An accurate protocol for transition metal systems

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Abstract

The explicitly correlated (F12) ab initio methods significantly reduce the basis set demands of high-accuracy quantum chemistry, enabling meaningful coupled cluster and multi-reference configuration interaction calculations to be carried out on a much wider range of systems. Advances in basis sets designed specifically for use in F12 calculations have pushed this even further. There are examples in the literature of F12 methods now being used to investigate transition metal complexes, which has typically been the reserve of density functional theory.

The accuracy of explicitly correlated coupled cluster methods for 3*d* transition metal-containing molecules will be demonstrated through analysis of geometries and atomisation energies of a recently proposed molecular database, 3*d*MLBE20. Comparison with experimental and composite thermochemistry derived data reveals accelerated convergence that will translate to significant computational savings. Nonetheless, explicitly correlated calculations using existing basis sets do not always converge smoothly, removing some of the attraction of using wavefunction-based methods. In order to tackle this problem, and to make explicitly correlated calculations more feasible, correlation consistent basis sets for the 4*d* transition metal elements Y-Pd have been developed and optimised specifically for use with F12 methods. These sets are designed with efficiency and smooth convergence in mind, and they hold the promise of accurate calculations on transition metal-containing complexes of a chemically relevant size. Furthermore, auxiliary basis sets matched to existing F12-specific orbital basis sets were developed and optimised for the elements H-Ar; these sets are expected to facilitate the performance of explicitly correlated calculations. Selected results from this thesis have been published in Kritikou, S.; Hill, J. G. *J. Chem. Theory Comput.* **2015**, 11, 5269.

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Chapter 1

Introduction

In 1929, Paul Dirac stated that "The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation."[1]

Almost a century later, the biggest bottleneck of modern quantum chemistry still remains this "compromise" between accuracy and efficiency. Expensive computational methods that are based on first principles are proven to be very accurate, but are, essentially, inapplicable to any chemically relevant systems (except for systems of very small size) due to the particularly high amount of computational resources (whether that is memory, disk space, or even simpler, time) that they require. On the other hand, methods that include some amount of empirical parametrisation, are not necessarily guaranteed to work for systems other than the ones used for their parametrisation. The degree of uncertainty associated with these methods allows us to use computational studies as auxiliary research findings, but is often prohibitive when it comes to utilising quantum mechanical calculations as a predictive tool that can guide any experiments.

This issue is being tackled from many directions; on one hand there has been a big advance and a vast improvement of computers over the past few decades. In 1965, Intel founder Gordon Moore stated that the number of transistors in a dense, integrated circuit doubles-up approximately every two years.[2] This came to be known as Moore's law and has essentially dictated the scaling progress of conventional (silicon) transistors up to this day. As the years go by, this qualitative rule for the electronics industry seems to be approaching its limits; at least with regards to silicon. Nonetheless, for the past few years the advances of modern computers and supercomputers have been tremendous, and one could assume that these advances will progress at a similar rate. On the other hand the theoretical approaches of solving the problem (essentially the Schrödinger equation) can vary dramatically. While density functional theory has become the "standard approach” that accompanies the vast majority of experimental investigations, it is still best used as a qualitative method, since its quantitative accuracy remains limited by the approximate electron exchange and correlation. Meanwhile, *ab initio* theories have been been struggling with their “inefficient”yet accurate nature for many decades; it is not uncommon for “new” methods (such as the explicitly correlated methods that are discussed here) to be based on quite old ideas, that have now become computationally feasible.

The work of this thesis is aimed at making *ab initio* calculations an option for transition metal systems of chemical interest. While the existing methodology is not revised, new basis sets are developed for the explicitly correlated method framework. The scope of this work is first to create a series of basis sets suitable for these sort of calculations, and to make them as small as possible, while ensuring their correct behaviour and physical representation. This is discussed in Chapters 5 and 6. Furthermore, composite approaches that potentially exploit fortuitous cancellation of error have been examined in Chapter 5 for 3*d* transition metal systems. The thesis is concluded by considering the goals set and achieved throughout this work, and by discussing the outlook and future work.

Before the presentation of any results, however, an overview of the theoretical methods, basis sets, and optimisation techniques required for the completion of this work is presented in Chapters 2, 3, and 4, respectively.

Chapter 2

Overview of electronic structure methods

Within the context of quantum chemistry, we are trying to calculate the energy of atoms and molecules, in order to predict equilibrium geometries, transition states, reaction rates, as well as many other properties of a system of interest. To do so, we are trying to solve the Schrödinger equation that, unfortunately, cannot be solved exactly for many-electron atoms and molecules. The inability of solving this problem exactly has led to the development of many electronic structure methods, split into two main categories: first-principle and semi-empirical ones. Both families of methods heavily depend on computers that have been routinely employed in the field of quantum chemistry for the past couple of decades. The scope of this chapter is to provide a standard overview of the majority of first-principle or *ab initio* methods in a brief manner, in order to create the solid background that is necessary for further exploration of the explicitly correlated (often called F12) framework, that includes the methods used throughout this work.

2.1 Schrödinger equation

Quantum mechanics and subsequently quantum chemistry arose at the beginning of the twentieth century with Planck's solution to the black-body radiation problem and Einstein's explanation of the photoelectric effect, which led to de Broglie's wave-particle duality formulation. Following up on de Broglie's ideas, Peter Debye stated that if particles behave as waves they should satisfy some sort of wave equation. Inspired by Debye's remark, Schrödinger formulated[3] what turned out to be the most famous equation in the field of quantum mechanics, a 3-dimensional wave equation for the electron that reproduced the correct spectral energies of hydrogen:

$$i\hbar\frac{\partial}{\partial t}\Psi = \hat{H}\Psi(\mathbf{r}, t)\,, \tag{2.1}$$

where $\hat{H}$ is the Hamiltonian operator acting upon the wavefunction $\Psi(\mathbf{r}, t)$ that describes the present state of the system. In many cases, especially in the context of chemical systems, the potential energy that is included in the Hamiltonian is time independent, and thus the above equation takes the form of a standing wave, hence being referred to as wavefunction. The wavefunction needs to meet some requirements in order to satisfy Schrödinger's formulation: it needs to be continuous, single-valued, differentiable, quadratically integrable and anti-symmetric since it describes electrons that are fermions.[4] Furthermore, its first derivative needs to be continuous as well. While the wavefunction itself lacks of physical meaning, the probability density $\langle\Psi(\mathrm{r}, t)|\Psi(\mathrm{r}, t)\rangle = \int_{\text{allspace}} |\Psi(\mathrm{r}, t)|^2 dr$ describes the probability that the system exists in space $[x, x + dx]$ at moment t (also known as the Born interpretation of quantum mechanics).[5] In cases where no external forces are acting upon the system, the potential energy of the system is time independent and it only depends on the position $\mathbf{r}$, and then the time independent Schrödinger equation is obtained. The molecular time independent Schrödinger can be written in its general form as:

$$(\hat{T}_e + \hat{V}_{ee} + \hat{V}_{eN} + \hat{T}_N + \hat{V}_{NN})\Psi(\mathbf{r}, \mathbf{R}) = E\Psi(\mathbf{r}, \mathbf{R})\,, \tag{2.2}$$

where E is the total molecular energy of the system represented by the wavefunction $\Psi(\mathbf{r}, \mathbf{R})$, $\mathbf{r}$ are the electron coordinates, $\mathbf{R}$ the nuclear coordinates, $\hat{T}_e$ and $\hat{T}_N$ the kinetic energy operators for electrons and nuclei respectively, $\hat{V}_{ee}$ the electron-electron repulsion, $\hat{V}_{eN}$ the electron-nuclear attraction, and $\hat{V}_{NN}$ the nuclear-nuclear repulsion.

While generating a potential energy requires many points in many dimensions, the focus of this work is mainly focused in solving for the electronic energies at or around the equilibrium distance, that are eigenvalues of the time independent form of the Schrödinger equation. Typically, the ground state energy is the focus, as excited electronic states are usually not populated at thermal equilibrium; however in fields such as photochemistry, excited states become important as optical photons cause transitions to excited states.

2.2 Born-Oppenheimer Approximation

The non-relativistic Hamiltonian for a molecule with N nuclei and n electrons can be expressed in atomic units as:

$$\hat{H} = \hat{T}_N(\mathbf{R}) + \hat{T}_e(\mathbf{r}) + \hat{V}_{eN}(\mathbf{r}, \mathbf{R}) + \hat{V}_{NN}(\mathbf{R}) + \hat{V}_{ee}(\mathbf{r})\,, \tag{2.3}$$

and

$$\hat{H} = -\frac{1}{2}\sum_{i}^{n}\nabla_i^2 - \frac{1}{2}\sum_{A}^{N}\frac{1}{M_A}\nabla_A^2 - \sum_{A,i}^{N,n}\frac{Z_A}{r_{Ai}} + \sum_{A>B}^{N}\frac{Z_A Z_B}{R_{AB}} + \sum_{i>j}^{n}\frac{1}{r_{ij}}\,. \tag{2.4}$$

It is evident that the $V_{eN}(\mathbf{r}, \mathbf{R})$ term prevents us from separating the hamiltonian into a nuclear and an electronic part, and thus express the the molecular wavefunction as a product of nuclear and electronic terms, $\Psi(\mathbf{r}, \mathbf{R}) = \Psi(\mathbf{r})\chi(\mathbf{R})$. To overcome this problem, the Born-Oppenheimer approximation is invoked. The Born-Oppenheimer approximation assumes that the wave function of a molecule can be expressed as a product of the nuclear wavefunction and the electronic wavefunction (that is parameterised by the nuclear coordinates) due to the huge difference in mass between electrons and nuclei; a proton is approximately 1827 times heavier than an electron. This approximation allows us to consider the nuclei fixed in space, with the electrons moving due to the static potential generated by the frozen nuclei. The electronic Schrödinger equation can then be solved separately from the nuclear one. The electronic wavefunction that is parameterised with the nuclear coordinates assumes that the electrons respond instantaneously to changes in nuclear coordinates, and is thus sometimes called the adiabatic approximation. The Born-Oppenheimer approximation is an essential step for solving the Schrödinger equation, due to the lack of an analytic solution for all cases other than the hydrogen and the hydrogen-like atoms.

2.3 Wavefunctions in electronic structure

Molecular orbitals can be expressed as linear combinations of atomic orbitals. Each molecular orbital is a single-electron wavefunction, and therefore N molecular orbitals should be combined in order to obtain an N electron wavefunction. However, since both atomic and molecular orbitals are single-electron wavefunctions, they are, in principle, not sufficient to describe any system that contains more than one electron; a many-body wavefunction (N-electron wavefunction) is required to do so. Yet, it is very common in quantum chemistry to use molecular orbitals in order to construct good approximations to the N-electron wavefunction. The simplest form for an N-electron wavefunction would be a product of one-particle functions (from now on only referred to as orbitals). Since there are N electrons and each of them has three spatial coordinates (Cartesian) plus one single spin coordinate, the N-electron wavefunction must be a function of $4N$ coordinates. Orbitals that depend on spin as well as on spatial coordinates are called spin-orbitals and are usually denoted as $\chi_i(\mathbf{x}_i)$. A simple N-electron wavefunction could then have the form of $\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) = \chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2)\ldots\chi_N(\mathbf{x}_N)$. Unfortunately the above expression (which is also called a Hartree Product) is not a suitable wavefunction, since it is not antisymmetric with respect to the interchange of coordinates of any pair of electrons. The wavefunction itself needs to be antisymmetric, and thus to obey the Pauli principle which states that two or more identical fermions (particles with half-integer spin) cannot occupy the same quantum state within a quantum system simultaneously. To ensure that the Pauli principle is obeyed, we can utilise a determinant of spin orbitals, called a Slater determinant (named after John Slater) that has the following form:

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) & \cdots & \chi_N(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) & \cdots & \chi_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\mathbf{x}_N) & \chi_2(\mathbf{x}_N) & \cdots & \chi_N(\mathbf{x}_N) \end{vmatrix} . \tag{2.5}$$

All N electrons are arranged in all $N!$ possible ways among the N spin orbitals. This ensures that the electrons are indistinguishable as required by the antisymmetry principle. Therefore, if we only know the list of the occupied orbitals $\{\chi_i(\mathbf{x})\}$, we can construct a determinant thus construct a wavefunction. It has not been made clear however how these spin-orbitals are obtained; this is the role of Hartree-Fock theory (discussed in section 2.5), which utilises the variational principle (section 2.4) in order to obtain the set of orbitals that minimize the total electronic energy. Typically, the spatial orbitals are expanded as a linear combination of contracted Gaussian-type functions (discussed extensively in Chapter 3) centered on the various atoms. Of course, this is a rather "simplified" wavefunction, and there are a few ways that it could become more sophisticated by adding flexibility; use a larger atomic orbital basis set so that the set of generated molecular orbitals is better (as discussed in Chapter 3) or expand the form of the wavefunction itself by making it a linear combination of different Slater determinants with different orbitals. The latter approach is used in the post-Hartree Fock Methods (see section 2.6) such as Configuration Interaction (subsection 2.6.2), Perturbation theory (subsection 2.6.1), and the Coupled-Cluster method (subsection 2.6.3).

2.4 Variational Principle

The variational principle states that the energy $E(\Phi)$ calculated using any well-behaved trivial wavefunction Φ, will always be no less than the exact energy of the system E_0

$$\frac{\langle\Phi|\,\hat{H}\,|\Phi\rangle}{\langle\Phi|\Phi\rangle} \geq E_0\,. \tag{2.6}$$

In other words, the energy that we compute using an approximate wavefunction can only be an upper barrier to the true energy. The basic idea of the method is to begin with a "trial" wavefunction that consists of some parameters that are called variational; these parameters are adjusted (optimised) until the energy of the trial wavefunction is minimised. The variational method is applied to problems that can't be solved analytically. The trial wavefunction Φ can be written as

$$\Phi = \sum_i c_i \Psi_i\,, \tag{2.7}$$

where Ψ_i is a set of suitably-behaved basis states. and the corresponding energy can be expressed as

$$E(\Phi) = \frac{\int \Phi^* \hat{H} \Phi \, d\tau}{\int \Phi^* \Phi \, d\tau}\,, \tag{2.8}$$

or by expanding the trial wavefunction with respect to the true wavefunction

$$E(\Phi) = \frac{\sum_{ij} c_i^* c_j \int \Psi_i^* \hat{H} \Psi_j \, d\tau}{\int \Psi_i^* \Psi_j \, d\tau}\,. \tag{2.9}$$

Since Ψ_i are the exact eigenfunctions of the Hamiltonian with corresponding ε_i eigenvalues, equation 2.9 can be written as

$$E(\Phi) = \frac{\sum_{ij} c_i^* c_j \varepsilon_i \int \Psi_i^* \Psi_j \, d\tau}{\sum_{ij} c_i^* c_j \int \Psi_i^* \Psi_j \, d\tau} \Rightarrow E(\Phi) = \frac{\sum_i c_i^* c_i \varepsilon_i}{\sum_i c_i^* c_i} \,, \tag{2.10}$$

and by subtracting the exact energy of the system E_0

$$E(\Phi) - E_0 = \frac{\sum_i c_i^* c_i \varepsilon_i}{\sum_i c_i^* c_i} - E_0 \Rightarrow E(\Phi) \geq E_0 \,. \tag{2.11}$$

The strategy of the variational method is based exactly on the fact that since the energy of any approximate trial wavefunction will always be above the true energy, then any variations to the trial wavefunction which lower its energy are making the approximate energy closer to the exact answer, and thus the corresponding trial wavefunction is also a better approximation to the true ground state wavefunction.

2.5 Hartree-Fock

2.5.1 Introduction

The Hartree-Fock (HF) method, is probably the most widely used wavefunction-based method of electronic structure when it comes to solving many-body problems in quantum chemistry, such as those encountered in electronic structure calculations. While a HF result is nowadays rarely used independently, as it is accompanied by a higher level, more "sophisticated" calculation it still holds a crucial role in any calculation, as it is the starting point.

The basic premise of HF theory is as follows. While the electronic problem for the hydrogen atom is solvable, trouble arises when there are more than one electron present. If we consider the hydrogen atom to which we add another electron in order to get H^- then we already have new terms that describe the interactions between electrons. As an initial approach, one could think that we can set the $\hat{V}_{ee}$ term of equation 2.2 equal to zero, and assume that electrons don't interact with each other. That way, the Hamiltonian would be separable and the total electronic wavefunction would simply be a product of two hydrogen atom wavefunctions. While such an approximation would be too crude to use, the Hartree Product formulation has been historically considered, as mentioned earlier in section 2.3 and eventually led to the antisymmetrized product (Slater determinant) wavefunctions. The assumption that electrons are properly (in terms of physical meaning) described by a Slater determinant is in line with the assumption that each electron moves independently of all other electrons, with only the Coulombic repulsion due to the average positions of all other electrons present. The antisymmetrisation of the wavefunction also ensures that exchange interaction is present, but this will be discussed in more detail later on, when the electron correlation is revisited (see section 2.8.1). Due to this fact, HF is referred to as a mean-field theory (and sometimes as an independent particle model). All mean-field theories capture interactions between particles in an average way, so that a single particle only experiences an average potential instead of an explicit interaction with all other particles. This simplifies the problem significantly, from a N-electron problem to an essentially single electron problem. The single electron problem is solved to figure out where the electrons are likely to be found, and the the mean-field is recomputed. The single electron problem is solved again using the newly computed mean-field potential, which, in turn, changes the potential which is recalculated to solve the individual electron problem, and so on. This process continues until the average potential and the solutions to the individual electron problem converge from one iteration to the next, and this procedure is known as self-consistent field (SCF) method. The HF SCF procedure generates the mean-field approximation for an N-electron system after a nuclear configuration has been fixed, under the BO approximation.

2.5.2 Hartree-Fock Equations

The electronic Hamiltonian can be simplified by utilising one and two-electron operators, $\hat{h}(i)$ and $\hat{u}(i,j)$, as

$$\hat{H}_{el} = \sum_i \hat{h}(i) + \sum_{i<j} \hat{u}(i,j) + \hat{V}_{NN} \, , \tag{2.12}$$

where

$$\hat{h}(i) = -\frac{1}{2}\nabla_i^2 - \sum_A \frac{Z_A}{r_{iA}} \tag{2.13}$$

and

$$u(i,j) = \frac{1}{r_{ij}} \, . \tag{2.14}$$

The HF wavefunction has the form of a Slater determinant, and the energy of the system is given by

$$E_{el} = \langle \Psi | \hat{H} | \Psi \rangle \Rightarrow E_{el} = \sum_i \langle i | \hat{h} | i \rangle + \frac{1}{2} \sum_{ij} [ii|jj] - [ij|ji] \, , \tag{2.15}$$

where the one electron integral is

$$\langle i | \hat{h} | i \rangle = \int d\mathbf{x}_1 \chi_i^*(\mathbf{x}_1) \hat{h}(\mathbf{r}_1) \chi_j(\mathbf{x}_1) \, , \tag{2.16}$$

while the two electron integral is given by

$$[ij|kl] = \int d\mathbf{x}_1 d\mathbf{x}_2 \chi_i^*(\mathbf{x}_1) \chi_j(\mathbf{x}_1) \frac{1}{r_{12}} \chi_k^*(\mathbf{x}_2) \chi_l(\mathbf{x}_2) \, . \tag{2.17}$$

The HF method determines the set of spin orbitals which minimise the energy and provide the best single determinant as a wavefunction. The minimisation of the energy provides us with a set of equations, the so-called HF equations:

$$f(\mathbf{x}_1) \chi_i(\mathbf{x}_1) = \epsilon_i \chi_i(\mathbf{x}_1) \, , \tag{2.18}$$

where $f(\mathbf{x}_1)$ is the newly introduced Fock operator:

$$f(\mathbf{x}_1) = \hat{h}(\mathbf{x}_1) + \sum_j \mathcal{J}_j(\mathbf{x}_1) - \mathcal{K}_j(\mathbf{x}_1) \, . \tag{2.19}$$

$\mathcal{J}_j(\mathbf{x}_1)$ and $\mathcal{K}_j(\mathbf{x}_1)$ are the Coulomb and exchange operators respectively, and are defined as:

$$\mathcal{J}_j(\mathbf{x}_1)\chi_i(\mathbf{x}_1) = \Big[\int d(\mathbf{x}_2)|\chi_j(\mathbf{x}_2)|^2 r_{12}^{-1}\Big]\chi_i(\mathbf{x}_1)\,, \tag{2.20}$$

which gives the mean local potential at point $\mathbf{x}_1$ due to the charge distribution from the electron in orbital χ_j, and

$$\mathcal{K}_j(\mathbf{x}_1)\chi_i(\mathbf{x}_1) = \Big[\int d\mathbf{x}_2\chi_j^*(\mathbf{x}_2)r_{12}^{-1}\chi_i(\mathbf{x}_2)\Big]\chi_j(\mathbf{x}_1) \tag{2.21}$$

which describes the quantum mechanical quantity of exchange that arises from the antisymmetry principle, and exchanges spin orbitals χ_i with χ_j. Introduction of a (non-orthonormal) basis set (usually of Slater or Gaussian type) transforms the HF equations into the so called Roothaan equations. The Hartree-Fock-Roothaan equations can be expressed in matrix notation as:

$$\sum_\nu F_{\mu\nu}C_{\nu i} = \epsilon_i \sum_\nu S_{\mu\nu}C_{\nu i}\,, \tag{2.22}$$

where $\tilde{\chi}$ denotes the atomic orbital basis functions, and

$$\mathbf{S} = \int d\mathbf{x}_1 \tilde{\chi}_\mu^*(\mathbf{x}_1)\tilde{\chi}_\nu(\mathbf{x}_1)\,, \tag{2.23}$$

and

$$\mathbf{F} = \int d\mathbf{x}_1 \tilde{\chi}_\mu^*(\mathbf{x}_1)f(\mathbf{x}_1)\tilde{\chi}_\nu(\mathbf{x}_1)\,, \tag{2.24}$$

or even simpler as

$$\mathbf{FC}{=}\mathbf{SC}\boldsymbol{\epsilon}\,, \tag{2.25}$$

where $\boldsymbol{\epsilon}$ is the diagonal matrix of the orbital energies, ϵ_i. In an orthogonal basis, the overlap matrix **S** vanishes, and the problem is reduced to diagonalising **F** in the self-consistent manner described earlier.

2.6 Post Hartree-Fock Methods

So far the basic method of quantum mechanics, the Hartree-Fock method has been discussed. However, the HF method only accounts for the average electron-electron interactions and consequently neglects the correlation between electrons. In a sufficiently large basis set, the HF wavefunction accounts for $\approx$ 99% of the total energy, but the remaining $\approx$ 1% is often very important for the description of chemical phenomena. Solving the Hartree-Fock-Roothan equations with an infinite basis set provides an energy limit which is called the Hartree-Fock limit, and describes the "best" energy one could get at the HF level. The energy difference between this HF limit and the exact, non-relativistic energy is defined as the electron correlation energy, and it corresponds to the motion of the electrons being correlated. Electron correlation is discussed in detail in section 2.8.1, it is however important to consider the "practical " aspect of the electron correlation as the missing energy from HF, in order to discuss possible ways of including it in an electronic structure protocol.

2.6.1 Perturbation Theory

Perturbation theory[6,7] provides one way of solution to finding the correlation energy. Perturbation theory (PT) partitions the Hamiltonian of the system into two parts, a known part $\hat{H}^{(0)}$ and a perturbation $\hat{H}^{(1)}$

$$\hat{H} = \hat{H}^{(0)} + \lambda \hat{H}^{(1)} \,. \tag{2.26}$$

The known part, $\hat{H}^{(0)}$, or unperturbed or reference Hamiltonian is the one we can solve (often the HF wavefunction). As long at the perturbation is small compared to the unperturbed Hamiltonian, PT provides the means to correct the reference energy. First the eigenfunctions and eigenvalues of the unperturbed Hamiltonian are obtained, and then a series of energetic corrections (as an infinite series of terms) are obtained $E_n = E_n^0 + E_n^1 + E_n^2 + \dots$, alongside a series of wavefunction corrections $\Psi_n = \Psi_n^0 + \Psi_n^1 + \Psi_n^2 + \dots$. Quite often, the corrections are only considered through the first or second order, as for well-behaved systems each consecutive term of the series decreases in -at least- quantitative significance. The first-order correction to the energy is given by

$$E_n^1 = \int \Psi_n^{(0)} \hat{H}^{(1)} \Psi_n^{(0)} d\tau \,, \tag{2.27}$$

while the second order one is given by

$$E_n^2 = \int \Psi_n^{(0)} \hat{H}^{(1)} \Psi_n^{(1)} d\tau \Rightarrow E_n^2 = \sum_{i \neq n} \frac{\left| \left\langle \Psi_n^{(0)} \middle| \hat{H}^{(1)} \middle| \Psi_i^{(0)} \right\rangle \right|^2}{E_n^0 - E_i^0} \,. \tag{2.28}$$

In electronic structure calculations, Møller-Plesset Perturbation Theory (MP) is commonly used.[8] In order to apply the Møller-Plesset method to calculate the correlation energy, the unperturbed wavefunction must be selected. This unperturbed, zeroth-order wave function is the HF determinant, and the zeroth-order energy is the sum of MO energies. Møller-Plesset theory goes on to calculate further corrections to the wave function and the energy, and the methods are named according to the n-th order of the perturbation theory as MPn. Adding the first order correction to the zeroth order energy yields the Hartree-Fock energy. To include correlation we need to go at least to the second order or MP2, since the energy up to the first order, MP1, is exactly the same as the HF energy. In practice only low orders of perturbation theory are carried out. In certain cases, higher order perturbation corrections will have errors greater than the HF solution. MPn does not always converge to the exact solution nor does higher order perturbation theory always improve the wavefunction, for example while MP2 tends to overestimate the true correlation energy, it often provides a better answer than MP3, especially in cases where a medium-sized basis set is used. Higher order perturbation corrections may give errors greater than the HF ones, and thus, in most cases MP2 is the point at which MP is truncated, since it is a relatively inexpensive way to recover around 85 to 95% of the correlation energy and higher orders of Møller-Plesset theory are mostly used for methodology testing rather than practical applications.

2.6.2 Configuration Interaction

Configuration Interaction (CI) is a post-HF method based on the variational method that solves the non-relativistic Schrödinger equation, under the BO framework. In contrast to HF that uses a single Slater determinant as the electronic wavefunction, CI utilises a linear combination of Slater determinants or configuration state functions ψ_k (CSFs) $\Psi = \sum_k c_k \psi_k$ for the wavefunction. CSFs are derived from different electronic configurations, from different assignments of electrons to orbitals. For any given configuration we can, in most cases generate several CSFs, and for this reason CSFs are sometimes also called N-particle symmetry adapted basis functions. In the CI framework the wavefunction is written as linear combination of CSFs with corresponding expansion coefficients that are determined by minimising the total energy of the system:

$$|\Psi\rangle = c_0 |\Phi_0\rangle + \sum_{ia} c_a^i |\Phi_a^i\rangle + \sum_{a<b,i<j} c_{ab}^{ij} |\Phi_{ab}^{ij}\rangle + \sum_{i<j<k,a<b<c} c_{abc}^{ijk} |\Phi_{abc}^{ijk}\rangle + \dots , \qquad (2.29)$$

where $|\Phi_a^i\rangle$ represents the Slater determinant formed by replacing spin orbital a with i in $|\Phi_0\rangle$. The first configuration, $|\Phi_0\rangle$, is usually called the reference configuration and all possible configurations generated as excitations from that reference state. Calculations that include all possible excitations from a given reference are called Full CI calculations. While very accurate, full CI calculations are unfeasible for all but very small systems and are mainly used in method development, since they provide the best results for any given basis set. In reality CI methods are truncated to include certain levels of excitations relative to the reference configuration, for example single (S), double (D), triple (T) etc. Truncated CIS, does not improve the HF ground state, since all matrix elements between the HF wavefunction and singly excited determinants are zero (Brillouin's Theorem). Therefore, in order to include electron correlation beyond the HF level, one must go beyond this CIS level, to at least CISD. While CI provides a systematic way of improving the Hartree-Fock energies, its truncated versions are not size-consistent. Size-consistency is a very important property of electronic structure methods, crucial to obtaining correct dissociation curves in most systems, that states that the energy of a system AB at infinite separation should be the sum of the energies of its non-interacting components A and B, or

$$E(AB)^\infty = E(A)^\infty + E(B)^\infty \qquad (2.30)$$

One of the great strengths of the CI method is its generality; the formalism applies to open-shell systems, closed-shell systems, excited states, and to systems far from their equilibrium geometries. By contrast, traditional single-reference perturbation theory and coupled-cluster approaches (see section 2.6.3) tend to assume that the reference configuration is dominant, and they may fail in cases that is not. The most common truncated version of CI is the CISD version that includes up to second order excitations from the reference state. Since only the doubles interact directly with the HF reference $|\Phi_0\rangle$, we expect and indeed see that the double excitations make the largest contributions to the CI wavefunction, after the reference state. Even though singles, triples, and higher do not interact directly with $|\Phi_0\rangle$, they can still become part of the CI wavefunction (i.e. have non-zero coefficients) due to their direct or indirect mixing with the doubles. Although singles are much less important to the energy than doubles, they are generally included in CI treatments because of their relatively small number and because of their low computational cost.

2.6.2.1 Davidson correction

The Davidson correction is an energy correction that is often applied in truncated CI calculations.[9] It allows the estimation of the full CI energy from a truncated CI expansion. More specifically, it estimates[10] a CISDTQ energy from the CISD energy

$$\Delta E_{\mathrm{Q}} = (1 - c_0^2)(E_{\mathrm{CISD}} - E_{\mathrm{HF}}) \,, \tag{2.31}$$

$$E_{\mathrm{CISDTQ}} \approx E_{\mathrm{CISD}} + \Delta E_{\mathrm{Q}} \,, \tag{2.32}$$

where c_0 is the coefficient of the HF wavefunction in the CISD expansion, E_{CISD} and E_{HF} are the CISD and HF energies respectively, and and ΔE_{Q} is the perturbative correction that estimates the CISDTQ energy, E_{CISDTQ}. Calculations that include this correction are usually denoted CISD(Q).

Davidson correction is quite popular due to its good perfomance and its low computational cost. The correction improves the correlation energy, it does not however improve the wavefunction in any way, and it cannot be used to improve quantities such as dipole moments, charge densities, vibronic couplings etc. As with most perturbative approaches, Davidson correction is not particularly reliable when the electronic structure of CISD differs significantly from the reference HF wavefunction, in other words the correction is not valid, when a_0^2 is not close to 1. In cases where there is significant multi-reference character present, or that CISD calculates an excited state, or a state with different spin multiplicity, then the Davidson correction provides poor results.

Finally, the Davidson correction improves the size consistency of CISD energies; however the correction itself, not the corrected energies, are actually size-consistent.[10,11] This is especially the case in larger molecules, where contribution from higher than quadruple excitations becomes more significant. Nonetheless Davidson correction is a rapid and economical way of improving the correlation energy, and thus is widely used. A multi-reference Davidson correction that improves the multi-reference CISD (MRCISD) exists as well and can be used to correct excited as well as ground state energies. The multi-reference Davidson correction utilises the multireference CI energy.

$$\Delta E_{\mathrm{Q}} = (1 - \sum_i |c_i^2|)(E_{\mathrm{MRCI}} - E_{\mathrm{MR}}) \,, \tag{2.33}$$

where E_{MRCI} is the multireference CI energy and E_{MR} is the energy obtained from the set of references. The multireference equivalent Davidson correction simply replaces the CISD correlation energy in the Davidson correction, with the analogous multireference correlation energy.

2.6.3 Coupled Cluster

Coupled-cluster (CC) methods are a class of pertubative techniques that look quite different from the perturbative MPn methods discussed earlier. CC methods focus on the physical nature of the excitations rather than the configurations emphasized in CI. The ground state wavefunction is obtained by the exponential ansatz

$$|\Psi_{cc}\rangle = e^{\hat{T}} |\Phi_0\rangle \Rightarrow |\Psi_{cc}\rangle = \left(1 + \hat{T} + \frac{\hat{T}^2}{2} + \frac{\hat{T}^3}{3} + \dots\right) |\Phi_0\rangle \ . \tag{2.34}$$

where $\hat{T}$ is the cluster operator that can be broken up to reflect the hierarchy of excitation levels:

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \dots \ . \tag{2.35}$$

Each $\hat{T}$ includes all excitations of nth order. For example, the first two excitation hierarchies are

$$\hat{T}_1 |\Phi_0\rangle = \sum_{i,a} t_i^a \Phi_i^a \,, \tag{2.36}$$

and

$$\hat{T}_2 |\Phi_0\rangle = \sum_{\substack{i>j \\ a>b}} t_{ij}^{ab} \Phi_{ij}^{ab} \,. \tag{2.37}$$

The exponential form of the wavefunction dictates different approaches than the ones seen so far. Instead of variational minimization, the projected Schrödinger equation is used; the idea is to project the CC wavefunction on to a particular excitation. The CC energy is obtained by a projection onto the Hartree-Fock state

$$E = \langle HF| \mathbf{H} |CC\rangle \,. \tag{2.38}$$

This equation is not necessarily variational. Usually, the variational principle for CC breaks down at the fourth and higher orders of perturbation theory, and so the CC theory is often called quasivariational. CC equations are always size-extensive for any level of truncation, unlike CI ones that are only extensive at the FCI level. When the cluster operator includes all possible excited determinants, the CC wavefunction is equivalent to the full CI one. Of course, in the same way that is inefficient to do a full CI calculation, in most cases the CC calculations are truncated. By truncating the $\hat{T}$ operator, some of the terms in the amplitude equations become zero and the energy becomes approximate, similarly to the energy generated from a truncated CI calculation. The accuracy of the calculation can again be improved by including more terms in the $\hat{T}$ operator. In most cases single and double excited states are included, and the contribution of the connected triples is estimated by a non-iterative MP calculation. This approach leads to the CCSD(T) method, what is considered to be the "Gold Standard" of Quantum Chemistry, since it provides great results for a large variety of systems. It should be noted that even the truncated CC wavefunctions include excitations of different orders due to the exponential nature of the wave function. For example, the 6th order excitations include contributions, not only from $\hat{T}_1$ up to $\hat{T}_6$ but also the so called disconnected amplitudes, in this case of a quadruple excitation and a double excitation, two triple excitations, three double excitation, and so on. These disconnected amplitudes allow the wave function to recover dynamic correlation in a systematic and efficient way.

2.6.4 Computational cost and scaling of Post Hartree-Fock methods

Hartree-Fock is a straightforward theory that satisfies the commonly known features of electronic wavefunctions: it generates wavefunctions that are antisymmetric with respect to the exchange of two electron positions and includes exchange between like-spin electrons. The cost of a Hartree-Fock calculation formally scales as n^4 where n is the number of basis functions, but depending on implementation the scaling can vary between n and n^2. This scaling makes HF method appropriately used in systems with up to a few hundred atoms. First and second analytical derivatives are readily available with respect to common perturbations. However, HF is insufficiently accurate for quantitative predictions of the properties of many compounds. By only taking into account the average potential generated by the rest of the electrons, interaction energies are typically very poor. Nonetheless, a HF wavefunction is a well-controlled approximation to the N-body wavefunction, and for this reason HF continues to be widely used.

Almost all post-HF methods share the combined limitations of a poor scaling with system size and a strong basis set dependence. In practice, post-HF methods typically scale as follows

- MP2 scales as n^5
- MP3, CISD, and CCSD scale as n^6
- MP4 and CCSD(T) scale as n^7
- MP5 and CISDT and CCSDT scale as n^8
- FCI scales as $n!$

where n is the number of basis functions. It is evident that their scaling limits application to small systems. CI and CC-based methods effectively transform the electron-correlation problem into a basis set problem, where the basis set is the set of molecular orbitals derived from a HF (or similar) calculation. Different approaches to this problem of poor scaling of post-HF methods is discussed in detail later on (see section 2.8.2).

2.7 Multireference methods

While we have seen that in many cases HF wavefunctions are a sufficient starting point for a calculation, there are a few problems that are not well represented by single configuration wavefunctions, such as diradicals, excited states, transition states, and systems with near degeneracies. These systems are known to be of "multirefeference" character, and they require a different approach in order to be accurately described. The two main methods that are vastly used within the multireference framework are the Multi-Configurational Self-Consistent Field (MCSCF) method and the multireference equivalent of CI, denoted MRCI.

2.7.1 Multi-Configurational Self Consistent Field

The Multi-Configuration Self-Consistent Field method (MCSCF) is a popular method that accounts for (statistical) electron correlation, in cases where the system is not well described by a single determinant. The MCSCF method can be considered a variation of CI, where the coefficients in front of the determinants optimised, as well as the MOs used for constructing the determinants are optimised. MCSCF methods are rarely used for calculating large fractions of the correlation energy; it is generally more efficient to include additional determinants and keep the MOs fixed (which is what the CI method does). The MCSCF method defines an active space in terms of orbitals and electrons, inside within it performs a full CI calculation. Of course this process can be quite computationally demanding, especially if we consider that the ideal active space would be the full valence. It is therefore not always feasible to use a full valence active space, and we are forced to truncate the active space in order to perform the calculation. Unfortunately, there is not one bulletproof way of selecting the active space, and this selection can become quite tricky. Once the active space has been selected, two sets of coefficient optimisations must take place. CI coefficients are being optimised by solving a linear variation secular equation, while the orbital optimisation follows an analogous to, but more complex, HF algorithm.

MCSCF wavefunctions are often used as reference states for multireference configuration interaction calculations (MRCI). These methods can deal with extremely complex chemical situations and, if computing power permits, may be used to reliably calculate molecular ground- as well as excited states.

2.7.2 Multi-Reference Configuration Interaction

The multireference configuration interaction (MRCI) method consists of a CI expansion of the eigenstates of the electronic molecular Hamiltonian in a set of Slater determinants which correspond to excitations of the ground state electronic configuration as well as to some excited states.[12–14] Similarly to CI, the Slater determinants from which the excitations are performed are called reference determinants, and the higher excited derterminants are then chosen by truncating excitations from these references to singly, doubly, *n*ly excitations resulting in MRCIS, MRCISD, etc. Similarly to CI, MRCI is usually truncated to MRCISD. For the ground state using more than one reference configuration means a better correlation and so a lower energy. The problem of size inconsistency of truncated MRCI methods is quasi treated by performing the Davidson +Q correction.[9]

MRCI calculations start with a MCSCF calculation, which describes the static electron which include the nearly degenerate CSFs in the wavefunction. Then occupied orbitals are substituted by virtual orbitals in each CSF. The number of CSFs usually mandates the truncation of MRCI to single and double substitutions, in order to keep the computational cost to a reasonable level. The MRCI method is very flexible and robust, but the use of extensivity corrections is by no means as straightforward in MRCI as in the single reference case.

2.8 Explicitly Correlated Methods

2.8.1 Revisiting Electron Correlation in Atoms and Molecules

In order to construct accurate trial wavefunctions, we need to make sure that we have a deep understanding of electron correlation. It is crucial that we identify the cases where electron correlation is represented accurately, and the cases where it is not. Although a more empirical discussion of correlation energy has been included when post-HF methods were reviewed, this subsection aims to focus on a mathematical description of correlation energy and of its underlying physical principles.

2.8.1.1 Statistical definition of electron correlation

The motion of two electrons is said to be statistically uncorrelated if their pair probability distribution function can be written as a product of the distribution functions for the individual electrons:

$$P_{12}(\mathbf{x}_1, \mathbf{x}_2) \; = P_1(\mathbf{x}_1) P_2(\mathbf{x}_2)\,, \tag{2.39}$$

where $\mathbf{x}_i$ is the spatial and spin coordinate of each particle i. This probability can be also written in terms of the conditional electron density[15] $P_{12}(\mathbf{x}_1|\mathbf{x}_2)$ which expresses the probability distribution for electron 1, when electron 2 is at $\mathbf{x}_2$. If there is no correlation, the conditional probability is independent of the position of particle 2:

$$P_{12}(\mathbf{x}_1|\mathbf{x}_2) = \frac{P_{12}(\mathbf{x}_1, \mathbf{x}_2)}{P_2(\mathbf{x}_2)} = P_1(\mathbf{x}_1)\,. \tag{2.40}$$

In other words, it is equally possible to find electron 1 right next to electron 2 as is to find them separated by some arbitrary distance r. Since electrons are indistinguishable particles, the individual electron probability for each electron of any electron pair is the same

$$P_1(\mathbf{x}) = P_2(\mathbf{x}) = \frac{1}{n}\rho(\mathbf{x})\,, \tag{2.41}$$

and the conditional probability $P_{12}(\mathbf{x}_1\mathbf{x}_2)$ can be expressed as

$$P_{12}(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{n(n-1)}\rho_2(\mathbf{x}_1, \mathbf{x}_2)\,, \tag{2.42}$$

where $\rho(\mathbf{x})$ is the electron density and $\rho_2(\mathbf{x}_1, \mathbf{x}_2)$ is the pair density

$$\rho(\mathbf{x}) = n \int d\mathbf{x}_2 ... \int d\mathbf{x}_n \Psi^*(\mathbf{x}, \mathbf{x}_2 ..., \mathbf{x}_n)\Psi(\mathbf{x}, \mathbf{x}_2 ..., \mathbf{x}_n) \tag{2.43}$$

$$\rho_2(\mathbf{x}_1,\mathbf{x}_2) = n(n-1)\int d\mathbf{x}_3 ... \int d\mathbf{x}_n \Psi^*(\mathbf{x}_1,\mathbf{x}_2 ...,\mathbf{x}_n)\Psi(\mathbf{x}_1,\mathbf{x}_2 ...,\mathbf{x}_n)\,. \tag{2.44}$$

The pair density $\rho_2(\mathbf{x}_1,\mathbf{x}_2)$, expresses the probability of electron 1 being at $\mathbf{x_1}$ while electron 2 is at $\mathbf{x}_2$. Since the electrons are countable, if electron 1 is at $\mathbf{x}_1$ there are can only be $n-1$ electrons at $(\mathbf{x}_2)$, and therefore ρ_2 integrates over $n(n-1)$. Therefore, the electrons in an n-electron system are statistically correlated if

$$\rho_2(\mathbf{x}_1,\mathbf{x}_2) = \frac{n-1}{n}\rho(\mathbf{x}_1)\rho(\mathbf{x}_2)\,. \tag{2.45}$$

Up to this point, $\mathbf{x}$ is a coordinate that consists of both space and spin, $\mathbf{x} = (r_x, r_y, r_z, m_s)$. However, since in most cases we work with non-relativistic Hamiltonians that do not have any spin components, the repulsion energy depends only on the spatial distribution of the electrons. Thus, we are usually focused on the spatial probability distributions, that can be obtained by integrating $\rho(\mathbf{x})$ and $\rho_2(\mathbf{x}_1,\mathbf{x}_2)$ over all the spin coordinates to obtain $\rho(\mathbf{r})$ and $\rho_2(\mathbf{r}_1,\mathbf{r}_2)$ respectively.

The origin of electron correlation can be attributed to two independent sources: The first source is easy to comprehend as it is based on the electrostatic interaction between two electrons. Coulomb's law dictates that electrons interact through a repulsive Coulomb force $e^2/4\pi\epsilon_0 r_{12}$, where r_{12} is the distance between electron 1 and 2. The second source, is more complicated, as it is purely quantum mechanical in nature. It arises from the fact that electrons are indistinguishable particles that obey Fermi statistics, and thus is called Fermi correlation. Electrons, along with all other fermions, are required to obey the Pauli exclusion principle. In other words, any wavefunction that describes fermions has to be anti-symmetric with respect to exchange of configurations $\mathbf{x}_1$ and $\mathbf{x}_2$ for any pair of fermions, in this case electrons.

2.8.1.2 Fermi correlation: shell structure and exchange

The Fermi correlation is taken into account somewhat automatically, by the use of Slater determinants, in other words fully antisymmetrized products of orbitals. The starting point of all calculations of electronic structure, namely the HF method, uses a single Slater determinant as a wavefunction. The ground-state of a n-electron atom can be expressed as:

$$\Psi(\mathbf{x}_1,\mathbf{x}_2 ...,\mathbf{x}_n) = \prod_{i=1}^{n}\phi_{k_i}(\mathbf{x}_i) \tag{2.46}$$

where ϕ_{k_i} are the orthonormal spin orbitals. By looking at the quantity

$$P_{ij}(\mathbf{x}_i,\mathbf{x}_j) = P_i(\mathbf{x}_i)P_j(\mathbf{x}_j)\,, \tag{2.47}$$

where

$$P_i(\mathbf{x}_i) = \phi^*_{k_i}(\mathbf{x}_i)\phi_{k_i}(\mathbf{x}_i) \tag{2.48}$$

and

$$P_j(\mathbf{x}_j) = \phi^*_{k_j}(\mathbf{x}_j)\phi_{k_j}(\mathbf{x}_j)\,, \tag{2.49}$$

one could say that the HF wavefunction is statistically uncorrelated, since for every pair the two-particle probability distribution function factorizes into a product of one-particle distribution functions. However, this would only be true if electrons were distinguishable, which they are not. It is clear to see that equation 2.46 is satisfied, since:

$$\rho(\mathbf{x}_1) = \sum_{i=1}^{n} P_i(\mathbf{x}_1) \tag{2.50}$$

and

$$\rho_2(\mathbf{x}_1, \mathbf{x}_2) = \sum_{\substack{i,j=1 \\ i \neq j}}^{n} P_{ij}(\mathbf{x}_1, \mathbf{x}_2) \tag{2.51}$$

and thus

$$\rho_2(\mathbf{x}_1, \mathbf{x}_2) = \rho(\mathbf{x}_1)\rho(\mathbf{x}_2) - \sum_{i=1}^{n} P_i(\mathbf{x}_1)P_i(\mathbf{x}_2)\,. \tag{2.52}$$

Therefore, the electron pair probability distribution derived from a Hartree product wavefunction is in fact statistically correlated. This reflects the shell structure of the electronic distribution, in accordance with the Pauli exclusion principle.

So far we have examined the “shell structure” component of Fermi correlation. We need, however, to examine the exchange component of Fermi correlation. For a wavefunction that consists of a single Slater determinant, the one-electron probability distribution is given by

$$P_1(\mathbf{x}) = \frac{1}{n}\rho(\mathbf{x}) \tag{2.53}$$

where

$$\rho(\mathbf{x}) = \sum_{i=1}^{n} \phi^*_{k_i}(\mathbf{x})\phi_{k_i}(\mathbf{x}) \tag{2.54}$$

and the pair density is given by

$$\rho_2(\mathbf{x}_1, \mathbf{x}_2) = \rho(\mathbf{x}_1)\rho(\mathbf{x}_2) - \sum_{i,j=1}^{n} \phi^*_{k_j}(\mathbf{x}_1)\phi_{k_i}(\mathbf{x}_1)\phi^*_{k_i}(\mathbf{x}_2)\phi_{k_j}(\mathbf{x}_2)\,. \tag{2.55}$$

A direct comparison of equations 2.52 and 2.55 shows that there is additional correlation component which arises from the antisymmetry of the wavefunction, which is often called the exchange component of Fermi correlation. Integration over spin coordinates show that the exchange lowers the probability of same-spin electrons being close in space, but has no effect on opposite-spin electron pairs.

2.8.1.3 Coulomb correlation: static and dynamic

As mentioned previously, Coulomb correlation is a result of the electrostatic repulsion between electrons dictated by Coulomb’s law. It is important to mention that although the Coulomb correlation occurs due to the interelectronic repulsion only, its effect on the probability density depends on the electron-nucleus relative coordinates. This picture is in contrast to the idealized model of the uniform electron gas, where the correlation effects are independent of position and depend only on the relative coordinates of electrons. For ground states the Coulomb correlation is always negative, and reduces the probability of two electrons being found in the same spatial region. In HF, the orbitals are optimised to minimize the expectation value of the energy, and the repulsion between the electrons only influences the wavefunction through an effective potential, making HF a mean-field theory. In most post-HF methods however, where the wavefunction expands beyond a single determinant, Coulomb correlation is included. We can intuitively distinguish two different contributions to this electrostatic correlation: A dynamic component that arises from the fact that each electron interacts instantaneously with all other electrons, and a static component[16] that is always present, but dominates in cases where near degenerate electron configurations are included. Cases of the latter need to be treated with multi-reference methods, that include all nearly degenerate electron configurations in the reference wavefunction.

Although presented here from a mathematical point of view, the traditional meaning of "electron correlation" in quantum chemistry is what the HF wavefunction fails to model. Löwdin defined[17] electron correlation as the difference between the HF energy and the "exact" non-relativistic BO energy:

$$E_{\mathrm{corr}} \equiv E_{\mathrm{exact}} - E_{\mathrm{HF}} \leq 0\,. \tag{2.56}$$

Since the HF wavefunction includes Fermi correlation, the term "electron correlation" as used by quantum chemists refers primarily to Coulomb correlation. It should be noted that Löwdin's definition is based on a restricted HF wavefunction. Pople and Binkley have extended[18] that definition, to an unrestricted HF wavefunction, but in unrestricted calculations, spin contamination makes the separation between Fermi and Coulomb correlation less clear.[19]

2.8.2 Motivation for Explicitly Correlated Wavefunctions

The success of *ab initio* calculations over the past years should be partly attributed to the use of Gaussian-type basis functions, for which efficient algorithms for integral evaluation are readily available. In order for calculations to rival experimental accuracy, it is essential to reproduce the electron correlation. Although HF can recover up to 99% of the total energy, the remaining 1% is critical for chemistry, especially in cases that involve the breaking and creation of bonds. Correlation is included in post-HF wavefunctions, such as CI, by taking linear combinations of excited HF determinants. Therefore, the accuracy of the wavefunction is improved by increasing the number of determinants in the expansion, which consequently depends on the number of HF orbitals, which is equal to the number of functions in the atomic orbital basis. Nevertheless, all post-HF calculations suffer from an extremely slow convergence of electron correlation with respect to basis set size. In order to achieve the so-called "chemical accuracy" with CISD or CCSD, a cc-pV5Z basis or larger is required. Even basis sets that are specifically designed for electron correlation[20–24] make calculations in larger systems computationally formidable, since high angular momentum terms are required in order to reproduce the electronic cusp. As charged particles approach one another, the Coulomb interaction, which scales like the reciprocal of the inter-particle distance, diverges. Nonetheless, the local energy $E = \langle \hat{H}\Psi \rangle / \langle \Psi \rangle$ is constant everywhere for the exact wavefunction. Thus the divergence in the Coulomb energy must be cancelled exactly by the kinetic energy operator. This can only be achieved if the wavefunction becomes linear in the inter-particle distance as the particle coalesces, because $-(1/2)\nabla^2 r = -1/r$. In other words, the cusp condition dictates that as the coordinates of two electrons converge, the wavefunction is linear in r_{12}. One way to account for the cusp condition is to explicitly include r_{12} in the expansion of the wavefunction. In that way, the cusp condition is satisfied explicitly, rather than modeled by including orbitals of high angular momenta. These methods that include explicitly the interelectronic distance in the expansion of the wavefunction, are called explicitly correlated methods. The idea that the interelectronic distances were universally useful for constructing efficient wavefunctions, although known from around the 1930s, became clear around the time of Kato's discovery of the cusp condition in 1957. Kato established properties of the exact wavefunction near Coulomb singularities (such as the electron-nucleus coalescence point):[25]

$$\left(\frac{\partial \Psi(r_{12})}{\partial r_{12}} \right)_{r_{12} \to 0, \mathrm{av}} = \frac{1}{2} \Psi(r_{12} = 0) \tag{2.57}$$

(av indicates a spherical averaging.) He showed that discrete-spectrum wavefunctions are continuous and have bounded continuous first derivatives, except at the Coulomb singularities. More specifically, he established that the structure of the wavefunction's first derivative can be universally described in terms of the inter-particle coordinates. It is the difficulty of reproducing this cusp feature in the wavefunction that makes convergence with respect to the orbital expansion so difficult.

2.8.2.1 Hylleraas-type methods

Around 1928, Hylleraas was looking for a way to refine his breakthrough variational function[26] for the He atom ground state, that computed an energy of He to within 0.1 eV. He realized that the slow convergence of his orbital expansion could be solved by introducing terms in the wavefunction that depend explicitly on interelectronic coordinates. By creating a very compact wavefunction with linear dependence on r_{12}, he managed to calculate the energy of $E = -2.902431\ E_h$, in error from the exact Born-Oppenheimer non-relativistic result by 0.035 eV.[27] His wavefunction included a linear r_{12} term

$$\Psi(r_1, r_2, r_{12}) = N(1 + c_1(r_1 - r_2)^2 + c_2 r_{12}) e^{-\alpha(r_1 + r_2)}, \tag{2.58}$$

where parameters α, c_1 and c_2 were determined variationally ($\alpha = -1.81607$, $c_1 = 0.130815$, $c_2 = 0.291786$, and N, the corresponding normalization constant is 1.330839). Many studies have been performed, trying to attribute the spectacular success of the Hylleraas's wavefunction to the inclusion of the linear r_{12} term. However, findings of these studies suggest that in order to produce compact wavefunctions that approach the exact energy, the use of r_{12} terms is necessary but not sufficient: appropriately accounting for the cusps of the electronic wavefunction is essential for the rapid decay of the basis set error of the many-electron wavefunction. Having to calculate high dimensional integrals that come along with the use of interelectronic distances is what prevented Hylleraas's idea being applied in practice.

2.8.3 Explicitly Correlated Methods for *n*-Electron Systems

Extending Hylleraas's idea to more systems might seem straightforward but is actually technically challenging. The main obstacle is the evaluation of the high dimensional integrals involved in these calculations. Specifically, application of explicitly correlated techniques to systems with more than two electrons faces the challenge of evaluating *n*-electron integrals. Even if we restrict each *n*-electron basis function to depend on only one of the interelectronic distances, up to four-electron integrals are necessary.

Let's consider the explicitly correlated MP2 method, in order to demonstrate the need for three- and four-electron integrals. In MP2, it is conventional to take advantage of the decomposition[28] of the second-order energy into a sum of pair contributions. This decomposition requires the first-order pair functions, $|u_{ij}\rangle$, to be strongly orthogonal to the occupied space. In orbital based methods, this is trivially achieved by expanding $|u_{ij}\rangle$ in products of virtual orbitals. In a more general approach though, it is necessary to use an explicitly projected form $\hat{Q}_{12}|u_{ij}\rangle$ where $\hat{Q}_{12}$ is a projection operator into the complete virtual space. The Hylleraas functional[27] can then be minimized for each pair to provide upper bounds for each MP2 pair energy:

$$\begin{aligned} H[u_{ij}] &= \langle u_{ij}|\, \hat{Q}_{12}(\hat{F}_1 + \hat{F}_2 - \epsilon_i - \epsilon_j)\hat{Q}_{12}\, |u_{ij}\rangle \\ &\quad + 2\,\langle u_{ij}|\, \hat{Q}_{12} r_{12}^{-1}\, |ij\rangle \geq \epsilon_{ij}^{(2)} \,. \end{aligned} \tag{2.59}$$

This is a spin-free formalism, where i and j denote spin-orbitals, in which the functions $|u_{ij}\rangle$ and $|ij\rangle$ are properly antisymmetrized, $\hat{F}$ is the Fock operator and ϵ_i is an orbital energy. For simplicity it is assumed that the spin-orbitals are canonical HF orbitals. Although in conventional MP2 calculations the pair functions $|u_{ij}\rangle$ are built from one-electron orbital products, in explicitly correlated MP2 theory these pair functions also contain terms that depend explicitly on the interelectronic coordinates. If the pair function $|u_{ij}\rangle$ is an explicit two-electron function, then the first term in equation 2.59 contains both three- and four-electron terms, while the second term contains only three-electron terms. The number of four-electron integrals scales as $\mathcal{O}(m^8)$, where m is the number of basis functions. Over the past years, different methods of evaluating these integrals have been developed, solving one of the main major challenges in explicitly correlated methods. The most pursued methods are the following:

- Weak orthogonality functional of Szalewicz *et al.* can be used to avoid some high-dimensional integrals.[29,30]

- Exact evaluation of integrals is possible in cases of atoms or certain types of explicitly correlated basis functions. For example, explicitly correlated Gaussian functions allow analytic evaluation of integrals for molecules with any number of electrons.[31]

- The transcorrelated method allows the Coulomb singularities to be eliminated from the Hamiltonian through a similarity transformation.[32,33] The resulting Hamiltonian, although more complicated, (it includes three-electron terms) is cusp-less and therefore can be represented efficiently by Slater determinants.

- Resolution-of-the-identity (RI) is the most heavily used method in explicitly correlated calculations in order to reduce three- and four-electron integrals to products of two-electron integrals only.

The two basic strategies (transcorrelated method and weak orthogonality functional) that have been developed in order to avoid the need to compute n-electron integrals in explicitly correlated theories will be outlined in the following subsections, while RI will be discussed along with the R12 nomenclature in section 2.8.4.

2.8.3.1 Gaussian Geminals

Boys[34] and Singer[35] independently realized that it was possible to analytically compute all of the necessary integrals for explicitly correlated calculations on molecules, provided that both the one- and two-electron basis functions are Gaussian basis functions (Gaussian geminals). In that case, all many-electron integrals that arise can be reduced exactly to expressions involving the Boys function $F_m(T)$.[34] Although this provided a significant advance, the problem of the rapidly scaling number of many-electron integrals, still obstructed application to larger systems. In the 1980s, Szalewicz *et al.* introduced[29,30] a scheme for performing MP2 calculations that uses the Gaussian geminals of Boys and Singer but avoids the need to compute any four-electron integrals at all[29,36]. This was achieved through the weak orthogonality functional (WOF), which retains a strict upper bound to the second-order energy. The WOF has the form:

$$\begin{aligned} W[u_{ij}] = {} & \langle u_{ij}| \hat{F}_1 + \hat{F}_2 - \epsilon_i - \epsilon_j |u_{ij}\rangle \\ & + 2 \langle u_{ij}| \hat{Q}_{12} r_{12}^{-1} |ij\rangle \\ & + \eta_{ij} \langle u_{ij}| \hat{O}_1 + \hat{O}_2 |u_{ij}\rangle \geq \epsilon_{ij}^{(2)} , \end{aligned} \tag{2.60}$$

where η_{ij} is a positive parameter that satisfies:

$$\eta_{ij} \geq \frac{\epsilon_i + \epsilon_j}{2} - \epsilon_1 \tag{2.61}$$

and ϵ_1 is the orbital eigenvalue of the lowest occupied orbital. The *Ansatz* used for the pair function in WOF calculations has the form

$$\langle u_{ij}| = \hat{\mathcal{A}} \left(\sigma(1)\sigma(2) \sum_p a_p e^{-\alpha_p |\vec{r}_1 \vec{A}_p|^2 - \beta_p |\vec{r}_2 \vec{B}_p|^2 - \gamma_p |\vec{r}_1 \vec{r}_2|^2} \right) , \tag{2.62}$$

where a_p are fully optimizable linear coefficients, α_p, β_p and γ_p are fully optimizable exponents, and $\vec{A}_p$ and $\vec{B}_p$ are fully optimizable function centers, which are not constrained to be coincident with the nuclei. $\hat{\mathcal{A}}$ is an antisymmetrizer and σ is a spin function. All parameters are optimised individually for each pair function, $|u_{ij}\rangle$. Szalewicz *et al.* applied this WOF formalism and obtained[30,37,38] highly converged MP2 and coupled-cluster results for a variety of atoms and small molecules.

Despite this success, the main disadvantage of the WOF Gaussian geminal method is the need for expensive non-linear optimisations of basis set parameters. These are necessary to obtain extremely high accuracy, but can be bypassed; geminal theories that only involve optimisation of linear expansion coefficients can exist. However, it remains the case that Gaussian geminals calculations (with or without non-linear optimisations) with exact three-electron integral evaluation are limited to high accuracy studies of small systems. Furthermore, it seems like the penalty function $\eta_{ij} \langle u_{ij}| \hat{O}_1\hat{O}_2 |u_{ij}\rangle$ in the WOF may lead to poor results if small basis sets are used.

2.8.3.2 Exponentially correlated Gaussians

The conclusion of subsubsection 2.8.3.1 that the Gaussian geminals method is limited to small systems, can also be applied to the method of exponentially correlated Gaussians (ECGs).[31] In ECGs, explicit dependence on r_{12} is introduced into the n-electron basis function:

$$\Phi(\mathbf{r}) = \exp\left(-\sum_{i=1}^{n} \alpha_i |\mathbf{r}_i - \mathbf{C}_i|^2 - \sum_{i<j=1}^{n} b_{ij} |\mathbf{r}_i - \mathbf{r}_j|^2\right). \tag{2.63}$$

The extra term correlates the motion of all pairs of electrons simultaneously, while keeping the ECGs straightforward, due to their Gaussian form. Although Gaussian geminals do not satisfy Kato's cusp condition, a linear combination of ECGs can efficiently approximate the shape of the electronic wavefunction near the electron cusp. This is achieved through the explicit dependence of the wavefunction on the interelectronic distance. All integrals involving ECGs are analytic, and the ECG method strategy involves variational minimization of linear and non-linear parameters. The highly flexible s-type Gaussians can adapt and shift to where they are most required. ECGs have been traditionally used[39] in accurate variational computations, and predict extremely accurate ground and excited PESs of small molecules, such as H_2, H_3, He_2^+, LiH. Unfortunately, the large number of non-linear parameter optimisations and integral evaluations[40] prevent ECGs being used for accurate calculations on systems with more than four electrons.

2.8.3.3 Transcorrelated method

The main idea of the transcorrelated method is to use a similarity transformation to produce a Hamiltonian that is free of electron-electron singularities

$$\hat{H}_G = e^{-\hat{G}} \hat{H} e^{\hat{G}} \tag{2.64}$$

$$\hat{G} = \sum_{i<j} f(\mathbf{r}_i, \mathbf{r}_j), \tag{2.65}$$

where $f_{ij} \equiv f(\mathbf{r}_i, \mathbf{r}_j)$ can be a general function[41]. The Hausdorff expansion of the non-Hermitian $\bar{H}$ truncates exactly after the second term, due to the multiplicative nature of $\hat{G}$

$$\bar{H} = \hat{H} + [\hat{T}, \hat{G}] + \frac{1}{2!}[[\hat{T}, \hat{G}], \hat{G}] + \dots . \tag{2.66}$$

Therefore, $\bar{H}$ contains only up to three-electron terms of type $(\nabla_i f_{ij}) \cdot (\nabla_i f_{ik})$.

Handy selected[42] the following form for f_{ij}

$$f_{ij} = \sum_k c_k g_k(\mathbf{r}_i, \mathbf{r}_j) + \sum_\mu d_\mu \phi_\mu(\mathbf{r}_i) , \tag{2.67}$$

where g_k is a primitive spherical Gaussian geminal, and ϕ_μ is an atomic orbital. The energy is obtained from

$$E = \langle \Phi_0 | \bar{H} | \Phi_0 \rangle , \tag{2.68}$$

where Φ_0 is a Slater determinant of MOs, which are also optimised. Handy successfully applied the transcorrelated method to several small systems, and obtained good results, using a very small numbers of parameters[42]. However, the challenge of choosing a universal operator $\hat{G}$ and the growing importance of the three-body terms in the transformed Hamiltonian are some of the reasons[43,44] why this method is not widely used nowadays.

2.8.4 R12/F12 Methods for Electronic Structure

So far, the use of various explicitly correlated methods, based on Gaussian geminals, ECGs and transcorrelated wavefunctions, has been outlined. The common basis of these approaches, is that the whole wavefunction (or the whole pair function $\langle u_{ij}|$) is expanded in explicitly correlated basis functions. In the 1980s, however, Kutzelnigg and Klopper proposed[45–47] a different MP2 approach, in which the pair function is expanded in a basis of products of virtual orbitals, the same way it is done in conventional MP2. This conventional expansion is then supplemented by only one (or a few) explicitly correlated basis function.

2.8.4.1 Definition

In R12 methods the pair function $|u_{ij}\rangle$ in the Hylleraas functional (equation 2.59) has the following form

$$|u_{ij}\rangle = |v_{ij}\rangle + |w_{ij}\rangle \tag{2.69}$$

where

$$|v_{ij}\rangle = \sum_{k<l} c_{ij}^{kl} \hat{Q}_{12} f_{12} |kl\rangle \tag{2.70}$$

and

$$|w_{ij}\rangle = \sum_{a<b} t_{ij}^{ab} |ab\rangle . \tag{2.71}$$

Herein, orbital indices i, j, k, l will be used for spin-orbitals that are occupied in the HF reference state, while indices a, b, c, d will be used for virtual spin-orbitals, and p, q, r, s for any molecular orbitals. All functions c_{ij}^{ab} and amplitudes t_{ij}^{ab} are restricted to be real. In the first implementations of R12 theory, the pair function was restricted to only the diagonal term:

$$\left|v_{ij}\right\rangle = c_{ij}\hat{Q}_{12}f_{12}\left|ij\right\rangle \tag{2.72}$$

with $c_{ij} \equiv c_{ij}^{ij}$.[45–47] However, although this "diagonal" *Ansatz* although avoids geminal BSSE[48,49] it is not invariant with respect to unitary transformations of the occupied orbitals. For example, different energies were obtained with canonical or localized HF orbitals. The projection operator $\hat{Q}_{12}$ that appears in equation 2.70, ensures the strong orthogonality of the pair function $\left|u_{ij}\right\rangle$. The factor f_{12} is called the correlation factor, and is a function of r_{12}, the distance between electrons 1 and 2. Originally, this factor was equal to the interelectronic distance, in other words $f_{12} = r_{12}$ and theories that use this correlation factor are referred to as R12 methods. More recently, the correlation factor was selected to be a function other than $f_{12} = r_{12}$, and in this case we speak of F12 theories, in order to highlight the fact that a particular correlation factor f_{12} is used instead of r_{12}.

2.8.4.2 Correlation factors

As already mentioned, all of the early studies that used the R12 methods have been based on the correlation factor

$$f_{12} = r_{12}. \tag{2.73}$$

Inclusion of r_{12} takes care of the correlation cusp, and satisfies the fact that the many-body wavefunction is linear in r_{12} for very small interelectronic distances. R12 calculations have been very successful for both small and medium sized systems, such as the benzene dimer,[50] water tetramer,[51] and ferrocene[52]. Despite its success, the use of r_{12} as a correlation factor has two main disadvantages. First, the three- and four-electron integrals involved in the electronic structure calculation cannot be evaluated analytically for a many-body problem. Even if we resort to the WOF approach in order to avoid the four-electron integrals, the evaluation of the three-electron ones still remains an obstacle. Second, although the linear r_{12} term yields a proper wavefunction for small interelectronic distances, it does not display the correct long-range behavior.

These two main drawbacks, can be addressed by altering the form of the correlation factor. Persson and Taylor[53,54] altered the correlation factor by fitting an expansion in Gaussian geminals to the linear r_{12} term:

$$r_{12} \approx \sum_{v} b_v[1 - \exp(-\gamma_v r_{12}^2)] \tag{2.74}$$

Using the WOF approach, we only need to evaluate three-electron integrals. Although these can be computed analytically, they are numerous and thus computationally expensive. Samson *et al.*[55] tried to eliminate the linear term, by multiplication with a Gaussian function:

$$f_{12} = r_{12}\exp(-\gamma r_{12}^2) = r_{12} + \mathcal{O}(r_{12}^3) \tag{2.75}$$

where γ is an exponent to be optimised, and $\mathcal{O}(r_{12}^3)$ are higher order terms of (r_{12}^3). By doing so, the correlation factor vanishes at large interelectronic distances, while it retains its linear form at small r_{12}. More recently, Ten-no suggested the use of a Slater-type geminal of the form

$$f_{12} = 1 - \exp(-\gamma r_{12}) = \gamma r_{12} + \mathcal{O}(r_{12}^2) \tag{2.76}$$

Calculations using this correlation factor returned excellent results[56,57]. If a given accuracy is obtained with the linear r_{12} term using an augmented correlation-consistent basis set of the type aug-cc-pVnZ, then the same accuracy can be obtained using the new correlation factors, and the next smaller basis set, aug-cc-pV($n-1$)Z. Since an increase in the cardinal number n causes an increase in computing time by an order of magnitude, it is clear that calculations with the new correlation factors can save significant, computing time.

2.8.4.3 Projection operators

In the first R12 publication,[46] the projection operator $\hat{Q}_{12}$ in the pair function equation 2.70, was chosen as

$$\hat{Q}_{12} = (1 - \hat{O}_1)(1 - \hat{O}_2) \tag{2.77}$$

in order to ensure that the pair function is strongly orthogonal to the HF reference state (on the basis of the Brillouin theorem). $\hat{O}_1$ is the projection operator onto the occupied Hartree-Fock orbitals

$$\hat{O}_1 = \sum_i |\phi_i(1)\rangle \langle \phi_i(1)| \;. \tag{2.78}$$

Klopper *et al.* suggested[58] to orthogonalize the two-electron basis function $\hat{Q}_{12} f_{12} |kl\rangle$ against all orbital products constructable in the given one-particle basis. This was achieved by the projection operator:

$$\begin{aligned} \hat{Q}_{12} &= (1 - \hat{P}_1\hat{P}_2)(1 - \hat{O}_1)(1 - \hat{O}_2) \\ &= 1 - \hat{O}_1(1 - \hat{P}_2) - (1 - \hat{P}_1)\hat{O}_2 - \hat{P}_1\hat{P}_2 \end{aligned} \tag{2.79}$$

where

$$\hat{P}_1 = \sum_p |\phi_p(1)\rangle \langle \phi_p(1)| \tag{2.80}$$

is the one-electron projection operator onto the given one-particle basis, in which the calculation is carried out.

Klopper *et al.* recognized,[58] that the many-electron integrals occurring due to the terms with the isolated projection operators onto the occupied space in equation 2.79, operators $\hat{O}_1$ and $\hat{O}_2$, can be approximated accurately using a resolution-of-the-identity (RI) approximation. This approximation implies that the operators $\hat{O}_1$ and $\hat{O}_2$ are replaced by the product operators $\hat{O}_1\hat{P}_2'$ and $\hat{P}_1'\hat{O}_2$, where

$$\hat{P}_1' = \sum p' \left|\phi_{p'}(1)\right\rangle \left\langle \phi_{p'}(1)\right| \tag{2.81}$$

is the projection operator onto an orthonormal auxiliary basis[59] $\{\phi_{p'}\}$. In this approximation the projection operator can be rewritten as:

$$\begin{aligned}\hat{Q}_{12} &= (1-\hat{V}_1\hat{V}_2)(1-\hat{O}_1)(1-\hat{O}_2) \\ &= 1-\hat{O}_1(1-\hat{P}_2)-(1-\hat{P}_1)\hat{O}_2-\hat{P}_1\hat{P}_2 \\ &\equiv 1-\hat{O}_1(\hat{P}'_2-\hat{P}_2)-(\hat{P}'_1-\hat{P}_1)\hat{O}_2-\hat{P}_1\hat{P}_2\,.\end{aligned} \tag{2.82}$$

In the case that the orbital basis set in which the wavefunction is expanded is used as auxiliary basis set for the RI approximation, then $\hat{P}_1 = \hat{P}'_1$, and then equation 2.82 reduces to

$$\hat{Q}_{12} \approx 1-\hat{P}_1\hat{P}_2 \tag{2.83}$$

So far, all equations incorporate equation 2.77, which is referred to as the original *Ansatz* of R12 theory, and known today as *Ansatz* 2. More details on the RI approximation and the *Ansatz* that is used in most calculations nowadays are discussed in sections 2.8.6.1 and 2.8.5.2 respectively.

2.8.5 Levels of F12 Theory

Concerning single-reference methods, the R12 approach has not only been implemented at the level of second-order Møller-Plesset perturbation theory (MP2), but also at higher orders of perturbation theory, as well as coupled-cluster theory. In this section the essential features of the MP2-F12 method will be described as an example.[60] The same basic technology can apply to coupled-cluster methods as well as multiconfigurational F12 wavefunctions.

2.8.5.1 Derivation of MP2-F12 equations

The first order Møller-Plesset wavefunction is obtained by minimizing the Hylleraas functional for the second-order MP energy (intermediate normalization is assumed):

$$H^{(2)}(\psi^{(1)}) = \left\langle \psi^{(1)} \middle| \hat{H}^{(0)} - E^{(0)} \middle| \psi^{(1)} \right\rangle + 2\left\langle \psi^{(1)} \middle| \hat{H}^{(1)} \middle| \psi^{(0)} \right\rangle \,. \tag{2.84}$$

The zeroth-order MP Hamiltonian is the Fock operator. The main difference between MP2 and MP2-F12 method, is the form of the second-order wavefunction: in conventional MP2 it contains only conventional doubly-excited determinants, whereas the MP2-F12 wavefunction also includes explicitly correlated geminal functions:

$$\left|\psi^{(1)}_{\mathrm{MP}}\right\rangle = \sum_{i<j,a<b} t^{ij}_{ab} \left|{}^{ab}_{ij}\right\rangle \tag{2.85}$$

$$\left|\psi^{(1)}_{\mathrm{MP-F12}}\right\rangle = \left|\psi^{(1)}_{\mathrm{MP}}\right\rangle + \sum_{i<j,x<y} t^{ij}_{xy} \left|{}^{xy}_{ij}\right\rangle \tag{2.86}$$

Indices i and j run over occupied orbitals, a and b over virtual orbitals, and α and β refer to a complete orthonormal one-electron basis, which in practice is a finite orbital basis that represent the resolution-of-the-identity (see section 2.8.6.1). The functions in the orthogonal complement are denoted complementary auxiliary orbitals and carry the indices x and y. The geminal basis functions are quasi-double excitations with respect to the reference:

$$\left|{}^{xy}_{ij}\right\rangle = \frac{1}{2}\bar{R}^{xy}_{\alpha\beta}\tilde{a}^{\alpha\beta}_{ij}\left|\psi^{(0)}\right\rangle \tag{2.87}$$

where $\bar{R}^{xy}_{\alpha\beta}$ are matrix elements of the explicitly correlated geminal factor $f(r_{12})$ projected by $\hat{Q}_{12}$:

$$\bar{R}^{xy}_{\alpha\beta} = \langle\alpha\beta|\,\hat{Q}_{12}f(r_{12})\,|xy\rangle\ . \tag{2.88}$$

The projector operator $\hat{Q}_{12}$ enforces strong orthogonality of the geminal functions $\left|{}^{xy}_{ij}\right\rangle$, in other words it ensures that the geminal functions are orthogonal to any single excitations and in most cases to the standard doubly excited determinants $\left|{}^{ab}_{ij}\right\rangle$. Traditionally the most common choice[61] for the projection operator was that of *Ansatz* 2, given by:

$$\hat{Q}_{12} = (1-\hat{O}_1)(1-\hat{O}_2) \tag{2.89}$$

but other forms of $\hat{Q}_{12}$ have been considered[59,62]. Nowadays, *Ansatz* 3C, and 3C(FIX) are the most commonly used. It should also be noted that the geminal-generating orbitals x and y are typically the (active) occupied orbitals, but other choices[63,64] have been considered.

In order to obtain the MP2-F12 energy, the Hylleraas functional is formally minimized by the following first-order wavefunction:

$$\left|\psi^{(1)}\right\rangle = -\hat{P}^{(1)}(\hat{H}^{(0)}-E^{(0)})^{-1}\hat{P}^{(1)}\hat{H}^{(1)}\left|\psi^{(0)}\right\rangle \tag{2.90}$$

where $\hat{P}^{(1)}$ projects on the first-order interacting space: in the case of MP method, it includes doubly excited determinants $\left|{}^{ab}_{ij}\right\rangle$ only, whereas MP-F12 it also includes geminal functions $\left|{}^{ab}_{ij}\right\rangle$. The matrix representation of equation 2.90 in the MP2-F12 method is:

$$\begin{pmatrix}\mathbf{T}_D\\ \mathbf{T}_R\end{pmatrix} = -\begin{pmatrix}\mathbf{H}^{(0)}_{DD} & \mathbf{H}^{(0)}_{DR}\\ \mathbf{H}^{(0)}_{RD} & \mathbf{H}^{(0)}_{RR}\end{pmatrix}^{-1}\begin{pmatrix}\mathbf{H}^{(1)}_{D}\\ \mathbf{H}^{(1)}_{R}\end{pmatrix} \tag{2.91}$$

where T_D and T_R are first-order coefficients of conventional doubly excited determinants and their geminal counterparts, as defined in equations 2.85 and 2.86 respectively. Although $\mathbf{H}^{(0)}_{DD}$ is diagonal in canoncal orbitals and can be easily inverted in the MP2 method, the zeroth-order matrix in MP2-F12 cannot be directly inverted since $\mathbf{H}^{(0)}_{DR} = (\mathbf{H}^{(0)}_{DR})^\dagger$ is non-zero. It can, however, be inverted by block-diagonalization, using the matrix $\mathbf{Y}$:

$$\mathbf{Y} = -(\mathbf{H}^{(0)}_{DD})^{-1}\mathbf{H}^{(0)}_{DR} \tag{2.92}$$

The transformation matrix

$$\begin{pmatrix}\mathbf{1} & \mathbf{Y}\\ \mathbf{0} & \mathbf{1}\end{pmatrix} \tag{2.93}$$

block-diagonalizes the zeroth-order Hamiltonian in equation 2.90

$$\begin{pmatrix}\mathbf{1} & \mathbf{0}\\ \mathbf{Y}^\dagger & \mathbf{1}\end{pmatrix}\begin{pmatrix}\mathbf{H}^{(0)}_{DD} & \mathbf{H}^{(0)}_{DR}\\ \mathbf{H}^{(0)}_{RD} & \mathbf{H}^{(0)}_{RR}\end{pmatrix}\begin{pmatrix}\mathbf{1} & \mathbf{Y}\\ \mathbf{0} & \mathbf{1}\end{pmatrix} = \begin{pmatrix}\mathbf{H}^{(0)}_{DD} & \mathbf{0}\\ \mathbf{0} & \bar{\mathbf{B}}\end{pmatrix} \tag{2.94}$$

where

$$\bar{\mathbf{B}} \equiv \mathbf{H}^{(0)}_{RR} - \mathbf{Y}^{\dagger}\mathbf{H}^{(0)}_{DD}\mathbf{Y} = \mathbf{H}^{(0)}_{RR} - \mathbf{H}^{(0)}_{RD}(\mathbf{H}^{(0)}_{DD})^{-1}\mathbf{H}^{(0)}_{DR}\,. \tag{2.95}$$

Transformation of equation 2.90 yields

$$\begin{pmatrix} \mathbf{T}_D \\ \mathbf{T}_R \end{pmatrix} = -\begin{pmatrix} \mathbf{1} & \mathbf{Y} \\ \mathbf{0} & \mathbf{1} \end{pmatrix} \begin{pmatrix} (\mathbf{H}^{(0)}_{DD})^{-1} & \mathbf{0} \\ \mathbf{0} & \bar{\mathbf{B}}^{-1} \end{pmatrix} \begin{pmatrix} \mathbf{H}^{(1)}_D \\ \bar{\mathbf{V}} \end{pmatrix}\,. \tag{2.96}$$

The final first-order MP2-F12 wavefunction is expressed as a sum of conventional F12 and "coupling" terms, respectively:

$$\begin{pmatrix} \mathbf{T}_D \\ \mathbf{T}_R \end{pmatrix} = -\begin{pmatrix} (\mathbf{H}^{(0)}_{DD})^{-1}\mathbf{H}^{(1)}_D \\ \mathbf{0} \end{pmatrix} - \begin{pmatrix} \mathbf{0} \\ \bar{\mathbf{B}}^{-1}\bar{\mathbf{V}} \end{pmatrix} + \begin{pmatrix} \mathbf{Y}\bar{\mathbf{B}}^{-1}\bar{\mathbf{V}} \\ \mathbf{0} \end{pmatrix}\,. \tag{2.97}$$

Although the standard doubles and geminal functions are orthogonal to each other, their coefficients are coupled via the off-diagonal $\mathbf{H}^{(0)}_{DR}$ block of the zeroth-order Hamiltonian. This zeroth-order coupling is relatively weak and vanishes rapidly as the basis set is enlarged.

The second order MP2-F12 energy can be represented as a sum of the conventional MP2 energy and the F12 correction term

$$\begin{aligned} E^{(2)}_{\mathrm{MP2-F12}} &= \left\langle \psi^{(0)} \middle| \hat{H}^{(1)} \middle| \psi^{(1)} \right\rangle \\ &= \begin{pmatrix} \mathbf{H}^{(1)}_D \\ \mathbf{H}^{(1)}_R \end{pmatrix}^{\dagger} \begin{pmatrix} \mathbf{T}_D \\ \mathbf{T}_R \end{pmatrix} \\ &= -(\mathbf{H}^{(1)}_D)^{\dagger} + (\mathbf{H}^{(0)}_{DD})^{-1}\mathbf{H}^{(1)}_D - \bar{\mathbf{V}}^{\dagger}\bar{\mathbf{B}}^{-1}\bar{\mathbf{V}} \\ &= E^{(2)}_{\mathrm{MP2}} + E^{(2)}_{\mathrm{F12}}\,. \end{aligned} \tag{2.98}$$

The above equation 2.98 is exact. Upon comparison to the conventional MP2 method, MP2-F12 involves several new matrices which are formulated in terms of four special intermediates of the F12 formulation:

$$\mathbf{H}^{(1)}_r : \left\langle \begin{smallmatrix} xy \\ ij \end{smallmatrix} \middle| \hat{H}^{(1)} \middle| \psi^{(0)} \right\rangle \equiv V^{xy}_{ij} \tag{2.99}$$

$$\begin{aligned} \mathbf{H}^{(0)}_{RR} : \left\langle \begin{smallmatrix} xy \\ ij \end{smallmatrix} \middle| \hat{H}^{(0)} - E^{(0)} \middle| \begin{smallmatrix} wz \\ ij \end{smallmatrix} \right\rangle &= \left\langle \begin{smallmatrix} xy \\ ij \end{smallmatrix} \middle| \hat{H}^{(0)} \middle| \begin{smallmatrix} wz \\ ij \end{smallmatrix} \right\rangle - E^{(0)} \left\langle \begin{smallmatrix} xy \\ ij \end{smallmatrix} \middle| \begin{smallmatrix} wz \\ ij \end{smallmatrix} \right\rangle \\ &\equiv B^{wz}_{xy} - (F^i_i + F^j_j)X^{wz}_{xy} \equiv (\tilde{B}^{(ij)})^{wz}_{xy} \end{aligned} \tag{2.100}$$

$$\mathbf{H}^{(0)}_{RD} : \left\langle \begin{smallmatrix} xy \\ ij \end{smallmatrix} \middle| \hat{H}^{(0)} - E^{(0)} \middle| \begin{smallmatrix} ab \\ ij \end{smallmatrix} \right\rangle = \left\langle \begin{smallmatrix} xy \\ ij \end{smallmatrix} \middle| \hat{H}^{(0)} \middle| \begin{smallmatrix} ab \\ ij \end{smallmatrix} \right\rangle \equiv C^{ab}_{xy}\,. \tag{2.101}$$

These intermediates, V^{xy}_{ij}, $(\tilde{B}^{(ij)})^{wz}_{xy}$ and C^{ab}_{xy} invoke different many-electron integrals. Intermediate B involves up to four-electron integrals, intermediates X and V up to three-electron integrals, and C is a two-electron integral:

$$B^{ow}_{xy} \equiv \langle xy|\, \hat{\gamma}_{12}\hat{F}_{12}\hat{\gamma}_{12}\, |ow\rangle \tag{2.102}$$

$$X^{ow}_{xy} \equiv \langle xy|\, \hat{\gamma}^{\dagger}_{12}\hat{\gamma}_{12}\, |ow\rangle \tag{2.103}$$

$$V^{xy}_{ij} \equiv \langle ij|\, \frac{1}{r_{12}}\hat{\gamma}_{12}\, |xy\rangle \tag{2.104}$$

$$C_{xy}^{ab} \equiv \langle xy| \, \hat{\gamma}_{12}\hat{F}_{12} \, |ab\rangle \tag{2.105}$$

where

$$\hat{\gamma}_{12} \equiv \hat{Q}_{12} f(r_{12}) \, . \tag{2.106}$$

These integrals can be evaluated analytically only in the case that the correlation factor is Gaussian. In addition, four-electron integrals can be avoided using the WOF. Although there have been analytical evaluations[53] of these integrals, the computational complexity of such calculations is high[65]. Approximate techniques of evaluating these integrals, have been extremely helpful for all F12 methods.

2.8.5.2 CCSD(T)-F12

Although the use of *Ansatz* 2, which was described earlier, is possible, most computational packages including MOLPRO[66] use the 3C diagonal *Ansatz* with fixed amplitudes [abbreviated as 3C(FIX)[67]] as the default. This *Ansatz* is based on the diagonal *Ansatz*, but the amplitudes T_{ij}^{ij} and T_{ji}^{ji} are not determined from the perturbation equation, but rather fixed to

$$T_{ii}^{ii} = t_s \tag{2.107}$$

$$T_{ij}^{ij} = \frac{1}{2}(t_s + t_p) \qquad (i \neq j) \tag{2.108}$$

$$T_{ji}^{ji} = \frac{1}{2}(t_s - t_p) \qquad (i \neq j) \tag{2.109}$$

(all other T_{kl}^{ij} are set to zero, as dictated by the diagonal *Ansatz*). In the closed-shell case and for spatial orbitals, the values $t_s = 1/2$ and $t_p = 1/4$ are obtained from the s- and p- wave cusp conditions, respectively[25,68]. The conventional external pair functions are augmented by terms of the form:

$$\left| u_{ijp}^{F12} \right\rangle = \sum_{p=\pm 1} \sum_{ij} T_{ij}^{ijp} \hat{Q}_{12} \hat{F}_{12} \, |ij\rangle \, . \tag{2.110}$$

This *Ansatz* is unitarily invariant, size consistent, and free of geminal BSSE, and yields the most accurate results for MP2-F12. Since the triples (T) correction in CCSD(T)-F12 calculations requires the use of canonical orbitals, the FIX approximation is used by default in CCSD-F12 and CCSD(T)-F12 calculations.

A CCSD calculation first performs a DF-MP2-F12 calculation, and then performs the CCSD-F12 without density fitting (details on density fitting techniques can be found in section 2.8.6.2). In this case the amplitudes of the explicitly correlated terms are determined in the MP2-F12 calculation and kept fixed in the CCSD-F12.[69,70]

Furthermore several approximations of CCSD-F12 have been proposed, with CCSD-F12x (x =a,b) to be one of the most widely used ones.[71,72] In CCSD-F12a only linear terms in the amplitudes T_{kl}^{ij} are kept as well as those are treated at second-order perturbation theory level. As for CCSD-F12b more coupling terms between the conventional and explicitly correlated amplitudes are included. Those rather strong simplifications are very good approximations to the CCSD basis set limit, even when a double-zeta basis set is used.

In addition, the perturbative triples correction can be invoked by using CCSD(T)-F12. In most cases explicit correlation is not implemented in the perturbative triples correction, and therefore the basis set error of the triples is not affected significantly by the F12 (although some small changes of the triples energy arise from the fact that the doubles amplitudes are affected by the F12 terms). In some cases, pragmatic improvement of the triples can be obtained by scaling the triples energy contribution as follows:

$$\Delta E_{(\mathrm{T}*)} = \frac{\Delta E_{(\mathrm{T})} E_{\mathrm{corr}}^{\mathrm{MP2-F12}}}{E_{\mathrm{corr}}^{\mathrm{MP2}}} \tag{2.111}$$

More technical details on coupled-cluster F12 methods can be found in appropriate review papers.[73,74]

2.8.6 Approximations of Many-Electron Integrals

It has already been shown that the slow convergence of dynamic correlation energies using conventional CI expansion can be efficiently bypassed in explicitly correlated electronic structure theory. However, there is a penalty associated with the latter, and that is the introduction of many-electron integrals which consist of one of the operators in the electronic Hamiltonian and a power of correlation factors. The success of the recent explicitly correlated methods is attributed to the progress of treatment of many-electron integrals.

2.8.6.1 Resolution-of-the-identity

The evaluation of three- and four- electron integrals that appear in matrix elements can be facilitated via an approximate resolution-of-the-identity (RI).[45,47,75] For example, the following three-electron integral, which appears in all linear R12 methods, is reduced to products of two-electron integrals:

$$\langle ijm | r_{12} r_{13}^{-1} | klm \rangle \approx \sum_{p'} \langle ij | r_{12} | p'm \rangle \langle p'm | r_{12}^{-1} | kl \rangle \tag{2.112}$$

For technical simplicity, an RI basis of atom-centered Gaussian functions is most often used. In addition, for the rest of this section, there is no implication that $\langle ij|$ and $|kl\rangle$ are antisymmetrized products of spin-orbitals. Rather, a simple spatial orbital picture is used, and we are concerned with integrals over spatial orbitals.

Kutzelnigg realized[45] that the partial wave analysis of the RI error in atoms can establish basic requirements on the RI basis $\{p'\}$, that could potentially apply to molecules as well. The above three-electron integral has a partial wave expansion that truncates at angular momentum $3\ell_{\mathrm{occ}}$ for atoms. In other words, the RI for such an integral is exact, if the RI basis is saturated to $3\ell_{\mathrm{occ}}$. The original implementation of F12 methods utilized the orbital basis set (OBS) for the RI. This meant that the OBS had to be very large. Klopper and Samson were the first to implement[59] a version of MP2-R12 theory, using a separate RI basis, known as the auxiliary basis set (ABS). The ABS method involves replacement of the projector $\hat{P}'$ on any orthonormal RI basis:

$$1 \to \hat{P}' \, . \tag{2.113}$$

This revolutionary ABS method allows us to control the RI error, as it can be made as small as desired by increasing the completeness of the ABS. Unfortunately, in cases where the ABS is not sufficiently complete, the RI error can rise too quickly. A key requirement of the RI basis set is that it spans the HF basis set exactly:

$$\hat{P}\hat{P}' = \hat{P} \, . \tag{2.114}$$

When this condition does not hold, the ABS approximation breaks down:

$$\text{exact: } \hat{P}(1 - \hat{P}) = 0 \tag{2.115}$$

$$\text{ABS: } \hat{P}(\hat{P}' - \hat{P}) \neq 0, \text{ if } \hat{P}\hat{P}' \neq \hat{P}' \, . \tag{2.116}$$

Unfortunately, the errors arising from a calculation with a small OBS can be significant, and in these situations it is recommended to include the HF basis set into the ABS, since that satisfies automatically the condition of equation 2.114. This approach is labeled Complementary auxiliary basis set, CABS+ and has a smaller RI error than the ABS method,[61] at the expense of a larger ABS, and thus a larger computation time. More details on methods of developing and optimising ABS for atomic and molecular calculations will be discussed in a later section 3.5.

2.8.6.2 Density fitting

Manby introduced[76,77] the density fitting (DF) technique in explicitly correlated theory. DF approximates all of the four-index 2-electron integrals in the explicitly correlated theories by representing orbital products in terms of auxiliary basis functions:

$$\phi_p(\vec{r})\phi_q(\vec{r}) \simeq \sum_A C^A_{pq} \Xi_A(\vec{r}) \, . \tag{2.117}$$

The expression above might seem like an RI approximation, and in fact such expansions are sometimes called RI approximations. However, the above is not a standard RI expression. Use of the DF approximation reduces significantly the computational time required for explicitly correlated calculations and is thus extremely efficient. The errors that arise from the fitting process are minimizing by using robust fitting formulas throughout all integral evaluations, such that the error in each fitted integral is quadratic in the error of the fitted orbital product densities.[78,79] Density fitting has been proven to be very helpful, and although it was originally designed for DFT,[80,81] it has nowadays been implemented in a variety of *ab initio* methods, including SCF,[82,83] MP2,[84,85] MCSCF[86,87] and CCSD.[88]

If we examine a conventional MP2 calculation, the most time-consuming step is actually the $\mathcal{O}(N^5)$ integral transformation [the energy evaluation scales as $\mathcal{O}(N^4)$]. The overall integral transformation is

$$(ia|jb) = \sum_{\mu\nu\rho\sigma} C^i_\mu C^a_\nu C^j_\rho C^b_\sigma (\mu\nu|\rho\sigma) \tag{2.118}$$

where $(ia|jb)$ are the required integrals in the MO basis. In equation 2.118 i and j are occupied orbitals, a and b are virtual orbitals, $(\mu\nu|\rho\sigma)$ are the AO-basis integrals, and C^i_μ is the contribution of AO basis function μ to molecular orbital i, etc. If there are N_{occ} occupied orbitals and N_{vir} virtual orbitals, then there are $N^2_{\text{occ}}N^2_{\text{vir}}$ of the required MOs integrals, ignoring permutational symmetry. Thus the transformation above would appear to require on the order of $N^2_{\text{occ}}N^2_{\text{vir}}N^4_{\text{OBS}}$ floating-point operations. However, due to factorization the actual cost is less:

$$(i\nu|\rho\sigma) = \sum_\mu C^i_\mu (\mu\nu|\rho\sigma) \qquad N_{\text{occ}}N^4_{\text{OBS}} \tag{2.119}$$

$$(ia|\rho\sigma) = \sum_\nu C^a_\nu (i\nu|\rho\sigma) \qquad N_{\text{occ}}N_{\text{vir}}N^3_{\text{OBS}} \tag{2.120}$$

$$(ia|j\sigma) = \sum_\rho C^j_\rho (ia|\rho\sigma) \qquad N^2_{\text{occ}}N_{\text{vir}}N^2_{\text{OBS}} \tag{2.121}$$

$$(ia|jb) = \sum_\sigma C^b_\sigma (ia|j\sigma) \qquad N^2_{\text{occ}}N^2_{\text{vir}}N_{\text{OBS}}. \tag{2.122}$$

Since N_{OBS} is the largest quantity, the first step, as given in equation 2.119, is the most time-consuming. In the DF approach, the factorization can be more effective:

$$b^Q_{i\nu} = \sum_\mu C^i_\mu b^Q_{\mu\nu} \qquad N_{\text{occ}}N^2_{\text{OBS}}N_{\text{aux}} \tag{2.123}$$

$$b^Q_{ia} = \sum_\nu C^i_\nu b^Q_{i\nu} \qquad N_{\text{occ}}N_{\text{vir}}N_{\text{OBS}}N_{\text{aux}} \tag{2.124}$$

$$(ia|jb) = \sum_Q b^Q_{ia} b^Q_{jb} \qquad N^2_{\text{occ}}N^2_{\text{vir}}N_{\text{aux}}. \tag{2.125}$$

The most expensive step of the DF transformation is the last one, with a cost of $\mathcal{O}(N^2_{\text{occ}}N^2_{\text{vir}}N_{\text{aux}})$ which is much less that $N^2_{\text{occ}}N^2_{\text{vir}}N^4_{\text{OBS}}$ from the conventional transformation, even considering the fact that $N_{\text{aux}} \approx 3N_{\text{OBS}}$. The error caused by the DF approximations is very small, as long as an appropriate DF auxiliary basis set is used. The different auxiliary basis sets that are typically used for different methods will be discussed on Chapter 3.

Chapter 3

Basis Sets: a condensed review

3.1 Introduction

In Chapter 2 the so called "methods" of electronic structure have been discussed. The scope of these methods is to expand the N-electron wavefunction to describe the system of interest as accurately as possible. The other main "approximation" that one needs to consider in order to perform a quantum mechanical calculation is the choice of basis set, in other words the way in which the one-electron wavefunctions (or orbitals) are expanded:

$$\phi_i = c_{1i}\chi_1 + c_{2i}\chi_2 + c_{3i}\chi_3 + \cdots + c_{ni}\chi_n \Rightarrow \phi_i = \sum_r c_{ri}\chi_r \,. \tag{3.1}$$

The combination of these two approximations dictates the overall accuracy of the calculation, as well as its corresponding computational cost.

3.1.1 Slater and Gaussian Type Orbitals

In mathematics, a basis set is a collection of vectors that spans a space in which a problem is solved. In most cases that includes a Cartesian, 3D linear vector space of $\hat{\imath}$, $\hat{\jmath}$, and $\hat{k}$. In the context of quantum mechanics, a basis set refers to the set of (non-orthonormal) one-electron wavefunctions (orbitals or atomic orbitals), centered at each nucleus within the molecule, that are utilised in order to construct molecular orbitals. This approximation is referred to as LCAO-MO and denotes that the molecular orbitals (or MOs) are built as a linear combination of atomic orbitals (LCAO) (see equation 3.1). Within the basis set, the wavefunction is represented as a vector of the coefficients of the linear combination of the basis functions (or atomic orbitals). One-electron operators correspond to rank two tensors or matrices, whereas two-electron operators correspond to rank four tensors.

The basis sets that provide the "best" physical representation of the system of interest are the so-called Slater-type orbitals (STOs). STOs are solutions to the Schrödinger equation of hydrogen-like atoms, that decay exponentially far away from the nucleus, and have the following form:

$$\phi_{abc}^{\mathrm{STO}}(x,y,z) = N x^a y^b z^c e^{-\zeta r} , \tag{3.2}$$

where N is a normalisation constant, a, b, and c control the angular momentum ℓ , and ζ (often referred to as the basis set exponent) controls the width of the orbital (large ζ corresponds to a tight function and small ζ to a diffuse one). STOs have the great advantage that they decay from the center in a similar manner as the "true" orbitals, and they also satisfy Kato's cusp condition at the nucleus, (discussed in section 2.8.2) thus accurately describing the electron density near the nucleus. STOs therefore provide both a correct short and long-range behaviour. The exponential dependence on the distance between the nucleus and the electron (r) mirrors the exact decay behavior of the orbitals for the hydrogen atom. However, STOs do not have any radial nodes, which are introduced by making linear combinations of STOs. While this exponential dependence ensures a rapid convergence with increasing number of functions, unfortunately, calculating the integrals that arise when STOs are used is computationally expensive. Since the electron-electron interactions are present in the Hamiltonian, three- and four-centre two electron integrals arise, which cannot be solved analytically. These integrals are difficult to calculate, and require excessive amounts of time and resources. For that reason STOs are primarily used for atomic and diatomic systems where high accuracy is required, and in some semi-empirical methods where all three- and four- center integrals are neglected.

In order to tackle the computational bottleneck associated with STOs, Gaussian-Type orbitals, or GTOs, were developed. The form of a GTO is quite similar with that of an STO, with the difference being the the quadratic r dependence within the exponential factor:

$$\phi_{abc}^{\mathrm{GTO}}(x,y,z) = N x^a y^b z^c e^{-\zeta r^2} . \tag{3.3}$$

It is evident that GTOs no longer have a cusp at the nucleus, and furthermore, they seem to fall off too rapidly for large values of r. They do therefore provide a "poorer" physical representation of the system. GTOs are able to address this issue, and can provide results as good as those arising from STOs, provided the GTO basis set is much larger than the STO one. That increase in number of basis functions, however, is more than compensated for by the ease by which the required integrals can be calculated, mainly due to the Gaussian Product rule (which states that any product of two Gaussians at different centers is equivalent to a single Gaussian function centered at a point between the two centers). Thus, in terms of computational efficiency, GTOs are almost always preferred, and are used almost universally as basis functions in electronic structure calculations. From this point onwards, all mentioned basis sets will be of the GTO type.

3.1.2 Quality of Basis Sets

Working inside the atom-centered GTO framework, basis sets are usually classified based on the number and type of functions that they contain. They typically come in hierarchies of increasing size, providing us with a systematic way to obtain increasingly accurate solutions, at increasing computational cost. The simplest basis sets that one can use, the ones that contain the smallest number of functions possible, are called "minimal" basis sets, as they only possess the necessary functions to contain the electrons within an atom. In practice, minimal basis sets are rarely used due to the fact that they allow for little or no electron correlation. Use of minimal basis sets results in energies and wavefunctions that are far from the desired limit of accuracy.

One way to improve upon a minimal basis set would be to double the number of functions on each atom. For example we could expand the minimal basis set of nitrogen (N), that would originally contain two s and one three-component p function, by doubling it, to a set that contains four s and two p functions, a double zeta (DZ) set. In a similar way we could triple, quadruple and so on the number of basis functions with respect to the minimal basis set, and obtain the corresponding triple zeta (TZ) and quadruple zeta (QZ) sets respectively. In order to balance between the inadequacy of a minimal basis set and the computational demand of a DZ or TZ basis set, split-valence basis sets were developed. Split-valence basis sets are slightly modified versions of the corresponding nZ basis sets where only the basis functions that corresponding to the valence electrons of a given element are increased in zeta. These sets are still referred to as DZ or TZ quality, but the abbreviations VDZ or VTZ (valence double zeta and valence triple zeta, respectively) are used to avoid mix-ups and provide additional clarity.

Another addition that leads to improved basis sets is that of polarisation functions. Polarisation functions are higher angular momentum functions, beyond those required to properly describe the atom of interest. In general to polarise a basis function with angular momentum ℓ, we would have to include with basis functions of angular momentum of at least $\ell + 1$. This results to "polarised n-zeta" quality basis sets. Polarisation functions are extremely significant for investigations using electron correlation.[89] Basis sets that include additional polarisation functions are often denoted with a $\star$, or with letters denoting the angular momentum shell that is being added, such as (p), (pd) and so on.

Finally, one can add extra functions to a basis set in order to achieve a better orbital representation. Diffuse functions (functions with small ζ exponent) help describe the "tail" portion of the atomic orbital, when the electron is held far away from the nucleus. Inclusion of additional diffuse functions is particularly important for anions, Rydberg states, and very electronegative atoms with a lot of electron density. Diffuse sets are often denoted with the word augmented, such as aVDZ or augmented valence double zeta, or with a $+$.

Combinations of the above schemes have resulted in several families of modern basis sets, suited to treat most electronic structure calculation problems.

3.1.3 Contraction Patterns

Basis functions in the form of equation 3.3 are known as Gaussian primitives (or just primitives). In most cases, for reasons of balance and efficiency, a linear combination of primitives is used to produce contracted functions.

$$\phi^{\text{contr}} = \sum_i n_i \phi_i^{\text{GTO}} , \tag{3.4}$$

where ϕ_i^{GTO} is a Gaussian primitive and n_i is the corresponding contraction coefficient.[90] While the above contraction scheme is simply a linear combination, there are two distinct methods of contraction that differ in which primitives are contracted and the way (or pattern) of contraction. The first contraction is scheme is called general contraction. In this scheme all primitives of the same angular momentum are present in every contracted function of the same angular momentum. Any given primitive has a different contraction coefficient for each contracted function. The second contraction scheme is called segmented contraction and includes disjointed contractions; here each primitive contributes to a single contraction. Occasionally, one or two primitives may appear in more than one contraction, but this is an exception and not the general rule.

In both contraction patterns, it is common to include a number of primitives in their uncontracted form (single primitives with a contraction coefficient of 1). When listing the basis set composition, both contraction schemes are expressed in the style $(14s8p5d3f2g) \rightarrow [7s6p3d2f1g]$, where the parenthesis denotes the primitive and the square brackets the contracted composition. This notation provides almost no information about the contraction pattern itself, and therefore in order to obtain details of the pattern one should refer to the original publication, or to some list of exponents and contraction coefficients.

While a general contraction scheme may seem more advantageous, segmented contraction schemes are more popular due to the fact that most popular *ab initio* packages do not implement efficient integral calculations with general contractions; integral calculations with general contractions are much more complex than those for the segmented case.

3.1.4 Basis Set associated errors

In practice, all quantum chemical calculations are performed using a finite number of basis functions. The truncation of the infinite basis set is an omnipresent important source of error in all electronic structure calculations. This error is referred to as basis set truncation error or basis set incompleteness error (BSIE). This error is addressed by creating basis sets in a systematic way, that reduces the basis set truncation error as the size of the basis increases. Furthermore, we can extrapolate results obtained with finite basis sets to a theoretical value that would correspond to that of an infinite basis set. When the finite basis set is expanded towards a theoretically infinite and complete set of functions, then the calculation is said to approach the complete basis set (CBS) limit.

Another source of error arises from the artifact that when two atoms A and B form the AB molecule, the basis set centered in A will be influenced by the basis set centered in B and viceversa. This will cause an improvement in the description of both atoms, and this error is called basis set superposition error (BSSE).[91,92] When large, saturated basis sets are used, BSSE is minimal. However, the increase of basis set size causes an increase in computational cost. Moreover, the saturation of the atomic basis set does not imply the saturation of the molecular basis set, since polarisation functions are often required for the proper bond description. Moreover, the basis sets commonly employed in molecular calculations are not saturated for atomic systems, due to the computational limitations of the calculation and storage requirements of the integrals.

Boys and Bernardi proposed a method that evaluates the BSSE, the so called counterpoise correction.[93] The molecular interaction energy of the dimer AB is given by

$$\Delta E_{\text{int}}(AB) = E_{AB}^{AB}(AB) - [E_A^A(A) + E_B^B(B)] \,, \tag{3.5}$$

where the subscript indicates the system of interest, while the superscript indicates the basis set used for the calculation. In order to remove the artificial stabilisation of each monomer that is caused by the presence of basis functions from the other monomer, the energy of each monomer is computed with the basis set used in the molecular calculation of AB, including polarisation functions if any, and with all the functions centered in the same points as they were centered in AB. The corrected interaction energy is then given by:

$$\Delta E_{\text{int}}^{\text{Corr}}(AB) = E_{AB}^{AB}(AB) - [E_A^{AB}(A) + E_B^{AB}(B)] \,. \tag{3.6}$$

This method is a useful evaluation and correction of the BSSE. However, following this procedure can lead to overestimation of the BSSE[94] since the atomic basis sets contain functions that shared between several atoms in the molecular environment, while describing only one in the atom. Different electronic structure methods can overestimate or underestimate the BSSE, and therefore in most cases a counterpoise correction is advisable. Unfortunately, this would lead to $2N+1$ computations for a system containing N atoms, and this is not always computationally feasible.

3.2 Atomic Natural Orbitals

The majority of modern basis set are somewhat influenced by the atomic natural orbital basis sets (ANO sets)[95–97] of Almlöf and Taylor, as well as from Ahlrichs's work, which can be considered as the origin of correlation consistent basis sets.[98] ANOs main goal was to reduce the contraction error (the energetic difference between calculations with a contracted and an uncontracted basis set) in post HF calculations. The development of ANOs was based on the work of van Duijneveldt,[99] that provided the primitive sp basis set. That primitive set was then generally contracted, with a well-controlled contraction error at the limit of chemical accuracy (1 kcal/mol). The contraction coefficients were the natural orbital coefficients of a CISD calculation (carried out using the uncontracted basis set). Polarisation functions were subsequently added to the sp set in an even-tempered manner and then contracted in the same way, until a family of basis sets for H-Ar was obtained.

$$\alpha_i = \alpha\beta^{i-1} \,. \tag{3.7}$$

A similar protocol was followed for transition metal elements; the main difference was that the natural orbitals were produced using the average of different density matrices obtained from several electronic states.[100,101] Different variations of ANOs that utilised a similar averaging of density matrices resulted in the development of alternative ANO-type basis sets (ANO-L) of Roos and coworkers,[102] as well as ANO basis sets for the second row elements,[103] and for the 3*d* transition metal elements.[104] Smaller ANO-type basis sets (ANO-S) for H-Ar were also developed by Roos and coworkers.[105] Newer iterations of ANO-style basis sets that aimed for basis sets of the same quality for the whole periodic table have also been created (ANO-RCC).[106–108,108–110] The ANO-S, ANO-L, and ANO-RCC basis sets are widely used and are the standard basis sets within the MOLCAS software.[111]

3.3 Correlation Consistent Basis Sets

The high computational cost associated with the large size of the original ANO basis sets, was a significant reason that hindered their use. An alternative approach, originally developed by Dunning[22] for the atoms H and B-Ne, led to the development of the correlation consistent (cc) family of basis sets. The cc basis sets are energy-optimised and follow a general contraction pattern for the functions describing the occupied orbitals. The main advance of the cc basis sets was the realization that when additional uncontracted higher angular momentum polarisation functions were added to the basis set, the incremental change in correlation energy at the CISD level could be split into discrete groups based on their magnitude. In Figure 3.1 it can be easily seen that the effect of adding a single *d* function has the biggest impact on the energy, while the addition of a second *d* function has approximately the same effect as the addition of a single *f* function. In a similar manner, groupings can be formed by adding a third *d* function, a second *f* function and a single *g* function. Each function within the grouping adds an approximately consistent amount of correlation energy, hence the correlation consistent naming. These groupings were combined with with split-valence DZ, TZ, and QZ quality groups of *s* and *p* functions, and a small number of *s* and *p* polarisation functions, to form the cc basis sets that are known as cc-pVDZ, cc-pVTZ, and cc-pVQZ (correlation consistent polarised valence *n* zeta). In order to avoid (methodological) repetition, more details on the optimisation procedure of the sets of interest will follow in the subsequent sections that discuss the explicitly correlated cc sets, as well as in Chapter 5.

The cc basis sets were designed to converge smoothly towards the CBS limit, since as the cardinal number *n* of the basis set increases, energies and various properties converge smoothly toward the CBS limit. This provides a way to systematically improve *ab initio* calculations with respect to the BSIE toward the exact solution of the time-independent non relativistic electronic Schrödinger equation. In order to reach the CBS limit, different extrapolation procedures have been developed, more details of which can be found in Reference 112.

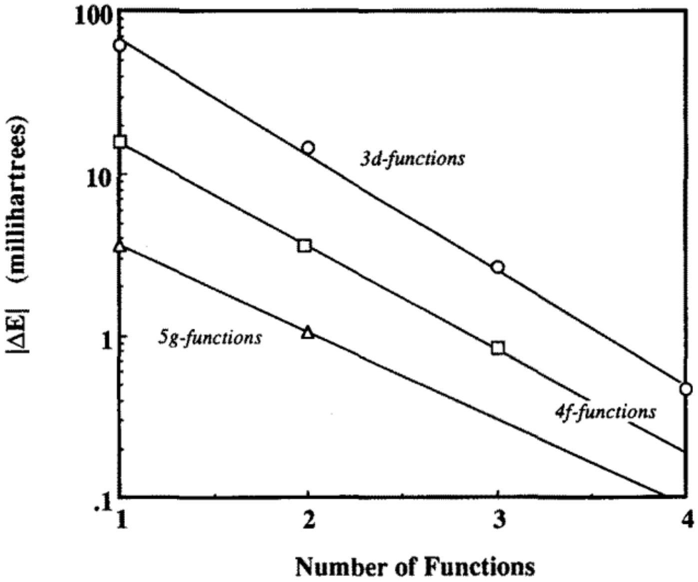


Figure 3.1: Incremental contributions of polarisation/correlating functions to the CISD correlation energy for the oxygen atom, as used in Reference 22 for the design of the correlation consistent basis sets. Figure reproduced with permission from AIP Publishing LLC.

The same protocol used in the original cc paper has been then extended to higher cardinal numbers, such as cc-pV5Z and cc-pV6Z for H-Ne (and even higher, such as cc-pV10Z for Ne)[113–116] as well as to cc basis sets for the second row elements (Na-Ar)[114,117,118] and third row main group elements (Ga-Kr).[119] In addition to the systematic improvement toward the CBS limit, cc basis sets exist in a multitude of variations that adapt the original idea to heavier elements, or augments the sets with diffuse functions or more generally with primitives that describe properties of interest.[120]

Correlation consistent sets that were augmented with additional diffuse functions, typically optimised for atomic anions, for every angular momentum present in the basis. These sets, denoted aug-cc-pV*n*Z sets were developed for accurate description of electron affinities (EAs) as well as non covalent interactions.[121] Since then, it has become common for researchers to develop diffuse augmented sets alongside their "parent set" and in some cases doubly (d-aug-cc-pV*n*Z) and triply (t-aug-cc-pV*n*Z) augmented basis sets are available.[115]

Most *ab initio* programs use the so-called frozen-core approximation when performing correlated electronic structure calculations and for that reason all original (parent) cc basis sets were designed alongside this fact. It is in some cases, however, important to correlate an additional shell of electrons (core electrons), by adding a number of optimised tight functions to the parent basis set. The exponents can be optimised with respect to the difference between valence-only and core and valence correlation energies, as done in cc-pCV*n*Z sets[24,122–124] or a weighted scheme can be utilised, in which the core-valence contribution to the correlation energy is strongly weighted over the core-core, as in cc-pwCV*n*Z sets.[24,122]

While scalar relativistic effects are typically small for the lighter elements of the periodic table, they may need to be included in cases where very-tight accuracy is the objective. This is most commonly done by utilising a Douglas-Kroll-Hess (DKH) Hamiltonian.[125] When DKH Hamiltonians are used in conjunction with standard cc basis sets, large errors can arise.[126] Rather than redesigning the basis set from scratch, a study by Dixon and coworkers showed that simply recontracting the primitives of basis sets in atomic DKH calculations, produced sufficiently good results for most elements, and was thus an appropriate solution.[114,126]

Although a succesful protocol for the design of cc basis sets for lighter elements has been established, heavier elements present a bigger heterogeneity of challenges, such as greater relativistic effects and many common oxidation states, on top of the main computational difficulty that arises from their larger total number of electrons. While cc sets for lighter elements are all-electron basis sets (i.e. they contain functions for all electrons) practical considerations render that imposible for heavier elements. Therefore cc basis sets that utilised pseudopotentials (PP), which are also called effective core potentials (ECPs), were developed. The use of PPs tackles two of these problems, since PPs accurately include scalar relativistic effects in a simple fashion, while replacing a number of core electrons, thus reducing the size of the basis set. PPs are most commonly split in two different sizes, large- and small-core . Large-core PPs replace all but the valence electrons, while small-core PPs maintain an additional core-valence shell of electrons on top of the valence ones. Some initial cc sets, matched to the large-core Stuttgart-Dresden-Bonn PPs,[127] were produced for elements Ga-Kr and In-Xe at TZ and QZ quality.[128] Subsequently, cc basis sets from DZ to 5Z quality, matched to the small-core Stuttgart-Köln PPs,[129–131] were developed for the post-*d* main group elements. These sets were denoted cc-pV*n*Z-PP and included diffuse augmented and core-valence variants.[132] As already mentioned,[128,133] inclusion of core-valence correlation is crucial for systems containing the group 13-15 elements, and the significance increases further down the groups.[132] Revised PP and accompanying cc sets that provide an increase in accuracy were also developed.[134] Additionally, cc sets for fully relativistic calculations on post-*d* main group elements of DZ-QZ quality were developed[135–139] along with a core-correlation variant.[140] Over the past few decades, a wide variety of cc sets have been developed for the majority of the periodic table. Details on the development of cc sets that involve transition metal elements, will be discussed in Chapter 6. Details on the different variations of cc sets that span the periodic table can be found in a recent review by Hill.[141]

3.4 Basis sets for Explicitly Correlated Methods

3.4.1 Introduction

As discussed in section 2.8.2, one of the biggest drawbacks of standard correlated electronic structure methods is the slow convergence with respect to one-particle basis set. The correlation energy in particular, converges towards the complete basis set (CBS) limit at a rate of about ℓ_{max}^{-3} where ℓ_{max} is the maximum angular momentum in the basis set. An efficient route around the basis set problem is the use of explicitly correlated techniques, as described in section 3.4. However, commonly used basis sets that are used to describe electron correlation effects, such as standard correlation consistent basis sets, are not optimal for use with explicitly correlated calculations. These basis sets attempt to describe not only the HF wavefunction, but also correlation effects involving both the correlation hole and the long-range portion of the electronic wavefunction. Since in F12 methods the correlation hole of the wavefunction can be accurately described by the (nonlinear) correlation factor, the one-particle basis set must only describe the HF wavefunction and the long-range electron correlation effects. This fact led to the development of new basis sets that are specifically designed for explicitly correlated methods, which substantially accelerate the calculations of electronic structure while recovering the maximum amount of correlation energy.

3.4.2 Correlation-consistent basis sets for explicitly correlated wavefunctions

Over the past few years, Peterson, Hill, and coworkers have developed new Gaussian basis sets specifically designed for use in F12 calculations. This has led to the series of cc-pV*n*Z-F12 (*n*=D, T, Q) orbital basis sets (OBSs)[142] for atoms H-Ar, the cc-pCV*n*Z-F12 (*n*=D, T, Q) and aug-cc-pV*n*Z-F12 (*n*=D, T, Q, 5) OBSs and corresponding ABSs[124] for atoms B-Ne and Al-Ar, the cc-pV*n*Z-F12 and cc-pCV*n*Z-F12 (*n*=D, T, Q) OBSs[143] for atoms Li, Be, Na and Mg, and finally the cc-pV*n*Z-PP-F12 OBSs along with ABSs[144] for post-*d* elements Ga-Rn. Each of these is reviewed in the subsequent section, while papers that focus solely on the development of ABS are discussed in Section 3.5.

3.4.2.1 cc-pV*n*Z-F12 (*n* = D-Q) for H, He, Be-Ne, and Al-Ar

Peterson and coworkers produced[142] basis sets for use with explicitly correlated methods (F12 methods) based on the original work of Dunning[22] for correlation consistent basis sets. These new sets were developed at the MP2-F12 level of theory, using the non-linear correlation factor $e^{-\beta r_{12}}$ for main group elements through the second row (H, He, B-Ne and Al-Ar). The resulting sets denoted cc-pV*n*Z-F12 (*n* = D, T, Q) exhibit improved convergence of MP2-F12 atomic and molecular correlation energies compared to both the standard (cc-pV*n*Z) and diffuse-augmented correlation consistent basis sets (aug-cc-pV*n*Z).

In all optimisations discussed in this section, only the valence electrons were correlated (frozen-core approximation), and the optimisation of basis set exponents employed numerical gradients using either the conjugate gradient or Simplex algorithms[145] (see Chapter 4). Conventional HF calculations were performed throughout, along with DF-MP2-F12 calculations that employed the cc-pV5Z/JKFIT auxiliary basis sets of Weigend[146] for the exchange and Fock operators and the aug-cc-pV5Z/MP2Fit sets of Hättig[147] for the remaining two-electron integrals. Additional information regarding the computational details can be found in the original paper.[142]

In analogy to the construction of standard correlation consistent basis sets (cc-pV*n*Z), the first order of action when creating a hierarchical basis set that converges to the CBS limit, was the determination of the identity and the number of the correlating functions for a given basis set. Similar to Dunning's work,[22] Peterson plotted the incremental correlation energy lowerings for the Ne atom, as optimal functions of increasing angular momentum were added to the basis set. Two different figures were plotted, as the correlation energy lowerings were calculated at both the conventional MP2 level of theory and the MP2-F12 level, with the 3C *Ansatz* and a geminal Slater exponent of $\beta = 1.4\,a_0^{-1}$.

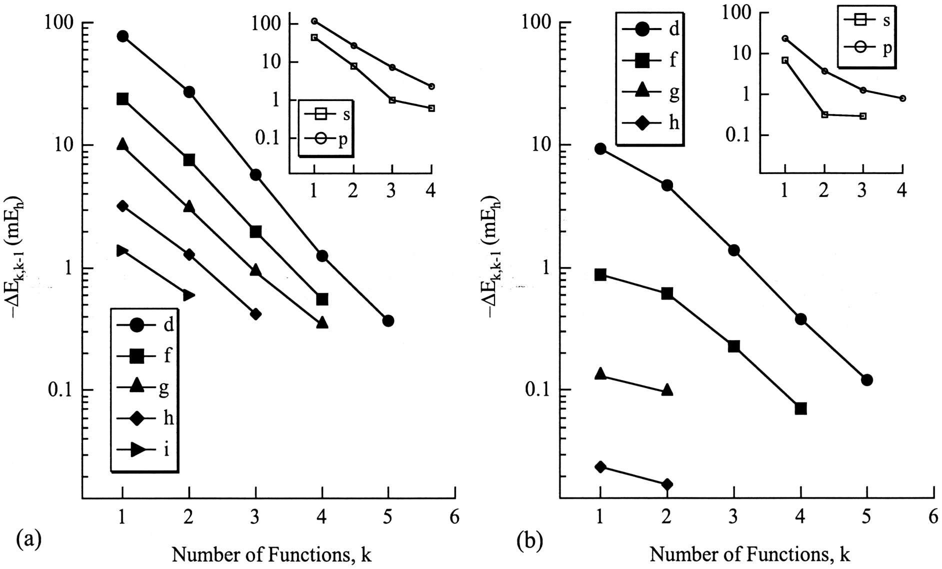


Figure 3.2: Incremental contributions of correlating functions to the frozen core correlation energy of the Ne atom, $\Delta E_{k,k-l}$ (in mE_h), calculated (a) at the MP2 and (b) at the MP2-F12/3C ($\beta = 1.4\,a_0^{-1}$) levels of theory, as used in Reference 142.
Figure reproduced with permission from AIP Publishing LLC.

Although the correlation consistent groupings of correlation functions of figure 3.2(a) looked very similar to those plotted by Dunning[22] for the oxygen atom, the MP2-F12/3C results were not so similar. More specifically, the convergence of the energy with respect to increasing angular momentum was much faster than in conventional MP2, and the overall magnitudes of the incremental lowerings were much smaller compared to conventional MP2, since the correlation factor alone recovered a large fraction of the correlation energy. The above results therefore indicated the necessity of a different set of "correlation consistent" groupings for F12 methods. However, the new basis set should not just depend on results obtained through atomic calculations, since in these cases the HF energy was known not to be sensitive to the presence or absence of higher angular momentum functions. Although in conventional molecular calculations this has previously been shown[22,117,119,148,149] not to be a problem, due to the fact that the optimal HF exponents and their relative energetic importance are very similar to those obtained in correlated calculations, in the case of F12 calculations this might not be true, due to the greatly decreased importance of higher angular momentum functions in explicitly correlated calculations as shown in Figure 3.3(b).

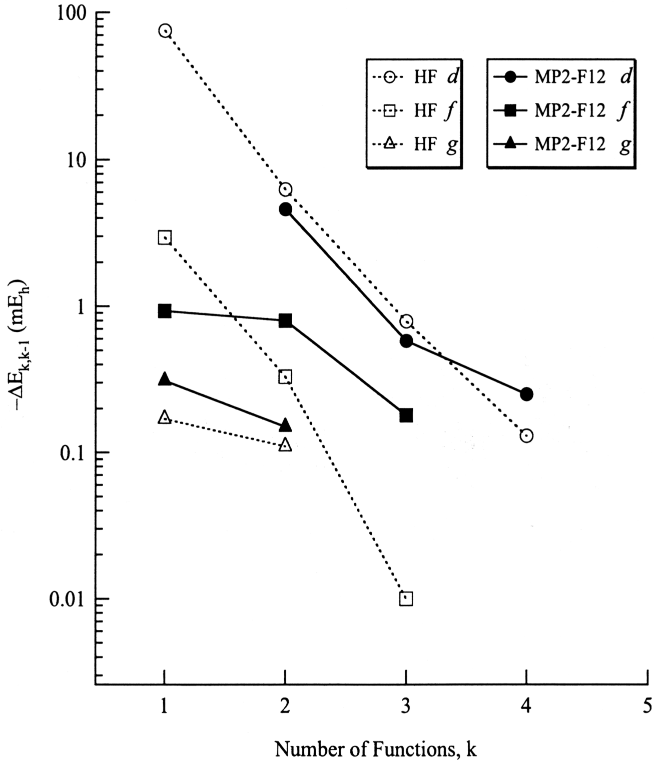


Figure 3.3: Incremental contributions of polarisation/correlating functions to the HF energy and frozen core MP2-F12/3C ($\beta = 1.4\,a_0^{-1}$) correlation energy for the N_2 molecule, $\Delta E_{k,k-l}$ (in mE_h),as used in Reference 142. The exponents were optimised for the total MP2-F12/3C energy.
Figure reproduced with permission from AIP Publishing LLC.

By plotting the incremental HF and MP2-F12 correlation energies calculated for the N_2 atom (Figure 3.3), it was clearly shown that the first function of each angular momentum symmetry contributed significantly to the HF wavefunction, and recovered less correlation energy at the MP2-F12 level of theory. The convergence of the HF energy with successive polarisation functions was however rapid and nearly exponential,[150, 151] so the addition of a second polarisation correlating function made strong contributions to the MP2-F12 correlation energy. In general the HF optimised exponents were much tighter than those required for the MP2-F12 correlation energy, and thus the resulting exponents obtained in (total energy) MP2-F12 optimisations were a compromise between minimising the HF energy and the MP2-F12 correlation energy. The above conclusions therefore suggested that the optimum strategy for basis set development was to optimise basis sets primarily in molecular calculations and to add at least two functions of each angular momentum symmetry to the basis set in order to describe both the HF and the correlation energies. Similar calculations were performed on P_2 (as an example of a second row molecule), and the resulting trends were completely analogous to those of N_2: the first optimised function of each angular momentum symmetry lowered primarily the HF energy, while the subsequent functions of that same symmetry recovered relatively more MP2-F12 correlation energy. Thus, for first row atoms, cc-pVDZ-F12 contained two d functions cc-pVTZ-F12 had a $3d2f$ set, and cc-pVQZ-F12 consisted of $4d3f2g$. Second row molecules had an additional d function added at each zeta level, analogous to the extra function added in the cc-pV$(n+d)$Z basis set[152] which is known to be required at the HF level. In a similar way, the basis sets for H and He were determined to be constructed with a $3p1d$ set for the cc-pVTZ-F12 set, while the cc-pVQZ-F12 set consisted of $4p2d1f$.

The selection of $dfghi$ correlating functions was followed by the determination of HF and s and p correlating functions. Unlike conventional calculations, the basis set error in the total energy in F12 methods is often dominated by the error in the HF energy, especially in small and moderate sized basis sets. The contracted HF s and p functions for the cc-pVnZ-F12 basis set, for all first row atoms, were obtained from the cc-pV$(n+1)$Z set. This choice decreased the HF error significantly while maintaining the low computational cost of the calculation. In addition, the most diffuse s and p augmenting functions of the aug-cc-pV$(n+1)$Z sets were also included in the cc-pVnZ-F12 basis set. A similar prescription was followed for the He atom, while in the case of the H atom, diffuse s functions were not included. In terms of choice for s and p correlating functions, Figure 3.2 indicated that the convergence of the MP2-F12 correlation energy with s functions was very rapid, while that of p functions was somewhat slower. Thus, the s-type correlating functions were simply taken from those of the cc-pV(n+1)Z basis set, while the p correlating functions were obtained from the cc-pV(n+1)Z basis set, augmented with an additional tight p in each case. This additional p function was an uncontracted p function from the HF set for the first row atoms, however this choice was not optimal for the second row atoms. Therefore, in the cc-pVDZ-F12 basis set for the second row atoms, the most diffuse p function was uncontracted from the cc-pVTZ HF set and this was combined with two functions that were explicitly optimised for MP2-F12. In the case of cc-pVTZ-F12 basis set, only one tight p function was explicitly optimised, while in cc-pVQZ-F12 it was possible to just uncontract the five most diffuse p functions from the underlying HF set. The composition of the resulting basis sets can be seen in Table 3.1:

Table 3.1: Composition of the cc-pVnZ-F12 basis sets, taken from references 142 and 124

Atoms	cc-pVDZ-F12	cc-pVTZ-F12	cc-pVQZ-F12
H	[$3s2p$]	[$4s3p1d$]	[$5s4p2d1f$]
He	[$4s2p$]	[$5s3p1d$]	[$6s4p2d1f$]
B-Ne	[$5s5p2d$]	[$6s6p3d2f$]	[$7s7p4d3f2g$]
Al-Ar	[$6s6p3d$]	[$7s7p4d2f$]	[$8s8p5d3f2g$]

Once the composition of the new sets was established, basis set optimisations were performed on molecules: the consistent choices for polarisation functions were based on energetical analysis for the set of molecules shown in Table 3.2. The main objective was to maintain a good balance between basis sets for a range of atoms, instead of having a good absolute energy for each individual atom.[148,149] In addition, a consistent number of functions for atoms of each row was also desired, and thus the basis set composition was the same for all elements on each row. Since open-shell F12 calculations were not possible at the time of the original investigation, the exponents of most elements were determined by closed-shell molecular calculations that covered a number of bonding environments (see Table 3.2).

Table 3.2: Set of atoms and molecules used in the cc-pVnZ-F12 basis set development, utilised in references 142 and 124

H_2, He_2
B: {BN, BH_3}, C: {C_2, $CH_2(^1A_1)$, CH_4, C_2H_4}, N: {N_2, NH_3, N_2H_2}
O: {H_2O, H_2O_2, H_2CO} F:{F_2, HF}, Ne
Al: {AlP, AlN, AlH}, Si: {Si_2, SiS, SiO, SiH_2, SiH_4}
P: {P_2, PN, PH_3}, S:{H_2S, H_2S_2, H_2CS} Cl: {Cl_2, HCl}, Ar

The geometries of the molecules were optimised at the CCSD(T) level of theory, using a cc-pCVQZ basis set[24,153]. It should be noted, that in the case of the H_2 molecule, a stretched bond length of 1.25 r_e was utilised in the basis set optimisations. In order to minimise geminal BSSE during the optimisation process, the 3C(D) *Ansatz* of MP2-F12 was used throughout, with orbital localization determined using the Pipek-Mezey method[154]. A relatively large value of the geminal exponent ($\beta = 1.4\, a_0^{-1}$) was used in all optimisations and only valence electrons were correlated. Initially, all correlating basis functions were optimised for each molecule separately and the final exponents were calculated by averaging the exponents for a particular element. This procedure however did not produce well behaved basis sets, and therefore the correlating basis functions for a given element were optimised for the weighted sum of the total MP2-F12/3C(D) energies of all the molecules utilised for that element.

Up to this point the dependence of the MP2-F12/3C correlation energies on the geminal exponent β had not been discussed. It was known[49,56] however, that the correlation energy can be very sensitive to its choice, particularly for small basis sets. The sensitivity of the MP2-F12/3C correlation energy to the choice of β was explored by calculating the basis set errors per correlated electron (pce) as a function of β. This study showed that the choice of β is an important factor that needs to be carefully considered in order to obtain accurate correlation energies. In order to avoid the optimisation of β in routine calculations, specific values of β were recommended[142] for cc-pVnZ-F12 as well as for aug-cc-pVnZ and aug-cc-pV$(n+d)$Z basis sets.

The convergence of the MP2-F12/3C correlation energy as a function of the cardinal number n of the basis set for Ne, Ar, N_2 between the new cc-pVnZ-F12 sets and the standard aug-cc-pVnZ (for first row) and aug-cc-pV$(n+d)$Z (second row) basis sets was compared, along with the recommended values of the geminal exponent $\beta = 1.4\, a_0^{-1}$. Substantially faster convergence was observed with the new basis sets. More specifically, cc-pVTZ-F12 and cc-pVQZ-F12 sets provided MP2-F12 correlation energies nearly equivalent to MP2-F12/aug-cc-pVQZ and MP2-F12/aug-cc-pV5Z results, respectively. In addition, estimated CBS limits for each set were obtained, by extrapolating the MP2-F12/3C correlation energies using the two largest sets (cc-pVTZ-F12 and cc-pVQZ-F12) and the following extrapolation scheme:

$$E(n) = E(\mathrm{CBS}) + A_1/n^4 \tag{3.8}$$

where A_1 is a fitting parameter and $E(\mathrm{CBS})$ is the estimated CBS limit correlation energy (in this case $n = 3$ and 4). The above extrapolation scheme was selected upon comparison of the resulting CBS limits with previously published[59,155] accurate benchmarking values. This comparison revealed that the basis set incompleteness error (BSIE) using the smallest set (cc-pVDZ-F12) was about 1% for systems containing only first row elements, and 1-3% for second row molecules. Upon increasing the size of basis set to cc-pVTZ-F12, the percent errors drop to just under 0.5% for first-row-containing systems and under 1% for second-row containing systems. Finally, when cc-pVQZ-F12 was used, nearly benchmark quality results were obtained for all molecules. Comparison of the BSIE with results obtained using the conventional aug-cc-pVnZ sets shows that the advantage of the new family of sets is clear for both the magnitude and variation in the percentage basis set errors.

One last thing that was examined was whether the new sets could be used in order to obtain accurate energy differences, in addition to accurate correlation energies. The reaction energies of several reactions of Werner's and Manby's paper[156] were calculated in different levels of theory, using different basis sets. The HF values were calculated using the aug-cc-pV6Z basis set, while three sets of MP2/CBS calculations were performed. The first set was obtained by extrapolation of individual molecular MP2-F12/3C correlation energies using the cc-pVTZ-F12 and cc-pVQZ-F12 basis sets and the previously shown extrapolation scheme (n^{-4}), while the other two sets were obtained from standard n^{-3} extrapolations of conventional MP2 correlation energies, using the aug-cc-pVQZ and aug-cc-pV5Z, and aug-cc-pV5Z and aug-cc-pV6Z basis sets, respectively. Both cc-pVDZ-F12 and aug-cc-pVDZ yielded similar results for the MP2 correlation contributions when using MP2-F12/3C, with mean absolute deviation values (MAD) between 0.3 and 0.4 kcal/mol, and maximum error values of 1 kcal/mol. In contrast, when HF contributions were included in the reaction energies, the new sets were significantly more accurate, with cc-pVTZ-F12 yielding better agreement with the reference CBS values (in comparison to aug-cc-pVTZ) by a factor of two.

3.4.2.2 cc-pV*n*Z-F12 and cc-pCV*n*Z-F12 (*n* = D-Q) for Li, Be, Na and Mg

Correlation consistent basis sets that accurately describe core-core as well as core-valence correlation in an F12 framework have also been published for the elements Li, Be, Na and Mg.[124,143]

The design and optimisation of the cc-pV*n*Z-F12 basis sets for these four atoms followed a similar procedure to the one described above for the rest of the first and second row elements. Li and Na atoms were treated differently (since there is only one valence electron), and all optimisations regarding those atoms were carried out for the dimers instead, Li_2 ($r = 2.6729$ Å) and Na_2 ($r = 3.0788$ Å). The HF *s* and *p* functions, along with the diffuse *s* and *p* augmenting functions were obtained from the aug-cc-pV($n + 1$)Z basis sets[119] in order to keep the HF basis set error to a minimum. While the *s*-type correlating functions were simply taken directly from the cc-pV($n + 1$)Z basis sets, the set of *p*-type correlating functions consisted of functions taken directly from the set, augmented with one (in case of Li and Be) or more (for Na and Mg) additional *p* functions, which were obtained by uncontracting tight functions from the HF set. The number of higher angular momentum correlating functions that were optimised for Li and Be matched those of B-Ne, while Na and Mg matched those of Al-Ar. The compositions of these new sets are shown in Table 3.3.

Table 3.3: Composition of cc-pV*n*Z-F12 basis sets for Li, Be, Na, and Mg, taken from reference 124

Atoms	cc-pVDZ-F12	cc-pVTZ-F12	cc-pVQZ-F12
Li, Be	[5*s*5*p*2*d*]	[6*s*6*p*3*d*2*f*]	[7*s*7*p*4*d*3*f*2*g*]
Na	[6*s*6*p*3*d*]	[7*s*7*p*4*d*2*f*]	[8*s*8*p*5*d*3*f*2*g*]
Mg	[6*s*6*p*3*d*]	[7*s*7*p*4*d*2*f*]	[8*s*8*p*5*d*3*f*2*g*]

Correlation energies were calculated using the new cc-pV*n*Z-F12 basis sets with MP2-F12 and the 3C *Ansatz*, and compared against conventional MP2 calculations that employed the aug-cc-pV*n*Z and aug-cc-pV($n + d$)Z basis sets. In the MP2-F12/3C calculations, the previously recommended[142] values of beta (β) were used. In all cases, and within the MP2-F12 framework, all sets yielded correlation energies within 0.5 mE_h of the CBS limit.

In addition to the cc-pVnZ-F12 set, an augmented set that accounted for both core-core and core-valence contributions to the correlated energy was developed (cc-pCVnZ-F12). Although in some cases core correlating calculations are all-electron calculations, in this case the $1s^2$ electrons of the second row atoms (Na and Mg) were treated using the frozen core approximation. In consistency with previously published sets for the rest of first and second row atoms,[157] the basis sets for the Li and Be were augmented with $1s1p$ core correlating functions at the double-zeta level and with $1s1p1d$ at the TZ and QZ sets. In the case of Na and Mg, $1s1p1d$ functions were added at the DZ set, while $1s1p1d1f$ were added for both TZ and QZ. These additional exponents were optimised on the difference between all-electron and valence-only MP2-F12/3C(D) correlation energies. In order for these sets to be efficiently employed in F12 methods, auxiliary sets for use in both the RI and the DF components of these calculations were developed. More details on the development and performance of these ABS can be found in Section 3.5.

The performance of the new orbital basis sets was tested by calculating optimised geometries, harmonic vibrational frequencies, and atomization energies for a group of molecules (see Table 3.4) that have been used in previous conventional CCSD(T) benchmark studies.[158–160]

Table 3.4: Set of atoms and molecules used in the testing of cc-pCVnZ-F12 basis sets, utilised in reference 124

Li: {Li_2, LiF, LiOH, Li_2O}
Be: {BeO, BeF, BeH_2, BeF_2}
Na: {Na_2, Na_2O, NaOH, NaF}
Mg: {MgO, MgF, MgH_2, MgF_2}

Use of the new basis sets in MP2-F12 calculations showed that bond lengths converge rapidly towards the basis set limit: in most cases results obtained at the double-zeta level are within a thousand of an Ångstrom of those obtained using a conventional method with a quadruple-zeta basis set. Explicitly correlated results are converging towards the same bond length CBS limit at a much quicker rate than results obtained using a conventional method (at the same level of theory). In certain cases the harmonic frequencies do not converge smoothly towards the basis set limit, and this is attributed to a small basis set superposition error. In most cases, the convergence of the harmonic frequencies is also very rapid, with the double-zeta results being only a few wavenumbers away from the conventional quadruple-zeta values. Estimates of the CBS limit atomization energies for the set of molecules were produced, by extrapolating the triple-zeta and quadruple-zeta CCSD-F12b and (T) contributions to the total correlation energy, using a Schwenke-type[161] extrapolation scheme:

$$E_{\mathrm{CBS}}^{\mathrm{corr}} = (E_{\mathrm{VQZ}}^{\mathrm{corr}} - E_{\mathrm{VTZ}}^{\mathrm{corr}})F + E_{\mathrm{VTZ}}^{\mathrm{corr}} \tag{3.9}$$

where F is a parameter previously optimised[162] for the cc-pVnZ-F12 sets, by reproducing high accuracy reference values for correlation energies of several molecules that contain first and second row p-block elements. In this case, the values of $F = 1.363388$ and $F = 1.769474$ were used for the extrapolation of CCSD-F12b and (T) correlation energies, respectively, with cc-pVTZ-F12 and cc-pVQZ-F12 basis sets. In order to get an estimate of the CBS limit for the total correlation energy, the previously extrapolated CBS correlation energies were then summed with HF energies (calculated using a quadruple-zeta basis set) that included a CABS singles correction.[163] The mean absolute error and the standard deviation of the basis set error showed a smooth convergence towards the estimated CBS limit in both all-electron and valence-only cases, with the mean absolute total error in the calculated atomization energies to be almost equivalent for both cases. Therefore, the error per correlated electron is much smaller in the all-electron case suggesting that the majority of the basis set error was due to valence correlation. Overall, the explicitly correlated CCSD(T)-F12b method using the new sets, approached similar results to those obtained with aug-cc-pV(5+d)Z and aug-cc-pwCV5Z basis set, at the triple-zeta level.

3.4.2.3 cc-pV*n*Z-PP-F12 (*n* = D-Q) for Ga-Rn

More recently, Hill and Peterson published[164] new correlation consistent basis sets, cc-pVnZ-PP-F12 (n = D, T, Q) for all post-d main group elements Ga-Rn. These sets have been optimised for use in explicitly correlated F12 calculations, include both OBS along with the matching ABS (MP2Fit ABS as well as OPTRI ABS).

These basis sets were designed for use with the previously published small-core MCDHF relativistic pseudopotentials[165–168] of the Stuttgart-Köln variety. The development of these sets is similar to the development of the basis sets for elements B-Ne, and Al-Ar.[142] Exponent optimisation calculations were carried out at the MP2-F12/3C level of theory, on the ground state of the neutral atoms. The value of β that was used throughout all optimisations was 1.4 a_0^{-1}. The auxiliary basis sets utilised corresponded to def2-QZVPP/JKFIT[169] for the DF of the exchange terms, with large, uncontracted even-tempered sets (18s17p15d12f10g8h7i) for both the DF of the conventional 2-electron integrals as well as the RI for the many-electron F12 integrals within the CABS.[61] The sp part of the basis set (contraction and correlating functions) was taken from the conventional aug-cc-pV($n+1$)Z-PP basis set[170,171,171] while the [1d] contracted HF d-type function was taken from the cc-pV($n+1$)Z-PP set, in order to ensure that the basis set convergence of the HF energy was synchronous with that of the correlation energy in the explicitly correlated calculations. To these base sets, an optimised, at the MP2-F12/3C level of theory, group of correlating functions was then added. These correlating functions included the usual F12 groupings of valence (sp) correlating functions (which were defined as even-tempered expansions), $2d$ for cc-pVDZ-PP-F12, $3d2f$ for cc-pVTZ-PP-F12, and $4d3f2g$ for cc-pVQZ-PP-F12. An additional $1d1f$ set that was also optimised for the MP2-F12 correlation energy of the $(m-1)d$ electrons (where m is the principal quantum number) was also added to the base set. This additional set addressed the drawback of the conventional cc-pVnZ basis sets,[172] which are missing sufficiently tight f functions for inner-shell polarisations, while it also provided a minimal set of functions necessary to describe the correlation of the $(m-1)d$ electrons. As a result, the new basis sets could accurately recover outer-core correlation effects, while being predominately valence correlating. The compositions of the new sets are presented in Table 3.5.

Table 3.5: Composition of cc-pVnZ-PP-F12 basis sets for the post-d elements

Element	cc-pVDZ-PP-F12	cc-pVTZ-PP-F12	cc-pVQZ-PP-F12
4p	$[6s5p4d1f]$	$[7s6p5d3f]$	$[8s7p6d4f2g]$
5p	$[6s5p4d1f]$	$[7s7p5d3f]$	$[8s8p6d4f2g]$
6p	$[6s5p4d1f]$	$[7s7p5d3f]$	$[8s8p6d4f2g]$

The convergence of the correlation energy using the cc-pVnZ-PP-F12 sets was evaluated in both conventional MP2 and MP2-F12 calculations. As expected, the F12 correlation energies were dramatically closer to the CBS limit (which was estimated by conventional MP2 n^{-3} extrapolations[173,174] of aug-cc-pwCVnZ-PP basis sets with n= Q and 5). At the DZ level, the F12 results were closer to the CBS limits than the conventional 5Z values. Even with the small $1d1f$ set of core correlating functions contained in the new basis sets, the F12 calculations recovered a significant amount of core correlation energy. In fact the cc-pVnZ-PP-F12 correlation energies are lower than the significantly larger conventional aug-cc-pwCV$(n+1)$Z-PP values. Although up to this point the geminal exponent used in all calculations was fixed equal to 1.4 a_0^{-1}, the sensitivity of the correlation energy with the choice of β is known to decrease as the size of the OBS increases. Unfortunately, in the case of post-d elements a single value of β was challenging, especially when the $(m-1)d$ electrons were correlated. In order to bypass this problem, the use of two geminals that used two exponents was examined, since in previous investigations[175] this method noticeably improved the observed d-correlation effects on $\mathrm{D_e}$, $\mathrm{r_e}$ and $!_\mathrm{e}$ for the DZ set (which was the most sensitive out of the three sets). The pairs of exponents that were used to examine the validity of this method for post-d elements were a compromise between As, Sb, and Bi: [0.70, 1.20] for DZ, [0.80, 1.25] for TZ, and [0.90, 1.35] for QZ. Nevertheless, the use of two geminals had nearly no effect on the calculated d-correlation effects, and therefore single values of β were used; 1.0 a_0^{-1} for valence-correlation calculations, and 1.4 a_0^{-1} for the cases were the $(m-1)d$ electrons were correlated. The validity of this selection was reflected in the excellent results of the benchmark calculations.

The effectiveness of the new sets for both valence and $(m-1)d$ electron correlation in molecular systems was examined through determination of spectroscopic constants (D_e, r_e, and ω_e) of 18 homonuclear and heteronuclear molecules at the CCSD(T) level. (see Table 3.6).

Table 3.6: Molecular systems used in calculations of spectroscopic constants

Ga_2, In_2, Tl_2, As_2, Sb_2, Bi_2, Br_2, I_2, At_2
GaCl, InCl, TlCl, AsN, SbN, BiN, BrF, IF, AtF

The selection of molecules was based on a previous study.[176] CCSD(T)-F12b/3C(FIX) benchmark calculations were performed on the above set of molecules (see Table 3.6), using the new cc-pV*n*Z-PP-F12, cc-pV*n*Z-PP-F12/MP2Fit and cc-pV*n*Z-PP-F12/OPTRI sets (*n*=D, T Q), along with def2-QZVPP/JKFIT on the post-*d* elements. The OBS as well as the OPTRI set for the lighter elements was cc-pV*n*Z-F12 and the MP2Fit sets were aug-cc-pV*n*Z-PP and aug-cc-pwCV*n*Z-F12. The ABSs for the exchange terms corresponded to cc-pV*n*Z/JKFIT (where *n*=T for DZ and TZ OBS and *n*=Q for QZ). Both frozen core (only sp valence electrons correlated) calculations, in which $\beta = 1.0\ a_0^{-1}$ as well as $msp + (m-1)d$ correlation calculations, in which $\beta = 1.4\ a_0^{-1}$ were performed. Results for the homonuclear diatomic molecules show that the convergence of the frozen-core quantities with respect to the basis set is very rapid with the F12b *Ansatz* and the new basis sets. For group 15 diatomic molecules, calculations using the F12b method, with the cc-pV*n*Z-PP-F12 basis sets, yielded dissociation energies for bond lengths comparable to at least *n*+1 in a conventional treatment, and bond lengths of *n*+2 quality, compared to results obtained with conventional methods and aug-cc-pV*n*Z-PP. Calculations for all diatomic molecules showed that cc-pVQZ-PP-F12 results differ in average by ~ -0.47 kcal/mol, 0.0009 Å and -0.5 cm^{-1} from the conventional CBS limits for D_e, r_e and ω_e, respectively. Use of CCSD(T)-F12b with the new cc-pV*n*Z-PP-F12 basis sets yielded very rapid convergence towards the respective CBS limit. In these cases when DZ quality calculations yielded reliable estimates of core correlation effects, to within a few tenths of a kcal/mol for D_e to a few mÅ for the bond length. This is in contrast with results obtained using conventional results where the *d*-electron correlation effects can often be underestimated (compared to the CBS limit) by a few kcal/mol and a few hundredths of an Å, for DZ and even TZ core-valence basis sets. Unfortunately, convergence of these effects with F12, although rapid is not always monotonic. This could be mainly attributed to BSSE that presumably arises from only using a $1d1f$ set of functions in order to recover *d*-electron correlation effects (in addition to the F12 correlation factor of course). Nevertheless, the improved convergence of the F12 results to the estimated CBS limits was much more rapid, both in frozen-core and outer-core *d*-electron correlated calculations. This increased rate of basis set convergence with F12 methods for these elements opens up the way to carrying out accurate CCSD(T) calculations of large molecular systems involving these elements using only relatively small basis sets.

3.5 Auxiliary basis sets

The principal difficulty in explicitly correlated methods is the necessity for computing numerous three and four electron integrals, as well as multiple many-index two electron integrals. This problem is bypassed by invoking two main approximations that make the explicitly correlated calculations computationally efficient, namely the resolution-of-the-identity (RI) and density fitting. Both approximations require their respective auxiliary basis sets (ABS). The necessity and properties of each ABS, as well as the methodology under which those sets are developed are discussed in the following subsections.

3.5.1 RI auxiliary basis sets

Explicitly correlated methods were not practically implemented until Klopper and Kutzelnigg employed the resolution-of-identity (RI) approximation, which computes many electron integrals as products of no more than two electron integrals.[45,47,75] Although the initial work utilised the OBS for the RI, the requirement of a large basis set maintained the high computational cost of the calculation. To avoid this drawback, Klopper and Samson[59] utilised a separate ABS that fulfilled the RI approximation, allowing the use of relatively small OBS in explicitly correlated calculations. This was subsequently extended by Valeev,[61] who indicated that the RI approximation was most accurate when the ABS spans exactly the OBS. This essentially means that the ABS must at least contain the OBS. Valeev furthermore suggested[177] that a complementary ABS (CABS) should be used by constructing a set that is the union of an ABS with the OBS minus the linear dependent functions [that are removed through a singular value decomposition (SVD) analysis], and then forming the orthogonal complement to the OBS for use in the RI. Hill, Peterson, and Yousaf have optimised accurate ABSs for use in CABS-based explicitly correlated methods. In all cases only functions complementary to the chosen OBS were optimised, and thus the size of the produced ABS was relatively small, with well-controlled RI errors.[143,144,178,179]

Previous work in the context of the RI-MP2 method[180] suggested that ABS functions could be optimised for the quantity $\delta\text{RI} = |E_{\text{MP2}} - E_{\text{MP2,RI}}|$ but this approach was not the followed, due to the possibility of a more efficient approach that could utilise analytical gradient technology. Initial efforts involved minimization of the absolute energy difference between MP2-F12 calculations using approximate and reference ABSs, i.e., $\delta\text{RI} = |E_{\text{MP2}-\text{F12,RI}_{\text{REF}}} - E_{\text{MP2}-\text{F12,RI}_{\text{OPT}}}|$. Unfortunately these methods were proven to be less than ideal for two, mainly practical, reasons. First, as a function of the basis set exponents, the value of δRI appeared to have many small discontinuities and therefore both gradient based (BFGS) and energy-based (Simplex) algorithms often failed to converge to a minimum. This could in principle be caused by the sensitivity of the reference ABS calculations to the chosen CABS SVD thresholds. Second, exponents that were optimised using this way seemed to introduce an explicit *Ansatz* dependence. In initial calculations the fixed-amplitude diagonal *Ansatz* of Ten-no[67] was used, since it is both orbital invariant and free of geminal BSSE. However, when ABSs optimised with this *Ansatz* were used to calculate MP2-F12 energies, the RI errors were an order of magnitude larger using the 3C(FIX) *Ansatz* than those obtained using *Ansatz* 3C. Thus it was observed that any optimisation that depended directly on the energy difference involved not only the accuracy of the F12 intergals, but also some error cancellation from the *Ansatz* itself. In order to overcome these difficulties, the general procedure for the design of OPTRI sets was set to be the optimisation of functions that would minimise the value for δRI for the atoms. The δRI functional involves the diagonal elements of the **V** and **B** matrices that arise in MP2-F12 theory[48] (see Equations 2.98-2.106) and has the following form:

$$\delta\mathrm{RI} = \sum_{ij} \frac{(V^{\mathrm{RI}}_{ij,ij} - V^{\mathrm{RI}_{ref}}_{ij,ij})^2}{|V^{\mathrm{RI}_{ref}}_{ij,ij}|} + \frac{(B^{\mathrm{RI}}_{ij,ij} - B^{\mathrm{RI}_{ref}}_{ij,ij})^2}{|B^{\mathrm{RI}_{ref}}_{ij,ij}|} \,. \tag{3.10}$$

The **V** and **B** matrices contain the many-electron integrals approximated by the RI, and the quantity of equation 4.7 is always positive. Similarly to the conventional methods, δRI is motivated by the energy expression and therefore has units of energy. The determination of the number of functions that is required in the ABS for a particular choice of OBS follows a similar prescription to that used in the construction of the correlation consistent OBS (including the F12 variants). For each angular momentum, successive uncontracted functions are added and optimised with respect to the reference RI that was truncated to contain only functions involving the angular momentum being optimised. ABS functions are included until δRI is below a chosen threshold (which depends on the the OBS and the angular momentum of the functions being optimised). The s, p and d functions are treated simultaneously, to reduce the number of calculations required and to account for the strong coupling between the functions of these angular momenta. In addition, in order for linear dependences to be minimised, the ratio of any two exponents in the combined CABS basis (within the same shell of angular momentum) is constrained to be greater than or equal to a fixed value which is often equal to 1.5.

Yousaf and Peterson developed[178,179] so called OPTRI ABSs for elements H, B-Ne, and Al-Ar, matched to the standard aug-cc-pVnZ and aug-cc-pV(n+d)Z (n= D-5) and the cc-pVnZ-F12 (n= D-Q) OBSs, for use as RI sets in explicitly correlated F12 calculations. optimisation of the exponents was performed using the Simplex algorithm,[145] and pure spherical harmonic basis functions were used throughout. Although specific values were used for the geminal exponent, molecular tests performed at the MP2-F12/cc-pVTZ-F12 level of theory with $\beta = 1.4\, a_0^{-1}$ indicated that the accuracy of the developed ABSs did not appear to depend on the choice of β. In order to determine the resulting RI errors a large reference ABS was chosen that consisted of the uncontracted $18s13p$ (for B-Ne), $20s15p$ (Al-Ar) sets of Partridge[181,182] combined with the $dfghi$ functions from the standard aug-cc-pV6Z basis sets.[183,184] In addition, a set of s and p diffuse functions, as well as two additional d and one f function were added for B-Ne, and three additional d and two f functions were added for Al-Ar in an even-tempered manner. The reference ABS for hydrogen consisted of the uncontracted aug-cc-pV6Z basis set without the h-type functions. A single tight

p function was then added to this set. In both papers discussed above, the final ABSs were benchmarked in calculations of atomization energies and electron affinities of a number of small molecules. The errors associated with the use of a number of RI sets were compared to those obtained from an extensive reference ABS. In each case the OPTRI sets resulted in RI errors more than an order of magnitude smaller than the basis set error. This was a demanding requirement since with the F12 methods the latter is already very small with the AVDZ OBS. The developed ABSs yielded essentially the same accuracies when used in other MP2-F12 methods besides 3C (such as the fixed amplitude *Ansatz*), as well as in CCSD-F12 calculations.

Hill, and Peterson optimised[143] RI auxiliary basis sets for use with the cc-pVnZ-F12 and cc-pCVnZ-F12 (n = D, T, Q) OBSs for elements Li, Be, Na and Mg. The general procedure of the minimization was the same as the one discussed before, and involved the minimization of δRI. In the cases of Li and Na where there was only one valence electron, the OPTRI sets were optimised for the Li_2 and Na_2 dimers. The reference RI set required in the δRI was constructed from an uncontracted aug-cc-pwCV5Z orbital basis set, which for Li and Be was also augmented with $3d3f3g$ functions that filled gaps between the cc-pV5Z and cc-pwCV5Z exponents, 2 tight h functions and $2i$ functions that were extrapolated from the cc-pCV6Z[124] basis sets for p-block elements, and a final tight i function that was obtained by multiplying the tightest of the previously extrapolated functions by 2.5. In a similar manner, the reference RI set for Na and Mg consisted of the uncontracted aug-cc-pwCV5Z orbital basis set augmented with $4d3f3g3h4i$ functions. However, during the optimisation of OPTRI auxiliary sets matched to the cc-pCVQZ-F12 OBSs, it was necessary to use a larger sp set in the reference since otherwise the orbital and reference sets would have the same set of HF primitives. In these cases the $18s10p$ sets from Partridge[182] were used for Li and Be, while $28s18p$ sets were optimised for both Na and Mg using 6-term Legendre expansions.[185] A diffuse p-type function was also added to these latter Li and Be reference sets. optimisation of OPTRI sets that matched the cc-pVnZ-F12 OBSs followed the procedure outlined in Yousaf and Peterson's papers with two modifications. First, due to the tighter spacing between exponents in the OBSs the constraint on the minimum ratio between the ABS exponent and an orbital basis set exponent of the same angular momentum was adjusted from 1.5 to 1.3. No linear dependency problems appeared due to this change. Second, in order for the desired level of accuracy in the δRI functional to be reached, an additional p exponent was required for Na and Mg, when matched to the cc-pVDZ-F12 OBS. The 3C *Ansatz* along with previously determined optimal geminal exponents β (0.9 for DZ, 1.0 for TZ and 1.1 for QZ) were used. For the cc-pVTZ-F12/OPTRI sets for Be, the gradients and Hessians of the functions with the highest angular momentum (g and h, respectively) were very flat, leading to optimisation problems. These functions were thus optimised for the ^3P_u excited states and then tested for the ground state. Additional functions were then added to the cc-pVnZ-F12 orbital basis sets in a procedure identical to that described in Hill's paper.[124] In all cases the resulting MP2-F12 energy differences between the OPRTI sets and the reference RI sets ranged from only a few μE_h for valence electron correlation and up to 55 μE_h for calculations where all-electrons were correlated. These errors were entirely consistent with the previous results for the adjacent *p*-block elements and are at least 1-2 orders of magnitude smaller than the orbital BSIE. The validity of the new ABSs was tested by benchmarking calculations of atomization energies, as well as equilibrium geometries and harmonic vibrational frequencies.

Recently, Hill and Peterson published[144] OPTRI sets for use in conjunction with cc-pV*n*Z-PP-F12 (*n*= D, T and Q) for the post-*d* main group elements, Ra-Rn. In order for linear dependencies to be minimised, the ratio of any two exponents (with the same angular momentum) in the combined CABS basis was constrained to be ≥ 1.5. The 3C *Ansatz* with a value for beta $\beta = 1.4\, a_0^{-1}$ was used. Comparing to previous development of OPTRI sets, this work was complicated by having F12 basis sets designed for correlating two different orbital spaces, primarily valence *sp* but also a minimal set for $(m-1)d$. Initial sets of OPTRI exponents were first optimised within the frozen-core approximation (valence *sp* correlation only). Each angular momentum was optimised separately and the *s*, *p*, *d* and *f* functions employed a reference RI that was truncated at *f*-type functions. The higher angular momentum functions utilised the full reference RI. The resulting sets were then frozen, and 0-4 additional functions in each angular momentum were optimised in MP2-F12 calculations that included the valence + $(m-1)d$ electrons. In general the OPTRI sets slightly decrease in size as the OBS becomes more complete. Using a set of test molecules the RI errors were assessed (relative to the reference RI) for the new OPTRI auxiliary sets. In general these errors are about 2 orders of magnitude smaller than the MP2-F12 BSIE.

3.5.2 DF-MP2 auxiliary basis sets

The evaluation of four-index two-electron integrals has traditionally been one of the main drawbacks in all post-HF methods. Density fitting (DF) reduces the required computational resources by a robust approximation of the integrals via an expansion of orbital product densities in an auxiliary basis set. While ABSs can be automatically generated,[186] in most cases DF calculations employ a pre-optimised fitting set that is matched to a specific OBS and this leads to a saving of at least an order of magnitude in computer time. Although similar to DF-HF,[146,187] DF for post-HF methods has its roots in related intergal approximation techniques applied to DFT[188,189] and usually requires a different ABS than DF-HF and DFT. In most cases the ABSs are designed in the framework of DF-MP2; however DF for post-HF methods is not limited to DF-MP2, with the approximate coupled-cluster singles-and-doubles model (CC2)[190] a popular example of a method that often utilises the same ABS.

The MP2 correlation energy can be expressed as

$$E_{\mathrm{MP2}} = -\frac{1}{4}\sum_{aibj}\frac{\langle ab||ij\rangle^2}{\epsilon_a - \epsilon_i + \epsilon_b - \epsilon_j} \tag{3.11}$$

where $\langle ab||ij\rangle = (ai|bj) - (aj|bi)$. The indices *i*, *j* denote occupied and *a*, *b* virtual (unoccupied) canonical SCF spin orbitals, while ϵ_p are the SCF orbital energies. In the DF approximation the four-index electron repulsion integrals (ERIs) are approximated as

$$(ai|bj) \approx (ai|bj)_{\mathrm{DF}} = \sum_{PQ} (ai|P) V^{-1}_{PQ} (Q|bj) \tag{3.12}$$

with $V_{PQ} = (P|Q)$, where P and Q are auxiliary basis functions and $(ai|P)$ and $(P|Q)$ are three- and two- index ERIs. The DF error in the MP2 correlation energy, which is defined as the difference between the result obtained in an DF-MP2 calculation and that of a conventional MP2, can be split into two contributions:

$$\Delta_{\mathrm{DF}} = E_{\mathrm{DF-MP2}} - E_{\mathrm{MP2}} \tag{3.13}$$

$$\Delta_{\mathrm{DF}} = -\frac{1}{2} \sum_{aibj} \frac{\langle ab||ij\rangle(\langle ab||ij\rangle_{\mathrm{DF}} - \langle ab||ij\rangle)}{\epsilon_a - \epsilon_i + \epsilon_b - \epsilon_j} - \frac{1}{4} \sum_{aibj} \frac{(\langle ab||ij\rangle_{\mathrm{DF}} - \langle ab||ij\rangle)^2}{\epsilon_a - \epsilon_i + \epsilon_b - \epsilon_j} \tag{3.14}$$

The errors in the individual four-index ERIs can be positive or negative, and therefore the first term in equation 3.14 cannot be used as a functional for a variational optimisation of the ABSs. The second term, however, which is quadratic in the error of the ERIs, is negative semi-definite and suitable for a variational optimisation. The negative of the latter term, i.e. the functional

$$\delta_{\mathrm{DF}} = \frac{1}{4} \sum_{aibj} \frac{(\langle ab||ij\rangle_{\mathrm{DF}} - \langle ab||ij\rangle)^2}{\epsilon_a - \epsilon_i + \epsilon_b - \epsilon_j} \tag{3.15}$$

is minimised to determine optimised auxiliary basis sets for the DF in DF-MP2 and DF-CC2 calculations. In δDF the SCF orbital energies appear as in the MP2 energy linear in the denominators. Compared to other choices for the denominators and in particular to a minimization of just the average squared errors in the ERIs, minimising δDF leads to an optimal convergence for correlation energies with the size of the thereby optimised ABSs. Early optimisations of auxiliary basis sets for DF-MP2 calculations[180,191] employed numerical gradients evaluated by finite differences for the minimization of δDF. This technique led to a rapid increase in computational time with the basis set size for fully optimised ABSs, as it required the evaluation of δDF at least once for each basis parameter that had to be varied. In addition, the numerical errors of the finite difference procedure hindered a tight convergence of the optimisation procedure. Therefore, optimisation of accurate ABSs for large one-electron OBSs required analytic basis set gradients as an important prerequisite. The gradients of δDF with respect to a parameter λ of the ABS $\{P\}$ can be expressed in a form which is very similar to that of some contributions to the gradient for the DF-MP2 correlation energy:

$$\frac{d\delta\mathrm{DF}}{d\lambda} = -\frac{1}{2} \sum_{aibj} \frac{\langle ab||ij\rangle_{\mathrm{DF}} - (\langle ab||ij\rangle d\langle ab||ij\rangle_{\mathrm{DF}}}{\epsilon_a - \epsilon_i + \epsilon_b - \epsilon_j} \tag{3.16}$$

$$\frac{d\delta\mathrm{DF}}{d\lambda} = \sum_{\mu\nu P} \tilde{\Delta}^{ao}_{\mu\nu P} (\mu\nu|\frac{dP}{d\lambda}) - 2 \sum_{PQ} \tilde{\gamma}^{ao}_{PQ} (\frac{dP}{d\lambda}|Q) \tag{3.17}$$

The intermediates $\tilde{\Delta}^{ao}_{\mu\nu P}$ and $\tilde{\gamma}^{ao}_{PQ}$ are three- and two-index two-electron densities which differ from corresponding intermediates in the calculation of DF-MP2 energy gradients[192,193] only in that the amplitudes calculated in the DF approximation,

$$^{\mathrm{DF}}t_{ij}^{ab} = -\frac{\langle ab||ij\rangle_{\mathrm{DF}}}{\epsilon_a - \epsilon_i + \epsilon_b - \epsilon_j} \tag{3.18}$$

are replaced by the difference amplitudes

$$\tilde{t}_{ij}^{ab} =^{\mathrm{DF}} t_{ij}^{ab} - t_{ij}^{ab} = -\frac{\langle ab||ij\rangle_{\mathrm{DF}} - \langle ab||ij\rangle}{\epsilon_a - \epsilon_i + \epsilon_b - \epsilon_j} \tag{3.19}$$

The three-index two-electron density matrix $\tilde{\Delta}^{ao}$ is defined as

$$\tilde{\Delta}_{\mu\nu P}^{ao} = \sum_i C_{\nu i} \sum_a C_{\mu a} \sum_{bj} \tilde{t}_{ij}^{ab} \sum_Q (bj|Q) V_{RQ}^{-1} \tag{3.20}$$

and the two-index two-electron density matrix $\tilde{\gamma}^{ao}$ is obtained as

$$\tilde{\gamma}_{PQ} = \sum_{\alpha\beta} \tilde{\Delta}_{\alpha\beta}^{ao,P} \sum_R (\alpha\beta|R) V_{RQ}^{-1} \,. \tag{3.21}$$

Based on the above equations, the derivatives of δDF with respect to the exponents and contraction coefficients of the ABS can be obtained by relatively simple modifications of a DF-MP2 energy gradient code. This has been exploited and these basis set gradients are implemented in the RICC2 module[147,190] of the TURBOMOLE package.[194] Since the canonical orbitals and the non-approximated four-index ERIs do not depend on the ABS, these need to be evaluated only once. This fact is what reduced the costs for a gradient calculation for δDF to about 2-3 times the costs of a DF-MP2 energy calculation.

ABSs matched to conventional basis sets have been developed in this way, and details can be found in a series of papers.[147,180,195–199] The only ABSs specifically matched to "explicitly correlated" basis sets however, are the ones for post-d elements Ga-Rn, that were recently developed[144] by Hill and Peterson. The development of ABSs specifically matched to the cc-pVnZ-PP-F12 (n =D, T, Q) OBS, and the optimisation of the uncontracted exponents proceeded through the minimization of the functional δDF. All atoms were in their respective ground electronic states, and the $(m-1)sp$ electrons were frozen, while the $(m-1)d$ electrons were included in the correlation treatment and evaluation of δDF. The guidelines established by Weigend[190] were followed: the number of basis functions in the ABS was not greater than four times the number of functions in the OBS, and the error in the correlation energy due to the DF should be less than 100 μE_h per atom in molecular calculations. To qualitatively describe the above DF error, and since the energetic error was not directly related to δDF, it was transformed to $\delta\mathrm{DF}/|E_{MP2}^{corr}| \leq 10^{-6}$. In addition, the error due to the density fitting in molecules had to be three to four of orders of magnitude smaller than the BSIE in the respective OBS. In order for the DF error to remain negligible in the F12 framework, where the BSIE was greatly reduced, the DF error was assessed at the MP2-F12 level. Evaluation of the new MP2Fit ABSs was carried out by comparing the DF error in the correlation energy with the BSIE for a test set of molecules containing post-d elements. In order to obtain the BSIE, (R)MP2-F12/3C(FIX) calculations were performed, with a Schwenke-type extrapolation of the TZ and QZ correlation energies, with the cc-pV*n*Z-F12 OBSs used for lighter elements. The large even-tempered ABSs that were described earlier were used for both DF and RI. However, the BSIE error was proven to be very sensitive to the selection of ABS used for the lighter elements, and thus future investigation and development of optimised ABSs specifically matched to cc-pV*n*Z-F12 for those lighter elements was proposed. Upon this finding, the ABSs were increased to aug-cc-pwCVQZ/MP2Fit and aug-cc-pwCV5Z/MP2Fit, for cc-pVTZ-F12 and cc-pVQZ-F12 OBSs respectively, and this reduced the errors by approximately an order of magnitude. A comparison of the DF error with the BSIE indicated that the errors due to the fitting were negligible, despite the large decrease of the BSIE due to the explicitly correlated nature of the wavefunction. The overall magnitude of errors was the same for all three sets, and in both instances, i.e. where the $(m-1)d$ electrons were correlated or not. Finally, although they required a large number of functions, the new ABSs were not expected to have significant consequences in computational time or resources, especially in the cases where more computationally expensive methods, such as CCSD(T)-F12b, would be used.

Chapter 4

Basics of unconstrained optimisation

4.1 Introduction to optimisation

Optimisation, within a mathematical framework, can be defined as the process that determines a set of "best" solutions to a problem, often of physical interest, manifested through mathematics. The process of optimisation usually involves the mathematical definition of the problem as a function, the study of optimality criteria that minimise (usually) or maximise that function, the algorithmic design that will lead to a solution, and often the computational implementation of that algorithm itself. The applicability of optimisation methods is widespread, and is present in the majority of activities in which numerical information is processed. In chemistry, optimisation (as defined here) is heavily used in the branch of theoretical and computational chemistry; it most usually corresponds to geometry optimisation of a molecule or a cluster of molecules, in which the geometry that corresponds to a minimum energy is found. Furthermore, optimisation is heavily used when a new theory or basis set is designed, but is often concealed from the end user. In this chapter, the basics of optimisation from a mathematical point of view will be covered in order to finally present the procedure followed during the design and optimisation of correlation consistent basis sets that is presented in the following chapters. An optimisation problem can be represented in the following way:

$$\begin{aligned} &\text{minimise } f(\mathbf{x}) \\ &\text{subject to } \mathbf{x} \in \Omega\,. \end{aligned} \tag{4.1}$$

Such formulation is called an optimisation problem. The function that we want to minimise $f : \mathbb{R}^n \to \mathbb{R}$ is a real-valued function and is called an objective function or a cost function and in certain fields, an energy function. The vector $\mathbf{x}$ is an n-vector of independent variables, $\mathbf{x} = [x_1, x_2, ..., x_n]^T \in \mathbb{R}^n$. The variables $x_1, x_2, ..., x_n$ are mostly referred to as decision variables. In basis sets optmisation the objective function may be the correlation energy with the exponents of the basis sets as decision variables. The set Ω is a subset of the Euclidean space $\mathbb{R}^n$ often specified by a set of constraints, equalities or inequalities that the members of Ω have to satisfy. The domain Ω of f is called the search space or the choice set, while the elements of Ω are called candidate solutions or feasible solutions. The above problem can be described as a decision problem that involves finding the "best" vector $\mathbf{x}$ of the decision variables in all possible vectors in Ω. That "best" vector is called the minimiser of f over Ω (it is possible that there may be more than one minimiser). In general there can be optimisation problems that require the maximisation of the objective function. Of course, maximising function f is equivalent to minimising $-f$, and so at this level we can think that all optimisations are essentially minimisations of an objective function. Furthermore, since all optimisations that are going to be described later are energy optimisations of bound states, we are only interested in minimising some energy of our systems. The above problem represents the general form of a constrained optimisation problem, since the decision variables are constrained in the set Ω. However, we are only interested in unconstrained optimisation problems, where $\Omega = \mathbb{R}^n$. When considering the general unconstrained optimisation problem

$$\begin{gathered} \text{minimise } f(\mathbf{x}) \\ \text{subject to } \mathbf{x} \in \mathbb{R}^n \, , \end{gathered} \tag{4.2}$$

we can distinguish between different kinds of minimisers:

- A point x^* is a global minimiser of f if for all $\mathbf{x} \in \mathbb{R}^n \setminus \{x^*\}$, $f(x^*) \leq f(\mathbf{x})$.
- A point x^* is a local minimiser of f if there is $\varepsilon > 0$ such that $f(x^*) \leq f(\mathbf{x})$ for all $\mathbf{x} \in \mathbb{R}^n \setminus \{x^*\}$ and $||\mathbf{x}x^*|| \ < \varepsilon$
- A point x^* is a strict global minimiser of f if for all $\mathbf{x} \in \mathbb{R}^n \setminus \{x^*\}$, $f(x^*) < f(\mathbf{x})$.
- A point x^* is a strict local minimiser of f if there is $\varepsilon > 0$ such that $f(x^*) < f(\mathbf{x})$ for all $\mathbf{x} \in \mathbb{R}^n \setminus \{x^*\}$ and $||\mathbf{x}x^*|| \ < \varepsilon$.

These different kinds of minimiser for $\mathbb{R}^1$ are illustrated in figure 4.1.

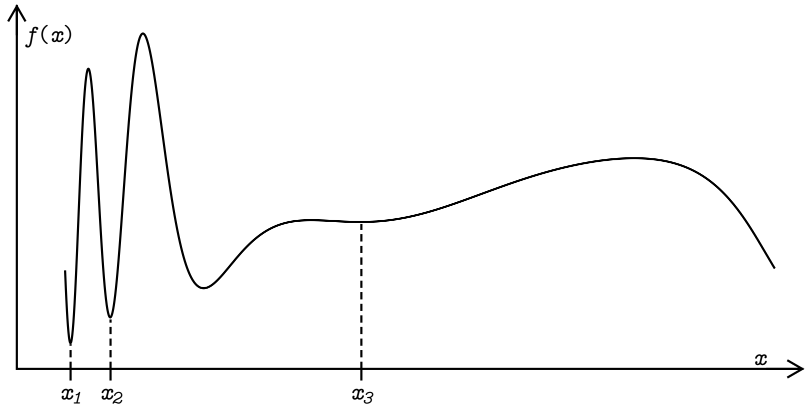


Figure 4.1: Different types of minimisers for the function $\sin(3x - x^2) - 4\sin(x^6)$ of $\mathbb{R}^1$: $\mathbf{x}_1$ is a strict global minimiser, $\mathbf{x}_2$ a strict local minimiser and $\mathbf{x}_3$ a local (not strict) minimiser.

Strictly speaking, an optimisation problem is solved only when a global minimiser is found. However, global minimisers are, in general, difficult to locate; thus most of the time optimisations are considered "complete" when local minimisers are found.

4.2 Conditions for local minimisers

This section explores the conditions required in order for $\mathbf{x}^*$ to be a local minimiser of a function $f\colon \mathbb{R}^n \to \mathbb{R}$. The first derivative f, denoted Df has the form

$$Df \equiv \left[\frac{\partial f}{\partial x_1}, \frac{\partial f}{\partial x_2}, ..., \frac{\partial f}{\partial x_n}\right], \tag{4.3}$$

while the gradient ∇f is the transpose of Df; $\nabla f = (Df)^T$. The second derivative of f is called the Hessian and has the form:

$$F(\mathbf{x}) \equiv D(Df(x)) = D^2 f(x) = \begin{bmatrix} \frac{\partial^2 f}{\partial x_1^2}(x) & \cdots & \frac{\partial^2 f}{\partial x_n \partial x_1}(x) \\ \vdots & & \vdots \\ \frac{\partial^2 f}{\partial x_1 \partial x_n}(x) & \cdots & \frac{\partial^2 f}{\partial x_n^2}(x) \end{bmatrix}. \tag{4.4}$$

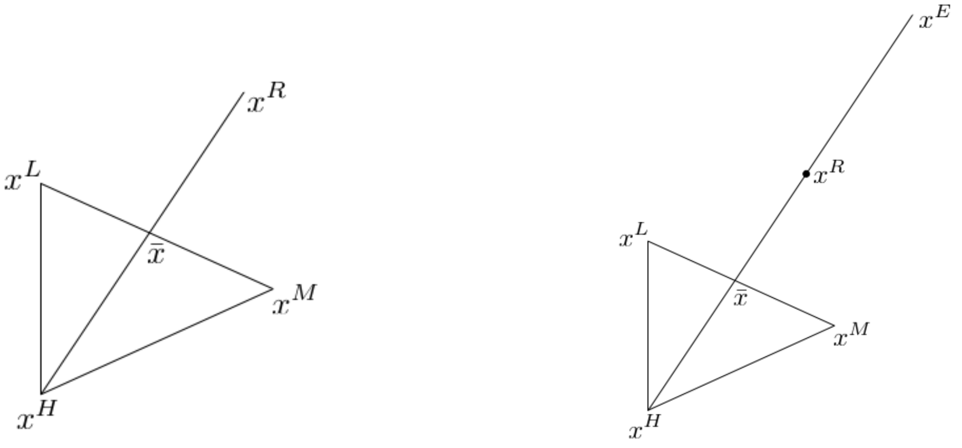
There are two necessary and two sufficient conditions in order for $\mathbf{x}^*$ to be a local minimiser of f over $\mathbb{R}^n$. The first-order necessary condition states that if $\mathbf{x}^*$ is a local minimiser of f and f is continuously differentiable in an open neighborhood (a set of points containing $\mathbf{x}^*$ where one can move away from $\mathbf{x}^*$ without leaving the set) of $\mathbf{x}^*$, then $\nabla f(\mathbf{x}^*) = \mathbf{0}$. The second-order necessary condition states that if $\mathbf{x}^*$ is a local minimiser of f and $\nabla^2 f(\mathbf{x}^*)$ is continuous in an open neighborhood of $\mathbf{x}^*$, then $\nabla f(\mathbf{x}^*) = \mathbf{0}$ and $\nabla^2 f(\mathbf{x}^*)$ is positive semi-definite. Note that in linear algebra, a self-adjoint (Hermitian) matrix M is said to be positive semi-definite if the scalar $z^* M z$ is real and non-negative for all non-zero column vectors z of n complex numbers (z^* denotes the conjugate transpose of z). The two second-order sufficient conditions state that if $\nabla^2 f(\mathbf{x}^*)$ is continuous in an open neighborhood of $\mathbf{x}^*$, and $\nabla f(\mathbf{x}^*) = \mathbf{0}$ and $\nabla^2 f(\mathbf{x}^*)$ is positive semi-definite, then $\mathbf{x}^*$ is a strict local minimiser of f. Despite the existence of two second-order sufficient conditions, certain minimisation methods are based only upon trying to locate a point $\mathbf{x}^*$ that satisfies $\nabla f(\mathbf{x}^*) = \mathbf{0}$, and do not check whether $\nabla^2 f(\mathbf{x}^*)$ is positive semi-definite. This results in points that may not be local minimisers, and these points are usually referred to as stationary points, and they can be minima, maxima or saddle points.

4.2.1 Iterative methods

While the above criteria are relatively "easy" to calculate, it is in practice very rare to be able to provide an explicit minimiser. Instead, so-called iterative methods are used in order to facilitate the optimisation. During an iterative method, a starting "guess " x_0 is used to generate a sequence $\{x_k\}$ with $k = 1, 2, ...$ The search direction d and step size λ that determine the sequence are controlled by setting $x_{k+1} = x_k + \lambda d$. Ideally, the sequence should have some favorable limiting properties, for example it should satisfy first and second order necessary conditions. The iterative method stops when x_k becomes optimal. One basic iterative approach in order to find a local minima $\mathbf{x}^*$ of an objective function $f : \mathbb{R}^n \to \mathbb{R}$ is the line search method. The line search approach first finds a descent direction along which the objective function f will be reduced and then computes a step size that determined how far $\mathbf{x}$ should move along that direction. The descent direction can be computed using various different methods such as gradient descent, Newton's method and Quasi-Newton methods. The step size can be determined exactly, or it can be approximated. In the early days, the line search used to be exact, i.e. a univariate minimisation, a fact that resulted in the search to be rather expensive. Modern methods are focused on inexact line searches, through which the the step size is not determined exactly, but rather a sufficient increase or decrease in the step size is evaluated. The loosely defined step sizes are ensured not to be too long nor too short, while trying to pick a "useful" stepsize that will facilitate the convergence.

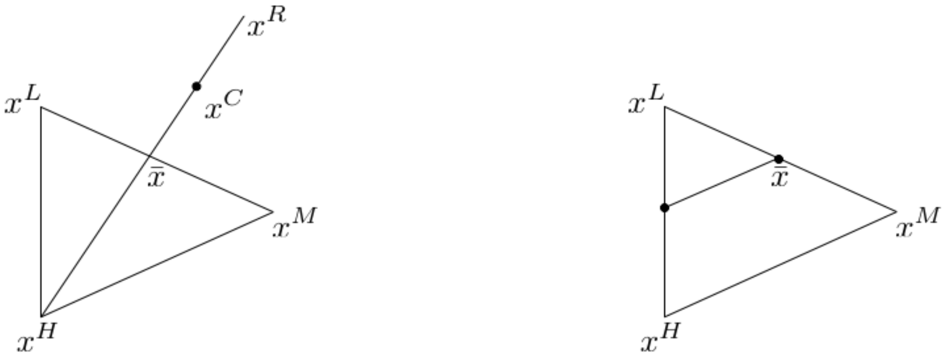
4.2.2 Nelder-Mead Simplex method

Many early methods of minimisation did not have a solid theoretical background. This was primarily the case for problems that only consisted of two to three variables, for which it was relatively easy to establish a region in which the minimum exists, and then address the problem systematically. These methods of optimisation are called *ad hoc* methods, since they are constructed for only a particular problem, with no previous planning. One of the most succesful methods which only compares function values is the Nelder-Mead simplex method.[200] A k-simplex is a k-dimensional polytope which is the convex hull of its $k+1$ vertices. The Nelder-Mead algorithm tries to minimise the objective function by successfully re-evaluating the simplices in the direction where the function decreases in value.[201,202] The aim of the algorithm is to replace the point which maximises the function in the current simplex with another point that makes the function smaller. Consider a two dimensional simplex (triangle) with vertices x^L, x^M, x^H with $x_i \in \mathbb{R}^2$ for which $f(x^L) \leq f(x^M) \leq f(x^H)$. The aim of the algorithm is to replace x^H, with a new improved point, denoted x', so that the new point minimises the function with respect to the first point. In other word the new point needs to satisfy $f(x') > f(x^H)$, and it thus generates a new simplex x^L, x^M, x'. The new point x', is obtained by reflecting, expanding, contracting or shrinking the initial point x^H. These operations are shown in Figure 4.2.



(a) Reflection of point x^H to x^R through the edge of the simplex that connects the remaining points x^L and x^M. $x^R = \bar{x} + \alpha(\bar{x} - x^H)$, where α is usually 1 and $\bar{x} = \frac{x^L + x^M}{2}$.

(b) Expansion step, a move further away in the direction of x^R that could further minimise the function: $x^E = \bar{x} + \gamma(x^R - \bar{x})$, and $\gamma \geq 1$ and in most cases $\gamma = 2$



(c) Contraction step, which is examined if x^R does not offer a significant improvement over $f(x^L)$; The new point, x^C is found from either $x^C = \bar{x} + \beta(x^R - \bar{x})$ or $x^C = \bar{x} + \beta(x^H - \bar{x})$, where $0 < \beta < 1$ with $\beta = 0.5$ most of the time.

(d) Shrinking step, in which if the contraction step fails and $f(x^C) \geq f(x^H)$ then the simplex shrinks by half, towards the current minimum $f(x^L)$.

Figure 4.2: Possible operations that occur during each simplex cycle , in order to determine a new point x' for which $f(x') \leq f(x^H)$.
Figure reproduced from http://www.jakubkonka.com/ with permission from owner.

To illustrate an example of a minimisation using the Nelder-Mead simplex algorithm, the consecutive generated simplices that are generated for the minimisation of the function $f(x_1, x_2) = x_1^2 + x_2^2 - 3x_1 - x_1x_2 + 3$ are shown in Figure 4.3. The function has one global minimum at $x = (2, 1)$.

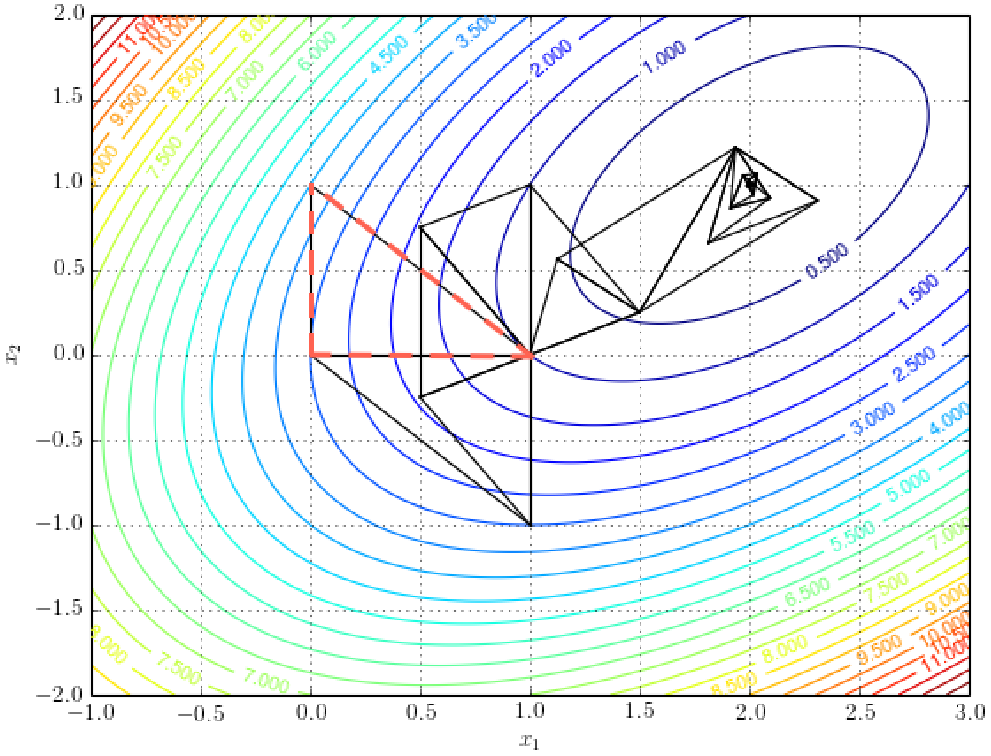


Figure 4.3: Path of the simplex algorithm, overlaid on the contour plot of the objective function $f(x_1, x_2) = x_1^2 + x_2^2 - 3x_1 - x_1x_2 + 3$. Starting state is indicated by the dashed, orange triangle. Figure reproduced from http://www.jakubkonka.com/ with permission from owner.

The Nelder-Mead simplex algorithm is one of the most widely used algorithms for multidimensional unconstrained optimisations.[203,204] Because the method does not require the evaluation of derivates, the method is suitable for problem with non-smooth functions. This method is widely used to solve parameter estimation and similar statistical problems. Nonetheless it is important to keep in mind that the Nelder-Mead simplex method is a so-called heuristic method; it can converge to a non-stationary point. Modern variations that often provide improvement over the basic method have been explored since 1979.[205–210]

4.2.3 Common types of iterative methods

Most optimisations follow some iterative method for finding the optimal solutions. The typical behaviour of such an algorithm is regarded as acceptable if the iterates x_k move steadily towards the neighborhood of a local minimiser x^* and then converge fast to the point x^* itself, where the iteration terminates upon convergence. As mentioned earlier, most modern optimisations rely on some sort of line-search algorithm. Of course different approaches of selecting the search direction and step size yield different methods (within the exact or inexact line-search framework). The most common method associated with inexact or partial line search is the concept of a descent method. This method is a line search for which the slope $\frac{df}{d\alpha}$ is always negative at $\alpha = 0$ unless x_k is a stationary point. This condition guarantees that the function could be reduced in the line search from some $\alpha_k > 0$. In practice the descent optimisation method is closely associated with global convergence. While this method appears appealing at first and while there is a theoretical proof of convergence, the rate of convergence is quite slow and the method usually terminates far from the solution. In order to accelerate the rate of convergence, a quadratic model can be utilised. Descent methods that are based on a quadratic model have been proven to be very powerful. One way to associate an algorithm with a quadratic model is to ensure that the iteration will terminate at the minimising point, in a known finite number of iterations when applied to a quadratic function; this property is known as quadratic termination. This is of course only one way to incorporate a quadratic model in an algorithm. Many algorithms and methods do not terminate for quadratic functions but are derived with quadratic functions in mind and converge rapidly for quadratic functions. Generally speaking, most modern optimisation methods are based on quadric models. If both first and second derivatives are calculated within the algorithm, then the set up of the quadratic model is straight-forward, and gives rise to the popular Newton or Newton-Raphson method.[211] Alternatively, the second derivates may not be evaluated but only estimated, resulting in the so-called quasi-Newton methods, such as the Broyden-Fletcher-Goldfarb-Shanno or BFGS, method that is described later on.

4.2.3.1 Newton and Quasi-Newton methods

Let's consider a function $f : \mathbb{R}^n \to \mathbb{R}$ which we are trying to optimize, without the presence of any constraints (unconstrained optimisation). All methods discussed from this point onwards are iterative methods that begin from point x_0 , produce a sequence x_k and converge to the optimum x^*. Newton's method finds the new iterate x_{k+1} as a function of x_k. First a new point $p = x - x_k$ is found, and then a quadratic model of the function is defined near the point x_k. The second order Taylor expansion around x_k that is utilised for the quadratic model definition is given by

$$m_k(p) = f_k + p^T \nabla f_k + \frac{1}{2} p^T \mathbf{H}_k p \,. \tag{4.5}$$

The gradient of the quadratic model $\nabla m_k(p) = \nabla f_k + \mathbf{H}_k p$ is evaluated and minimised at $p_k = -\mathbf{H_k}^{-1} \nabla f_k$. It is clear, that in order to evaluate p_k the inverse of the Hessian $\mathbf{H}_k$, needs to be computed (or the linear system $B_k p = -\nabla f_k$ needs to be solved). Once p_k is found, then the next point of the sequence x_{k+1} is found using a line-search in the direction of p_k, with $x_{k+1} = x_k + \alpha P_k$, with a step size α that usually has an initial value of 1. While Newton's method is an extremely powerful technique that achieves quadratic convergence, an analytic expression for the derivative and especially for the Hessian may not be easily obtainable and expensive to calculate.

In cases where both the gradient and the Hessian cannot be analytically evaluated, approximate ways of calculating one or both can be used. For example the gradient can be approximated by using the slope of a line through two nearby points on the function; the use of such approximation would result in a variance of the secant method, which converges slower than Newton's method but bypasses the need of a direct gradient evaluation. There can be cases where the first derivative is easily obtainable, while the Hessian is significantly more expensive to evaluate. In such cases quasi-Newton methods are used to find the desired optimum. In quasi-Newton methods, the Hessian does not need to be computed, but it is instead approximated and updated by analyzing successive gradient vectors instead.

The first quasi-Newton method, DFP named after Davidson, Fletcher and Powell, uses an approximation that is based on the change in gradient between iterations in order to approximate the Hessian, $\mathbf{H}$.[212,213] Different properties are used to characterize $\mathbf{H}$ and derive an expression for the unique $\mathbf{H}$ that satisfies these properties. In certain cases before this procedure begins an initial evaluation of $\mathbf{H}$ is performed, but it is possible to avoid this all together simply by using a scalar multiple of the identity matrix, where a scaling factor that is within the range of the eigenvalues of the true Hessian is used.

4.2.3.2 BFGS method

DFP was soon replaced by the superior BFGS method, which is still considered the most effective quasi-Newton method. BFGS is named after its four discoverers, who all discovered it individually in 1970: Broyden, Fletcher, Goldfarb and Shanno.[214] BFGS is quite similar to the DFP method, but bares a single, elegant modification; It does not approximate the Hessian $\mathbf{H}$, but instead it approximates its inverse $\mathbf{H}^{-1}$, using the same criteria as the DFP method. By doing so, it eliminates the need for solving a linear system in order to get the search direction; the only operation required is a matrix/vector multiplication. It is also more numerically stable and is considered to have effective "self-correcting properties" not shared by DFP, a fact that results in its superior performance in practice. The necessary condition of BFGS for a solution to be optimal is that the gradient has to be zero. In other words, a BFGS solution satisfies the first-order necessary condition of unconstrained optimisation. However, since BFGS is a quasi-Newton method, it only requires the gradient of the objective to be computed at each iteration, and it does not compute the Hessian.

If we consider the usual function $f : \mathbb{R}^n \to \mathbb{R}$ which we are trying to optimize then the algorithm starts by making an initial guess of $\mathbf{x}_0$ at the minimum, where k is set to be zero. The initial guess for the inverse Hessian $\mathbf{H}^{-1}(\mathbf{x}_k)$ is set $\mathbf{H}^{-1}(\mathbf{x}_k)= \mathbf{I}$, the n by n identity matrix. Then the gradient $\nabla f(\mathbf{x}_k)$ is computed and the search direction is obtained as $\mathbf{h}_k = \mathbf{H}^{-1}(\mathbf{x}_k)\nabla f(\mathbf{x}_k)$.

Subsequently, a line search is performed, starting from point $\mathbf{x}_k$ in the direction $\mathbf{h}_k$ following the sequence $\mathbf{x}_{k+1} = \mathbf{x}_k + t^*\mathbf{h}_k$ where t^* minimises $f(\mathbf{x}_k + t\mathbf{h}_k)$. Finally the inverse Hessian is updated and $\mathbf{H}_{k+1}^{-1}$ by appropriate modification of $\mathbf{H}_k^{-1}$. This is usually done by setting $\mathbf{H}_{k+1}^{-1} = \mathbf{H}_k^{-1} + \mathbf{U}_k$, where $\mathbf{U}_k$ is some easy to compute "updating" matrix. Then k is set to $k+1$ and a new iteration begins. The key part in the above algorithm is of course the update of $\mathbf{H}_k^{-1}$ to $\mathbf{H}_{k+1}^{-1}$. The criteria that DFP as well as BFGS uses in order to ensure that the approximate Hessian maintains the "essential features" of the true Hessian are the following:

- Symmetry:
  The true Hessian is symmetric (and so is the inverse Hessian that is utilised in the BFGS method), and so it is crucial to insist that the initial $\mathbf{H}_k^{-1}$ should be symmetric. If the initial Hessian (or its inverse) is symmetrical then all subsequent matrices $\mathbf{H}_{k+1}^{-1}$ will be inherently symmetrical.

- Quasi-Newton Condition:
  If we consider the special case where f is quadratic, i.e. $f(\mathbf{x}) = \frac{1}{2}\mathbf{x}^T\mathbf{x} + \mathbf{x}^T + c$ and has a constant Hessian $\mathbf{H}$, then it trivial that any vectors $\mathbf{x}$ and $\mathbf{y}$ satisfy

  $$\mathbf{x} - \mathbf{y} = \mathbf{H}^{-1}(\nabla f(\mathbf{x}) - \nabla f(\mathbf{y}))\,. \tag{4.6}$$

  The new $\mathbf{H}_{k+1}^{-1}$ is required to obey equation 4.6 but not for possible pairs of $\mathbf{x}$ and $\mathbf{y}$, but only for the case that $\mathbf{x} = \mathbf{x}_{i+1}$ and $\mathbf{y} = \mathbf{x}_i$ for $i = 0$ to $i = k$. In other words $\mathbf{x}_{i+1} - \mathbf{x}_i = \mathbf{H}_{k+1}^{-1}(\nabla f(\mathbf{x}_{i+1}) - \nabla f(\mathbf{x}_i))$ for $0 \leq i \leq k$. This is called the quasi-Newton condition.

- Positive-Definiteness:
  The Hessian (and its inverse) should be positive definite, in order for $\mathbf{h}_k$ to be a descent direction.

Quasi-Newton methods have been shown to converge much faster than other methods, such as the descent methods, and since they don't required the use of a Hessian, they are sometimes more efficient (in "wall-clock computational time") than Newton methods.

4.2.3.3 Exponent optimisation for basis set development

During the next chapters, different cases of basis set development will be discussed. These basis sets can be split in two main categories, orbital basis sets (OBSs) and auxiliary basis sets (ABSs). In both cases, exponents of Gaussian functions are optimized by minimising some relevant term (usually the correlation energy of an atom).

Orbital basis set development is carried out within the minimising program of the MOLPRO computational package.[215] There are two implemented options in terms of the optimisation method, simplex and BFGS. As mentioned earlier, simplex method only uses function evaluations, and BFGS uses numerical derivative information. The default optimisation occurs in the space of initial value scaling, however the option to optimize in the space of $\ln(x)$ can be selected. The corresponding convergence thresholds for simplex and BFGS are 1×10^{-7} for the function value, and 1×10^{-5} for the gradient respectively; these thresholds are more strict than the default thresholds of MOLPRO. In most cases the optimisation was carried on using the simplex method, as it provided an overall more stable alternative. While the optimisation of the exponents is unconstrained, the exponents should always remain real, positive numbers, otherwise they are rejected from the energetic calculation. During initial efforts to optimize functions using the BFGS algorithm, the Hessian was not always positive definite and did not maintain this essential feature of the true Hessian, thus causing the optimisation to stop. This of course did not happen when simplex was used (since the Hessian was not evaluated), and for this reason, the majority of optimisations were performed using simplex. Nonetheless, in certain cases the BFGS algorithm was used, in order to obtain the initial gradient over our initial set of exponents in order to get a better idea of where the exponents that were to be for optimised should roughly be.

Auxiliary Basis Sets (ABSs) that were optimized, can be split in two categories, MP2Fit ABSs and OPTRI ABSs. MP2Fit ABSs were optimized using the TURBOMOLE program.[216] The optimisation followed the approach of Hättig,[217] where the following functional, δRI, is minimised for neutral ground-state atoms, using the analytical ABS gradients available in RICC2 module of TURBOMOLE.[217–219] OPTRI sets that were designed, minimised the value for δRI for the atoms where

$$\delta\mathrm{RI} = \sum_{ij} \frac{(V_{ij,ij}^{\mathrm{RI}} - V_{ij,ij}^{\mathrm{RI}_{ref}})^2}{|V_{ij,ij}^{\mathrm{RI}_{ref}}|} + \frac{(B_{ij,ij}^{\mathrm{RI}} - B_{ij,ij}^{\mathrm{RI}_{ref}})^2}{|B_{ij,ij}^{\mathrm{RI}_{ref}}|}\,. \tag{4.7}$$

Additional details on the specifics of the minimisation are given in chapters 5 and 6.

Chapter 5

Auxiliary basis sets for density fitting in explicitly correlated calculations: The atoms H-Ar

5.1 Introduction

The principal difficulty in explicitly correlated methods is the necessity for computing numerous three- and four-electron integrals, as well as multiple many-index two electron integrals. This problem is bypassed by invoking two main approximations that make the explicitly correlated calculations computationally efficient, namely the resolution-of-the-identity (RI) and density fitting (DF), both of which require a respective auxiliary basis sets (ABS). Density fitting reduces the steep computational cost associated with the evaluation of multi-index two-electron integrals, by approximating these integrals through an expansion of orbital product densities in an auxiliary basis sets (ABS).[220–222] This technique[223] has been traditionally used in second-order Møller-Plesset perturbation theory, where it is denoted DF-MP2,[224–227] but can also be used in explicitly correlated methods such as DF-MP2-F12 (DF is sometimes called resolution-of-the-identity, however the former is preferred to prevent confusion in the context of explicit correlation).[180,228]

Two primary methods exist for the optimisation of ABSs (denoted MP2Fit) for use in DF-MP2. ABSs can be either automatically generated on-the fly[229,230] using the Cholesky decomposition (CD) and related methods of Aquilante *et al.*,[231] or they can be individually pre-optimised and matched to a specific orbital basis set (OBS), following the procedure of Ahlrichs,[180] and Hättig.[147] In the present investigation explicitly correlated ABSs of this latter approach were constructed. The pioneering work of Weigend *et al.*[180] in the optimisation of ABSs for conventional frozen-core DF-MP2 established guidelines that were utilised in the development of MP2Fit ABSs. These guidelines suggest that the number of functions in the ABS should be no greater than four times the number of functions in the OBS, and that the error in the correlation energy due to the density fitting (ΔDF error) should be less than 100 μE_h per atom. An additional rule-of-thumb has also been established; the error due the density fitting in molecules should be two to three orders of magnitude smaller than the error due to basis set incompleteness (BSIE) in the OBS.[141,232] Following the establishment of these guidelines, MP2Fit ABSs matched to correlation consistent[180,232,233] and def2 series of basis sets,[234–236] have been produced for the biggest part of the periodic table.

Although the above guidelines can be utilised to examine the behavior of the newly developed MP2Fit ABSs at an initial level, they should be challenged in order to reflect any variations between conventional and explicitly correlated methods. For instance, MP2Fit ABSs for post-d elements Ga-Rn that were recently published by Hill and Peterson[144] exhibit an average ΔDF error much smaller than the 100 μE_h per atom threshold, somewhat expected due to the known fact that F12 methods greatly reduce the BSIE. Furthermore, although previous publications[141,147,237] have pointed out that in order to obtain an accurate resolution of the identity for products of one occupied and one virtual orbital MP2Fit ABSs should include at least functions with angular momenta up to $\ell_{\mathrm{occ}} + \ell_{\mathrm{OBS}}$, where ℓ_{occ} is the highest angular momentum symmetry occupied in neutral atom and ℓ_{OBS} is the highest angular momentum symmetry occupied in the OBS, Hill's paper suggests that MP2Fit ABSs for use in explicitly correlated methods should include functions of angular momenta up to $\ell_{\mathrm{ABS}} = \ell_{\mathrm{occ}} + \ell_{\mathrm{OBS}} + 1$. It is therefore clear that although helpful the above guidelines must be re-evaluated in order to accurately represent explicitly correlated methods.

In this present investigation, the error in the electron repulsion integrals (ERIs) that establishes a satisfactory fitting of the two-electron integrals is assessed at the atomic level. Furthermore, examination of the effect of density fitting on the evaluation of the many-electron integrals at the atomic level reveals that the new ABSs are optimal for use in the context of explicitly correlated methods. Finally, the behavior of the new ABSs in molecular calculations is estimated through the ΔDF error (where $\Delta\mathrm{DF} = E_{\mathrm{MP2}} - E_{\mathrm{DF-MP2}}$) that is assessed at the conventional MP2/DF-MP2 level but compared against the BSIE at the MP2-F12 level for a test set of 104 molecules.

5.2 Basis set construction and optimisation

Auxiliary basis sets for the density fitting of the conventional two-electron integrals were developed using similar design and optimisation strategies as previously employed for a large number of DF-MP2 ABSs (Refs. 3, 25, 30, and references therein). The ABSs presented in this work are designed and optimised to be used in conjunction with the correlation consistent cc-pV*n*Z-F12 and cc-pCV*n*Z-F12 (where n = D, T, Q) OBSs, for elements H-Ar.[124,143,238] The optimisation of the uncontracted exponents proceeded via the minimisation of the functional[180]

$$\delta_{\mathrm{DF}} = \frac{1}{4} \sum_{aibj} \frac{(\langle ab||ij\rangle_{\mathrm{DF}} - \langle ab||ij\rangle)^2}{\epsilon_a - \epsilon_i + \epsilon_b - \epsilon_j} , \tag{5.1}$$

where $\langle ab||ij\rangle = (ai|bj) - (aj|bi)$ with i, j denoting occupied orbitals, a, b virtual orbitals, and ϵ_x representing the HF orbital energies.[180] The above optimisations used the analytical auxiliary basis set gradients of Hättig,[147] implemented within the RICC2 module[219,239] of the TURBOMOLE package.[216]

The new MP2Fit ABS were designed so that the number of basis functions within a particular ABS will remain the same for the elements of each row of the periodic table, namely H and He, Li-Ne and Na-Ar. In consistency with Hättig's paper,[147] optimisations of the cc-pV*n*Z-F12 and cc-pCV*n*Z-F12 ABSs were carried out for the atoms in their electronic ground state, while for hydrogen the optimisation was performed for the H_2 molecule ($R_{\mathrm{HH}} = 1.40\ a_0$). More specifically, the exponents for H_2 were optimised within the MOLPRO[215,240] computational package, by minimising the ΔDF error with respect to each exponent, using a Broyden-Fletcher-Goldfarb-Shanno (BFGS) conjugate gradient method,[214] which uses numerical gradients. Since the cc-pV*n*Z-F12 sets have been designed to correlate only the valence electrons, the usual frozen core approximation ($1s^2$ core electrons frozen for Be-Ne and $1s^22s^22p^6$ core electrons frozen for Mg-Ar). In a similar manner, only the $1s^2$ electrons were frozen for elements Mg-Ar with the remaining electrons correlated during the optimisation of cc-pCV*n*Z-F12 ABSs. In all cases, all the Li electrons were correlated, and only the $1s^2$ electrons of the Na atom were frozen. All exponents were optimised at the atomic level, with the exception of the atoms Li-Ne, at the cc-pVTZ-F12/MP2Fit level, for which the highest angular momentum function was poorly determined due to the lack of gradient on the functional δ_{DF}. The exponent of this single h function was interpolated from the exponents of the next lowest angular momentum as suggested by Hättig.[147] More specifically, the cc-pVTZ-F12/MP2Fit set for Li-Ne contains $4g$ functions (α_{g_1}, α_{g_2}, α_{g_3}, α_{g_4}) where a larger subscript indicates a more diffuse exponent, and a single defined h function α_{h_1}. The initial h exponent was interpolated as $\alpha_{h_1} = \sqrt{\alpha_{g_3}\alpha_{g_4}}$, however that exponent was too diffuse, and caused an increase in ΔDF at the molecular level; hence the exponent was defined as $\alpha_{h_1} = \sqrt{\alpha_{g_2}\alpha_{g_3}}$. It is worth noticing that the exponents of the cc-pCV*n*Z-F12/MP2Fit sets have been completely re-optimised in order to assure their optimal performance both at the atomic and molecular level.

As mentioned earlier, ABSs that were optimised for use in conventional DF-MP2 calculations included functions with angular momenta at least up to $\ell_{\mathrm{occ}} + \ell_{\mathrm{OBS}}$. One exception of the above rule is the hydrogen atom, often strongly polarised in covalent bonds, includes functions up to $\ell_{\mathrm{occ}} + \ell_{\mathrm{OBS}} + 1$. It was, however found that the new ABSs presented herein require functions with angular momenta up to $\ell_{\mathrm{occ}} + \ell_{\mathrm{OBS}} + 1$ for all atoms. This became evident mainly through the molecular calculations, in which it was found that the highest angular momentum functions contributed significantly to the correlation energy of each molecular system, and was maintained throughout the rest of the elements.

In the present investigation, although the ABSs were developed for use in explicitly correlated calculations, the exponent optimisation was carried out at the MP2 and DF-MP2 level instead of the MP2-F12 and DF-MP2-F12 level, due to the fact that there is no "DF-free" MP2-F12 code implemented in any of the computational packages available at the time of the investigation. To overcome this issue, the effect of the DF on the many-electron integrals was evaluated, estimating how effective the resolution-of-identity part of the F12 calculation would be, and the energetic ΔDF error was compared against the BSIE obtained at the MP2-F12 level.

5.3 Results and Discussion

The compositions of the resulting ABSs and their matched OBSs are presented in Table 5.1 (ABSs matched to cc-pV*n*Z-F12) and Table 5.2 (ABSs matched to cc-pCV*n*Z-F12), with the optimised exponents included in Appendix C.

Table 5.1: Composition of the cc-pV*n*Z-F12/MP2Fit auxiliary basis sets (*n* = D, T , Q) compared to the orbital basis sets. The ratio of functions (ABS:OBS) assumes spherical orbitals.

OBS	Atoms	OBS Composition	ABS Composition	Ratio of Functions
cc-pVDZ-F12	H	[3*s*2*p*]	(6*s*4*p*2*d*1*f*)	3.9
	He	[4*s*2*p*]	(6*s*4*p*2*d*1*f*)	3.5
	Li-Ne	[5*s*5*p*2*d*]	(9*s*8*p*7*d*3*f*2*g*)	3.6
	Na-Ar	[6*s*6*p*3*d*]	(12*s*10*p*9*d*5*f*2*g*)	3.6
cc-pVTZ-F12	H	[4*s*3*p*1*d*]	(7*s*5*p*3*d*2*f*1*g*)	3.3
	He	[5*s*3*p*1*d*]	(7*s*5*p*3*d*2*f*1*g*)	3.2
	Li-Ne	[6*s*6*p*3*d*2*f*]	(11*s*10*p*9*d*5*f*4*g*1*h*)	3.2
	Na-Ar	[7*s*7*p*4*d*2*f*]	(14*s*12*p*11*d*7*f*4*g*1*h*)	3.2
cc-pVQZ-F12	H	[5*s*4*p*2*d*1*f*]	(8*s*6*p*4*d*3*f*2*g*1*h*)	2.8
	He	[6*s*4*p*2*d*1*f*]	(8*s*6*p*4*d*3*f*2*g*1*h*)	2.7
	Li-Ne	[7*s*7*p*4*d*3*f*2*g*]	(13*s*12*p*11*d*7*f*6*g*3*h*1*i*)	2.9
	Na-Ar	[8*s*8*p*5*d*3*f*2*g*]	(16*s*14*p*13*d*9*f*6*g*3*h*1*i*)	3.0

Table 5.2: Composition of the cc-pCVnZ-F12/MP2Fit auxiliary basis sets (n = D, T , Q) compared to the orbital basis sets. The ratio of functions (ABS:OBS) assumes spherical orbitals.

OBS	Atoms	OBS Composition	ABS Composition	Ratio of Functions
cc-pCVDZ-F12	Li-Ne	$[6s6p2d]$	$(11s10p8d3f2g)$	3.6
	Na-Ar	$[7s7p4d]$	$(14s12p10d6f2g)$	3.6
cc-pCVTZ-F12	Li-Ne	$[7s7p4d2f]$	$(13s12p10d6f4g1h)$	3.0
	Na-Ar	$[8s8p5d3f]$	$(16s14p12d8f5g1h)$	2.8
cc-pCVQZ-F12	Li-Ne	$[8s8p5d3f2g]$	$(16s15p13d9f7g3h1i)$	3.1
	Na-Ar	$[9s9p6d4f2g]$	$(18s16p14d10f7g3h1i)$	2.8

By comparing the size of the new ABSs to existing MP2Fit ABSs it is apparent that cc-pVDZ-F12/MP2Fit is similar in size to aug-cc-pVTZ/MP2Fit, cc-pVTZ-F12/MP2Fit to aug-cc-pVQZ/MP2Fit and cc-pVQZ-F12/MP2Fit to aug-cc-pV5Z/MP2Fit. Core-valence cc-pCVnZ-F12/MP2Fit ABSs are approximately 16% smaller than the aug-cc-pwCV(n+1)Z/MP2Fit.

The errors due to the DF approximation for the neutral atoms are detailed in Table 5.3 in the form of the difference between conventional MP2 and DF-MP2 correlation energies per correlated electron (pce), from now on denoted ΔDF error and the difference in the electron repulsion integrals (ERIs) per atom expressed as $\delta_{\mathrm{DF}}/|E^{\mathrm{corr}}_{\mathrm{MP2}}|$ (see equation 5.1).

Table 5.3: Errors in the MP2 density fitting for atoms He-Ar, as errors in correlation energy (ΔDF error) per correlated electron and electron repulsion integrals ($\delta_{\mathrm{DF}}/|E^{\mathrm{corr}}_{\mathrm{MP2}}|$) per atom for the cc-pV$n$Z-F12/MP2Fit and cc-pCV$n$Z-F12/MP2Fit auxiliary basis sets (n= D, T, Q)

	ΔDF error (μE$_h$)			$\delta_{\mathrm{DF}}/|E^{\mathrm{corr}}_{\mathrm{MP2}}|$		
Basis	MUE	σ	MAX	MUE	σ	MAX
cc-pVDZ-F12	0.116	0.175	0.732	1.563×10^{-9}	1.916×10^{-9}	8.371×10^{-9}
cc-pVTZ-F12	0.106	0.113	0.467	1.640×10^{-9}	1.753×10^{-9}	6.033×10^{-9}
cc-pVQZ-F12	0.061	0.068	0.307	4.545×10^{-9}	1.226×10^{-9}	5.218×10^{-9}
cc-pCVDZ-F12	0.273	0.225	0.698	3.403×10^{-9}	2.522×10^{-9}	8.420×10^{-9}
cc-pCVTZ-F12	0.182	0.135	0.494	2.099×10^{-9}	1.421×10^{-9}	4.499×10^{-9}
cc-pCVQZ-F12	0.037	0.033	0.099	2.441×10^{-9}	3.044×10^{-9}	9.650×10^{-9}

It can be seen that the average performance of the ABSs at the atomic level improves as the cardinal number increases, as the ΔDF and δ_{DF} error decreases, from double- to quadruple-ζ. The mean unsigned DF error is always less than 0.2 μE$_h$ pce for cc-pVnZ-F12/MP2Fit and less than 0.3 μE$_h$ pce for cc-pCVnZ-F12/MP2Fit while the maximum of this error is always less than 1 μE$_h$, significantly smaller than the original criteria of 100 μE$_h$ by Weigend *et al*.[180] As the energetic error is not directly related to δ_{DF}, a similar criteria for the error in the integrals was established[180] for optimisation purposes in which $\delta_{\mathrm{DF}}/|E^{\mathrm{corr}}_{\mathrm{MP2}}|$. As δ_{DF} is of the order of 10^{-4} $\mathrm{E_h}$ in ppm, all of the ABSs developed in this work produce negligible errors both in the correlation energy and the ERIs. It should be noted that hydrogen is excluded from the above discussion, since it was only assessed at a molecular level.

In addition to exploring the error in the evaluation of two-electron integrals due to the density fitting, the error in evaluation of many-electron integrals (using the RI method) was also examined. Since the RI approximation requires the use of an auxiliary basis set, compact ABSs matched to correlation consistent basis sets have been developed specifically for use as CABS RI sets in explicitly correlated F12 calculations, and they are commonly denoted as OPRTI.[143,241–243] These OPTRI sets are used for the evaluation of the multi-electron F12 integrals within the complementary auxiliary basis set (CABS+) approach.[244] The general procedure for the design of OPTRI sets is the optimisation of functions that minimise the value for δ_{RI} functional for each element. The δ_{RI} functional involves the diagonal elements of the **V** and **B** matrices that arise in MP2-F12 theory and has the following form:

$$\delta_{\mathrm{RI}} = \sum_{ij} \frac{(V_{ij,ij} - V^{\mathrm{ref}}_{ij,ij})^2}{|V^{\mathrm{ref}}_{ij,ij}|} + \frac{(B_{ij,ij} - B^{\mathrm{ref}}_{ij,ij})^2}{|B^{\mathrm{ref}}_{ij,ij}|} \tag{5.2}$$

The **V** and **B** matrices contain the many-electron integrals approximated by the RI,[245,246] and the quantity of equation 6.4 is always positive. Since the RI approximates many-electron integrals as sums of products of two-electron integrals, the way that the two-electron integrals are approximated through density fitting affects the evaluation of the many-electron integrals. In order to examine how the fitting of the two-electron integrals affects the evaluation of many-electron integrals, $\sqrt{\delta_{\mathrm{RI}}}$ was evaluated using the cc-pV*n*Z-F12 and cc-pCV*n*Z-F12 OBSs, along with the matched cc-pV*n*Z-F12/OPTRI and cc-pCV*n*Z-F12/OPTRI auxiliary basis sets.[143,147,247] The cc-pVTZ/JKFIT[232] basis set was employed for the Fock and exchange matrices at the DZ level (cc-pVTZ/JKFIT and cc-pVQZ/JKFIT were used at TZ and QZ respectively). The reference MP2Fit ABS used is the large even-tempered set constructed by Hill *et al*.[248] with a 21*s*18*p*14*d*12*f*10*g*8*h*6*i* configuration for H-He, 28*s*26*p*22*d*22*f*20*g*18*h*15*i* for Li-Ne, and 29*s*27*p*23*d*20*f*18*g*17*h*15*i* for Na-Ar, while the MP2Fit sets were selected between the cc-pV*n*Z/MP2Fit, aug-cc-pV*n*Z/MP2Fit, and aug-cc-pwCV*n*Z/MP2Fit families of sets. By using the large even-tempered set as reference MP2Fit ABS and one of the existing MP2Fit ABS mentioned above, we are comparing the error caused to the RI approximation by the density fitting when the existing MP2Fit set is used, to the minimum error caused to the RI approximation by the density fitting when the large reference MP2Fit ABS is used. Following the same procedure we also assess the error caused by the newly developed cc-pV*n*Z-F12/MP2Fit, and compare it to those of the existing MP2Fit ABSs. The functional $\sqrt{\delta_{\mathrm{RI}}}$ was evaluated at the atomic level for all elements other than H, for which $\mathrm{H_2}$ was used. In all cases, the geminal Stater exponent for the fixed amplitude *Ansatz* was set to 1.4 α_0^{-1} for all zeta levels. The calculated values of $\sqrt{\delta_{\mathrm{RI}}}$ for all atoms He-Ar and $\mathrm{H_2}$ are presented below in statistical form as the mean average error (MAE), standard deviation, and maximum unsigned error (MAX).

Table 5.4: Effect of density fitting on the many electron integrals, as expressed by $\sqrt{\delta_{\mathrm{RI}}}$ in $\sqrt{\mathrm{mE_h}}$, using the newly developed cc-pV*n*Z-F12 (n = D, T, Q) sets, and a series of existing MP2Fit sets. (cc-pV*n*Z-F12 has been shortened to V*n*Z-F12, aug-cc-pV*n*Z to aV*n*Z and aug-cc-pwCV*n*Z to awCV*n*Z)

OBS	ABS	MAE	σ	MAX
VDZ-F12	VDZ-F12/MP2Fit	0.052	0.028	0.105
	awCVDZ/MP2Fit	0.549	0.283	0.937
	aVTZ/MP2Fit	0.095	0.053	0.210
	awCVTZ/MP2Fit	0.057	0.028	0.100
VTZ-F12	VTZ-F12/MP2Fit	0.020	0.010	0.034
	awCVTZ/MP2Fit	0.830	1.123	4.523
	aVQZ/MP2Fit	0.103	0.070	0.344
	awCVQZ/MP2Fit	0.043	0.081	0.344
VQZ-F12	VQZ-F12/MP2Fit	0.015	0.009	0.031
	awCVQZ/MP2Fit	0.369	0.575	2.333
	aV5Z/MP2Fit	0.068	0.028	0.121
	awCV5Z/MP2Fit	0.027	0.016	0.079

Table 5.5: Effect of density fitting on the many electron integrals, as expressed by $\sqrt{\delta_{\mathrm{RI}}}$ in $\sqrt{\mathrm{mE_h}}$, using the newly developed cc-pCV*n*Z-F12 (n = D, T, Q) sets, and a series of existing MP2Fit sets. (cc-pCV*n*Z-F12 has been shortened to CV*n*Z-F12 and aug-cc-pwCV*n*Z to awCV*n*Z)

OBS	ABS	MAE	σ	MAX
CVDZ-F12	CVDZ-F12/MP2Fit	0.164	0.124	0.407
	awCVDZ/MP2Fit	3.261	3.212	10.377
	awCVTZ/MP2Fit	0.368	0.381	1.227
CVTZ-F12	CVTZ-F12/MP2Fit	0.037	0.022	0.080
	awCVTZ/MP2Fit	11.949	10.638	25.732
	awCVQZ/MP2Fit	0.154	0.197	0.559
CVQZ-F12	CVQZ-F12/MP2Fit	0.027	0.016	0.070
	awCVQZ/MP2Fit	0.782	0.727	2.364
	awCV5Z/MP2Fit	0.030	0.011	0.051

Data presented in Tables 5.4 and 5.5 suggest that the new sets perform statistically better than the default MP2Fit ABSs as suggested by MOLPRO and TURBOMOLE MOLPRO pairs cc-pV*n*Z-F12 OBS with the aug-cc-pV(*n*+1)Z/MP2Fit while turbomole recommends aug-cc-pwCV(*n*+1)Z/MP2Fit ABS in conjunction with the cc-pV*n*Z-F12 OBS). In statistical terms, cc-pVDZ-F12/MP2Fit behaves a bit better than aug-cc-pwCVTZ/MP2Fit, cc-pVTZ-F12/MP2Fit much better than aug-cc-pwCVQZ/MP2Fit, and cc-pVQZ-F12/MP2Fit roughly the same as aug-cc-pwCV5Z/MP2Fit. Correspondingly, cc-pCVDZ-F12/MP2Fit behaves much better than aug-cc-pwCVTZ/MP2Fit, cc-pCVTZ-F12/MP2Fit surpasses aug-cc-pwCVQZ/MP2Fit significantly, while cc-pCVQZ-F12/MP2Fit is roughly equivalent to aug-cc-pwCV5Z/MP2Fit. In all cases it is clear that the error in $\sqrt{\delta_{\mathrm{RI}}}$ produced by the use of the new cc-pV*n*Z-F12/MP2Fit and cc-pCV*n*Z-F12/MP2Fit ABSs is well controlled, with a mean average value of less than 0.05 $\mathrm{mE_h}$ for the valence sets and less than 0.2 $\mathrm{mE_h}$ for the core-valence ABSs. It is therefore expected that the new sets will be optimal for use in explicitly correlated calculations.

In order to estimate the basis set incompleteness error (BSIE) and assess the performance of the newly developed ABSs at a molecular level, (R)MP2-F12/3C(FIX) calculations were carried out using the MOLPRO computational package. The standard frozen core approximation was used in all molecular calculations that used the valence-only cc-pV*n*Z-F12/MP2Fit ABSs, while the $1s^2$ electrons of elements Na-Ar were frozen in all calculations that employed the core-valence ABSs cc-pCV*n*Z-F12/MP2Fit. All calculations employed cc-pV*n*Z-F12 (*n*= D - Q) as the orbital basis set[238] and the corresponding cc-pV*n*Z-F12/OPTRI auxiliary sets[242] for the resolution-of-identity. The large aug-cc-pwCV5Z/MP2Fit[143,147] was used for the DF of the integrals in the MP2-F12 calculations, while the cc-pVTZ/JKFIT basis was used for the evaluation of exchange integrals at the DZ level (cc-pVTZ/JKFIT and cc-pVQZ/JKFIT were used at TZ and QZ respectively). The geminal Slater exponent for the diagonal fixed amplitude *Ansatz* was set to 0.9 α_0^{-1} for the DZ level and 1.0 α_0^{-1} for the TZ and QZ level, as recommended from previous work of *et al*.[248] The molecular set selected to test the performance of the new ABSs is a subgroup of the molecules used by Weigend[249] (with the additions of Ne, Ar and O_2) and consists of 104 small- to medium-sized molecules. The molecular test set consisted of 56 molecules containing only first row elements and 48 molecules containing both first and second row elements the following compounds: B_2H_6, $B_3N_3H_6$, B_4H_4, Be_2F_4, Be_2H_4, Be_4, BeC_2H_6, $BeF_2O_2H_4$, BeH_2, BF_3, BH_3CO, BH_3, BH_3NH_3, C_2H_2, C_2H_3N, C_2H_4, C_2H_6, C_4H_4, C_6H_6, CF_4, CH_2O_2, CH_2O, CH_3N, CH_3OH, CH_4, CO_2, CO, F_2, H_2CO_3, H_2, H_2O_2, H_2O, HCN, He_2, HF, HNC, HNO_2, HNO_3, HNO, Li_2, Li_2O, Li_4H_4, Li_8, $LiBH_4$, LiF, LiH, N_2, N_2H_2, N_2H_4, N_4, NF_3, NH_3, NH_4F, Ne, OF_2, O_2, Al_2O_3, Al_2S_3, $AlCl_3$, AlF_3, AlH_3, AlN, Ar, BeS, Cl_2, ClF_3, ClF, CS_2, H_2SO_4, H_3PO_4, HCl, HCP, HSH, HSSH, Li_4Cl_4, LiCl, LiSLi, Mg_4, $MgCl_2$, MgF_2, MgF, MgH_2, Na_2O, Na_2S, Na_3N, Na_3P, NaCl, NaF, NaH, P_2, PF_3, PF_5, PH_3, PLi_3, S_2, S_5, SF_2, SF_4, SF_6, $SiCl_4$, SiF_4, SiH_4, SiO_2, SiS_2.

Estimates of the CBS limit have been obtained from (R)MP2-F12/3C(FIX) calculations, that were carried out with a Schwenke-type extrapolation scheme:[250]

$$E^{\mathrm{corr}}_{\mathrm{CBS}} = (E^{\mathrm{corr}}_{\mathrm{large}} - E^{\mathrm{corr}}_{\mathrm{small}})F + E^{\mathrm{corr}}_{\mathrm{small}}, \tag{5.3}$$

where $E_{\text{large}}^{\text{corr}}$ and $E_{\text{small}}^{\text{corr}}$ are the correlation energies evaluated with the larger and smaller of two basis sets, respectively. The value of F was set to the optimal values of 1.495083 for the VDZ-F12/VTZ-F12 extrapolation and 1.414800 for the VTZ-F12/VQZ-F12 extrapolation, as suggested by Hill *et al*.[248]

The BSIE and DF errors for the cc-pV*n*Z-F12/MP2Fit and cc-pCV*n*Z-F12/MP2Fit ABSs respectively, can be seen in Tables 5.6 and 5.7. The errors are presented in statistical form as the mean average error (MAE), standard deviation (σ), and maximum unsigned error (MAX) and the molecule that corresponds to the MAX error in parentheses, for the whole test set of molecules.

Table 5.6: MP2-F12/cc-pV*n*Z-F12 correlation energy errors (ΔDF) per correlated electron (in μE_h) due to orbital BSIE and the DF approximation, assessed at the DF-MP2/MP2 level of theory, for a test set of molecules containing elements H-Ar.

OBS	Error Type	MAE	σ	MAX
cc-pVDZ-F12	BSIE	590.369	292.793	1189.003
	ΔDF	0.727	0.656	3.763 (Li_2)
cc-pVTZ-F12	BSIE	173.325	87.916	367.641
	ΔDF	0.363	0.373	2.399 (NaH)
cc-pVQZ-F12	BSIE	49.525	25.121	105.049
	ΔDF	0.317	0.437	2.999 (Li_2)

Table 5.7: MP2-F12/cc-pCV*n*Z-F12 correlation energy errors (ΔDF) per correlated electron (in μE_h) due to orbital BSIE and the DF approximation, assessed at the DF-MP2/MP2 level of theory, for a test set of molecules containing elements H-Ar.

OBS	Error Type	MAE	σ	MAX
cc-pCVDZ-F12	BSIE	1271.511	792.449	3971.284
	ΔDF	0.483	0.410	1.785 (BH_3)
cc-pCVTZ-F12	BSIE	276.362	178.315	1200.659
	ΔDF	0.316	0.238	0.884 (N_2H_4)
cc-pCVQZ-F12	BSIE	78.967	50.951	343.072
	ΔDF	0.186	0.144	0.963 (Li_2)

The average of the ΔDF error is three orders of magnitude smaller than the BSIE when cc-pVDZ-F12/MP2Fit was used, and this became three and two orders of magnitude when cc-pVTZ-F12 and cc-pVQZ-F12 were used respectively. Similarly, the average of the ΔDF error is four orders of magnitude smaller than the BSIE when cc-pCVDZ-F12/MP2Fit was used, and this became three and two orders of magnitude when cc-pCVTZ-F12 and cc-pCVQZ-F12 were used respectively. A comparison of BSIE with ΔDF errors indicates that the energetic error caused by the DF is always at least 2 orders of magnitude smaller than the respective BSIE, with an average ΔDF error less than 1 μE_h for cc-pVnZ-F12/MP2Fit, and less than 0.5 μE_h for cc-pCVnZ-F12/MP2Fit, and can thus be considered negligible in all cases, despite the large decrease in BSIE due to the explicitly correlated wavefunction.

Figure 5.1 displays the cc-pVnZ-F12 and cc-pVnZ-F12 (n = D, T, Q) ΔDF errors graphically as normalised Gaussian distributions, while it indicates that the ΔDF error generally decreases as the cardinal number n of the basis sets increases. Although the increase in fitting accuracy is immediately apparent between CVDZ, CVTZ, and CVQZ, it can be seen that the standard deviation of VTZ and VQZ is the roughly the same at 0.373 and 0.437 μE_h respectively, and only the central position of the Gaussian demonstrates the lower MAE for QZ, by 0.06 μE_h. This is also accompanied by the small reduction in MAX displayed in Table 5.6.

The ΔDF error per correlated electron for each molecule in the test set, is also presented in bar chart form in Figures 5.2 and 5.3. Figure 5.2 plots the ΔDF error per correlated electron (pce) for each molecule in the test set with the cc-pVnZ-F12 (n = D, T, Q) series of OBSs and ABSs, while figure 5.3 plots the ΔDF error pce for the molecular set, using the cc-pCVnZ-F12 (n = D, T, Q) series of OBSs and ABSs. Inspection of the heights of the bars indicates that the majority of the time the DF error decreases monotonically as the cardinal number increases. For both set series, Li complexes seem to produce pce errors that are larger than the average for this basis (probably due to the somewhat different treatment of this element - all 3 electrons correlated at all times), but the overall DF errors are still around four orders of magnitude smaller than the BSIE.

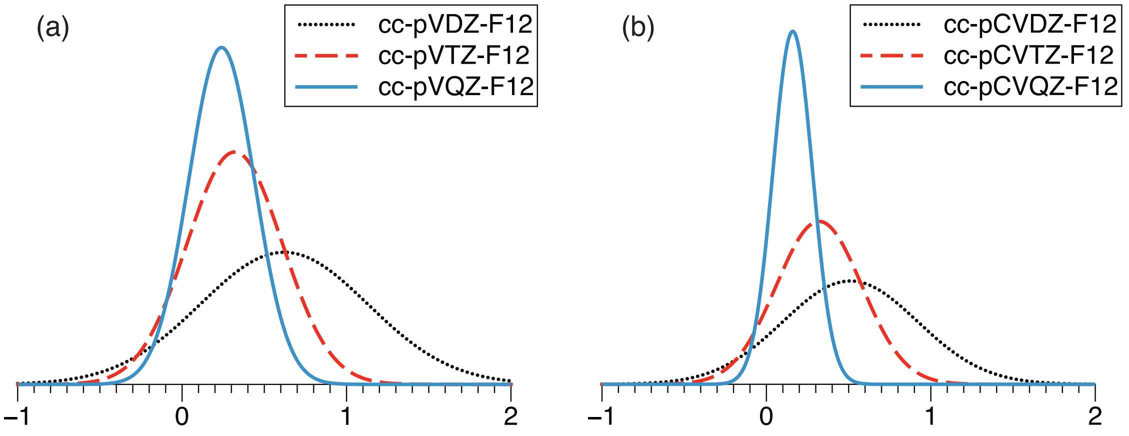
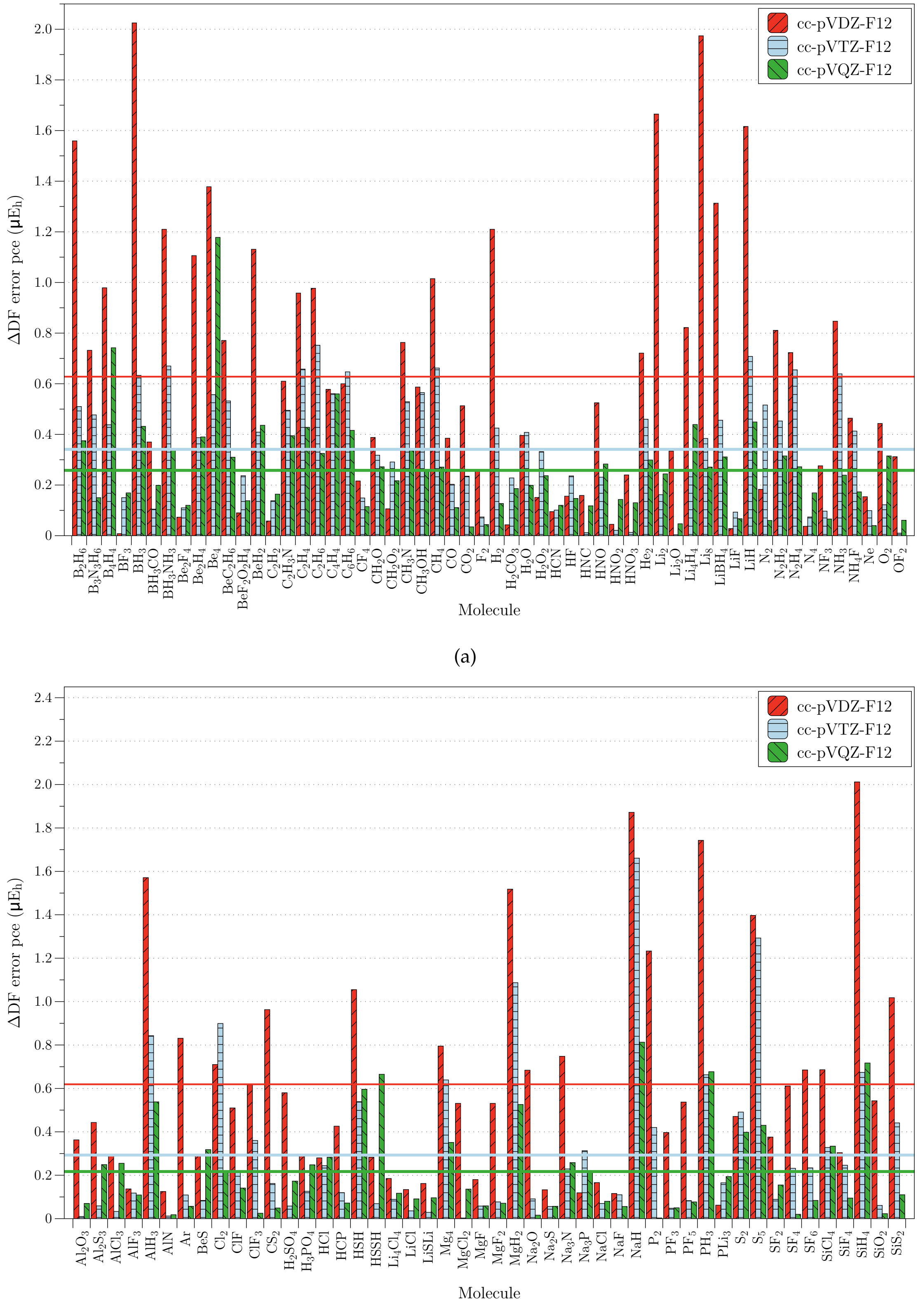


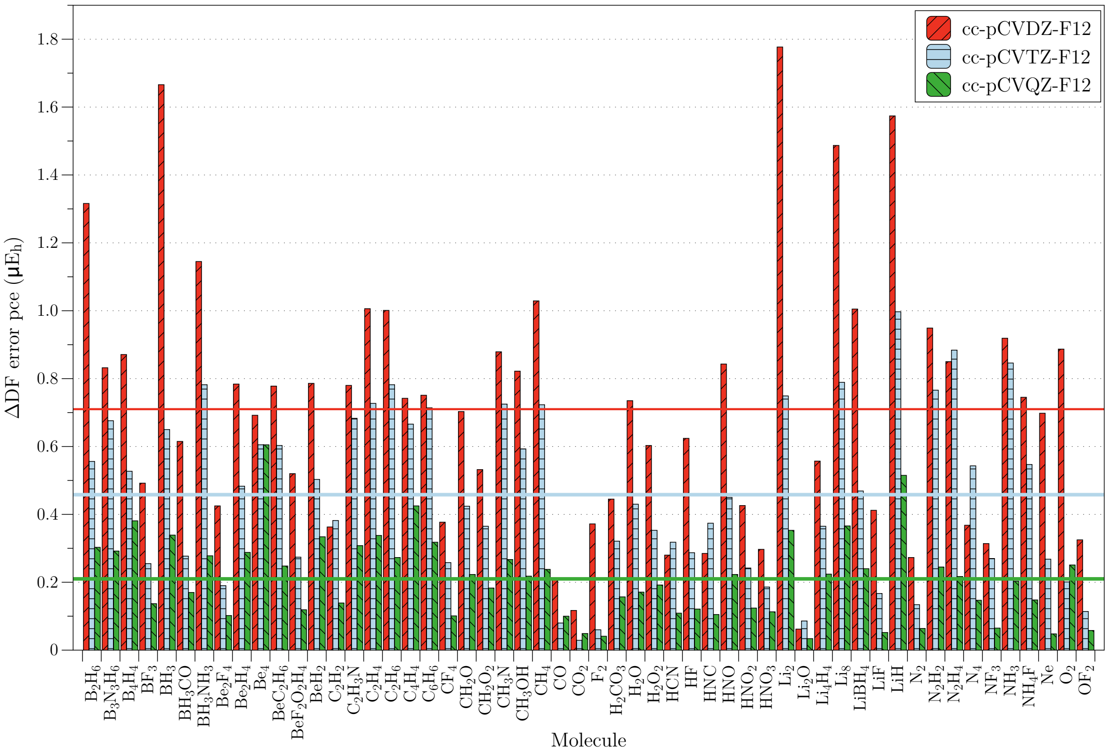
Figure 5.1: Normalised Gaussian distributions of the DF error pce in MP2 correlation energy for a test set of molecules that include elements H-Ar, using
(a) cc-pVnZ-F12 OBSs and the corresponding cc-pVnZ-F12/MP2Fit ABS and (b) cc-pCVnZ-F12 OBSs and the corresponding cc-pCVnZ-F12/MP2Fit ABS.



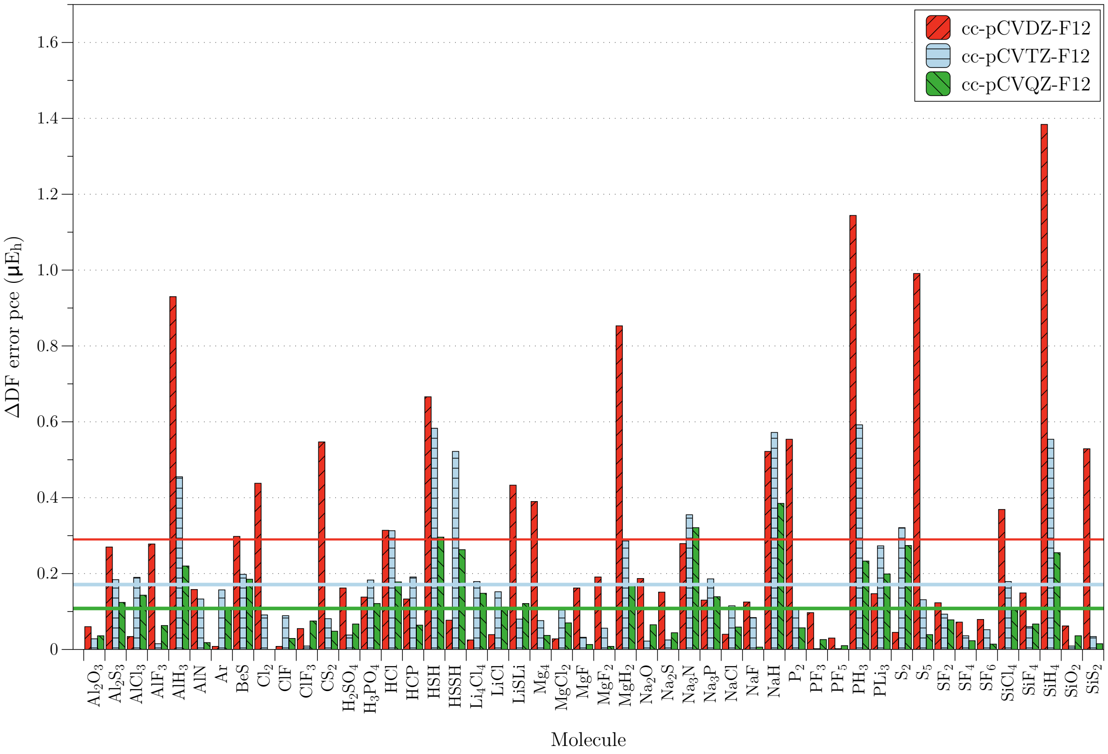
(a)

(b)

Figure 5.2: ΔDF error (pce, μE_h) from the MP2Fit auxiliary basis sets specifically matched to cc-pVnZ-F12 for a test set of molecules that include (a) elements H-Ne and (b) elements H-Ar.



(a)



(b)

Figure 5.3: ΔDF error (pce, μE_h) from the MP2Fit auxiliary basis sets specifically matched to cc-pCV*n*Z-F12 for a test set of molecules that include (a) elements H-Ne and (b) elements H-Ar.

5.4 Conclusions

New auxiliary basis sets for use in the density fitting approximation at the MP2-F12 level have been optimised for use with the cc-pV*n*Z-F12 and cc-pCV*n*Z-F12 (n = D, T, Q) orbital basis sets for the elements H-Ar. The performance of these sets has been assessed both at the atomic and molecular level. At the atomic level, the ΔDF error meets Hättig's guideline as it is significantly lower than 50 μE_h, and it appears that the guideline for this atomic energetic error, calculated using F12 methods for these lighter elements, can be updated to 1 μE_h. In addition, $\sqrt{\delta_{\mathrm{RI}}}$ was evaluated in order to examine how the fitting of the two-electron integrals affects the evaluation of many-electron integrals, and the errors produced by the use of the new cc-pV*n*Z-F12/MP2Fit and cc-pCV*n*Z-F12/MP2Fit ABSs is well controlled, with a mean average value of less than 0.05 $\mathrm{mE_h}$. It is therefore expected that the new sets will be optimal for use in explicitly correlated calculations. Furthermore, the error introduced by utilising the new ABSs in the DF approximation have been assessed by comparing the BSIE error with the ΔDF error for a test set of molecules that contain elements H-Ar. In all cases the mean average error, standard deviation and maximum error of the DF error were three to four orders of magnitude smaller than the BSIE, indicating that the errors introduced by using these ABSs is negligible and that they are suitable for use in MP2-F12 calculations; the 100 μE_h per atom threshold that was suitable for conventional calculations appears to be much smaller, around 5 μE_h pce for explicitly correlated calculations. Overall, the new ABSs outperform existing sets of similar size, and are shown to be particularly efficient in MP2-F12 calculations, when used in conjunction with the cc-pV*n*Z-F12 and cc-pCV*n*Z-F12 OBS. These ABSs can also be employed in other explicitly correlated methods such as CCSD(T)-F12. All of the ABSs optimised in this work can be found in Appendix C, and are available for electronic download from the Basis Set Exchange website (https://bse.pnl.gov/bse/portal).[251,252]

Chapter 6

Basis Sets for explicitly correlated calculations: The atoms Y-Pd

High-accuracy calculations involving transition metal elements are known to be particularly demanding with regards to both the method and the basis set selection, mainly due to the large number of low lying electronic states that likely exist. It is important to ensure that the selected basis set provides an accurate and balanced description of all states (as already seen in the ANO basis sets framework where a state averaged density matrix was used).[21] Correlation consistent basis sets for some transition metals have been available for almost two decades, published for Ti and Fe based on the primitive functions previously developed by Partridge.[182,253,254] All-electron basis sets of TZ-5Z quality for all 3*d* transition metals (Sc-Zn) elements were later produced by Balabanov and Peterson, with consideration to ensure the flexibility of the sets when describing the 4*p* orbitals and multiple (up to three) electronic states.[255] Correlation consistent sets for use in DKH calculations, as well as diffuse augmented and core-valence variants were also developed and reported in the same publication. Furthermore, smaller basis sets of DZ quality were developed later and are included in packages such as MOLPRO.[215,240,256]

The importance of relativistic effects that can no longer be neglected once the 4*d* and 5*d* transition metal elements are reached, as well as their increased number of electrons, led to the development of cc basis sets matched to the small-core Stuttgart-Köln relativistic PPs for those elements as well as Cu and Zn.[257–261] While the existing relativistic ECPs and the corresponding series of basis sets (cc-pV*n*Z-PP, cc-pwCV*n*Z-PP, aug-cc-pV*n*Z-PP) for 4*d* transition metals have been proven to be well-controlled and convergent towards the CBS limit, nonetheless they still suffer from slow convergence with respect to their cardinal number; it is common for sets of at least QZ if not 5Z quality to be required in order to achieve chemical accuracy. As already discussed, the introduction of explicitly correlated methods improves the convergence significantly by including one or more nonlinear correlation factors such as $e^{-\gamma r_{12}}$ into the wavefunction. The F12 philosophy has been implemented in numerous methods, many of which are described briefly in Chapter 2 as well as in several reviews.[60,74] While standard basis sets can be effectively used in an F12 framework, it has been established that Gaussian basis sets optimised specifically for use in F12 methods are advantageous.[142,157] However, the technical difficulties of basis set development for transition metal systems has hindered their progress; basis sets designed for explicitly correlated methods for transitions metal elements have not yet been reported. In the present work, this "gap" is addressed as new F12-based correlation consistent basis sets, denoted cc-pV*n*Z-PP-F12 as well as cc-pCV*n*Z-PP-F12, have been developed for the 4*d* transition metal elements Y-Pd. These sets are based upon the existing standard aug-cc-pV*n*Z-PP sets that are matched to the small-core Stuttgart-Köln relativistic PPs.[259] To accompany the new orbital basis sets, new auxiliary basis sets were also necessary; auxiliary basis sets used for the density fitting of the standard 2-electron integrals, denoted MP2Fit, as well as auxiliary basis sets used for the resolution of identity of the many-electron F12 intergals, denoted OPTRI, were also developed. The preliminary atomic and molecular performance of these sets in CCSD(T)-F12b calculations exhibit excellent and accelerated convergence to the basis set limit.

6.1 Basis Set Development

The MOLPRO suite of *ab initio* programs was used unless otherwise stated.[215] All of the bais sets of this work were paired with small-core, Stuttgart-Köln relativistic PPs (denoted ECP28MDF since they replace 28 electrons for atoms Y-Pd) as previously seen in the conventional cc-pV*n*Z-PP basis sets.[259]

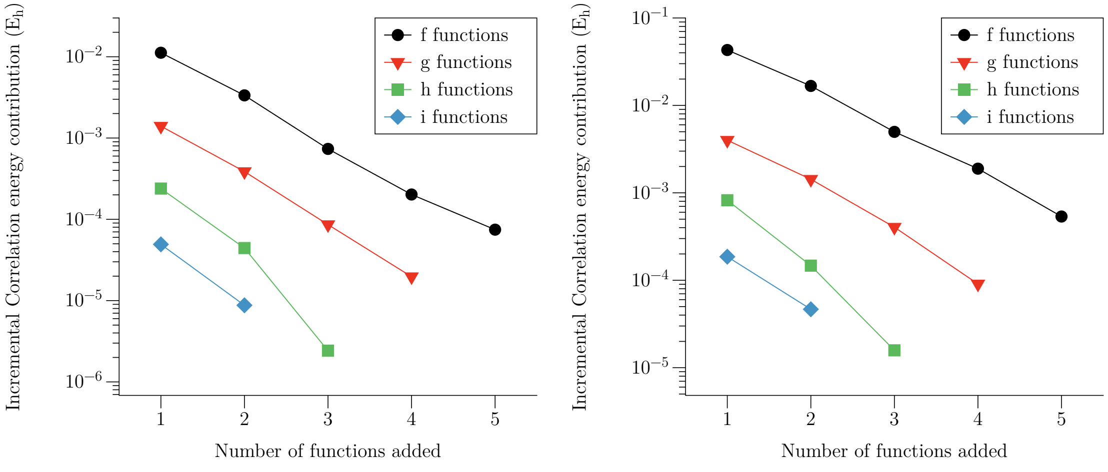
6.1.1 Atomic Orbital Basis Sets

The development of the F12 atomic orbital basis sets (OBS) of this work, follows the general procedure utilised for the development of correlation consistent basis sets, with a few modifications in order to address the multitide of common oxidation states of the elements, as well as to fit in the F12 framework. All exponent optimisations were carried out using the Nelder-Mead simplex or the BFGS methods (discussed in Chapter 4). All orbitals were fully symmetry equivalenced, and only the pure spherical harmonic components of the angular momentum functions were used. As already mentioned, one of the main challenges of developing basis sets for transition metal systems is the multitude of low-lying electronic states. In order to include a balanced description of these states, the exponents were always optimised with respect to the average energy of several states, in most cases the three; lowest states corresponding to the $4d^{m-2}5s^2$, $4d^{m-1}5s^1$, and $4d^m$ configurations (seen in Table 6.1). Exponent optimisations were performed at the CCSD-F12b level of theory[71,72] with the 3C(FIX) ansatz[262] and a geminal exponent γ of 1.4 α_0^{-1} at all cardinal levels. While the optimisation could in principle be performed at the MRCI-F12 level, numerical instabilities arose from using big, even-tempered RI fitting sets, which did not occur with CCSD-F12b.

Table 6.1: Electronic configurations and corresponding states (ground states in bold, cation ground states in parentheses, and anion ground states in square brackets) of elements Y-Pd, used in the present work, along with their corresponding term symbols. Atomic states were utilised for exponent optimisations while cations and anions were used for atomic property evaluation. Note that m refers to the total number of valence electrons ($4d$ and $5s$).

		Electronic configuration		
Element	m	[Kr]$4d^{m-2}5s^2$	[Kr]$4d^{m-1}5s^1$	[Kr]$4d^m$
Y	3	^{2}**D**, (^{1}S)	^{4}F	^{4}F, [^{1}D]
Zr	4	^{3}**F**, [^{4}F]	^{5}F, (^{4}F)	^{5}D
Nb	5	^{4}F, [^{5}D]	^{6}**D**, (^{7}S)	^{6}S, (^{5}D)
Mo	6	^{5}D, [^{6}S]	^{7}**S**	^{5}S, (^{6}S)
Tc	7	^{6}**S**, [^{5}D]	^{6}D	^{4}F
Ru	8	^{5}D, [^{4}F]	^{5}**F**	^{3}F, (^{4}F)
Rh	9	^{4}F, [^{3}F]	^{4}**F**	^{2}D, (^{3}F)
Pd	10	^{3}F	^{3}D, [^{2}S]	^{1}**S**, (^{2}D)

The auxiliary basis sets (ABSs) utilised in the OBS development corresponded to def2-QZVPP/JKFIT[73] for density fitting of the exchange terms, aug-cc-pwCV5Z-PP/MP2Fit[195] for the density fitting of the conventional 2-electron integrals, and a large even-tempered RI set of $18s17p16d12f10g8h7i$ composition comprised of the most diffuse function of aug-cc-pV5Z-PP[259] with a step size of 1.8.[196]



(a)

(b)

Figure 6.1: Incremental correlation energy contributions of higher angular momentum functions to the uncontracted spd primitive set of functions of cc-pV5Z-PP at the MP2-F12/3C(FIX) ($\beta = 1.4\alpha_0^{-1}$) level for ground states of (a) Zr and (b) Ru atoms.

These latter RI ABSs can be found in Appendix D. Similarly with previously developed cc-pV*n*Z-F12 basis sets,[263,264] the *spd* primitives for each new set were obtained from the existing aug-cc-pV(*n*+1)Z-PP set.[259] The *spd* HF contracted sets, with composition [2*s*2*p*1*d*] for all cardinal levels, was also taken from the existing aug-cc-pV(*n*+1)Z-PP sets, in order to ensure smooth basis set convergence of the HF energy. Groups of correlating functions were optimised on top of the uncontracted primitive *spd* sets of aug-cc-pV(*n*+1)Z-PP at the CCSD-F12b/3C(FIX) as well as at MP2-F12 ($\beta = 1.4\alpha_0$) levels of theory, to assess the sensitivity of the groupings with respect to the method.[71,72,262] The two sets of groupings were quite similar (i.e. led to the same correlation groupings); MP2-F12 groupings are displayed in Figure 6.1 since they produce a slightly clearer pattern.

During the development of cc-pV*n*Z-F12 basis sets for elements H, He, B-Ne, and Al-Ar, Peterson and coworkers advocated the construction of cc sets for both atomic and molecular calculations by including at least two functions of each new angular momentum symmetry to the basis set in order to describe both the HF and correlation energies.[142] With that information in mind, and by inspecting Figure 6.1, initial groupings were determined as 2*f* for DZ, 3*f*2*g* for TZ and 4*f*3*g*2*h* for QZ. Groupings that included a higher number of correlating functions were also considered, but preliminary atomic and molecular benchmarks indicated that adding extra functions was not beneficial. Once the groupings were obtained as preliminary even-tempered expansions, the exponents were freely optimised (not in an even-tempered form) at the CCSD-F12b/3C(FIX) level of theory. After higher angular momentum functions were optimised, contracted correlating *spd* functions were added. While one common technique when developing correlation consistent basis sets is to include the more diffuse primitives as uncontracted correlating functions, Blaudeau and coworkers indicated that when cc sets were used along with ECPs they benefitted significantly from inclusion of contracted correlating functions.[265] In order to ensure the sets were as small and flexible as possible, these contractions were not taken directly from the conventional aug-cc-pV(*n*+1)Z-PP sets, but instead an investigation on the number of contracted correlating functions was performed. The number of contracted correlating functions required ended up matching that of the existing aug-cc-pV($n+1$)Z-PP set (2*s*2*p*2*d* for DZ, 3*s*3*p*3*d* for TZ, and 4*s*4*p*4*d* for QZ). However they were re-contracted using the atomic orbital coefficients from a three-state averaged density matrix (see Table 6.1) obtained from a full-valence complete active space (CAS) MRCI-F12 calculation. The contraction coefficients were obtained using the primitive set of aug-cc-pV($n+1$)Z-PP as well as the optimised higher angular momentum functions. The MRCI-F12 calculations utilised def2-QZVPP/JKFIT[73] for density fitting of the exchange terms, aug-cc-pwCV5Z-PP/MP2Fit[195] for the density fitting of the conventional 2-electron integrals, and aug-cc-pwCVTZ-PP/MP2Fit[195] for the many-electron F12 integrals. Finally, the most diffuse primitive in each angular momentum of the cc-pV($n+1$)Z-PP was uncontracted and added to cc-pV*n*Z-PP-F12, along with the augmented diffuse uncontracted function of aug-cc-pV($n+1$)Z-PP. The compositions of the final contracted basis sets are shown in Table 6.2.

Table 6.2: Composition of basis sets sets developed in this work for the $4d$ transition metal elements, Y-Pd. The ratio of functions (MP2Fit:OBS and OPTRI:OBS) assumes spherical angular momenta.

Basis Set	OBS	MP2Fit	Ratio	OPTRI	Ratio
cc-pVDZ-PP-F12	$[6s6p5d2f]$	$(12s12p10d9f7g4h1i)$	4.6	$(6s6p6d5f3g3h2i)$	2.9
cc-pVTZ-PP-F12	$[7s7p6d3f2g]$	$(14s14p12d11f9g6h4i1k)$	4.4	$(7s7p7d6f5g4h3i)$	2.5
cc-pVQZ-PP-F12	$[8s8p7d4f3g1h]$	$(16s16p14d13f11g8h6i3k1l)$	4.0	$(7s7p7d8f6g4h3i)$	1.8
cc-pCVDZ-PP-F12	$[7s7p6d3f]$	$(13s13p11d10f8g5h2i)$	4.4	-	-
cc-pCVTZ-PP-F12	$[8s8p7d4f3g]$	$(15s15p13d12f10g7h5i2k)$	4.0	-	-
cc-pCVQZ-PP-F12	$[9s9p8d5f4g2h]$	$(17s17p15d14f12g9h7i4k2l)$	3.7	-	-

Figure 6.2 shows the basis set convergence of the CCSD correlation energy both in conventional and CCSD-F12b/3C(FIX) calculations for the atoms Y-Pd, on their respective ground states. The frozen-core correlation energies from conventional CCSD with aug-cc-pVnZ-PP basis sets are compared to CCSD-F12b/3C(FIX) calculations with the new cc-pVnZ-PP-F12 sets. The F12 calculations utilised the new auxiliary sets described below. The convergence with basis is monotonic in all cases, and as expected, the F12 correlation energies converge much faster with respect to the cardinal number compared to conventional results. Similarly to the behaviour of lighter elements, Figure 6.2 indicates that the convergence pattern obtained with an explicitly correlated method/basis set of cardinal number n corresponds, at worst, to that of a conventional calculation/basis set of cardinal number $n + 1$ and that convergence is quicker as the number of the electrons of the system increase.

Since the cc-pVnZ-PP-F12 basis sets do not generally provide an adequate description of outer-core $4s4p$ correlation, cc-pCVnZ-PP-F12 sets were also developed. A set of uncontracted $1s1p1d$ functions were optimised for $4d^{m-2}5s^2$ state and added to the cc-pVnZ-PP-F12 sets. Higher angular momentum functions were also included ($1f$ for DZ, $1f1g$ for TZ, and $1f1g1h$ for QZ), but since there was some overlap between the core and existing valence correlating functions, the new functions were optimised together with all but the most diffuse valence function of each angular momentum. Therefore the newly developed cc-pCVnZ-PP-F12 core-valence sets for elements Y-Pd are not constructed by a simple addition of tight functions. The exponents were optimised with respect to the difference in correlation energy between a standard frozen core calculation (where $4s$ and $4p$ electrons are frozen and not treated as correlating electrons) and a core-valence calculation (where the above electrons are included in the correlation treatment). The convergence of core-core and core-valence correlation energies, calculated both at CCSD/aug-cc-pwCVnZ-PP conventional level and explicitly correlated CCSD-F12b/cc-pCVnZ-PP-F12 level are shown in Figures 6.3 and 6.4. It is evident that the new sets recover significantly more core-core as well as core-valence correlation energy; cc-pV*n*Z-PP-F12 sets roughly correspond to aug-cc-pwCV$(n+2)$Z-PP results, and they can be considered almost converged.

Lastly, in order to accurately describe weak interactions, additional higher angular momentum diffuse functions (f, g, h functions) were also obtained for use with the new valence-only sets cc-pV*n*Z-PP-F12, thus creating an aug-cc-pV*n*Z-PP-F12 series of sets (for $n =$ D-Q). These functions were added as an even-tempered extension, based on the most diffuse function in that angular momentum shell multiplied by the ratio of the two most diffuse functions in the following form (here for shell h):

$$\alpha_{h_n} = \frac{\alpha^2_{h_{n-1}}}{\alpha_{h_{n-2}}}, \tag{6.1}$$

The necessity of these sets will be evident when electron affinities are presented, among other atomic properties, below. These initial atomic results presented here only focus on the convergence of electronic energy with respect to the cardinal number, to ensure smooth convergence is achieved. The performance of the sets will be later examined through a series of atomic and molecular calculations that aim to cover a variety of bonding environments and properties. These are discussed in section 6.1.4.

6.1.2 Density fitting auxiliary basis sets, MP2Fit

Auxiliary basis sets for the density fitting of the two-electron integrals (suffixed MP2Fit) were developed using a similar design pattern employed for previously developed MP2Fit sets (as seen in References 141 and 180 and references therein, as well as in Chapter 5). Auxiliary basis sets specifically matched to cc-pV*n*Z-PP-F12 and cc-pCV*n*Z-PP-F12 orbital sets described above were optimised by minimising the functional, δ_{DF} (see equation 3.15) using the analytical auxiliary basis set gradients of Hättig,[147] implemented within the RICC2 module[219,239] of the TURBOMOLE package.[216]

In order to be able to describe the various oxidation states of the transition metal elements, a range of different ionic states was used, following an optimisation protocol similar to that described in References 147 and 266. More specifically, elements Y, Zr, and Tc, which are generally found in a single oxidation state, had their exponents divided into two categories, diffuse and tight, while the remaining elements had their exponents split into three categories, diffuse, intermediate and tight. The optimisation always began from the cation of greatest charge (which corresponds to optimization of the tight exponents) and proceeded towards the neutral state, and the optimisation of the diffuse exponents. This layered optimisation ensured a satisfactory representation of most common oxidation states of elements Y-Pd, by including their corresponding cations. The electronic configurations utilised in the MP2Fit development is shown in Table 6.3.

The principal design goals for the MP2Fit ABSs were that the number of functions will remain constant for all elements (Y-Pd), and that the total number number of auxiliary basis functions should not be greater than $6 \times N_{OBS}$ (number of orbital basis set functions).[267] The accuracy of MP2 fitting basis sets was verified by comparing the mean error, standard deviation, maximum error, and mean unsigned error introduced by the DF approximation (ΔDF) at the MP2 level with the same statistics for the error in orbital basis set incompleteness for explicitly correlated MP2-F12 (BSIE MP2-F12) over a test set of representative transition metal complexes. The ΔDF error in atoms should be less than 1.0 μE_{h} per correlated electron, with an optimization criteria of $\delta_{\mathrm{DF}}/|E^{\mathrm{corr}}_{\mathrm{MP2}}| \leq 10^{-8}$, and in molecules the ΔDF error should be at least two orders of magnitude smaller than the BSIE at the explicitly correlated MP2-F12 level. Similarly with previously developed MP2Fit ABSs for explicitly correlated calculations (Chapter 5), while only the functions up to $\ell_{\mathrm{occ}} + \ell_{\mathrm{OBS}}$ possessed a δ_{DF} gradient, inclusion of functions up to $\ell_{\mathrm{occ}} + \ell_{\mathrm{OBS}} + 1$ was crucial for the adequate performance of the sets in molecular calculations.

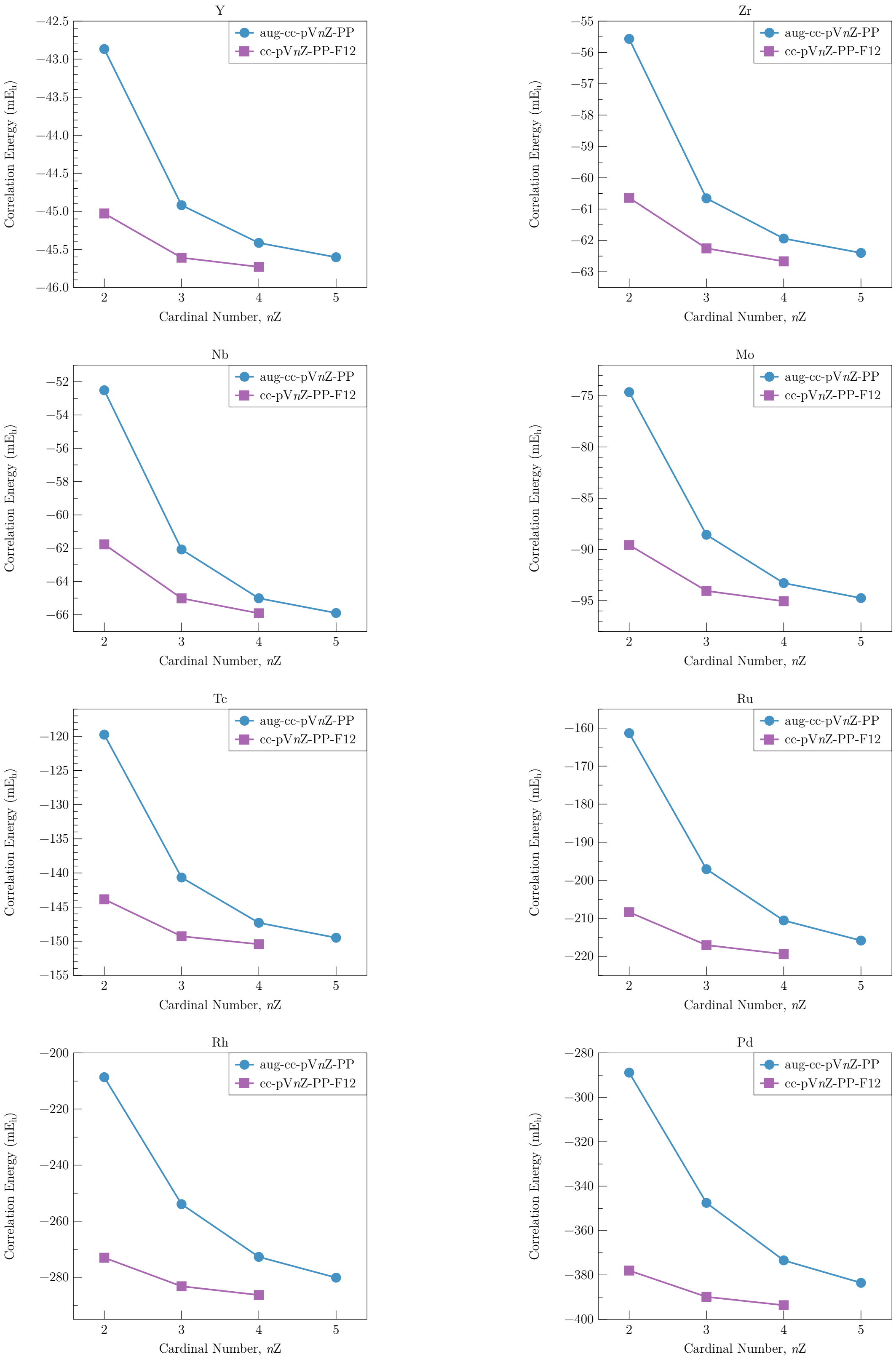


Figure 6.2: Convergence of frozen-core CCSD correlation energies from conventional (aug-cc-pVnZ-PP) and explicitly correlated (cc-pVnZ-PP-F12) CCSD-F12b/3C(FIX) ($\beta = 1.4\alpha_0^{-1}$) calculations.

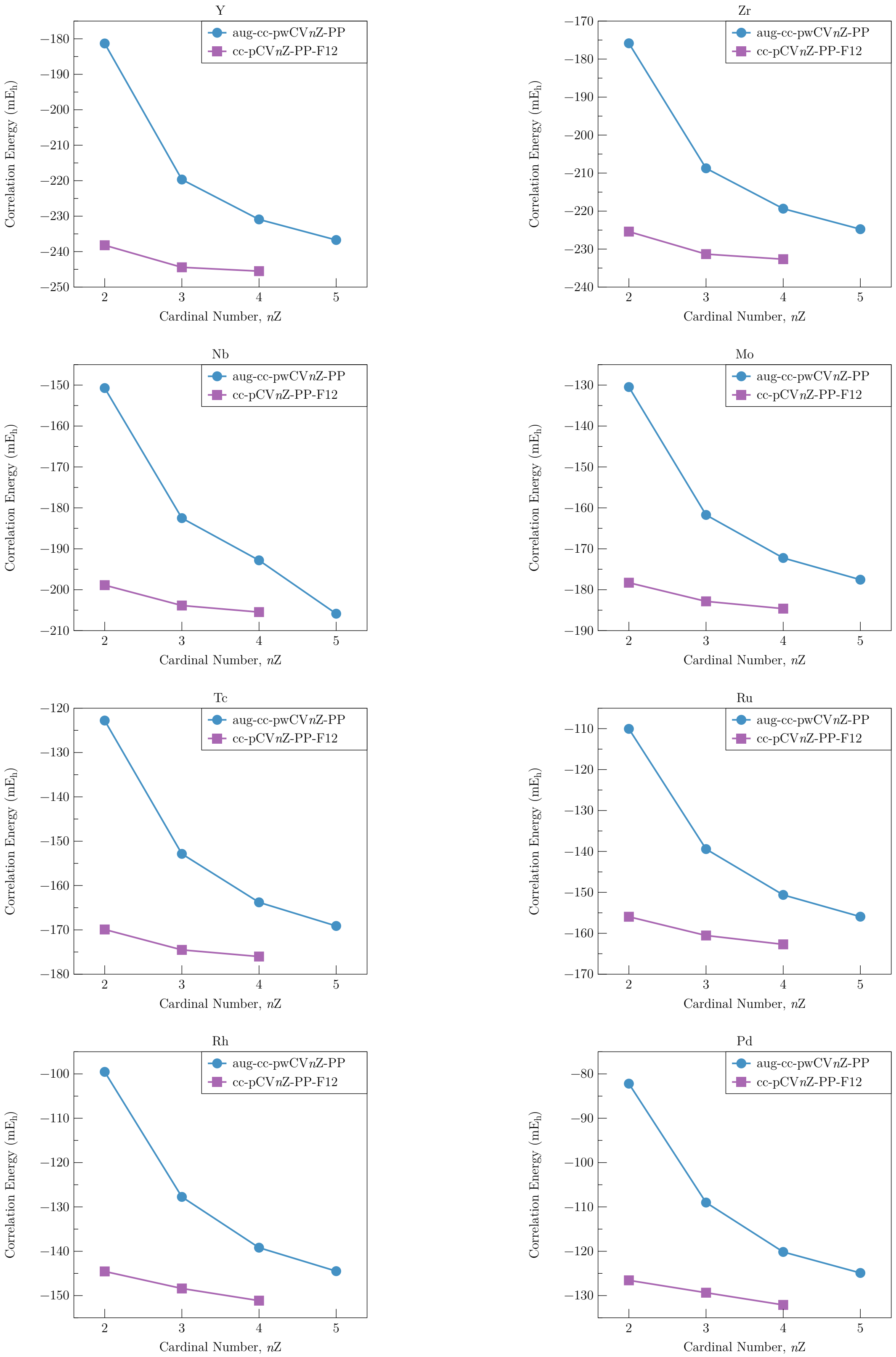


Figure 6.3: Convergence of CCSD core-core correlation energies from conventional (aug-cc-pwCV*n*Z-PP) and explicitly correlated (cc-pCV*n*Z-PP-F12) CCSD-F12b/3C(FIX) ($\beta = 1.4\alpha_0^{-1}$) calculations.

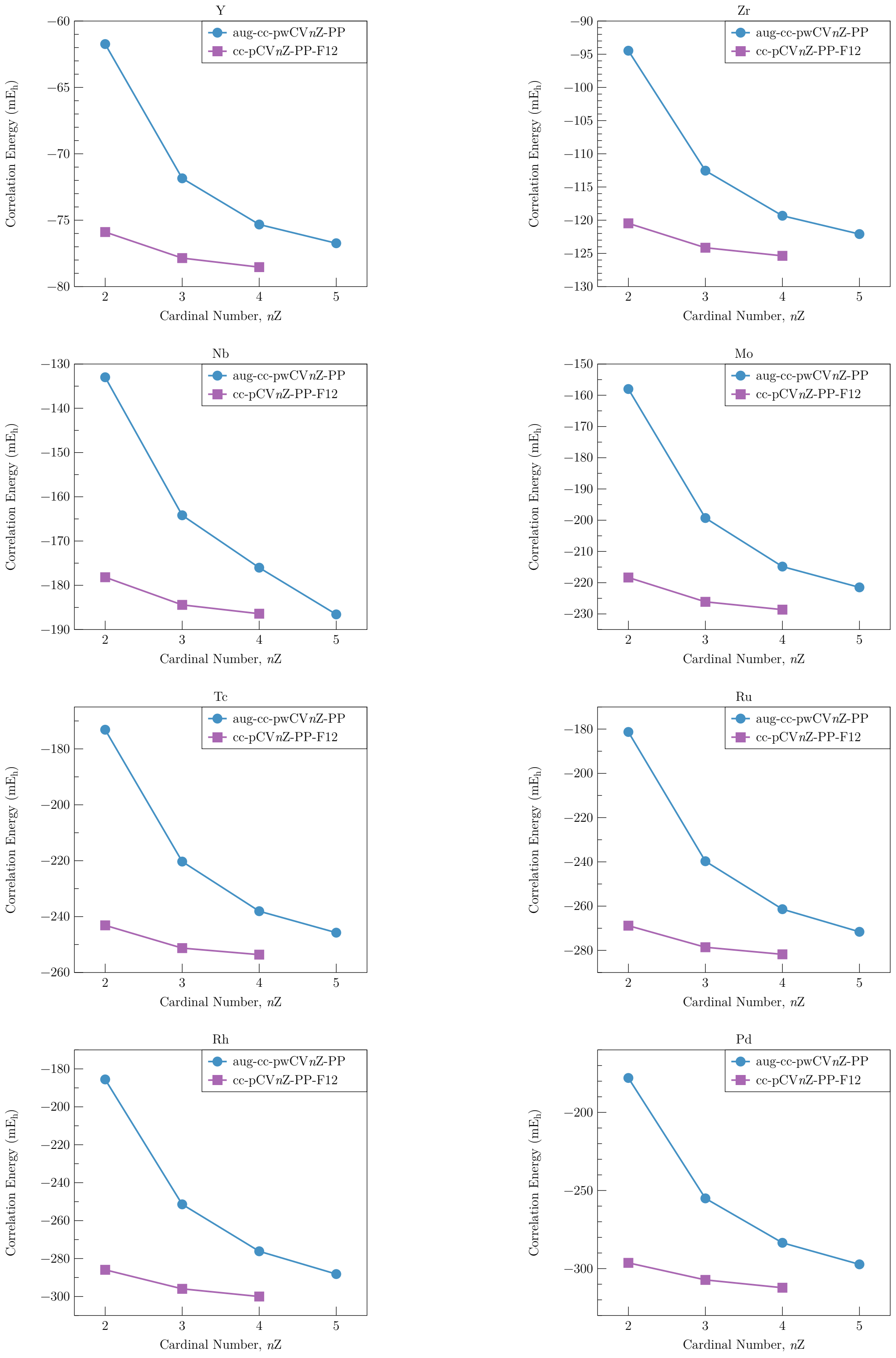


Figure 6.4: Convergence of CCSD core-valence correlation energies from conventional (aug-cc-pwCVnZ-PP) and explicitly correlated (cc-pCVnZ-PP-F12) CCSD-F12b/3C(FIX) ($\beta = 1.4 a_0^{-1}$) calculations for ground states of atoms Y-Pd.

Table 6.3: Atoms and cations of $4d$ transition metals utilised in the development of MP2Fit auxiliary basis sets.

Atom/Ion	Electronic Configuration
Y	[Kr]$4d^1 5s^2$
Y^{+3}	[Kr]
Zr	[Kr]$4d^2 5s^2$
Zr^{+4}	[Kr]
Nb	[Kr]$4d^3 5s^2$
Nb^{+3}	[Kr]$5s^2$
Nb^{+5}	[Kr]
Mo	[Kr]$4d^4 5s^2$
Mo^{+3}	[Kr]$4d^1 5s^2$
Mo^{+6}	[Kr]
Tc	[Kr]$4d^5 5s^2$
Tc^{+4}	[Kr]$4d^1 5s^2$
Tc^{+7}	[Kr]
Ru	[Kr]$4d^7 5s^2$
Ru^{+3}	[Kr]$4d^3 5s^2$
Ru^{+4}	[Kr]$4d^2 5s^2$
Rh	[Kr]$4d^8 5s^1$
Rh^{+3}	[Kr]$4d^6$
Pd	[Kr]$4d^{10}$
Pd^{+2}	[Kr]$4d^8$
Pd^{+4}	[Kr]$4d^6$

Such functions that were required for molecules but had no gradient in the atomistic optimisation, were interpolated from the previous angular momentum symmetry as:

$$\alpha_\ell = \sqrt{\alpha_{(\ell-1),x}\alpha_{(\ell-1),y}}, \tag{6.2}$$

where $\alpha_{(\ell-1),x}$ and $\alpha_{(\ell-1),y}$ were the two most diffuse exponents of the previous angular momentum symmetry. MP2Fit ABSs for use in explicitly correlated methods should include functions of angular momenta up to $\ell_{\mathrm{ABS}} = \ell_{\mathrm{occ}} + \ell_{\mathrm{OBS}} + 1$, which is in agreement with the resulting compositions of the new sets.[144,267]

A similar procedure to the one described above was followed for the design of ABSs specifically matched to the core-valence correlating OBSs, cc-pCV*n*Z-PP-F12/MP2Fit. While in some cases ABSs matched to conventional core-valence OBSs have typically fixed the exponents of the corresponding valence-only sets and added a number of additional tight functions, in the present investigation such an approach was not followed. Initial tests demonstrated that, in order to reach the desired levels of accuracy, a complete reoptimisation of all exponents led to much smaller sets, and thus this approach was preferred. Furthermore this procedures seems to follow the same design protocol used for the development of cc-pCV*n*Z-PP-F12 OBSs; an almost complete reoptimisation was performed there as well.

The compositions of the resulting ABSs are presented in Table 6.2. The performance of the new MP2Fit auxiliary sets has been initially validated for atoms by inspection of both the error in the conventional MP2 correlation energy (ΔDF) and the quantity $\delta_{\mathrm{DF}}/|E_{\mathrm{MP2}}$ which represents the error in the two-electron integrals at the conventional MP2 level. This data is presented in statistical form in Table 6.4 as the mean unsigned error (MUE), the standard deviation of the error (σ) and the maximum absolute error (MAX), on a per-correlated electron basis. It can be seen that the errors in the integrals are roughly equivalent for all zeta-levels, and that the overall magnitude of the error is very small. The ratios between the number of functions in the MP2Fit ABSs and the corresponding OBSs are displayed in Table 6.2. The ratios range from 3.7 to 4.6, with valence-only sets cc-pV*n*Z-PP-F12/MP2Fit holding the larger values, in comparison with the core-valence sets cc-pCV*n*Z-PP-F12. These ratios are well within the established guidelines of $N_{\mathrm{ABS}} \leq 6 \times N_{\mathrm{OBS}}$, ensuring small yet flexible MP2Fit ABSs.

Table 6.4: Errors in the MP2 density fitting for atoms Y-Pd, as errors in correlation energy (ΔDF error) pce and electron repulsion integrals ($\delta_{\mathrm{DF}}/|E^{\mathrm{corr}}_{\mathrm{MP2}}|$) per atom for the cc-pV*n*Z-PP-F12/MP2Fit and cc-pCV*n*Z-PP-F12/MP2Fit auxiliary basis sets (*n*= D, T, Q)

	ΔDF error (μE$_h$)			$\delta_{\mathrm{DF}}/|E^{\mathrm{corr}}_{\mathrm{MP2}}|$		
MP2Fit Basis	MUE	σ	MAX	MUE	σ	MAX
cc-pVDZ-PP-F12	0.43	0.35	1.47	2.95×10^{-13}	1.73×10^{-13}	8.36×10^{-13}
cc-pVTZ-PP-F12	0.63	0.52	1.81	3.50×10^{-13}	2.75×10^{-13}	9.75×10^{-13}
cc-pVQZ-PP-F12	0.25	0.25	1.15	3.42×10^{-13}	2.75×10^{-13}	8.34×10^{-13}
cc-pCVDZ-PP-F12	0.34	0.34	1.29	3.83×10^{-13}	2.89×10^{-13}	9.81×10^{-13}
cc-pCVTZ-PP-F12	0.39	0.27	0.99	3.55×10^{-13}	1.65×10^{-13}	6.56×10^{-13}
cc-pCVQZ-PP-F12	0.29	0.23	0.87	5.31×10^{-13}	2.34×10^{-13}	8.61×10^{-13}

Further validation of the new sets was obtained by comparing the ΔDF error with the BSIE for a test set of molecules that contained 4*d* transition metal elements [Mo(CO)$_6$, MoF$_3$, MoH, MoO$_2$, MoO$_3$, NbF$_3$, NbO$_2$F, NbO$_2$, NbO, Pd(CO)$_4$, PdF, PdO$_2$, RhF$_4$, RhF$_6$, RhF, RhO, Ru(CO)$_5$, RuF, RuO$_2$, RuO$_4$, RuO, Tc$_2$O$_7$, TcO$_3$F, TcO, YF$_3$, YF, YO, ZrF$_3$, ZrF, ZrO$_2$, ZrO]. The test set of molecules used to evaluate the performance of the new MP2Fit sets is comprised by 31 molecules utilised in Hill's previous work.[198] The BSIE was obtained by extrapolating MP2-F12 correlation energies using the new cc-pVTZ-PP-F12 and cc-pVQZ-PP-F12 (and cc-pCVTZ-PP-F12 and cc-pCVQZ-PP-F12 for CV calculations) basis sets to the CBS limit. To obtain an estimate of the CBS limit, a Schwenke-type[161] extrapolation was used:

$$E^{\mathrm{corr}}_{\mathrm{CBS}} = (E^{\mathrm{corr}}_{\mathrm{QZ}} - E^{\mathrm{corr}}_{\mathrm{TZ}})F + E^{\mathrm{corr}}_{\mathrm{TZ}}\,, \tag{6.3}$$

where QZ and TZ refer to the zeta level of the basis sets and F takes the value 1.4148.[162] Separate estimates of the CBS limit were produced for valence-only and core-valence correlation, and while the value of F used has not been well-tested for core-valence correlation or transition metal containing species, it is expected to be sufficient for the purposes of estimating BSIE rather than establishing benchmark data on the CBS limits. The above calculations were performed at the MP2-F12/3C(FIX) level, using the new cc-pVnZ-PP-F12 and cc-pCVnZ-PP-F12 OBSs for the transition metals and the cc-pVnZ-F12 and cc-pCVnZ-F12 sets for the lighter elements.[142,143] The auxiliary basis sets for the lighter elements were those matched to the OBSs (see Chapter 5), namely cc-pVnZ-F12/MP2Fit and cc-pCVnZ-F12/MP2Fit,[267] cc-pVnZ-F12/OPTRI and cc-pCVnZ-F12/OPTRI,[142,143] and the cc-pVTZ/JKFIT and cc-pVQZ/JKFIT sets, while the auxiliary basis sets for elements Y-Pd were the ones developed in this work along with def2-QZVPP/JKFIT.[73]

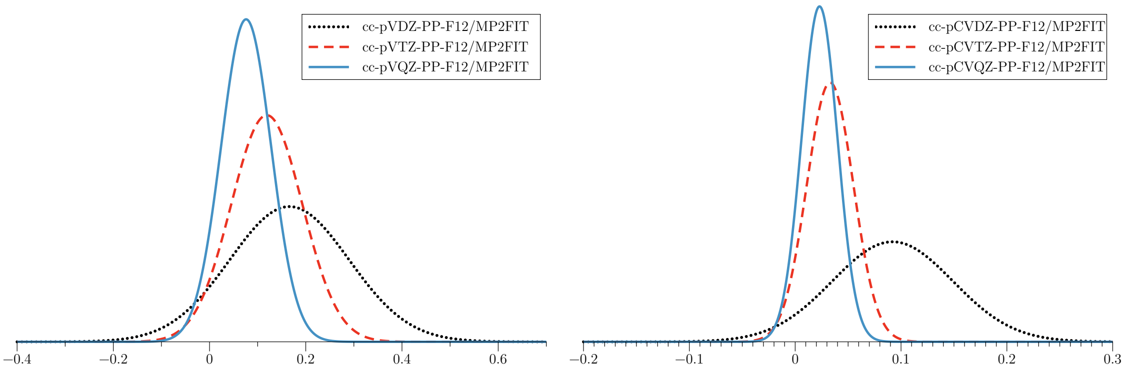
Table 6.5: cc-pVnZ-F12 and cc-pCVnZ-F12 correlation energy errors (μE_h, per correlated electron) due to MP2-F12 explicitly correlated basis set incompleteness error (BSIE) and conventional density fitting (ΔDF) using the auxiliary sets developed in this work, for a test set of molecules containing elements Y-Pd.

OBS	Error Type	MAE	σ	MAX
cc-pVDZ-PP-F12	BSIE	638	199	1037
	DF	0.167	0.123	0.512
cc-pVTZ-PP-F12	BSIE	183	48	289
	DF	0.137	0.056	0.235
cc-pVQZ-PP-F12	BSIE	52	14	83
	DF	0.076	0.054	0.173
cc-pCVDZ-PP-F12	BSIE	1207	331	1484
	DF	0.092	0.057	0.230
cc-pCVTZ-PP-F12	BSIE	206	312	1456
	DF	0.033	0.022	0.082
cc-pCVQZ-PP-F12	BSIE	59	89	416
	DF	0.023	0.017	0.075

From Table 6.5 it is evident that the MP2-F12 basis set incompleteness error is significantly larger than that due to density fitting. In terms of ΔDF, all of the error statistics presented are three to four orders of magnitude smaller than the error in the orbital basis, hence the density fitting errors due to the MP2Fit sets developed in this work can be considered negligible. At the molecular level as the basis set cardinal number is increased all of the error statistics related to ΔDF are reduced, as expected. A comparison between the valence and core-valence sets indicates that in all cases, core-valence sets appear to provide a better fitting (expressed in smaller ΔDF values per correlated electron), potentially indicating a particularly accurate density fitting for core-valence in this case. The fitting errors reported herein are of similar magnitude to those reported for the cc-pV*n*Z-PP-F12 sets for the post-d main group elements.[144]

The accuracy of the density fitting for the molecular test set is presented visually as normalised Gaussian distributions in Figure 6.5, where the tight grouping of the Gaussians reflects the high accuracy at all zeta-levels. For both the valence and core-valence correlation cases, as the cardinal number increases the accuracy of the density fitting also increases.

The ΔDF error per correlated electron for each molecule in the test set is also presented in bar chart form in Figures 6.6 and 6.7. Inspection of the heights of the bars indicates that the ΔDF error is reasonably consistent across all of the molecules and it does not appear that the fitting accuracy is noticeably worse for any given element.



(a) (b)

Figure 6.5: Gaussian distributions of the ΔDF error (μE_h, per correlated electron) in the MP2-F12/3C(FIX) correlation energy for a test set of molecules that include elements Y-Pd, using (a) valence cc-pV*n*Z-PP-F12 basis sets and (b) core-valence cc-pCV*n*Z-PP-F12 basis sets.

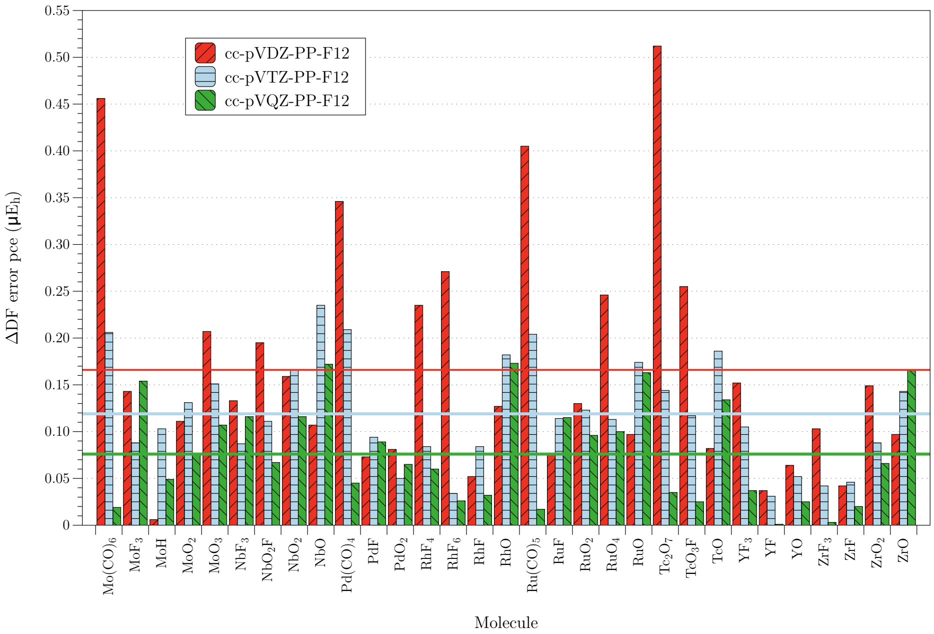


Figure 6.6: MP2 ΔDF error (pce, μE$_h$) from the MP2Fit auxiliary basis sets specifically matched to cc-pVnZ-PP-F12 for a test set of molecules that include elements Y-Pd.

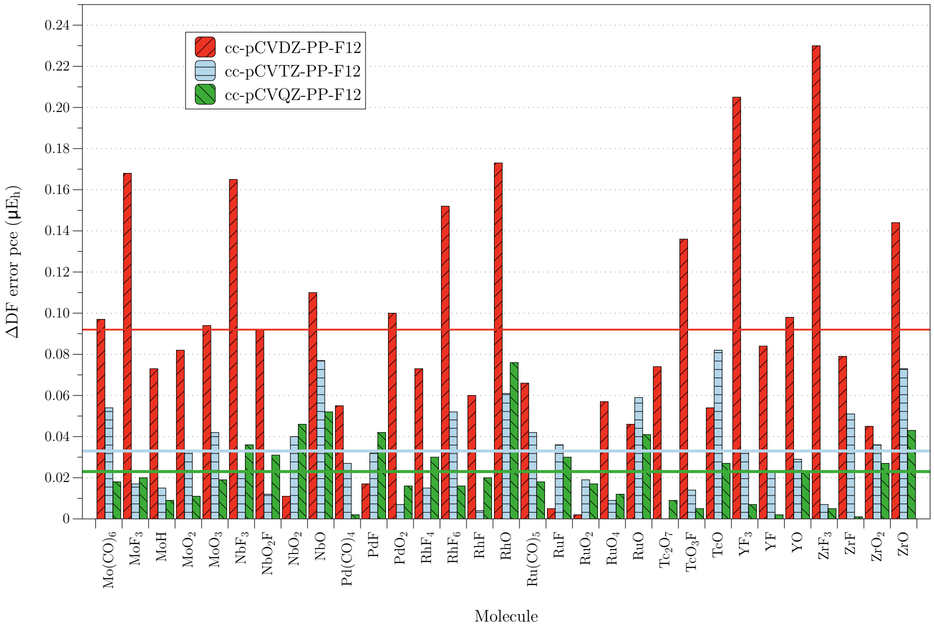


Figure 6.7: MP2 ΔDF error (pce, μE$_h$) from the MP2Fit auxiliary basis sets specifically matched to cc-pCVnZ-PP-F12 for a test set of molecules that include elements Y-Pd.

6.1.3 Complementary auxiliary basis sets, OPTRI

The RI auxiliary basis sets that are required for the evaluation of the many-electron integrals that arise within the F12 framework were optimised for use within the CABS+ approach[61] of MOLPRO.[215] The resulting OPTRI ABSs, cc-pV*n*Z-PP-F12/OPTRI, are specifically matched to cc-pV*n*Z-PP-F12 OBSs; it is crucial that the sets are combined in the expected manner, since the full CABS+ basis sets is a result of the union of the OPTRI set and the orbital basis set. The OPTRI sets were produced by minimising the value δRI for the atoms:

$$\delta\mathrm{RI} = \sum_{ij} \frac{(V_{ij,ij} - V_{ij,ij}^{\mathrm{ref}})^2}{|V_{ij,ij}^{\mathrm{ref}}|} + \frac{(B_{ij,ij} - B_{ij,ij}^{\mathrm{ref}})^2}{|B_{ij,ij}^{\mathrm{ref}}|}\,, \tag{6.4}$$

which involves the diagonal elements of the **V** and **B** matrices that arise in the MP2-F12 theory. The reference matrices were defined by the large, even-tempered RI basis sets described earlier. In order to account for multiple oxidation states, the root mean square of the above functional for each state, as detailed in Table 6.1 was minimised. In order to avoid linear dependencies in the optimised OPTRI set (and the resulting CABS basis set), the ratio of any two exponents, within the same angular momentum shell, in the combined CABS basis set was constrained to be $\geq$ 1.4. The 3C(FIX) ansatz with a geminal exponent of 1.4 α_0^{-1} was used throughout. Each angular momentum shell was optimised separately, and the s, p, d and f functions were optimised using the reference RI set truncated at the f shell. Higher angular momentum functions were then optimised, per shell, on top of a hybrid set that included the optimised $spdf$ functions and the higher angular momentum functions of the reference RI set. The compositions of the final sets are given in Table 6.2. Not surprisingly, the OPTRI sets are much smaller than the corresponding MP2Fit sets, since the final CABS sets include the OBS exponents as well. In general the OPTRI sets do not change in size significantly as the OBS increases size (as the MP2Fit sets do), since the total CABS set slowly approaches "completeness" .

In order to assess the performance of the new OPTRI sets, the RI errors (difference in energy between a calculation with a large, even tempered, reference RI and with the optimised one) were calculated for the same set of test molecules as used in testing of the MP2Fit sets, are shown in Table 6.6. Due to time limitations, OPTRI sets specifically matched to core-valence cc-pCV*n*Z-PP-F12 were not developed, and are part of the suggested future work of Chapter 8.

Table 6.6: ΔRI errors (OPTRI relative to the reference ABS) per correlated electron (μE$_h$) in the MP2-F12/3C(FIX) correlation energies for the combined set of molecules containing elements Y-Pd.

OBS	Error Type	MAE	σ	MAX
cc-pVDZ-PP-F12	BSIE	638	199	1037
	RI	3.003	1.824	6.224
cc-pVTZ-PP-F12	BSIE	183	48	289
	RI	0.409	0.273	1.193
cc-pVQZ-PP-F12	BSIE	52	14	83
	RI	0.287	0.270	1.084

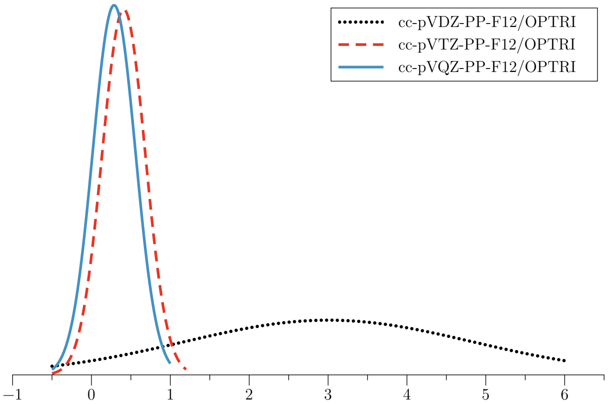


Figure 6.8: Gaussian distributions of the ΔRI error (μE$_h$, per correlated electron) in MP2-F12/3C(FIX) correlation energy for a test set of molecules that include elements Y-Pd, using cc-pV*n*Z-PP-F12 basis sets.

The accuracy of the resolution-of-identity for the molecular test set is presented visually as normalised Gaussian distributions in Figure 6.8. As expected, as the cardinal number increases, the accuracy of the fitting basis set also increases. The ΔRI error per correlated electron for each molecule in the test set, is also presented in bar chart form in Figure 6.9. Inspection of the heights of the bars indicates that the ΔRI error is reasonably consistent across all of the molecules and it does not appear that the fitting accuracy is noticeably worse for any given element. Figures 6.8 and 6.9 clearly exhibit the accelerated convergence between DZ and TZ that is associated with explicit correlation; at the TZ level the sets are close to the complete ABS limit as the fitting errors are negligible.

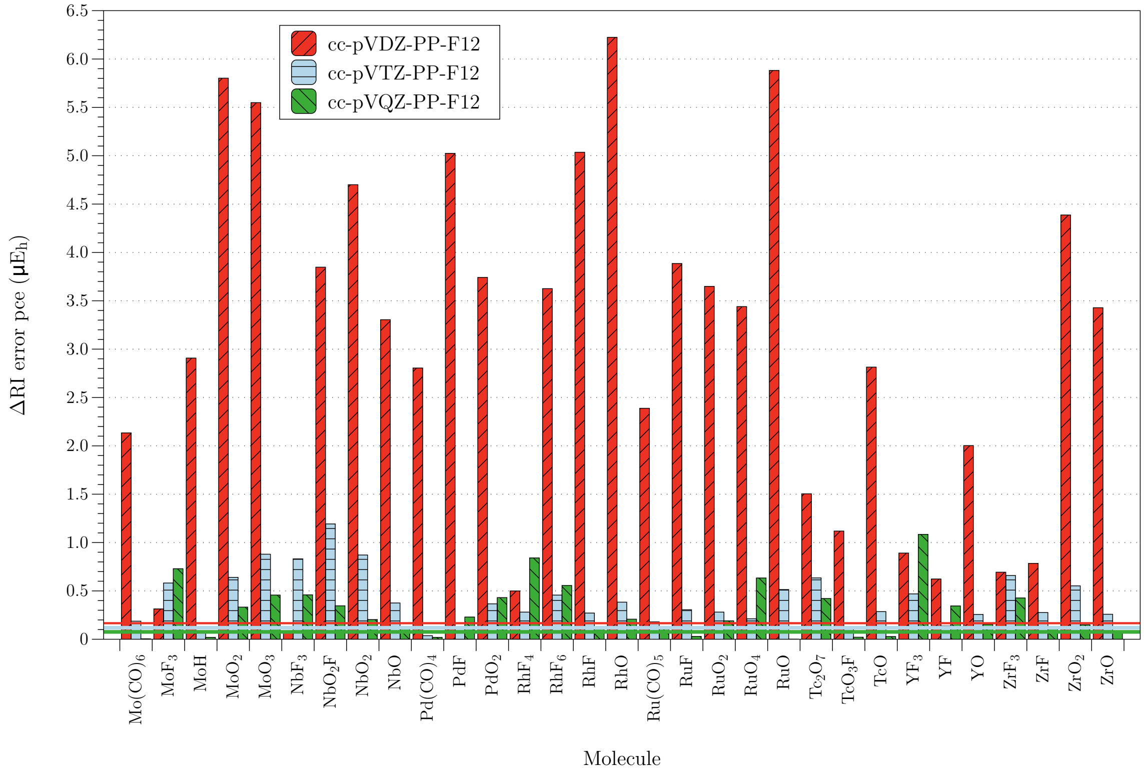
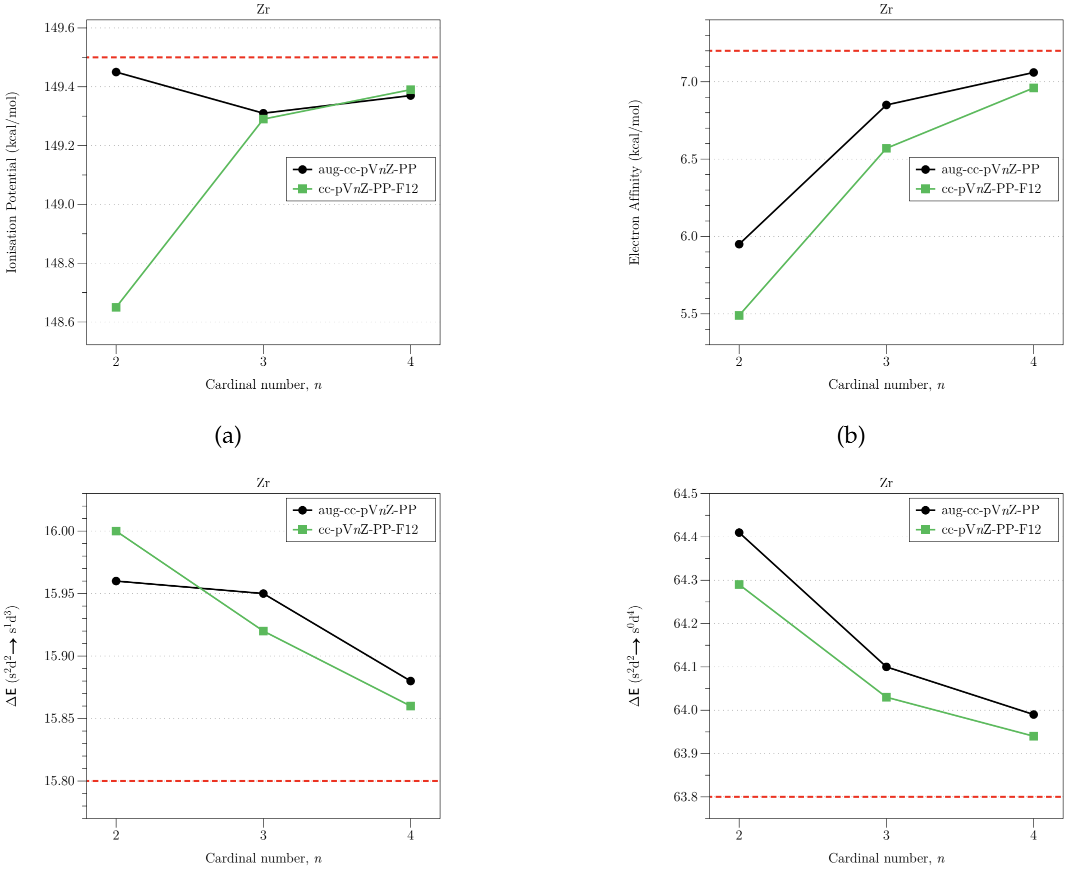


Figure 6.9: ΔRI error (pce, μE_h) from the OPTRI auxiliary basis sets specifically matched to cc-pVnZ-PP-F12 for a test set of molecules that include elements Y-Pd.

6.1.4 Benchmark Calculations

In order to demonstrate the effectiveness of the newly developed orbital and auxiliary basis sets for both valence and core-valence calculations, CCSD(T)-F12b atomic and molecular calculations were carried out. At the atomic level ionization potentials (IPs), electron affinities (EAs), and one- and two-electron excitation energies $4d^{m-2}5s^2 \rightarrow 4d^{m-1}5s^1$ and $4d^{m-2}5s^2 \rightarrow 4d^m5s^0$ were calculated. The performance of the new sets with regards to these atomic properties was assessed by comparing CCSD(T)-F12b calculations with existing aug-cc-pV*n*Z-PP and new cc-pV*n*Z-PP-F12 basis sets.

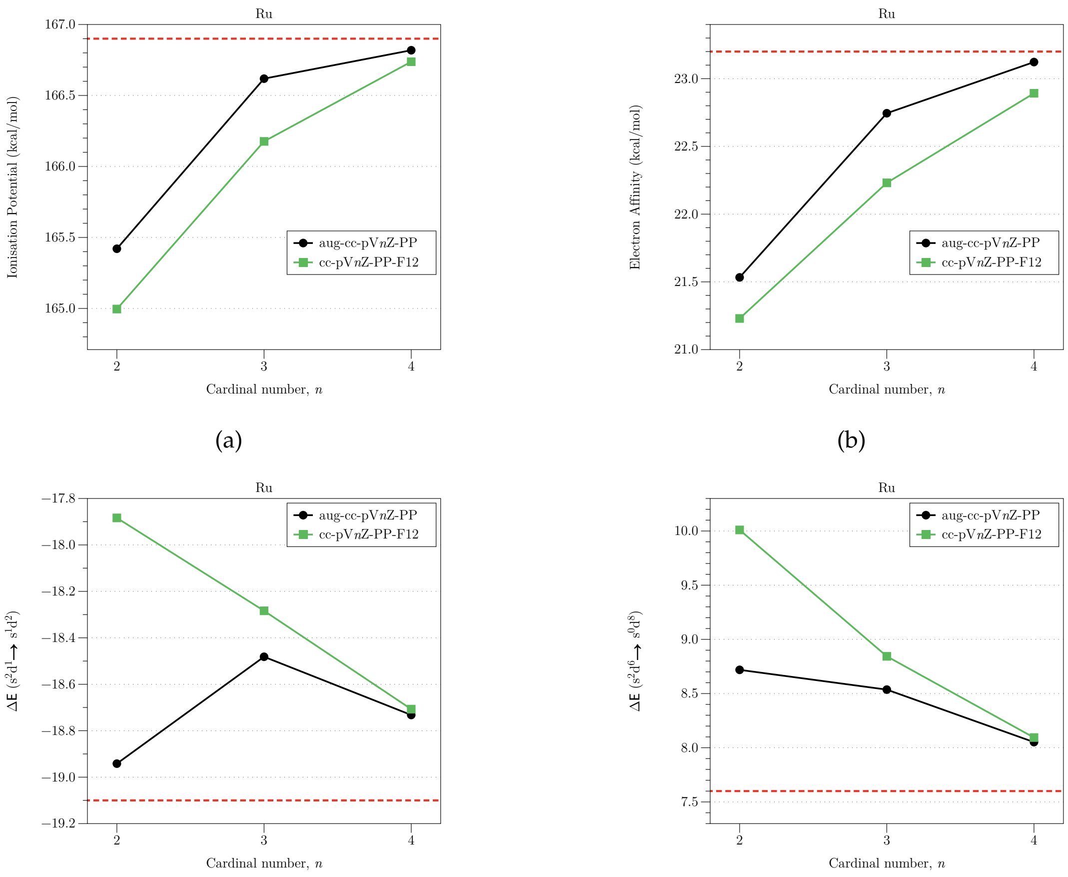


(a) (b)

(c) (d)

Figure 6.10: Atomic properties [(a) ionization potential, (b) electron affinity, (c) one- and (d) two-electron excitation energies $4d^25s^2 \rightarrow 4d^35s^1$ and $4d^25s^2 \rightarrow 4d^45s^0$] for the Zr atom, calculated at CCSD(T)-F12b/3C(FIX) level of theory with β =1.4 α_0^{-1}, using existing aug-cc-pwCV*n*Z-PP (n = D - 5) and new cc-pV*n*Z-PP-F12 (n= D - Q) basis sets. The estimated complete basis set limits (dashed horizontal lines) were obtained from conventional CCSD(T)/aug-cc-pwCV*n*Z-PP (n = Q, 5) calculations, from References 259 and 260.

While in practice, performing an F12 calculation without the appropriate (matched) basis set would not be recommended, and one would perform its conventional equivalent calculation, the CCSD(T)-F12b/3C(FIX) aug-cc-pwCV*n*Z-PP sets of calculations were used to highlight the need for explicit-correlation-specific basis sets. All atomic properties calculated below are within the F12 framework, and thus the improvement in the performance between existing and new sets can be directly and doubtlessly associated with the basis sets. All atomic calculations utilised the 3C(FIX) ansatz with a geminal exponent of 1.4 α_0^{-1} and the def2-QZVPP/JKFIT[73] for density fitting of the exchange terms.



(a)

(b)

(c)

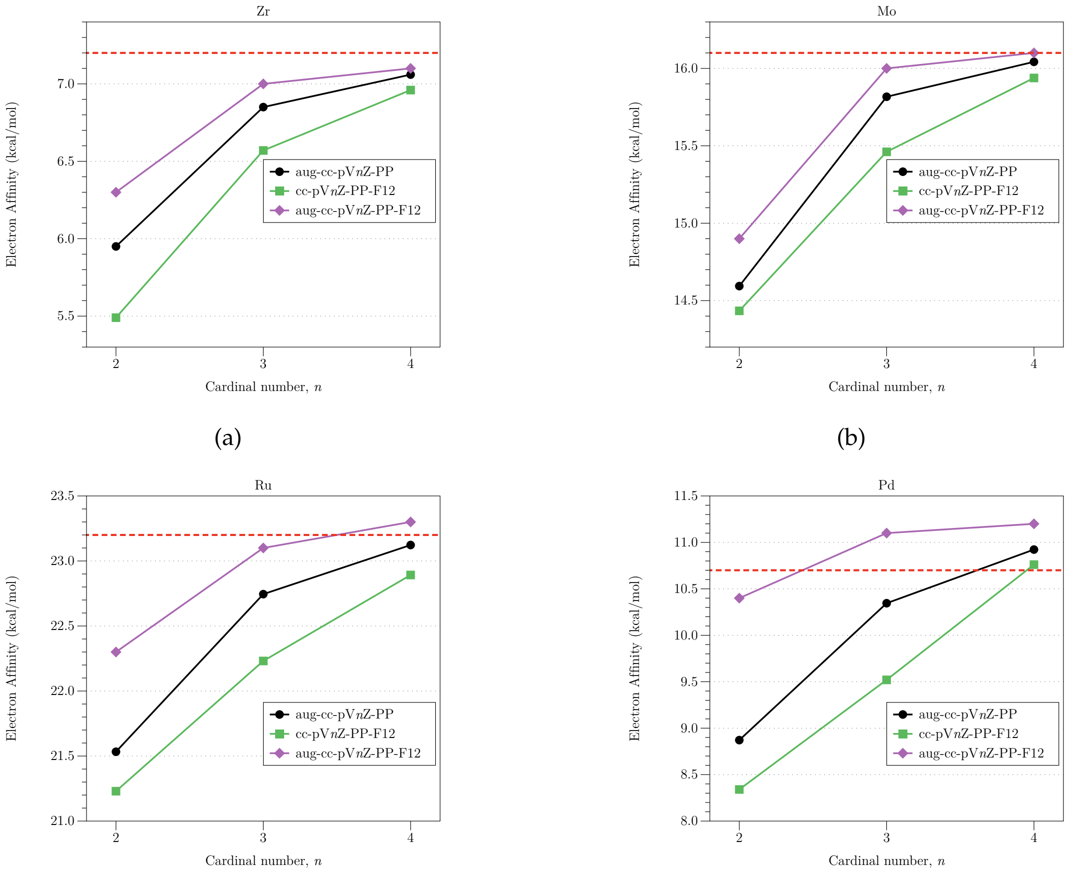
(d)

Figure 6.11: Atomic properties [(a) ionization potential, (b) electron affinity, (c) one- and (d) two-electron excitation energies $4d^65s^2 \rightarrow 4d^75s^1$ and $4d^65s^2 \rightarrow 4d^85s^0$] for the Ru atom, calculated at CCSD(T)-F12b/3C(FIX) level of theory with β =1.4 α_0^{-1}, using existing aug-cc-pwCV*n*Z-PP (n = D - Q) and new cc-pV*n*Z-PP-F12 (n= D - Q) basis sets. The estimated complete basis set limits (dashed horizontal lines) were obtained from conventional CCSD(T)/aug-cc-pwCV*n*Z-PP (n = Q, 5) calculations, from References 259 and 260.

All calculations with conventional sets utilised the largest possible sets available for both MP2Fit and OPTRI sets namely aug-cc-pwCV5Z-PP/MP2Fit[195] for the density fitting of the conventional 2-electron integrals and the large even tempered set mentioned in section 6.1.1 as the RI set. The new OBSs utilised the matching new ABSs. Indicative results for elements Zr and Ru are shown in Figures 6.10 and 6.11, respectively. In the case of core-valence sets, due to the lack of OPTRI sets, the MP2Fit sets cc-pV*n*Z-PP-F12/MP2Fit were used for the evaluation of the many-electron F12 integrals as well.

If we examine one property at at time, it is evident that the new cc-pV*n*Z-PP-F12 sets provide a smoother and faster convergence to the CBS limit, with respect to cardinal number. In a number of cases, such as the Zr IP and the Zr and Ru one-electron excitation energies, it is evident that the combination of an explicitly correlated protocol with a "conventionally developed " set yielded results that are not well converged; discrepancies are observed especially between the DZ and TZ results; the systematic increase of recovered correlation energy is no longer present. Once the new cc-pV*n*Z-PP-F12 sets are utilised, the convergence pattern improves and the convergence towards the CBS is, as expected, rapid and monotonic. In terms of the magnitude of the correlation energy recovered by each family of sets, it can be seen that in certain cases (the vast majority of cases in elements Y-Pd) the new sets do recover more correlation energy (as shown in Figures 6.10c and 6.10d). One should also keep in mind, especially for cases such as that of Figure 6.11c, that the CBS estimates presented in Figures 6.10 and 6.11 are obtained by two point extrapolation of the conventional QZ and 5Z CCSD(T) correlation energies, as provided in Reference 259. Therefore, while the CBS values provide a useful tool in evaluating the convergence pattern of the new sets, their absolute value should be treated with caution. Figures 6.10b and 6.11b suggest that the new sets may not be particularly effective for the description of electron affinities; it is evident that the new sets are outperformed by the existing ones. This result is due to the fact that while the new cc-pV*n*Z-PP-F12 basis sets are "augmented" with respect to *spd* functions, they lack augmentation with diffuse functions of angular momentum f and higher. In order to assess this shortcoming, additional higher angular momentum functions were interpolated (see Equation 6.1), and a new family of aug-cc-pV*n*Z-PP-F12 sets for EAs was created. Figure 6.12 shows the much improved behavior of aug-cc-pV*n*Z-PP-F12 sets, and their smooth convergence towards the CBS limit.

Results for the atomic properties are shown in Table 6.7 at the frozen core ($4d5s$ correlation) CCSD(T)-F12b/3C(FIX) (β =1.4 α_0^{-1}) level of theory, as a function of the cc-pV*n*Z-PP-F12 basis set. Smooth and rapid convergence towards the CBS limit is clearly observed in each case. The atomic trends in all four properties are analogous to previously reported trends for $4d$ transition metal elements.[259,260] The effects of $4s4p$ electron correlation in all four atomic properties are given in Table 6.8. As expected, outer-core correlation effects are far from negligible, and are required in cases where spectroscopic accuracy is of interest. Present core-valence effects demonstrate smaller overall effects for the early metals, which increases as the d shell becomes fuller (more than half-filled). Core-correlation seems to increase the value of the ionisation potential in all elements but Pd, whose IP is slightly decreased compared to the valence-only result, at the CBS limit. Regarding the electron affinities, correlation of the $4s4p$ electrons generally increases the EA value, except for the case of Nb. The effect of core-correlation on the atomic properties is found to be consistent with that previously reported in References 259 and 260, as demonstrated by the convergence towards the CBS limit.



(a)

(b)

(c)

(d)

Figure 6.12: Electron affinities for elements (a) Zr, (b) Mo, (c) Ru, and (d) Pd, calculated at CCSD(T)-F12b/3C(FIX) level of theory with β =1.4 a_0^{-1}, using existing aug-cc-pwCVnZ-PP (n = D - Q), new cc-pVnZ-PP-F12, and new aug-cc-pVnZ-PP-F12 (n= D - Q) basis sets. The estimated complete basis set limits were obtained from conventional CCSD(T) with aug-cc-pwCVnZ-PP (n = Q, 5) basis sets, as described in References 259 and 260.

Table 6.7: Calculated CCSD(T)-F12b/3C(FIX) (β =1.4 α_0^{-1}) ionization potentials, electron affinities, one-electron excitation energies $4d^2 5s^2 \rightarrow 4d^3 5s^1$ and two-electron excitation energies $4d^2 5s^2 \rightarrow 4d^4 5s^0$ with valence electrons ($4d5s$) correlated only. All values in kcal/mol. CBS estimates are taken from References 259 and 260.

Basis Set	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd
Ionisation potentials								
cc-pVDZ-PP-F12	132.9	148.7	150.5	157.5	160.3	165.0	167.3	196.1
cc-pVTZ-PP-F12	133.4	149.3	151.1	158.4	161.5	166.2	168.7	197.0
cc-pVQZ-PP-F12	133.5	149.4	151.3	158.6	161.7	166.7	169.3	197.1
CBS	133.6	149.6	151.5	158.9	162.2	167.3	169.9	197.8
CBS (aug sets)	133.6	149.5	151.4	158.7	161.9	166.9	169.5	197.2
Electron affinities								
cc-pVDZ-PP-F12		5.5	18.2	14.4	4.7	21.2	23.4	8.3
cc-pVTZ-PP-F12		6.6	19.1	15.5	6.6	22.2	24.4	9.5
cc-pVQZ-PP-F12		7.0	19.6	15.9	7.6	22.9	25.0	10.9
CBS		7.2	19.8	16.1	8.2	23.2	25.5	10.7
CBS (aug sets)		7.2	19.8	16.1	8.2	23.2	25.5	10.7
$4d^{m-2}5s^2 \rightarrow 4d^{m-1}5s^1$								
cc-pVDZ-PP-F12	35.2	16.0	−3.5	−37.6	14.1	−17.9	−36.5	−54.9
cc-pVTZ-PP-F12	34.8	15.9	−3.7	−37.6	13.5	−18.3	−37.0	−55.5
cc-pVQZ-PP-F12	34.7	15.9	−3.8	−37.5	13.0	−18.7	−37.5	−55.7
CBS	34.6	15.8	−3.9	−37.7	12.7	−19.1	−37.8	−57.4
CBS (aug sets)	34.6	15.8	−3.9	−37.7	12.7	−19.1	−37.8	−57.4
$4d^{m-2}5s^2 \rightarrow 4d^{m}5s^0$								
cc-pVDZ-PP-F12	87.2	64.3	26.0		58.4	10.0	−28.0	−81.0
cc-pVTZ-PP-F12	87.0	64.0	25.9		56.9	8.8	−29.1	−82.2
cc-pVQZ-PP-F12	86.9	64.0	25.8		56.1	8.0	−29.6	−82.8
CBS	86.8	63.7	25.6		55.5	7.4	−31.1	−83.3
CBS (aug sets)	86.9	63.8	25.5		55.7	7.6	−30.4	−83.0

Table 6.8: Effects of $4s4p$ correlation ΔE_{CV} at the CCSD(T)-F12b/3C(FIX) ($\beta = 1.4\ \alpha_0^{-1}$) ionization potentials, electron affinities, one-electron excitation energies $4d^2 5s^2 \rightarrow 4d^3 5s^1$ and two-electron excitation energies $4d^2 5s^2 \rightarrow 4d^4 5s^0$ with valence electrons ($4d5s$) correlated only. All values in kcal/mol. CBS estimates are taken from References 259 and 260.

Basis Set	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd
Ionisation potentials								
cc-pVDZ-PP-F12	6.9	2.5	5.0	5.0	1.8	3.8	3.3	1.6
cc-pVTZ-PP-F12	8.0	2.5	4.8	4.8	1.8	3.6	3.1	−0.1
cc-pVQZ-PP-F12	8.4	2.4	4.7	4.7	1.8	3.5	3.1	−0.9
CBS	8.7	2.4	4.6	4.7	1.7	3.4	2.9	−1.3
CBS (aug sets)	8.7	2.5	4.6	4.7	1.7	3.4	2.9	−1.3
Electron affinities								
cc-pVDZ-PP-F12		1.8	−0.1	0.2	1.2	0.5	0.7	1.4
cc-pVTZ-PP-F12		2.1	−0.2	0.1	1.6	0.5	0.7	1.5
cc-pVQZ-PP-F12		2.2	−0.3	0.0	1.8	0.5	0.7	1.6
CBS		2.2	−0.5	−0.1	2.1	0.4	0.6	1.6
CBS (aug sets)		2.2	−0.5	−0.1	2.1	0.4	0.6	1.6
$4d^{m-2}5s^2 \rightarrow 4d^{m-1}5s^1$								
cc-pVDZ-PP-F12	−3.0	−2.3	−1.4	0.7	−0.7	−1.1	2.4	2.5
cc-pVTZ-PP-F12	−3.7	−2.8	−1.8	0.4	−1.4	−0.7	2.1	2.6
cc-pVQZ-PP-F12	−4.0	−3.1	−2.0	0.3	−1.6	−0.5	2.0	2.8
CBS	−4.2	−3.3	−2.2	0.0	−2.1	0.1	1.7	3.6
CBS (aug sets)	−4.2	−3.3	−2.2	0.0	−2.1	0.1	1.7	3.6
$4d^{m-2}5s^2 \rightarrow 4d^{m}5s^0$								
cc-pVDZ-PP-F12	−1.5	−1.6	0.4		0.9	2.8	8.6	8.0
cc-pVTZ-PP-F12	−2.5	−2.5	−0.4		0.0	2.2	3.4	8.0
cc-pVQZ-PP-F12	−3.1	−2.9	−0.7		−0.4	1.9	3.9	8.0
CBS	−3.4	−3.3	−1.1		−1.3	1.2	4.0	7.5
CBS (aug sets)	−3.4	−3.3	−1.1		−1.3	1.2	4.0	7.5

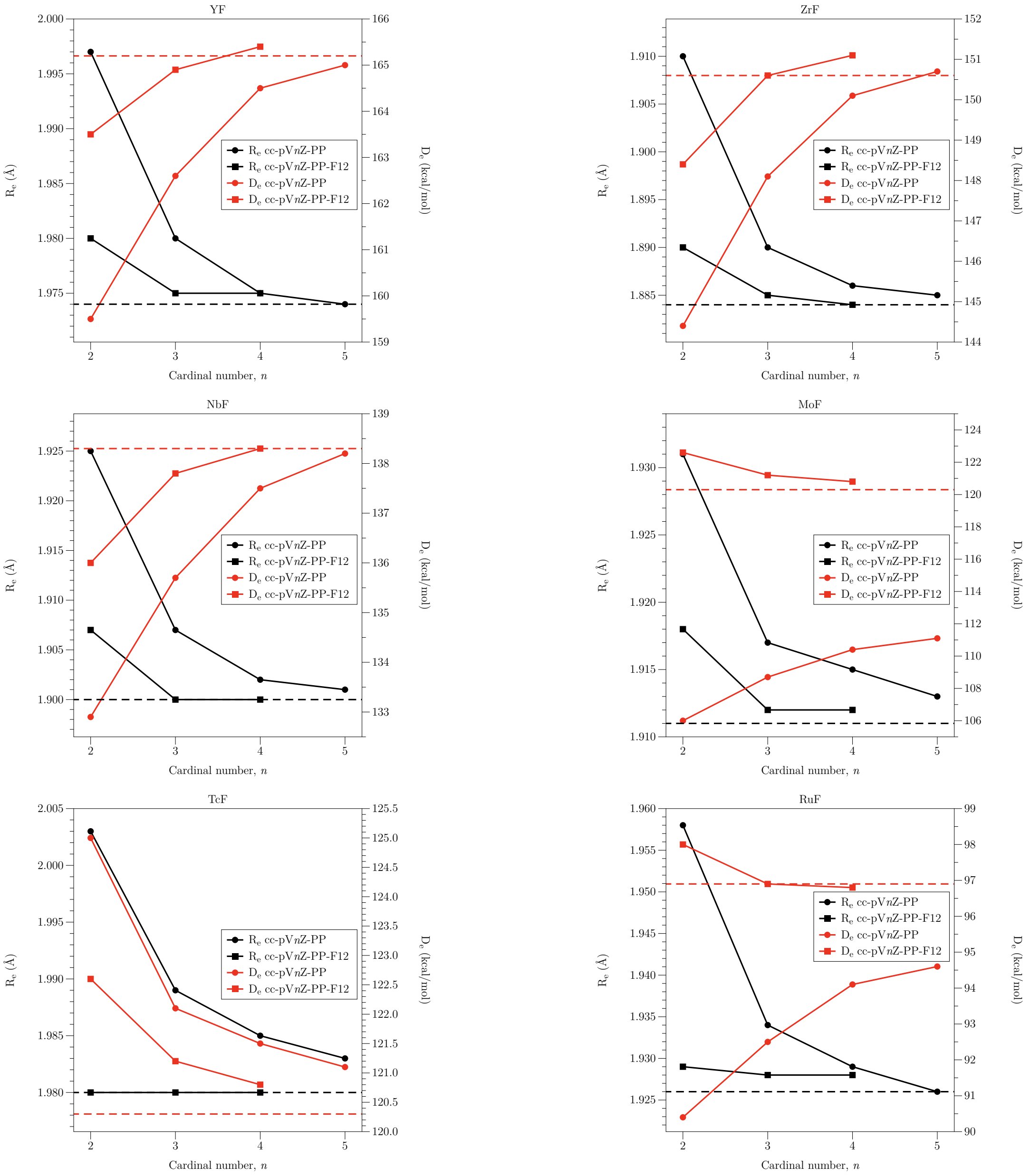
The effectiveness of new basis sets, for both valence-only and core-valence cases, was assessed at the molecular level by performing CCSD(T) and CCSD(T)-F12b calculations in order to determine the spectroscopic constants of fluorides. The CCSD(T)-F12b/3C(FIX) method was used with new cc-pVnZ-PP-F12 OBS, cc-pVnZ-PP-F12/MP2Fit, cc-pVnZ-PP-F12/OPTRI (n =

D - Q) ABSs on the 4*d* elements. The auxiliary basis set utilised for the density fitting of the exchange terms of 4*d* TMs was def2-QZVPP/JKFIT. The basis sets for F were the corresponding cc-pV*n*Z-PP-F12 (*n* = D - Q) sets as described earlier.

Seven single-point calculations were performed around the previously reported R_e,[141] and then a sixth order polynomial was fit to the data; in all cases the new calculated values of R_e and D_e^0 that are reported throughout the work are obtained through this process of polynomial fitting. Molecular results displaying the convergence of spectroscopic properties R_e and D_e for fluorides of 4*d* TMs are displayed in Figure 6.13, while the corresponding values of the spectroscopic constants are reported in table 6.9. Figure 6.13 compares the performance of new cc-pV*n*Z-PP-F12 basis sets at the CCSD(T)-F12b/3C(FIX) level of theory, with existing cc-pV*n*Z-PP F12 calculations. For both properties, the accelerated performance associated with explicit correlation is evident; CCSD(T)-F12b method yields bond lengths of approximately *n*+1 quality or better. The convergence with respect to the cardinal number appears to be quite monotonic, a fact that should make the F12 results amendable to CBS extrapolation. There appear to be some cases, for which the CCSD(T) and CCSD(T)-F12b results converge from different directions, towards a similar CBS limiting value. This can be seen in cases of TcF, RuF, RhF, and PdF. While the reason for this behaviour is not apparent, it could be attributed to the different magnitude of BSSE for conventional and F12 calculations. Furthermore, cases like RuF have a somewhat ambiguous ground state, as for example the energetic error between $^4\Phi$ and $^6\Delta$ state is very, very small, and the corresponding spectroscopic constants are almost indistinguishable.[260] Nonetheless, the newly developed sets exhibit smooth and monotonic behaviour towards the previously estimated CBS limit, a fact that reassures their behaviour in molecular systems. Due to the fact that experimental molecular information is not widely available for small molecular systems that contain 4*d* TMs, and that the information available is most of the time accompanied by significantly large error margins that don't allow for conclusive "evidence" regarding the expected convergence pattern. The effects from 4*s*5*p* correlation appear to be particularly significant for dissociation energies, as the core-valence contributions Δ_{CV}, are bigger than our goal value of chemical accuracy. On the other hand, equilibrium bond lengths appear to be less sensitive.

6.2 Conclusions

New correlation consistent basis sets for 4*d* transition metal elements Y-Pd, from double- to quadruple-zeta quality, were developed for use in explicitly correlated F12 calculations. Orbital basis sets (cc-pV*n*Z-PP-F12 and cc-pCV*n*Z-PP-F12) have been developed, along with the necessary auxiliary basis sets, both those for density fitting the conventional 2-electron integrals (MP2Fit) and those for CABS procedure for the F12 many electron integrals (OPTRI). The sets were designed for use along with the same small-core relativistic pseudopotentials as employed in the standard cc-pV*n*Z-PP basis sets. Atomic results exhibit smooth and accelerated convergence towards the CBS limit compared to conventional CCSD(T) calculations, witnessed from electronic energies and atomic properties. Molecular results, energies and spectroscopic properties of 4*d* TM fluorides, also show smooth and accelerated convergence that ensures overall well-behaved basis sets. The increased rate of basis set convergence with F12 methods for 4*d* transition metal elements frees up the way to carrying out accurate CCSD(T) calculations on larger molecular systems, using smaller basis sets. All of the OBSs and ABSs optimised in this work can be found in Appendix D.



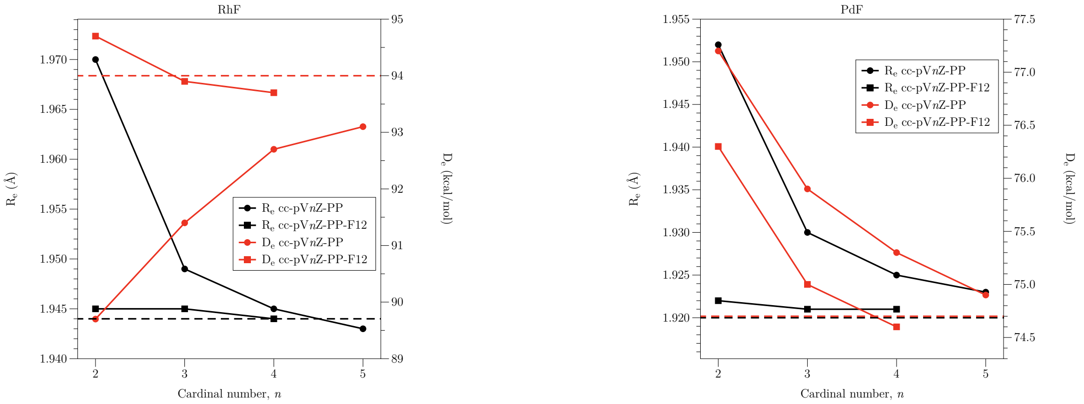


Figure 6.13: Calculated spectroscopic constants [r$_e$ (in Å) and D$_e$ (in kcal/mol)] for fluorides of elements Y-Pd, as a function of basis set for CCSD(T)-F12b/cc-pVnZ-PP-F12 and aug-cc-pwCVnZ-PP. The estimated complete basis set limits (dashed horizontal lines) were obtained from conventional CCSD(T) with aug-cc-pwCVnZ-PP (n = Q, 5) basis sets.

Table 6.9: Calculated CCSD(T)-F12b frozen-core and core-valence contributions for spectroscopic constants of 4*d* fluorides. The estimated complete basis set limits were obtained from conventional CCSD(T) with aug-cc-pwCV*n*Z-PP (n = Q, 5) basis sets.

		D_e (kcal/mol)		r_e (Å)		ω_e (cm^{-1})	
Molecule	Basis	Valence	Δ_{CV}	Valence	Δ_{CV}	Valence	Δ_{CV}
YF $^1\Sigma^+$	cc-pVDZ-PP-F12	163.5	−0.72	1.980	−0.0490	614.2	21.2
	cc-pVTZ-PP-F12	164.9	−1.27	1.975	−0.0471	615.2	23.1
	cc-pVQZ-PP-F12	165.4	−1.52	1.975	−0.0475	614.7	23.3
	CBS(Q5)	165.2	−1.04	1.974	−0.0477	615.1	22.4
ZrF $^2\Delta$	cc-pVDZ-PP-F12	148.4	−0.06	1.890	−0.0337	677.2	24.5
	cc-pVTZ-PP-F12	150.6	−0.98	1.885	−0.0316	683.9	21.7
	cc-pVQZ-PP-F12	151.1	−1.12	1.884	−0.0315	681.4	23.0
	CBS(Q5)	150.6	−0.24	1.884	−0.0322	682.9	22.5
NbF $^5\Pi$	cc-pVDZ-PP-F12	136.0	−0.31	1.907	−0.0227	630.9	15.9
	cc-pVTZ-PP-F12	137.8	−0.78	1.900	−0.0202	638.2	15.7
	cc-pVQZ-PP-F12	138.3	−0.80	1.900	−0.0206	636.8	16.0
	CBS(Q5)	138.3	−0.62	1.900	−0.0209	638.1	15.5
MoF $^2\Delta$	cc-pVDZ-PP-F12	109.6	0.56	1.918	−0.0167	611.5	8.0
	cc-pVTZ-PP-F12	111.2	0.34	1.912	−0.0165	617.8	7.5
	cc-pVQZ-PP-F12	111.7	0.40	1.912	−0.0172	618.1	7.5
	CBS(Q5)	112.0	0.23	1.911	−0.0172	619.5	6.5
TcF $^7\Sigma^+$	cc-pVDZ-PP-F12	122.6	−3.22	1.980	−0.0026	558.0	−0.1
	cc-pVTZ-PP-F12	121.2	−2.46	1.980	−0.0084	557.2	5.9
	cc-pVQZ-PP-F12	120.8	−2.55	1.980	−0.0097	557.2	5.7
	CBS(Q5)	120.3	−2.17	1.980	−0.0093	557.3	5.5
RuF $^4\Phi$	cc-pVDZ-PP-F12	98.0	−4.41	1.929	−0.0052	535.3	13.1
	cc-pVTZ-PP-F12	96.9	−1.42	1.928	−0.0114	536.2	14.3
	cc-pVQZ-PP-F12	96.8	−0.89	1.928	−0.0121	536.1	14.6
	CBS(Q5)	96.9	−0.56	1.926	−0.0115	535.5	14.7
RhF $^3\Delta$	cc-pVDZ-PP-F12	94.7	−2.72	1.945	−0.0053	536.3	11.2
	cc-pVTZ-PP-F12	93.9	−1.41	1.945	−0.0077	538.4	11.1
	cc-pVQZ-PP-F12	93.7	−0.91	1.944	−0.0080	538.1	11.5
	CBS(Q5)	94.0	−0.91	1.944	−0.0073	542.8	6.4
PdF $^2\Sigma^+$	cc-pVDZ-PP-F12	76.3	−0.60	1.922	−0.0008	562.7	5.3
	cc-pVTZ-PP-F12	75.0	1.68	1.921	−0.0041	563.7	5.4
	cc-pVQZ-PP-F12	74.6	2.19	1.921	−0.0047	563.3	4.7
	CBS(Q5)	74.7	1.99	1.920	−0.0049	563.3	5.2

Chapter 7

Explicitly correlated composite thermochemistry of 3*d* transition metal species

7.1 Background on composite thermochemistry methods

Transition metal (TM) containing systems have always been important from both a scientific and industrial point of view. Quantitative energetics of these molecules can be used to predict ground states, find intermediates and elucidate reaction mechanisms. However, TM species often present substantial experimental difficulties when it comes to determining quantitative thermochemical properties due to material instability, incomplete combustion and non-stoichiometric oxide formation.

As developments in transition metal chemistry continue to find applications in a growing number of areas, the need for theoretical calculations capable of accurately describing such systems becomes more and more important. Density functional theory (DFT)[268] gained popularity over the past decades, contributing significantly to a broad range of transition metal applications.[13,269–272] However, the lack of systematic improvement of DFT methods, as well as the functional dependence of the method, hints at the need for more accurate calculations.

High accuracy *ab initio* methods that determine chemically accurate energetics for TM containing systems have unfortunately proven to be much more difficult than for similar-sized main group elements. The computational difficulties are largely due to the compact nature of the 3*d* shell, which results in large electron correlation effects as well as the high density of states of these systems. The large correlation effects are best treated with methods like coupled cluster (CC) theory, while the dense states can be tackled with multireference methods such as multireference configuration interaction (MRCI). Unfortunately, both of these methods scale steeply with the number of correlated electrons and the system size. An additional limitation that affects the size of the treatable systems is the slow convergence with respect to the orbital basis set, an effect that often requires large basis sets and extrapolation to the complete basis set (CBS) limit in order for accurate results to be obtained. One way to bypass these difficulties and move closer to "chemically accurate" results on TM containing systems is to perform a series of quantum chemistry calculations; an approach that is called a composite method (or "thermochemical recipe"). These methods utilize results of several calculations; they combine methods with high levels of theory as well as lower levels of theory with appropriate basis sets (usually smaller sets for the expensive methods, and larger sets for the affordable calculations). These methods are commonly used to calculate thermodynamic properties such as enthalpies of formation, atomisation energies, ionization energies, electron affinities, excitation energies etc. The first systematic model chemistry of this type is called Gaussian-1 (G1)[273] and was introduced by John Pople; this method has been modified over the years, and a series of methods denoted Gaussian-*n* (G*n*) have been introduced.[274–276] Furthermore, different composite thermochemical schemes have also been developed, the most important of which are the Weizmann-*n* theories (W*n*: W1-W4),[277–279] the Petersson CBS models[280–283] the Feller-Peterson-Dixon method (referred to as FPD),[284,285] the correlation consistent Composite Approach (ccCA),[286,287] the focal point analysis (FCA)[288,289] and the HEAT protocol (High Accuracy Extrapolated Ab Initio Thermochemistry).[290] These methods will be briefly reviewed, with some focus on the FPD approach, since its modified version for explicitly correlated calculations is the approach utilized in this work.[291]

7.1.1 Gaussian-*n* Theories

In 1989, Pople and co-workers introduced a composite procedure named "Gaussian-1 theory" (G1) that was intended to predict properties that depended upon energy differences, such as total atomisation energies, ionization potentials, as well as proton and electron affinities.[273,292] G1 tried to approximate a high-level calculation [QCISD(T)/6-311+G(2df,p)][293] at a greatly reduced computational cost. G1 combined high-level methods with an empirical correction to achieve a target accuracy of ± 2 kcal/mol in atomisation energies for the majority of a 31-molecule test set containing elements taken from the first row of the periodic table. Subsequent extension to second-row elements yielded an accuracy of approximately ± 3 kcal/mol.[294]

As already mentioned, G1 theory is a composite procedure, which belongs to the G-*n* family of composite methods. G*n* theories assume that some higher level corrections of the total energies of the examined molecules could be treated separately and combined in an additive manner. The general objective of the theory was to obtain an equilibrium geometry, a total electronic energy, and a set of harmonic frequencies for all structures associated with local minima on a potential surface. The G1 procedure begins at the Hartree-Fock level (spin-restricted RHF for singlet states, and spin-unrestricted UHF for all other states), on which initial equilibrium structures are obtained, using the 6-31G* basis set.[295] Equilibrium geometries are then obtained at the second-order Møller - Plesset perturbation theory (MP2)[296] level with the 6-31G* basis set with all electrons (both valence and core electrons) correlated. Once the geometries are obtained, single point calculations at higher levels of theory are performed. The first set of higher level calculations is carried out at full fourth-order Møller - Plesset perturbation theory (MP4SDTQ)[297] using the 6-311G** basis set[298] and the standard frozen core approximation. While more accurate, the MP4SDTQ/6-311G** energies are still insufficiently accurate in order to provide good electronic energies; they were therefore modified by a number of corrections to take account of further theoretical refinements. These corrections are performed at higher levels of theory and involve extensive computations; these corrections are computed individually and combined in an additive manner. The approximation that the corrections can be added to provide one accurate composite energy is justified by its level of success relative to experiment. The first of the higher corrections is the inclusion of diffuse sp basis functions, known to be important for anions and molecules with lone pairs of electrons.[299] This correction is obtained at the MP4 level and compares the 6-311+G** and 6-311G** basis sets, in a form of a correction $\Delta E(+)$:

$$\Delta E(+) = E[\text{MP4/6-311+G}^{**}] - E[\text{MP4/6-311G}^{**}]\,. \tag{7.1}$$

The second correction adds additional (higher) polarization functions to non-hydrogen atoms. This correction is also obtained at the MP4 level and compares the 6-311G**(2df) and 6-311G** basis sets.

$$\Delta E(2df) = E[\text{MP4/6-311G}^{**}(2df)] - E[\text{MP4/6-311G}^{**}]\,. \tag{7.2}$$

In cases where the $\Delta E(2df)$ correction is positive, in which the f functions are considered unimportant since the single set of d functions yields a larger energy lowering than separate inner and outer sets of d's, the correction is set to zero. A third correction accounts for the deficiencies of the MP4SDTQ theory; it is known that MP4 converges slowly for molecules with stretched bonds[300] and that MP4 sometimes overestimates the interaction energies in some molecules with multiple bonds.[301,302] This correction which is also called a "post-MP4"correction for residual correlation effects, is based on the quadratic configuration interaction theory QCISD(T), which is known to reproduce full configuration interaction (FCI) results quite well, particularly near equilibrium geometries.[293] The QCISD(T) correction incorporates the 6-311G** basis, and has the form:

$$\Delta E(\text{QCI}) = E[\text{QCISD(T)/6-311G}^{**}] - E[\text{MP4/6-311G}^{**}]\,. \tag{7.3}$$

Up to this point the total (composite) energy of the system, can be written as:

$$E(\text{composite}) = E[\text{MP4/6-311G}^{**}] + \Delta E(+) + \Delta E(2df) + \Delta E(\text{QCI})\,, \tag{7.4}$$

and it corresponds to an approximate QCISD(T)/6-311+G$^{**}(2df)$ calculation. However this energy remains incomplete, mainly due to the deficiencies of the basis set. In order to avoid additional calculations, an empirical overall "higher level correction" ΔE(HLC) is added, which leads to the correct electronic energies of the hydrogen atom and molecule. More specifically -3.07 mE$_h$ are added for each bound paired valence electron, which corrects the hydrogen molecule, and then -0.19 mE$_h$ for each bound unpaired electron to correct the electronic energy of the hydrogen atom. If we consider the spin component state with the maximum number of electrons, the total correction in mE$_h$ is given by:

$$\Delta E(\mathrm{HLC}) = -0.19 n_\alpha - 3.07 n_\beta \,, \tag{7.5}$$

where n_α and n_β are the number of α and β valence electrons respectively. While this correction is not *ab initio* in nature, it is reasonable in cases where a balanced basis set is used, meaning that residual errors per electron are approximately constant over a wide range of molecules. At this point we have reached the G1 value for the electronic energy; the G1 estimate of the total energy if the nuclei have infinite mass and all electron correlation involving inner-shell electrons is ignored:

$$E_e = E(\mathrm{composite}) + \Delta E(\mathrm{HLC})\,. \tag{7.6}$$

Finally the harmonic frequencies and the zero-point correction ΔE(ZPE) are calculated and the total energy, E_0 is obtained:

$$E_0 = E_e + \Delta E(\mathrm{ZPE})\,. \tag{7.7}$$

The frequencies are obtained at HF/6-31G* (using the HF structures) and then scaled uniformly by a factor of 0.8929 to take account of known inadequacies at this level.[303]

G1 theory has been assessed against experimental data, such as atomisation energies. The main findings show that reaction energies of 61 small first-row compounds agree with experimental values to ± 2 kcal/mol. However, since the higher-level correction is based on the hydrogen atom and molecule, the success of G1 is dependent on the "balance" of the basis sets between hydrogen and other atoms. Furthermore, the fact that the higher-level correction depends on a count of paired electrons shows that G1 cannot be used to produce continuous potential curves or surfaces which connect bound with unbound regions. Finally, the theory performs poorly for triplet states, a fact that suggests the theory is giving an inadequate description of the correlation between electrons in different orbitals. The "black box" nature of G1 made it accessible to researchers who preferred to use an off-the-shelf, calibrated procedure. Due to G1's focus on energy differences, the use of single point calculations at reference geometries obtained from a much lower level of theory was justified. The practice of using reference geometries obtained at a much lower level of theory than the ultimate desired level, as well as frequencies (often scaled) from a lower-level calculation, is a general characteristic shared by nearly all composite techniques that followed.

In 1991, the need for improved accuracy led Pople and coworkers to introduce Gaussian-2 theory (G2).[274] G2 began from the G1 energy and added two corrections: a two-part MP2 correction designed to account for the error arising from an additivity assumption in G1 and a basis set correction involving an additional (third) *d* function on non-hydrogen atoms and a second set of *p* functions on hydrogen. Furthermore, an empirical, "higher-level correction" (HLC) based on the number of electron pairs was added. This empirical HLC was determined from the best fit to the atomisation energies of 55 molecules for which the experimental values were well established. This pushed the need to develop an experimental data set of energetic properties that are known to chemical accuracy (± 1 kcal/mol) in order to test existing composite theories as well as to develop a database used for necessary parameterization. For a set of 39 small first- and second row compounds, the average error dropped from 1.4 kcal/mol (G1) to 0.9 kcal/mol (G2), while differences exceeding 5 kcal/mol were still observed in some atomisation energies. Minor modifications to one or more of the steps in G2 theory in order to reduce the computing requirements led to a number of related methods, including: G2(MP2) and G2(MP3),[304] G2(B3LYP/MP2/CC),[305] G2(MP2,SVP),[306] and G2(MP2,SV).[307]

The subsequent major modification of the G*n* family, Gaussian-3 theory (G3), appeared in 1998.[275] G3 replaced several steps in the G2 procedure, while incorporating a new, still empirical, higher-level correction. It furthermore added corrections for spin-orbit effects in atoms and a core-valence correlation correction. When tested, G3 reduced the mean unsigned error from 1.56 (G2) to 0.94 kcal/mol, for a test set of 148 experimental enthalpies of formation at 298 K. As with G2, there were a number of derivative theories based on a range of smaller modifications to the procedure, such as G3(MP2),[308] G3//B3LYP, G3(MP2)//B3LYP,[309] G3(CCSD), G3(MP2,CCSD),[310] G3X, G3X(MP2), G3X(MP3), G3SX,[311] G3-RAD and G3X-RAD.[312]

The latest development of the Gaussian-*n* theories, namely the Gaussian-4 theory, was proposed in 2007 by Curtiss *et al*.[276] It incorporated five important modifications to G3:

1. An extrapolation procedure was included in order to obtain the Hartree-Fock limit for inclusion in the total energy calculation.

2. Additional *d* polarization functions were added to 3*d* on the first-row atoms and to 4*d* on the second-row atoms, with reoptimization of the exponents for the 4*d* set. More specifically, the 2*df* polarization set on the first row is replaced by a 3*df*, while the 3*d*2*f* polarization functions on the second row (Al-Cl) are replaced by 4*d*2*f* and no changes are made for Na, Mg, K, Ca, and Ga-Kr.

3. CCSD(T) replaced QCISD(T).

4. Geometries and zero-point energies were obtained at the B3LYP/6-31G(2*df*,*p*) level.

5. Two new higher-level corrections replaced the former ones, in order to account for deficiencies in radicals and in species having only one electron pair in the valence space. However, the correction for scalar relativistic effects was removed and is now included in the HLCs.

On the G3/05 test set of 454 experimental energy differences, G4 showed a mean error of 0.83 kcal/mol versus 1.13 kcal/mol for G3. Follow-up variants of G4, G4(MP2) and G4(MP3) whose performance on the G3/05 test set was only slightly worse than G4, were established that same year.[313] Looking back we can observe that the original G1 procedure, published in 1989, eventually spawned a family of 22 different methods based on four primary forms, each with their own strengths and weaknesses.

7.1.2 Weizmann-*n* Theories

Following the development of the Gaussian-1 method, Martin and co-workers introduced the Weizmann-1 (W1) and Weizmann-2 (W2) "black box" composite methods.[277] The W*n* family of models intended to include all terms that contributed approximately 1 kJ/mol to atomisation energies. Furthermore the goal was for all components of the theory to converge with respect to the 1-particle basis set, to approximately the same level of accuracy. One big difference from the G*n* methods was that empirical parameters derived from experiments were not to be used. While these were the original aims, W1 included a molecule-independent, empirical parameter which was not present in the more expensive W2 theory. Although atomic electron affinities were used to guide the selection of the best CBS extrapolation formula, W*n* theories were primarily intended for the prediction of heats of formation.

In W1, equilibrium geometries were obtained at the B3LYP/cc-pV(T+*d*)Z level; alternatively the B3PW91 exchange-correlation functional may be preferable for certain systems. The "+*d*" notation indicates the addition of a tight *d* function for second-row elements. Next, zero-point energy was obtained from B3LYP/cc-pV(T+*d*)Z, or B3PW91/cc-pV(T+*d*)Z harmonic frequencies scaled by a factor of 0.985. Corrections are carried out in the form of single point calculations; first CCSD(T)/aug-cc-pVDZ+2*d* and CCSD(T)/aug-cc-pVTZ+2*d*1*f* calculations, followed by a CCSD/aug-cc-pVQZ+2*d*1*f* calculation. Separate CBS extrapolations were performed on the SCF, CCSD and (T) energy components, since their convergence behaviors are fundamentally different; the SCF energy appears to converge exponentially, while the valence correlation energy converges as an inverse-power series in the maximum angular momentum present in the basis set. Core correlation contributions are obtained at the CCSD(T)/MTsmall level. Furthermore, scalar relativistic and, where necessary, spin-orbit coupling effects are treated at the ACPF/MTsmall level; ACPF which stands for averaged coupled-pair functional, is a size-extensive modified version of MRCISD.[314] W1 theory can be applied to fairly large systems. CPU times are dominated by the inner-shell correlation contribution (particularly for second-row compounds), which is reflected in the relatively small time reduction compared to W2 theory. In addition – contrary to W2 theory – W1 theory exhibits a pronounced difference in performance between first-row and second-row compounds: MAE is 0.26 kcal/mol for first-row, but 0.40 kcal/mol for second-row compounds. Imperfections in the CCSD(T) correlation method, which can be decomposed into effects of connected quadruple excitations on the one hand, and imperfections in the treatment of connected triple excitations on the other, are the largest remaining sources of error in the W1 theory. Upon taking these effects into account, the results for atomic electron affinities (where it is practical to do so) improve by an order of magnitude and on average agree with experiment to within 0.001 eV.

The more expensive W2 method performs a geometry optimization at the CCSD(T)/cc-pVQZ+1 level while zero-point energy is obtained from a CCSD(T)/cc-pVTZ+1 anharmonic force field or from B3LYP/cc-pV(T+d)Z frequencies scaled by 0.985. Single point calculations at the CCSD(T)/aug-cc-pVTZ+2d1f and CCSD(T)/aug-cc-pVQZ+2d1f levels were carried out, followed by a CCSD/aug-cc-pV5Z+2d1f single-point calculation. Separate CBS extrapolations were performed on the SCF, CCSD and (T) energy components respectively, similarly to W1. Core correlation is computed at the CCSD(T)/MTsmall level while scalar relativistic corrections and, if necessary, spin-orbit splittings are computed at ACPF/MT level.

Performance of the two theories was tested using a test set of 28 small, well-behaved, first- and second-row molecules. W1 was reported to yield a mean unsigned deviation of 0.30 kcal/mol for atomisation energies, while W2 reduced that to 0.23 kcal/mol; for comparison purposes, the corresponding G3 mean unsigned deviation was 0.86 kcal/mol. The maximum errors were 1.01 kcal/mol for W1 and 0.64 kcal/mol for W2. Since the CPU time gap between W1 and W2 theory is fairly narrow for second-row species, it is recommended to carry out a W2 rather than a W1 calculation for accurate work on second-row species. For first-row systems, on the contrary, W1 may seem the more attractive of the two. A number of W1 and W2 variants were subsequently introduced, including W1U, W1USc, W1BD and W1RO[315] and W1w, W2w and W2.2.[316] Mintz *et al*. discussed additional modifications labeled W2C, W2C-CAS-ACPF and W2C-CAS-AQCC methods.[317]

The next major Weizmann-n revision appeared 5 years later; the Weizmann-3 (W3) theory.[278] In W3, the contribution of triple excitations was determined from CCSDT calculations with the cc-pVDZ and cc-pVTZ basis sets. The effects of quadruple excitations were based on CCSDTQ/cc-pVDZ calculations scaled by a factor of 1.2532, a value derived from a small training set. The theory was tested against atomisation energies, ionization potentials and electron affinities. For the same set of 28 small molecules used with the W2 method, W3 provided a smaller mean unsigned deviation (0.22 vs. 0.40 kcal/mol) as well as a reduced maximum error of 3.00 (W2) compared to -0.78 kcal/mol (W3). A number of variations of W3 were also implemented, including W3a, W4a and W4b.

The latest revision of the Weizmann family, the Weizmann-4 (W4) model for first- and second-row compounds, was introduced by Karton *et al*. 2 years later.[279] In this implementation, reference geometries were based on CCSD(T)/cc-pVQZ calculations. The vibrational zero-point energies were taken from the best available sources, which often translated to a combination of experimental fundamentals and theoretical anharmonic corrections. For a test set of 26 small molecules for which highly accurate atomisation energies were available, W4 yielded a mean unsigned deviation of 0.15 kcal/mol. As with the earlier Wn models, a number of related theories were subsequently proposed, including W4lite, W4.2, W4.3,[318]W3.2[316] and W4.4.[318]

In an attempt to extend the applicability of the W1 and W2 thermochemistry methods, explicitly correlated versions, denoted W1-F12 and W2-F12, were proposed in 2012.[319] In W2-F12, it is possible to "save"one cardinal number in the basis set sequences without loss in accuracy; in W1-F12, this applies to first-row compounds but not for second-row compounds. The ability of the original W1/2 theories to successfully reproduce the CCSD(T)/CBS energy relied on a combination of very large Gaussian basis sets with extrapolation techniques. In practice however, for systems consisting of more than 7-8 non-hydrogen atoms, even W1 theory becomes prohibitively expensive. The explicitly correlated version of W1 and W2 theories (W1-F12 and W2-F12) are based on the well established fact that the inclusion of terms that explicitly depend on the interelectronic distance, r_{12} into the wavefunction drastically accelerates the basis set convergence.[280,320,321] Experience with CCSD-F12 has shown that basis set convergence is faster than for conventional calculations, with the typical gain to be approximately one basis set cardinal number.[281,322] This fact hinted at the possibility that the use of the CCSD-F12 method could accelerate the basis set convergence up to the point where basis sets of no larger than $spdf$ quality would be used in an "explicitly correlated"version of W1 theory. Although this is the case for systems that contain only first-row elements, second-row elements still need to employ basis sets of up to $spdfg$ quality, due to the small size of the VDZ basis set. The computationally more economic W1-F12 theory showed excellent performance for systems containing only first-row elements. Specifically, over the 97 first-row systems W1-F12 attained a RMSD of 0.19 kcal/mol against all-electron, relativistic CCSD(T) reference atomisation energies at the basis set limit. When considering reference atomisation energies at the FCI basis set limit, an RMSD of 0.45 kcal/mol was obtained. The more expensive W2-F12 protocol showed excellent performance for both first- and second-row systems. In particular, against all-electron, relativistic CCSD(T) reference atomisation energies a RMSD of 0.20 kcal/mol was obtained over the entire W4-11 test set.[323]

7.1.3 Petersson-style CBS models

Petersson and co-workers have produced a large body of work focused on procedures that estimate the correlation energy at the complete basis set limit.[280] Their earliest model chemistry was the CBS$^{(\infty,3)}$(Full)/DZ+P atomic pair natural orbital model, which was limited to closed-shell systems.[320] This method achieved an RMS accuracy of ±0.9 kcal/mol in total energies, even with the use of a double-zeta plus polarization quality basis set. A subsequent unrestricted Hartree-Fock quadratic-CI-based method, CBS-CI(Full)/($14s9p4d2f$,$6s3p1d$)/[$6s6p3d2f$,$4s2p1d$] was reported to yield total energies accurate to ± 0.8 kcal/mol.[321]

Further development work led to several new procedures. The CBS2(FC)/6-311+G**-QCI/6-311+G model was found to produce dissociation energies, electron affinities and ionization energies that were only slightly worse than G1 values while being 10 times faster.[322] These conclusions were based on a small set of first-row atoms and diatomic molecules. A further reduction in computer time, of a factor of ten, was found with the CBS2(FC)/6-311+G model, but the RMS error in dissociation energies increased from 1.91 to 4.23 kcal/mol, and the error in electron affinities increased from 0.18 to 1.58 eV. Following the release of the previously discussed Gaussian-2 method, further refinements in the approach of Petersson and co-workers led to the CBS-QCI/APNO model.[281] This model included a higher-order correction based on QCISD(T)/6-311++G(2df,p) calculations and a size-consistent empirical correction. Validations on a test set of 64 first-row compounds showed a MUD of 0.53 kcal/mol for various energy differences (dissociation energies, ionization potentials and electron affinities). While the maximum errors were not explicitly stated, several errors exceeding 1 kcal/mol were evident in the work.

Three new methods (CBS-4, CBS-q and CBS-Q) were introduced a year later in an attempt to increase the size of the systems that could be handled by significantly lowering the computational cost.[282] The mean unsigned deviations measured with respect to the 125-molecules of the G2 test set were 2.0, 1.7 and 1.0 kcal/ mol, respectively, for the three methods. Maximum errors of 5.4, 4.6 and 2.3 kcal/mol were obtained for atomisation energies. These three methods and the CBS-QCI/APNO method all utilized the asymptotic convergence of the MP2 pair energies. CBS-Q was later modified to use B3LYP geometries and frequencies, leading to a method labeled CBS-QB3.[324] That modification produced a reduction in the maximum error for the entire G2 test set from 3.9 to 2.8 kcal/mol. Following that, an additional modification was made to the CBS-QB3 method that allowed the spin correction to be removed. The resulting ROCBS-QB3 method did not perform quite as well as the method it was meant to replace, with an increase in the MUD of the G2/97 test set from 0.391 kcal/mol for CBS-Q to 0.69 kcal/mol for CBS-QB3.[283] Radom and co-workers proposed a modification to the CBS-Q method in which the geometries and zero-point vibrational energies were obtained from QCISD/6-31G(d) calculations and the highest level of theory involved CCSD(T) rather than QCI.[325] This method, which was intended for free radical thermochemistry, was called CBS-RAD. It included an empirical correction of 0.30 kcal/mol per triple or double bond.

Like the G-*n* family of methods, the collection of Petersson-style CBS models has undergone continuous evolution, which resulted in many different versions and implementations.

7.1.4 Feller-Peterson-Dixon procedure

Unlike fixed-recipe “model chemistries” the Feller-Peterson-Dixon or FPD approach consists of a flexible sequence of up to 13 components that vary with the nature of the chemical system under study and the desired accuracy in the final results.[284,326–330] In most instances, the primary component relies on coupled cluster theory, such as CCSD(T), or configuration interaction theory combined with large Gaussian basis sets and extrapolation to the complete basis set limit. Corrections for core-valence, scalar relativistic and higher order correlation effects are considered additive to the CBS extrapolated energy. Attention is paid to the uncertainties associated with each of the corrections in order to estimate the uncertainty of the overall results. A rough knowledge of the uncertainty in the individual components helps to avoid combining pieces with widely different accuracies, so that computational resources can be directed to the most problematic areas where they can be used most effectively. While the FPD method calculates molecular properties that can be highly accurate, its computationally intensive nature limits the size of the chemical system to which it can be applied to roughly 10 or fewer first- and second-row atoms.

The general strategy of the FPD approach was developed for the studies of thermochemical or spectroscopic properties such as molecular structures and vibrational frequencies and bares similarities with the focal-point analysis technique,[288,289] (see section 7.1.7) in that it is a flexible, multi-step approach intended to address all of the major sources of error, instead of a fixed-recipe model chemistry. The overall goal of FPD was to include all physically significant effects that contribute to the property of interest at a level of theory which guarantees results within the target accuracy. Consequently, the basic approach can be easily modified to only include effects that contribute significantly. This enables the method to address many properties across a large portion of the periodic table.

For thermochemical studies, the initial step in the procedure involves a series of frozen-core CCSD(T) geometry optimizations using the aug-cc-pVnZ and aug-cc-pV(n+d)Z basis sets, with n = D, T, Q, 5,...,10. The wide variation in basis set sizes allows the treatment of fairly large systems.[238,331,332] In the FPD approach, a combination of up to five CBS extrapolation formulas is sometimes utilized, taking the average as the best estimate and half the spread in the values as a first measure of the associated uncertainty.[284] The accuracy and the effectiveness of this approach has been verified across a collection of 141 small-to-medium size chemical systems, for which reliable estimates of the CBS limit were available.[237] Open-shell calculations were based on the R/UCCSD(T) method; a method that utilizes restricted open-shell Hartree-Fock (ROHF) orbitals but allows a small amount of spin contamination in the solution of the CCSD equations for open-shell systems.

Calculations on isolated atoms imposed full atomic symmetry on the orbitals. Higher-order (HO) correlation effects were handled with the CCSDT and CCSDTQ or CCSDT(Q) methods. Combinations such as CCSDT/cc-pVQZ+CCSDTQ/cc-pVTZ or CCSDT/cc-pVTZ+CCSDTQ/cc-pVDZ were typically used to provide a balanced treatment. Corrections for outer core-valence (CV) correlation effects used the weighted core-valence basis sets,[122] cc-pwCVnZ, n = D, T, Q and 5 with extrapolation to the CBS limit using the same procedure as for the frozen-core energies. For molecules with 4-6 “heavy”atoms, it seemed that generally the HO CV correction typically fell between the 0.1-0.2 kcal/mol range. Thus, these corrections were only required in studies that aim for the highest possible accuracy. Scalar relativistic (SR) effects were described with second-order Douglas-Kroll-Hess (DKH) CCSD(T) calculations,[333,334] using the cc-pVnZ-DK basis sets.[335] Spin-orbit coupling effects in the atoms were taken from the experimental zero-field splittings, while, when applicable, molecular SO corrections were taken either from experiment or calculated with the state-interacting approach using CI wavefunctions. Anharmonic zero-point vibrational energies (ZPEs) for diatomic molecules were obtained from sixth-degree Dunham fits of the potential energy curves.[336] For triatomic systems, fits to potential energy surfaces were often used with ZPEs calculated using second-order vibrational perturbation theory. Anharmonic ZPEs for general polyatomic species were determined by combining CCSD(T) harmonic frequencies with anharmonic corrections obtained from MP2. Whenever possible, the degree of convergence in the ZPE was tracked as the underlying basis sets were improved. Another factor considered, in order to ensure very high accuracy, especially when the molecule contained hydrogen atoms, was the effect of the diagonal Born-Oppenheimer correction.[337] The FPD approach utilizes the aug-cc-pVTZ basis set at either the CISD or CCSD levels of theory, in order to evaluate this component. The performance of the FPD procedure for atomisation energies had a mean signed deviation of -0.04 kcal/mol, RMS of 0.28 kcal/mol and MAD of 0.17 kcal/mol for a test set of 121 molecules whose experimental uncertainties were ±1 kcal/mol or less.[284] When the comparison is restricted to molecules with an experimental uncertainty of ±0.3 kcal/mol or smaller, the MAD fell to 0.10 kcal/mol. Molecular structures were also accurately predicted using this method. Mean unsigned deviations for CCSD(T) bond lengths between non-hydrogen atoms dropped from 0.029 Å with the aug-cc-pVDZ basis set to 0.012 Å with aug-cc-pVTZ and 0.007 Å with aug-cc-pVQZ.[284]

Recent advances in explicitly correlated methods have demonstrated a big improvement over conventional methods, in terms of their fast convergence with respect to the basis set and their computational cost.[338–342] Explicitly correlated methods allow the use of smaller basis sets to get results near the basis set limit. The CCSD(T)-F12x [x = a, b] methods in particular have been successfully used for main group elements, and have achieved this accelerated accelerated convergence, often with near complete basis set limit results being obtained with triple-zeta correlation consistent basis sets.[343]

The FDP method has been applied to transition metal systems in order to get accurate frozen core CCSD(T)-F12b basis set limit results as well as converged CCSD(T) corrections that account for core correlation. These were then combined into a FPD composite thermochemistry approach which gave chemically accurate atomisation energies and heats of formation.[291] While the number of molecules tested with this explicitly correlated FPD method is small (19 molecules) the results are expected to be indicative of the accuracies achievable with the current method. The FPD composite approach[284] has been used to determine atomisation energies of transition metal containing systems, which are utilized together with the known enthalpies of formation of the atoms to determine molecular enthalpies of formation, $\Delta\mathrm{H_{at}}(298\mathrm{K})$ that are defined as:

$$\Delta\mathrm{H_{at}}(298\mathrm{K}) = \Delta\mathrm{E_{at}}/\mathrm{CBS} + \Delta\mathrm{CV} + \Delta\mathrm{DK} + \Delta\mathrm{SO} + \Delta\mathrm{HC} + \Delta\mathrm{ZPE} + \Delta\mathrm{H}(298-0)\,. \tag{7.8}$$

The first two terms of equation 7.8 are the most important ones, since they represent the frozen-core CCSD(T) atomisation energy at the CBS limit ($\Delta\mathrm{E_{at}}/\mathrm{CBS}$) and the contribution to the atomisation enthalpy from core-valence (CV) electron correlation (ΔCV). The use of CCSD(T)-F12b instead of conventional CCSD(T) has been proven to be advantageous for the $\Delta E_{at}(FC)/CBS$ and ΔCV contributions.[343] The next term, ΔDK, includes the effects of scalar relativity through the use of the 2nd-order Douglas-Kroll-Hess (DKH) Hamiltonian,[333,334] while ΔSO accounts for atomic spin-orbit coupling. The term ΔHC extends the correlation treatment beyond the CCSD(T) level by including frozen-core CCSDT and CCSDT(Q) calculations. Based on previous experience,[344] harmonic frequencies calculated at the CCSD(T)-F12a/aug-cc-pVDZ level of theory were utilized for the zero-point vibrational corrections ΔZPE and are expected to be within 0.1 kcal/mol of the CCSD(T) basis set limit. These were then combined with standard statistical mechanical expressions for the thermal corrections $\Delta H(298-0)$. All calculations were carried out with the MOLPRO suite of *ab initio* programs, except for the higher order correlation work, which was performed with the MRCC program as interfaced to MOLPRO.[345,346]

For those cases that had experimental uncertainties on the order of 3 kcal/mol or less, the average deviation of the *ab initio* composite results was 1.3 kcal/mol, slightly less than that of the average of the experimental uncertainties, which was 1.8 kcal/mol. Even without considering the most expensive higher order correlation contributions, the mean unsigned deviation increased to just 2.1 kcal/mol. The main reason behind the high accuracy of these composite results lies in the accurate CBS limits obtained for both the frozen-core and CV contributions to the atomisation energies; in this case efficiently attained with the CCSD(T)-F12b method with basis sets only as large as aug-cc-pVQZ and aug-cc-pwCVTZ, respectively.

7.1.5 Correlation Consistent Composite Approach: ccCA

The MP2-based correlation consistent Composite Approach (ccCA)[286] of Cundari, Wilson and co-workers was proposed as an alternative to the Gaussian-*n* methods.[273–276,292] The design goal was to achieve a mean unsigned deviation of ±1 kcal/mol for the same energetic quantities targeted by G*n* (enthalpies of formation, electron affinities, ionization potentials and proton affinities) but without the use of any empirical corrections.

The original paper discussed five different implementations, ccCA-DZ, ccCA-TZ, ccCA-aTZ, ccCA CBS-1 and ccCA CBS-2, with all of them using reference geometries and scaled harmonic frequencies obtained at the B3LYP/6-31(d) level of theory. The first three methods, ccCA-DZ, ccCA-TZ and ccCA-aTZ begin with an MP4/cc-pV*n*Z (n = D,T) or MP4/aug-cc-pVTZ calculation, while the last two, namely ccCA-CBS-1 and ccCA-CBS-2 involved an extrapolation to the MP2 complete basis set limit using aug-cc-pV*n*Z (n = D,T,Q) basis sets with either an exponential[347] or mixed Gaussian/exponential formula.[348] Finally, a QCISD(T)/cc-pVTZ correction was added to better account for correlation effects. On a collection of 28 molecules taken from the G2-2 and G3/99 test sets, the ccCA-CBS2 method had a mean unsigned deviation of 1.16 kcal/mol after incorporating additional corrections for atomic spin-orbit effects and scalar relativistic effects based on theoretical values reported by Kedziora *et al*.[349] Subsequent modifications of ccCA (ccCA-F, ccCA-P, ccCA-S4, ccCA-S3 and ccCA-WD) explored the use of different MP2/CBS extrapolation formulas.[350] Furthermore, additional changes in some of the theories included the following, replacing QCISD(T) with CCSD(T), using MP2 Douglas-Kroll calculations for computing scalar relativistic corrections and using cc-pV(*n*+*d*)Z basis sets for second-row elements. The mean unsigned deviation for the complete G3/99 test set was 0.96 and 0.97 kcal/mol with the mixed Gaussian/exponential and $1/(\ell_{\max} + 1/2)^4$ formulas, respectively, compared to 0.95 kcal/mol for G3X.

A year after the ccCA method was published, further changes were introduced in order to handle transition metal compounds, leading to the ccCA-TM variant.[351,352] In ccCA-TM, a less rigid definition of "transition metal chemical accuracy" that corresponded to ± 3 kcal/mol, was adopted.[351,352] Further modifications that allowed the description of potential energy surfaces were introduced in the multireference ccCA (MR-ccCA) method.[353] The replacement of the standard self-consistent field and MP2 steps with its corresponding DF counterparts, led to improved computational efficiency with the development of the DF-ccCA and DF-ccCA+L methods, as reported by Prascher *et al*.[354] The +L notation indicates that the density fitting local CCSD(T) method of Schütz and Werner was used.[355,356] The average savings in computer time for the DF-ccCA method was 72% and 76% with the +L alternative. However, both approximations introduced additional error relative to ccCA. For DF-ccCA, the average unsigned error relative to ccCA was 0.27 kcal/mol, compared to 2.63 kcal/mol for DF-ccCA+L on a test set of 120 molecules. Five more modifications to ccCA were proposed in 2009, including changes to the basis set used in the B3LYP calculations, separate extrapolations of the SCF and MP2 energies and the use of new vibrational scaling factors.[357] When applied to the G3/05 test set, the latest version (ccCA-PS3) produced a mean unsigned deviation of 1.01 kcal/mol, when the corresponding G4(MP2) value was 1.04 kcal/mol.

7.1.6 HEAT

In 2004, Tajti *et al*. introduced the high-accuracy extrapolated *ab initio* thermochemistry model (abbreviated HEAT) which was intended to "achieve high accuracy for enthalpies of formation of atoms and small molecules" without resorting to empirical scale factors.[358] HEAT was not intended strictly for the purpose of computing atomisation energies, but rather for estimating the total energies of molecules. Reference geometries were determined at the CCSD(T)/cc-pVQZ level of theory, and open-shell systems were described with unrestricted Hartree-Fock (UHF) wavefunctions.[290] The CCSD(T)(CV) basis set limit was estimated by a $\frac{1}{\ell^3}$ extrapolation[359] of aug-cc-pCVQZ and aug-cc-pCV5Z energies. A frozen-core higher-order correction was determined by combining a $\frac{1}{\ell^3}$ extrapolation of CCSDT/cc-pVTZ and CCSDT/cc-pVQZ energies with a CCSDTQ/cc-pVDZ energy. Anharmonic zero-point vibrational energies (ZPE) were evaluated at the CCSD(T)(CV)/cc-pVQZ level of theory. For a test set of 26 small molecules involving 5 atoms (H, C, N, O and F), HEAT produced a mean unsigned deviation of 0.09 kcal/mol relative to well-established experimental Δ_fH(0 K) values.

Bomble *et al*. discussed a number of improvements to the original theory that lead to the creation of HEAT345-Q, HEAT345-(Q), HEAT345-Q(P) and HEAT345-Q(P) methods.[360] When applied to a set of 18 small molecules, these variants yielded mean unsigned deviations that were marginally better than the original HEAT method, with the most accurate method being HEAT345-QP. In 2008, Harding *et al*. explored the impact of extending the basis sets used in the HEAT protocol up through aug-cc-pCV6Z and including a diagonal Born-Oppenheimer correction; these corrections led to the HEAT456-Q and HEAT456-QP methods.[361] A statistical comparison based on a collection of 18 small molecules showed small increases in the RMS errors for the larger basis set variants, a fact that suggested that the earlier implementations may have benefited from some fortuitous cancellation of errors.[361]

7.1.7 Focal Point Analysis

The focal-point approach (FPA) of Allen, Császár and co-workers was introduced as a flexible strategy that can be tailored for particular research interests.[362,363] In the initial paper, the method was used to determine the heats of formation of cyanato radical (NCO^-) and isocyanic acid (HNCO), using a mixture of experimental and theoretical reference geometries. For cyanato radical a CISD/DZ(d,p) optimized structure was adopted, although the CO bond length differed substantially from the experimental r_0 value. Five independent reactions, involving a mixture of experimental and theoretical data, were used to determine the cyanato radical Δ_fH(0 K). A variety of basis sets, the largest of which was $[13s8p6d4f]/(8s6p4d)$, were combined with various levels of perturbation theory and coupled cluster theory, all of which utilized the frozen-core approximation. CCSD(T)/$(2d1f/2p1d)$ reaction energies were adjusted by MP2 energies evaluated using the largest basis set, allowing the expensive CCSD(T) calculations in the large basis set to be avoided. The analysis was carried out using two sequences of methods: MP2 to MP3 to MP4(SDTQ) to MP5(SDTQ) and MP3 to CCSD and finally CCSD(T). A focal-point analysis of conformational energies (e.g., the torsional barrier in ethane) replaced the basis sets used in earlier studies with members of the correlation consistent basis set family up through cc-pV6Z, aug-cc-pV5Z and cc-pCVQZ.[364]

A more recent investigation that utilized the focal point analysis re-examined the heats of formation of NCO^- and HNCO by Allen and co-workers.[365] The original focal point analysis paper had reported Δ_fH(0 K) values of 35.3 kcal/mol (NCO^-) and −26.1 kcal/mol (HNCO).[366] Another study by the same authors offered revised values of 31.4 ± 0.5 kcal/mol (NCO^-) and −27.5 ± 0.5 kcal/mol (HNCO).[363] In this investigation of 2004, the heat of formation of NCO^- was established via two formation reactions. The corresponding heat of formation for HNCO involved seven additional reactions. After accurately determining the reaction energies, reference heats of formation for component species were taken from experiment or in a few cases from theory. This approach avoided the calculation of total atomisation energies in favor of the use of isogyric reactions. The MP*n* (*n* = 2-5) scheme used in previous focal point analysis studies was abandoned in favor of the HF to MP2 to CCSD to CCSD(T) to CCSDT sequence of methods. The largest CCSD(T) calculation employed the cc-pV5Z basis set. Separate extrapolations were performed on the Hartree-Fock and correlation energy components. core-valence correlation effects were treated with up to CCSD(T)(CV)/cc-pCVQZ and MP2(CV)/cc-pCV5Z calculations, which were then extrapolated to the CBS limit. For closed-shell systems, the MP2/CBS limit was estimated with explicitly correlated MP2-R12/A calculations performed with an uncontracted cc-pV5Z basis set augmented with additional tight and diffuse functions. Open-shell systems were described with conventional UHF-MP2(FC)/cc-pVnZ (n = D-5), extrapolated to the CBS limit. While up to this point the highest level of correlation treatment was obtained from CCSDT calculations, the impact of quadruple excitations was explored via a series of homolytic bond breaking reactions, three of which involved a single bond and four of which involved a multiple bond. The Brueckner orbital coupled cluster theory, BD(TQ) and CCSD(2) methods were used to calculate quadruple excitations. Although the impact of quadruple excitations was not negligible in all cases, the two approaches that including quadruples gave anomalously large corrections in certain cases, and were therefore not recommended until CCSDTQ calculations became affordable for all of the species in their formation reactions. The final recommended heats of formation at 0 K were 30.5 ± 0.2 kcal/mol (NCO^-) and -27.6 ± 0.2 kcal/mol (HNCO).

7.2 Computational Methodology

7.2.1 Composite methodology

In the present work, a form of FPD composite approach[284] has been used to determine atomisation energies, which are utilized together with the known enthalpies of formation of the atoms, in order to determine molecular enthalpies of formation, which can be defined as

$$\Delta H_{at}(298K) = \Delta E_{at}(FC)/CBS + \Delta CV + \Delta DK + \Delta SO + \Delta HO + \Delta ZPE + \Delta H(298-0)\,. \qquad (7.9)$$

The first two terms of equation 7.9 represent the frozen core CCSD(T)-F12b atomisation energy at the CBS limit and the contribution to the atomisation energy from core-valence electron correlation. The use of explicitly correlated CCSD(T)-F12b instead of the conventional CCSD(T) is very advantageous as demonstrated in the Section 7.3. The next term, ΔDK, includes the scalar relativistic effects by utilizing the second order Douglas-Kroll-Hess (DKH) Hamiltonian,[333,334,367] while the ΔSO term accounts for spin-orbit coupling. The term ΔHO stands for higher order corrections and extends the correlation treatment beyond the CCSD(T) level by including frozen-core CCSDT and CCSDTQ calculations. All calculations were carried out using the MOLPRO suite of *ab initio* programs,[215] except for the higher order correlation work, which was performed with the MRCC program[345,346] as interfaced to MOLPRO.

7.2.2 Basis sets and methods

In the present work, the composite methodology proposed by Bross *et al.*,[291] which is a modified version of the FPD approach discussed earlier, was followed for a test set of 20 3*d* transition metal containing diatomics named 3*d*MLBE20, which was proposed in the recent work by Truhlar.[368]

Throughout this work both conventional and explicitly correlated coupled cluster calculations with single, double, and perturbative triple excitations CCSD(T) and CCSD(T)-F12b were carried out. Open-shell systems employed restricted open-shell Hartree-Fock (ROHF) orbitals, without spin restrictions in the CCSD equations.[343,369,370] Conventional calculations employed the standard diffuse-augmented correlation consistent basis sets, aug-cc-pV*n*Z (n = D-5), with the second-row elements (i.e., Cl) including an additional tight *d* function, aug-cc-pV$(n+d)$Z.[22,117,121,255,256,371] The explicitly correlated coupled cluster calculations utilized the CCSD(T)-F12b method of Werner and co-workers[246,343] with the fixed amplitude Ansatz 3C(FIX).[372–374] These calculations employed the same orbital sets as the conventional calculations, namely aug-cc-pV*n*Z (n = D-5) for the 3*d* transition metals, and the aug-cc-pV$(n+d)$Z sets for the second row elements.[22,117,121,255,256,371] For the required auxiliary basis sets (ABSs), density fitting (DF) of the Fock and exchange matrices utilized the def2-QZVPP/JKFIT ABSs of Weigend[235] for the transition metal elements and the cc-pV*n*Z/JKFIT sets of Weigend *et al.*[232] for the remaining elements (note that aug-cc-pVTZ/JKFIT sets were used for both aug-cc-pVDZ and aug-cc-pVTZ orbital basis sets). The ABSs required for the DF of the remaining two-electron integrals were the aug-cc-pV*n*Z/MP2FIT basis sets of Weigend *et al.*[232] for frozen-core calculations with n = T used for both double- and triple- ζ quality orbital basis sets in each case. The analogous DF sets were used for the transition metals: the aug-cc-pVTZ/MP2FIT basis sets of Hill and Platts[266] used along with the aug-cc-pVDZ and aug-cc-pVTZ orbital basis sets,[291] while the aug-cc-pVQZ/MP2FIT basis set was used along the aug-cc-pVQZ orbital basis set. The complementary auxiliary basis sets (CABS)[244] required for the resolution-of-identity (RI) utilized the aug-cc-pV*n*Z/OPTRI sets of Yousaf and Peterson[375] for the light elements and the MP2FIT sets mentioned above for the transition metal elements. The value of the geminal slater exponent, β, was chosen to be 1.0 for all three basis sets (aug-cc-pV*n*Z, n=D-Q), as previously proposed by Bross and coworkers.[291]

When evaluating the ΔCV term, core-valence CCSD(T)-F12b calculations utilizing the same ansatz as for valence-only, and a geminal slater exponent of 1.4 α_0^{-1} were performed. The aug-cc-pwCV*n*Z basis sets (n=T-5) were used for the orbital basis sets.[22,117,121,122,255,256,371] The RI CABS used were the aug-cc-pwCV*n*Z/MP2FIT sets of Hättig, with n = T used for both double- and triple- ζ quality orbital basis sets in each case. ABSs for DF of the Fock and exchange matrices were the same as those used for frozen-core CCSD(T) calculations, while the ABSs required for the DF of the remaining two-electron integrals were the same as the RI CABS. For calculations beyond the CCSD(T) level, smaller sets were utilized for practical reasons; namely the cc-pVTZ set was used for all atoms in CCSDT calculations and the cc-pVDZ set was used for all atoms in CCSDTQ calculations. Scalar relativistic calculations utilized the aug-cc-pVTZ-DK orbital basis set for the transition metal and the aug-cc-pVTZ+d-DK orbital basis set for the non-metal atom.[255,256] Spin-orbit coupling calculations were performed using the Breit-Pauli operator[376,377] at the triple zeta level, using the aug-cc-pVTZ orbital basis set for all elements except Cl and the aug-cc-pV(T+d)Z-DK orbital basis set for Cl. The spin-orbit energies of molecules which have a non-Σ ground state were calculated at the CASSCF level; the active space used in these calculations was the full valence space of each molecule, and can be seen in table 7.1. The atomic spin-orbit energies were taken from references 378–380.

Finally, harmonic frequencies at the CCSD(T)-F12b/aug-cc-pVQZ level of theory were utilized for the zero-point vibrational correction ΔZPE, and were combined with standard statistical mechanical expressions for the thermal corrections $\Delta H(298 - 0\text{K})$.

Table 7.1: Active spaces for the full-valence CAS calculations, the SO correction, ΔSO, and the ic-MRCI+Q calculations.

Molecule	(Electrons,Orbitals)	Molecule	(Electrons,Orbitals)
TiCl	(11,10)	FeH	(9,7)
VH	(6,7)	FeCl	(15,10)
VO	(11,10)	CoH	(10,7)
VCl	(12,7)	CoCl	(16,10)
CrO	(12,9)	NiCl	(17,10)

In certain cases where the composite results deviated significantly from existing experimental values (see the following section for more details), internally contracted multi-reference configuration interaction that includes the Davidson correction, ic-MRCI+Q calculations[381,382] were employed, using the aug-cc-pVTZ basis set for the metal atom and the aug-cc-pV(T+d)Z basis set for the non-metal atoms. In all the ic-MRCI+Q calculations the reference space was a full-valence complete active space with the number of electrons in orbitals shown in Table 7.1 Furthermore, to accurately describe the orbitals of the transition metal atoms, an additional *d* shell has been added to the active space of the ic-MRCI+Q calculation. The inclusion of these orbitals has been indicated to have in important effect in the correct description of the orbitals of transitions metals: Dunning *et al*. indicated that the "$(n + 1)$ " $3d$ orbital of the $4s3d^{n+1}$ states and the "$(n + 1)$" and "$(n + 2)$" $3d$ orbitals of the $3d^{n+2}$ states of the transition metal atoms are functionally inequivalent to the other $3d$ orbitals, being much more diffuse.[383] So-called double-*d* shell correlation effects are related to the presence of a large number of electrons in compact *d* shells, resulting in large radial correlation effects in these shells. The second more diffuse *d* shell gives additional flexibility to describe such correlation effects, and for many $3d$ transition metal compounds the second d shell must be present to obtain quantitative accuracy with the CASPT2 method.[201]

7.3 Results and Discussion

7.3.1 Calculation of Composite atomisation Energies

Atomisation energies were calculated using the modified Feller-Peterson-Dixon approach[291] with correlation consistent basis sets for a series of 20 diatomics containing 3*d* transition metal atoms. The molecular set, named 3dMLBE20, was initially introduced by Truhlar and co-workers, as the 20 3*d* transition metal-containing diatomic molecules, for which the most reliable experimental data is available.[368] The molecules and their corresponding ground state can be seen in Table 7.2

Table 7.2: Molecules considered in the present study and their corresponding term symbol

Molecule	Term Symbol	Molecule	Term Symbol
TiCl	$^4\Phi$	FeCl	$^6\Delta$
VH	$^5\Delta$	CoH	$^3\Phi$
VO	$^4\Sigma^-$	CoCl	$^3\Phi$
VCl	$^5\Delta$	NiCl	$^2\Pi$
CrH	$^6\Sigma^+$	CuH	$^1\Sigma^+$
CrO	$^5\Pi$	CuCl	$^1\Sigma^+$
CrCl	$^6\Sigma^+$	ZnH	$^2\Sigma^+$
MnS	$^6\Sigma^+$	ZnO	$^1\Sigma^+$
MnCl	$^7\Sigma^+$	ZnS	$^1\Sigma^+$
FeH [1]	$^6\Delta$,$^4\Delta$	ZnCl	$^2\Sigma^+$

Seven single-point calculations were performed around the minima of the respective potential curves of each of the investigated states, to which a sixth-order polynomial was fit, in order to provide the ground molecular electronic energy as well as the corresponding equilibrium bond length R_e. The modified Feller-Peterson-Dixon approach[291] was followed, starting by obtaining the complete basis set (CBS) limit by extrapolating aug-cc-pVTZ/aug-cc-pVQZ CCSD(T)-F12b calculations.[255,343] The extrapolation scheme used, as described by Hill *et al.*,[384] can be seen in equation 7.10:

$$E^{\text{corr}}_{\text{CBS}} = (E^{\text{corr}}_{\text{QZ}} - E^{\text{corr}}_{\text{TZ}})F + E^{\text{corr}}_{\text{TZ}}\ , \tag{7.10}$$

where $F = 1.416422$ for CCSD(T)-F12b and 1.663388 for (T). While these values of F^c were obtained by calibrating only 1st and 2nd row main group molecules, the resulting CBS limits are not expected to be particularly sensitive due to the proximity of the aug-cc-pVQZ result, to the CBS limit.

Once the CBS limit was obtained, a series of additive contributions for core correlation, relativity, higher order correlation, and zero-point vibrations were included, as shown in equation 7.11.

$$D^0_{e_{comp}} = \Delta E_{at}(FC)/CBS + \Delta CV + \Delta DK + \Delta SO + \Delta HO\,. \tag{7.11}$$

In all cases except for the evaluation of ΔSO, seven single-point calculations were performed around the previously reported R_e,[368] and then a sixth order polynomial was fit to the data; in all cases the new calculated values of R_e and D^0_e that are reported throughout the work are obtained through this process of polynomial fitting. Therefore a ΔD^0_e and a corresponding ΔR^0_e were obtained after each correction. The spin-orbit correction, ΔSO was calculated at the "best" composite R^0_e, which corresponded to the value obtained after the final correction ΔHO. The magnitude of each correction on D^0_e and R^0_e in terms of ΔCV, ΔDK, ΔHO split in two terms ΔT and ΔQ, and ΔSO can be seen in tables 7.3 and 7.4.

Table 7.3: Summary of contributions to the final atomisation energies D^0_e (kcal/mol).

	CCSD(T)-F12b/CBS[TQ]	ΔCV	ΔDK	ΔHO		ΔSO	ΔZPE
Molecule				ΔT	ΔQ		
TiCl	101.49	2.78	−1.33	−0.28	0.18	−1.08	0.557
VH	56.38	2.66	−1.59	0.16	0.00	−0.45	2.324
VO	149.09	3.76	−0.55	−0.94	1.14	−1.10	1.445
VCl	100.03	1.42	−1.82	−0.19	0.10	−1.21	0.573
CrH	50.30	−1.09	1.65	0.91	0.10	0.00	2.379
CrO	103.85	−1.18	4.07	0.13	0.68	0.05	1.435
CrCl	90.06	−2.34	1.10	0.72	0.17	−0.80	0.577
MnS	67.93	1.35	−1.51	0.50	0.18	−0.60	0.686
MnCl	84.94	−0.64	−1.55	−0.18	0.10	−0.80	0.547
FeH($^6\Delta$)	41.65	−0.01	−1.39	0.10	0.02	0.04	2.344
FeH($^4\Delta$)	35.11	3.29	−4.41	1.73	0.85	−0.07	2.486
FeCl	84.97	−0.39	−2.09	−0.04	0.13	−0.75	0.578
CoH	52.67	2.23	−3.75	2.07	1.46	−0.19	2.660
CoCl	83.14	1.42	−5.73	2.18	1.42	−1.03	0.597
NiCl	101.94	3.46	−8.19	−3.27	0.07	−2.71	0.580
CuH	62.17	−0.31	2.51	0.04	0.09	0.00	2.664
CuCl	88.95	−0.63	−0.21	−0.06	0.16	−0.80	0.578
ZnH	23.34	−0.41	−1.37	0.19	0.00	0.00	2.310
ZnO	38.54	−0.52	−2.09	0.02	1.28	−0.20	1.055
ZnS	36.21	−0.43	−1.91	−0.21	0.50	−0.60	0.658
ZnCl	54.32	−0.57	−3.00	0.01	0.13	−0.80	0.561

Table 7.4: Summary of contributions to the final bond length R_e^0 (Å).

	CCSD(T)-F12b/CBS[TQ]	ΔCV	ΔDK	ΔHO	
Molecule				ΔT	ΔQ
TiCl	2.3083	−0.0318	−0.0018	−0.0033	−0.0013
VH	1.7079	−0.0240	0.0001	0.0001	−0.0001
VO	1.5974	−0.0101	−0.0017	−0.0023	0.0054
VCl	2.2554	−0.0215	−0.0018	−0.0006	0.0000
CrH	1.6577	−0.0245	−0.0071	0.0060	0.0001
CrO	1.6551	−0.0067	−0.0046	0.0055	−0.0021
CrCl	2.2053	−0.0286	−0.0089	0.0052	0.0002
MnS	2.0880	−0.0156	−0.0080	0.0002	0.0023
MnCl	2.2535	−0.0096	−0.0054	−0.0002	0.0002
FeH($^6\Delta$)	1.6847	−0.0072	−0.0046	0.0003	−0.0002
FeH($^4\Delta$)	1.5588	−0.0066	−0.0147	0.0075	−0.0003
FeCl	2.1900	−0.0074	−0.0050	−0.0004	0.0002
CoH	1.5199	−0.0051	−0.0172	0.0032	−0.0025
CoCl	2.0886	−0.0070	−0.0210	0.0052	−0.0035
NiCl	2.0790	0.0014	−0.0237	−0.0007	−0.0005
CuH	1.4839	0.0015	−0.0249	0.0011	−0.0002
CuCl	2.0747	0.0026	−0.0246	0.0009	0.0000
ZnH	1.6012	0.0020	−0.0130	0.0015	0.0003
ZnO	1.7116	0.0011	−0.0122	0.0036	0.0002
ZnS	2.0581	0.0016	−0.0134	0.0017	0.0010
ZnCl	2.1399	0.0021	−0.0107	−0.0305	0.0004

The core-correlation effects that are not present in a "usual" frozen-core calculation can be calculated by including the $3s3p$ electrons for $3d$ TMs and the $1s$ and $2s2p$ for elements of first and second row respectively, in the valence space. These contributions to the atomisation energies and equilibrium bond-lengths are expressed through the ΔCV term and can be seen in tables 7.3 and 7.4. It is well known that core-valence correlation effects have to be considered especially for atoms with large and polarizable cores. The mean signed contribution of ΔCV on D_e^0 is +0.66 kcal/mol, while the mean unsigned contribution of ΔCV on D_e^0 is +1.47 kcal/mol. With respect to the bond length, R_e^0, the mean signed contribution of ΔCV is -0.0092 Å while the mean absolute contribution is +0.0104 Å. The maximum contribution occurs for vanadium oxide (VO) with a contribution of +3.76 kcal/mol and titanium chloride (TiCl) with a contribution of -0.0318 Å. The contributions to the atomisation energies due to scalar relativistic effects are examined through the ΔDK term. These were calculated as the differences between DKH-CCSD(T) and non-relativistic CCSD(T) calculations, with the aug-cc-pVTZ basis sets, contracted for DKH2 in the former case. The ΔDK correction contributed -1.58 kcal/mol to the atomisation energies on average and reached a maximum of -8.19 kcal/mol for NiCl. the contribution to the atomisation energies due to spin-orbit coupling, ΔSO, was also calculated. The spin-orbit energies of molecules that have a non-Σ ground state were calculated, while the atomic spin-orbit orbit energies are from References 378–380. In most cases the ΔSO contributions to the dissociation energy were small but not negligible, with an mean signed value of -0.62 kcal/mol that reach a maximum of -2.71 kcal/mol for NiCl. The effects of higher order electron correlation have been previously found to be important in composite thermochemistry schemes in order to achieve kcal/mol accuracy in some transition metal containing molecules,[385–387] as well as for molecules containing post-3d main group elements.[388] These effects were split into two terms, ΔT which is the difference between a CCSDT and a CCSD(T) calculation and ΔQ which is the difference between a CCSDTQ and a CCSDT calculation. As expected ΔT has a greater contribution than ΔQ, with an average absolute contribution of 0.66 and 0.42 kcal/mol and a maximum of -3.27 and +1.46 kcal/mol, respectively. It should be noted that sometimes the quadruples correction ΔQ is of opposite sign to ΔT, which is often the case in main group molecules and leads to the often fortuitously high accuracy of the CCSD(T) method; however in many cases the contributions here have the same sign such that they do not effectively cancel. This could be an indication that in order to accurately describe certain systems, corrections higher than ΔQ need to be computed. It is clear that the above corrections are quite substantial in order to help us achieve chemical or even spectroscopic accuracy, especially when compared with the basis set incompleteness error (BSIE).

7.3.2 Comparison of Composite Values to Experimental Data

In order to assess the quality of our composite values, comparisons with experimental results were carried out. We first evaluated the dissociation energy from the ground vibrational state, D_0^0 (the superscript denotes that the term is evaluated at 0 K). To do so, we utilized molecular data $\Delta\mathrm{H}_\mathrm{f}^{298}(M)$ [where (M) denotes molecular] or D_0^{298} taken from references 378, 389–399 as well as atomic data $\Delta\mathrm{H}_\mathrm{f}^{0}(A)$ [where (A) denotes atomic] and $\mathrm{H}_\mathrm{therm}(A)$, which is the thermal correction that accounts for the temperature difference (0 - 298 K), taken from reference 400. The dissociation energy D_0^0 for a molecule (M) that has the formula XY was evaluated using the following equations:

$$\mathrm{D}_0^0 = \mathrm{D}_0^{298} - \mathrm{H}_\mathrm{therm}(M)\,, \tag{7.12}$$

and

$$\mathrm{D}_0^0 = \Delta\mathrm{H}_\mathrm{f}^0(X) + \Delta\mathrm{H}_\mathrm{f}^0(Y) - \Delta\mathrm{H}_\mathrm{f}^0(M)\,, \tag{7.13}$$

where

$$\Delta\mathrm{H}_\mathrm{f}^0(M) = \Delta\mathrm{H}_\mathrm{f}^{298}(M) - \mathrm{H}_\mathrm{therm}(M) + \mathrm{H}_\mathrm{therm}(X) + \mathrm{H}_\mathrm{therm}(Y)\,. \tag{7.14}$$

This experimental D_0^0 was then compared with the composite calculated value of dissociation energy denoted $D_{0_{\mathrm{comp}}}^0$ which was calculated using the method described earlier; since the comparison is made to the experimental values, ΔSO was included in the composite values, as mentioned above. In order to facilitate the comparison ΔD_0^0 was evaluated and is shown in Table 7.5. To evaluate the performance of the composite method, the composite calculated values or equilibrium bond lengths $R_{e_{\mathrm{comp}}}$ are compared with the best estimated bond lengths R_e taken from reference 368.

Table 7.5: Comparison of experimental D_0^0 and composite $D_{0_{\mathrm{comp}}}^0$ dissociation energies in kcal/mol as well as of composite $R_{e_{\mathrm{comp}}}$ bond lengths and best estimate R_e for molecules of the 3*d*MLBE20 database. The deviation of $D_{0_{\mathrm{comp}}}^0$ from the experimental D_0^0 is expressed through ΔD_0^0 (in kcal/mol). The deviation of R_e from the composite $R_{e_{\mathrm{comp}}}$ is expressed through ΔR_e (also in Å).

Molecule	Molecular State	D_0^0 (kcal/mol)	$D_{0_{\mathrm{comp}}}^0$ (kcal/mol)	ΔD_0^0 (kcal/mol)	$R_{e_{\mathrm{comp}}}$ (Å)	R_e (Å)	ΔR_e (Å)
TiCl	$^4\Phi$	100.3 ± 2.0	101.2	0.95	2.270	2.265	5.00×10^{-3}
VH	$^5\Delta$	46.9 ± 1.6	54.8	7.92	1.684	1.730	-4.60×10^{-2}
VO	$^4\Sigma^-$	147.4 ± 2.0	149.9	2.54	1.589	1.589	-3.00×10^{-4}
VCl	$^5\Delta$	99.6 ± 2.0	97.8	-1.88	2.231	2.215	1.64×10^{-2}
CrH	$^6\Sigma^+$	42.5 ± 1.6	49.5	6.96	1.632	1.656	-2.38×10^{-2}
CrO	$^5\Pi$	109.9 ± 1.6	106.2	-3.75	1.647	1.621	2.62×10^{-2}
CrCl	$^6\Sigma^+$	87.4 ± 1.6	88.3	0.90	2.173	2.194	-2.08×10^{-2}
MnS	$^6\Sigma^+$	69.8 ± 2.0	67.2	-2.59	2.067	2.070	-3.10×10^{-3}
MnCl	$^7\Sigma^+$	77.9 ± 1.6	81.3	3.40	2.239	2.243	-4.50×10^{-3}
FeH	$^6\Delta$	35.4 ± 1.9	37.7	2.30	1.673	1.630	-4.30×10^{-2}
FeH	$^4\Delta$	35.4 ± 1.9	34.0	-1.37	1.545	1.630	-8.53×10^{-2}
FeCl	$^6\Delta$	75.8 ± 1.6	81.3	5.42	2.177	2.179	-1.60×10^{-3}
CoH	$^3\Phi$	44.5 ± 3.2	51.8	7.31	1.498	1.530	-3.17×10^{-2}
CoCl	$^3\Phi$	77.7 ± 1.6	80.8	3.05	2.062	2.087	-2.47×10^{-2}
NiCl	$^2\Pi$	86.9 ± 1.6	90.7	3.79	2.056	2.073	-1.75×10^{-2}
CuH	$^1\Sigma^+$	58.8 ± 1.4	61.8	2.99	1.461	1.463	-1.60×10^{-3}
CuCl	$^1\Sigma^+$	87.2 ± 0.4	86.8	-0.33	2.054	2.050	3.60×10^{-3}
ZnH	$^2\Sigma^+$	19.5 ± 0.5	19.4	-0.03	1.592	1.590	2.00×10^{-3}
ZnO	$^1\Sigma^+$	37.0 ± 0.9	36.0	-1.00	1.704	1.800	-9.57×10^{-2}
ZnS	$^1\Sigma^+$	32.4 ± 1.0	32.9	0.47	2.049	2.100	-5.10×10^{-2}
ZnCl	$^2\Sigma^+$	52.9 ± 1.0	49.5	-3.41	2.101	2.100	1.20×10^{-3}
MUE				1.60			-1.48×10^{-2}
MSE				2.97			2.29×10^{-2}
σ				3.44			3.14×10^{-2}
|MAX|				7.92			8.99×10^{-2}

Let's first examine the case of FeH independently, due to the debate regarding its ground electronic state. In reference 368 the ground state of FeH is reported to be a $^4\Delta$ state with a bond length of 1.630 Å and a corresponding D_0^0 of 35.4 ± 1.9 kcal/mol. However, during the initial CCSD(T)-F12b/aug-cc-pVQZ calculations the $^6\Delta$ state was found to be approximately 7 kcal/mol lower in energy than the $^4\Delta$ state; the difference corresponds to the difference of electronic energies at the respective minima of the potential energy curves as can be seen in Figure 7.1. Upon application of the composite corrections described above, the splitting of the two states became smaller but did not change sign; the $^6\Delta$ state still remained 3.56 kcal/mol lower in energy than the $^4\Delta$ state. Schultz and Armentrout examined the dissociation energy of FeH using guided-ion beam mass spectrometry, reporting[395] a D_0^0 of 35.4 ± 1.9 kcal/mol while a few years later a D_0^0 of 35.1 ± 4.4 kcal/mol was reported by studying gas-phase reactions of atomic Fe with a selection of common acids.[401] In general, multireference calculations have given D_0^0 values larger than the upper bounds of the Armentrout experiment, such as D_0^0 of 41.5 kcal/mol as reported by Tanaka *et al*.[402] The calculated composite $D_{0_{\text{comp}}}^0$ of FeH is 37.7 kcal/mol for the $^6\Delta$ state and 34.0 for the $^4\Delta$ state. A theoretical paper by DeYonker and Allen used focal point analysis to describe the low-lying electronic states of FeH, and reported a $^4\Delta$ ground state, with a dissociation energy D_0^0 of 42.0 kcal/mol, while the $^6\Delta$ state was found to be 4.4 kcal/mol higher.[403] Both $^6\Delta$ and $^4\Delta$ were investigated within the composite protocol of this work. Despite its importance, only a small amount of the spectroscopic information about the iron mono-hydride is known. Furthermore, it is difficult to carry out an analysis of the molecular electronic spectra due to its complicated electronic structure, which is incurred by the many low-lying states of high spin multiplicity. While a few computational papers place the $^4\Delta$ state lower than the $^6\Delta$ state[402,403] there are no studies using explicitly correlated (F12) methods. The CCSD(T)-F12b calculations with MOLPRO using the aug-cc-pVQZ basis set for iron and the aug-cc-pVQZ for hydrogen, place the $^6\Delta$ state 7 kcal/mol lower than the $^4\Delta$ state. This energy difference corresponds to total electronic energy of the molecule in the respective minima of both states (i.e. it does not correspond to a vertical transition between the minimum of one state and the corresponding place in the second state, but to an energy difference between the respective minima of the curves). Therefore both states were included in this work, and further analysis on which state may be the ground state can be found in section 7.3.2.

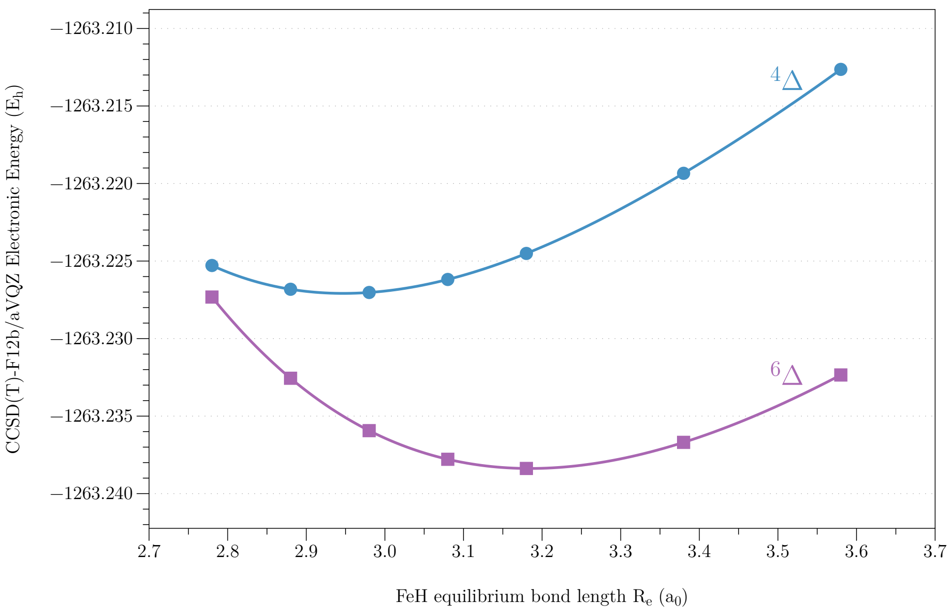


Figure 7.1: CCSD(T)-F12b/aug-cc-pVQZ electronic energies of states $^4\Delta$ and $^6\Delta$ of FeH (E_h).

It is evident that the present calculations (regarding of which state) appear to be in better agreement with the experimental dissociation energies than with the previously considered experimental energies. Furthermore, while Reference 403 argues that core-correlation is the key parameter in order to assign the states correctly, our composite calculations that include a core-correlation correction place the $^6\Delta$ state lower than the $^4\Delta$ state. While at first it appears that the $D^0_{0_{comp}}$ of the $^4\Delta$ state is closer to the D^0_0 value of 35.4 ± 1.9 kcal/mol, if one accounts for the error margin associated with the experiment, then the $^6\Delta$ state is also in reasonable agreement with the D^0_0. By examining the bond length, the composite $R_{e_{comp}}$ are 1.673 Å and 1.545 Å for states $^6\Delta$ and $^4\Delta$ respectively, while the ΔR_e was reported to be 1.630 Å; This suggests that the $^4\Delta$ state is probably misidentified as the ground state in the experiment, since ΔR_e was found to be twice as big for the $^4\Delta$ state than for the $^6\Delta$ state. While the computational procedure and the corresponding results are considered trustworthy, possible reasons that could impede a straightforward assignment of the states would be lack of confidence in the additivity scheme of the composite thermochemical recipe used (implying that the core-valence effects need to be considered from the beginning and not as added on corrections), a need for higher order correlation to be included (although this is not supported by any of the multireference diagnostics that were computed and evaluated - see Table 7.6) or the fact that the there is rather limited and relatively outdated experimental information available. In order to facilitate the comparison of the composite $D^0_{0_{comp}}$ values for all 20 molecules with the experimental D^0_0, ΔD^0_0 was plotted as single points within the error margins associated with the respective experiment plotted as a blue region (see Figure 7.2).

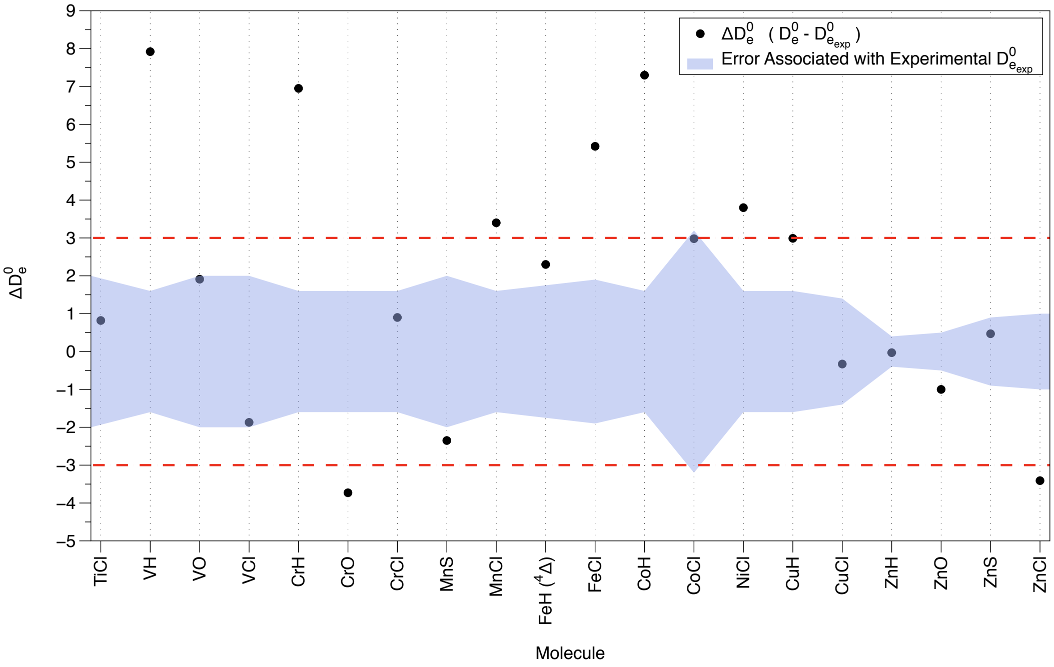


Figure 7.2: Difference in dissociation energies ΔD_0^0 (in kcal/mol) between the composite $D_{0_{comp}}^0$ and the experimental D_0^0, in presence of the experimental error associated with D_0^0.

Figure 7.2 demonstrates that seven out of twenty systems have a $D_{0_{comp}}^0$ that lies within the error associated with the experiment, while it is evident that the composite values for the molecules VH, CrH, CrO, MnS, MnCl, FeH($^6\Delta$), FeCl, CoH, CoCl, NiCl, CuH, ZnO and ZnCl (12 molecules) are lying outside the error margin of their respective experimental values for D_0^0. If, however, the so-called "chemical accuracy" is considered, (represented by the red dashed lines in the above figure), that for transition metal containing systems has been proposed to be 3 kcal/mol, then only the ΔD_0^0 of eight of the above molecules (VH, CrH, CrO, MnCl, FeCl, CoH, NiCl and ZnCl) are outside that range. As a first approach, one could think that the reason why these values are quite different from the experimental ones lies in the multireference character of the system, which may not be properly accounted for through the single reference CCSD(T) method. Although higher order correlation effects are treated through the inclusion of ΔT and ΔQ, it is not conclusive that these are sufficient to treat the potentially multi-reference nature of the system. In order to identify the single or multi-reference nature of the systems studied, several diagnostics of multi-reference nature were calculated and analyzed, with the results shown in Table 7.6. The T_1 diagnostic[404,405] is defined as the Frobenius norm of the single substitution amplitudes vector (t_1) of the closed-shell CCSD wave function (utilizing restricted HF orbitals) divided by the square root of the number of correlated electrons to address size consistency concerns.

$$T_1 = \frac{||t_1||}{\sqrt{N}} \,. \tag{7.15}$$

Single reference methods typically perform well for molecules with a T_1 value smaller than 0.020, as suggested by Lee and Taylor in a study of 23 main group species.[406,407] 3*d* transition metal containing molecules, tend to exhibit multireference behavior for T_1 values larger than 0.050, as proposed by Wilson *et al*. in Reference 400.

Table 7.6: Values of established and proposed multi-reference diagnostics for the 3*d*MLBE20 database. Cells in blue represent molecules that meet the cutoff criteria for the respective diagnostic, and could thus be characterized as multi-reference systems.

Molecule	T_1	D_1	C_0^2	%TAE$_e$[(T)]	%TAE$_e$[Q]
TiCl	0.0586	0.2230	0.265	9.6	2.0
VH	0.0659	0.2013	0.323	13.5	0.1
VO	0.1413	0.4987	0.992	2.9	0.3
VCl	0.1688	0.4283	0.963	2.0	0.3
CrH	0.0880	0.1915	0.827	17.9	0.1
CrO	0.0274	0.1001	0.996	2.9	0.1
CrCl	0.0392	0.1212	0.980	3.6	0.2
MnS	0.0238	0.0458	0.997	1.0	0.0
MnCl	0.0315	0.0781	0.845	5.0	0.1
FeH	0.0186	0.0318	0.994	1.6	0.1
FeCl	0.0599	0.0999	0.850	11.7	0.5
CoH	0.0366	0.1262	0.993	5.3	0.1
CoCl	0.0400	0.1177	0.489	1.4	0.2
NiCl	0.0601	0.1952	0.825	2.1	0.1
CuH	0.0999	0.2270	0.988	0.4	0.0
CuCl	0.0543	0.0973	0.896	12.8	0.9
ZnH	0.0191	0.0478	1.000	1.6	0.3
ZnO	0.0282	0.0729	1.000	2.9	0.0
ZnS	0.0327	0.0792	0.848	30.0	8.1
ZnCl	0.0254	0.0848	0.928	18.3	1.1

The D_1 diagnostic by Janssen and Nielsen[404] is based on the matrix 2-norm of t_1 from single excitations of the closed-shell CCSD wave function and is closely related to the value of the largest single excitation amplitude. Molecules are commonly dominated by dynamic correlation if the

D_1 diagnostic is larger than 0.05.[408] Both T_1 and D_1 diagnostics have been extended to open-shell CCSD wave functions.[405,409]

$$D_1 = ||t_1||_2\,. \tag{7.16}$$

Lee *et al*. performed a correlation analysis of T_1 and D_1 diagnostics and determined a squared correlation coefficient (R^2) of 0.96 based upon 10 open-shell main group species and of 0.90 based on 29 closed-shell main group molecules.[405] This high degree of correlation between the T_1 and D_1 diagnostics shows that both tools will likely provide similar predictions of the single and multireference character, since both diagnostics are related by the t_1 amplitudes, and it has thus been suggested that both diagnostics should be used together as one.[405]

An additional energy-based diagnostic, based on total atomisation energies (TAE), was proposed during the development of the W4 theory.[410,411] The original diagnostic $\%TAE_e[(T_4 + T_5)]$,is the percentage of the coupled cluster CCSDTQ5 total energy that arises from connected quadruple and quintuple excitations. Although $\%TAE_e[(T_4 + T_5)]$ provided a useful indicator of nondynamic correlation effects, it could not be used as a practical diagnostic due to its immense computational cost. Instead, the diagnostic $\%TAE_e[(T)]$ was proposed by Martin *et al*.[411] $\%TAE_e[(T)]$, which represents the percentage of the CCSD(T) TAE resulting from perturbative triple excitations, has following form:

$$\%TAE[(T)] = 100 \times \left| \frac{TAE_e[CCSD(T)] - TAE[CCSD]}{TAE[CCSD(T)]} \right|\,. \tag{7.17}$$

$\%TAE_e[(T)]$ has been shown to provide a prediction that strongly correlates with the $\%TAE_e[(T_4 + T_5)]$ diagnostic for 20 mostly main group diatomic molecules.[410] Martin and co-workers suggested $\%TAE_e[(T)] \leq 2\%$ could serve as the cutoff for reliable SR calculations, while $\%TAE_e[(T)] \geq 10\%$ was evidence for significant nondynamic correlation.[411] The historical interpretation of the T_1, D_1, and $\%TAE_e[(T)]$ diagnostics was developed based on small, well-behaved main group species. However, transition metal containing species are often open-shell systems that have degenerate or low-lying nearly degenerate electronic states that may require a multi-reference wave function based approach to properly describe the near degeneracies.[408,412,413] This is mainly due to partially filled d orbitals and the similar spatial extent and energy of the (n + 1) s and n d orbitals of transition metal containing systems. The need to address these nondynamical electron correlation effects is the main reason why the computational study of TM-containing species becomes quite challenging.[256,414–418] Furthermore, since TM species tend to have more degenerate states and a smaller atomic energy gap between n d and (n + 1) s orbitals than main group species and thus a greater MR character as a result, the historical diagnostic criteria ($T_1 \leq 0.02$, $D_1 \leq 0.05$, and $\%\ TAE_e[(T)] \leq 10\%$) may be not appropriate for TM-containing molecules.

Another common diagnostic is the square of the CI coefficient, C_0, the leading configuration in CISD or CASSCF calculations.[406,419–421] Systems with significant multireference character typically are indicated by a $C_0 \leq 0.95$ ($C_0^2 \leq 0.90$).[419] For 3*d* TM-containing systems considered in a study by Jiang *et al.*,[400] C_0^2 was not used for molecules of more than a few atoms due to the computational impracticality of using large full-valence CASSCF to establish the criteria.

For the current study, all of the above criteria were utilized in order to establish which of the molecules exhibit multireference character. Furthermore, one additional diagnostic, denoted $\%TAE_e[Q]$ was created, with the following form

$$\%TAE[Q] = 100 \times \left| \frac{TAE_e[CCSDTQ] - TAE[CCSDT]}{TAE[CCSDT]} \right| . \tag{7.18}$$

This diagnostic was created in order to estimate whether the correlation effects were sufficiently described through the ΔHO or whether additional treatment is required via a multi-reference technique. While this diagnostic is more expensive than the $\%TAE_e[(T)]$, it provides useful insight, and it can be obtained relatively easily for the test set of the twenty diatomics of this work. While there was no previously suggested cutoff for the value of this new diagnostic, comparison with the existing criteria helped provide a cutoff. Therefore $\%TAE_e[Q] \geq 1$ could indicate that the use of a CCSDTQ correction is insufficient to accurately describe the multi-reference nature of the system of interest.

Looking at the values of the different diagnostics it is clear that while there is some correlation between T_1 and D_1 (R^2 value of 0.88), there is no correlation between any other diagnostics mentioned above. If we use the above mentioned cutoffs, then the T_1 diagnostic indicates a subset of 9 multi-reference systems (CoCl, CoH, CrCl, CrH, CrO, MnS, VCl, VH and VO), D_1 a subset of 8 (CoCl, CoH, CrCl, CrH, CrO, CuH, NiCl and VH), C_0^2 a subset of 9 systems (CoCl, CoH, CrO, FeH, MnS, TiCl, VCl, VO, ZnO), $\%TAE_e[(T)]$ a subset of 6 (CoH, CrO, MnS, VO, ZnO, ZnS), and $\%TAE_e[Q]$ a subset of 3, (CoCl, ZnO, ZnS). It is evident that each diagnostic provides different indicators for the MR character of the systems, and it is therefore not easy to assess them individually. If we use a combination of diagnostics (in the order T_1, D_1, C_0^2, $\%TAE_e[(T)]$ and $\%TAE_e[Q]$) then the use of one diagnostic indicates 9 potentially multi-reference molecules, two diagnostics indicate 6 multi-reference systems, three diagnostics bring that number down to three (CoCl, CoH and CrO), four diagnostics only leave two multi-reference systems(CoH and CrO) while if we use all existing diagnostics plus the new diagnostic $\%TAE_e[Q]$, no molecules can actually be categorized as multi-reference systems. Of course, there is no guarantee that the above order of the diagnostic criteria should be followed; the reason of the above prioritization is solely based on the “popularity” of the existing diagnostics. In order to get a more clear picture of how each diagnostic performs, the multi-reference molecules as suggested by that diagnostic are highlighted in blue, in Table 7.6.

It can be seen that the molecules for which the composite value of atomisation energy differed significantly from the experimental value cannot be conclusively referred to as single or multi-reference systems. Nonetheless, to test whether this was the case, internally contracted multi-reference configuration interaction (ic-MRCI+Q) calculations were performed at the TZ level (aug-cc-pVTZ for the metal atom and aug-cc-pV(T+d)Z for the non-metal). Due to the demanding nature of these calculations, those were only performed on the five molecules with the maximum ΔD_0^0, as well as ZnH, which as can be seen in figure 7.2 and table 7.5 has the minimum ΔD_0^0. Furthermore, to accurately describe the orbitals of the transition metal atoms, an additional *d* shell has been added to the active space of the MRCI calculation. The inclusion of these orbitals has been indicated to have in important effect in the correct description of the orbitals of transitions metals: Dunning *et al*. indicated that the "$(n+1)$ " $3d$ orbital of the $4s3d^{n+1}$ states and the "$(n+1)$" and "$(n+2)$" $3d$ orbitals of the $3d^{n+2}$ states of the transition metal atoms are functionally inequivalent to the other $3d$ orbitals, being much more diffuse.[383] Double-*d* shell correlation effects are related to the presence of a large number of electrons in compact *d* shells, resulting in large radial correlation effects in these shells. The second more diffuse *d* shell gives additional flexibility to describe such correlation effects, and for many $3d$ transition metal compounds the second d shell must be present to obtain quantitative accuracy with the CASPT2 method.[201] Table 7.7 compares the overall higher order correlation correction term ΔHO, which is the sum of the ΔT and ΔQ terms as mentioned before, to a correction denoted ΔMRCI which accounts for the contribution of the MRCI calculation to the correlation energy, and $\Delta \mathrm{MRCI}^{\mathrm{dd}}$ which includes the extended active space.

Table 7.7: Comparison of corrections ΔHO, ΔMRCI and $\Delta \mathrm{MRCI}^{\mathrm{dd}}$ to the atomisation energies D_e^0 (in kcal/mol) and equilibrium bond lengths R_e (in Å), for the five molecules with the maximum ΔD_0^0

	D_e^0			R_e		
Molecule	ΔHO	ΔMRCI	$\Delta \mathrm{MRCI}_{\mathrm{dd}}$	ΔHO	ΔMRCI	$\Delta \mathrm{MRCI}_{\mathrm{dd}}$
VH	0.15	−0.36	−0.50	0.000	0.000	0.002
CrH	1.00	1.72	1.96	0.006	0.015	0.010
FeCl	0.09	−0.21	1.28	0.000	0.010	0.001
CoH	3.53	–	10.68	0.001	–	−0.004
ZnH	0.19	0.25	0.35	0.002	−0.017	0.000
ZnCl	0.14	–	−8.95	−0.030	–	0.047

Inspecting the ΔHO and ΔMRCI terms, one would expect that if the system under consideration is well described with the ΔT and ΔQ corrections and is not multireference in nature, the magnitude of the two terms, namely ΔHO and ΔMRCI will be roughly equivalent, with respect to the atomisation energy. As we can see in table 7.7 for the case of the well described ZnH, the corrections have very similar results in both the atomisation energy and the bond distance. On the other hand, if we examine CoH, a molecule that is considered multireference according to most of the diagnostics, we can see that that the ΔMRCI is roughly three times as big as the ΔHO , indicating a severe deficiency of the treatment of correlation when single-reference methods are used. Somewhat more surprising is the value of the ΔMRCI for ZnCl, since it is not expected to be of particularly multi-reference nature; these two results are "suspiciously" large, and can therefore be considered too large to trust. Furthermore, in these two cases, CoH and ZnCl the conventional ΔMRCI term was unobtainable, due to technical problems that arose because of the limiting/not big enough active space of the molecular system. By examining Table 7.7 and by comparing the difference between $\Delta\mathrm{MRCI}_{\mathrm{dd}}$ and ΔMRCI , it is evident that the addition of the second *d* shell could contribute a significant amount of correlation energy (as seen in the cases of CrH and FeCl), and thus, although computationally expensive, must be used in order to get the most accurate description of a molecular system (especially if multireference character is suspected). However, even if the expensive correction $\Delta\mathrm{MRCI}_{\mathrm{dd}}$ is taken into account, the composite $\mathrm{D}^{0}_{0_{\mathrm{comp}}}$ are still not in good agreement with the experimental D^{0}_{0}; the average $\Delta\mathrm{D}^{0}_{0_{\mathrm{comp}}}$ is approximately 8 kcal/mol, with a maximum of 11.47 kcal/mol for the case of CoH. It is, therefore, evident that the poor agreement with the experimental results does not appear to be a result of the multireference character of the systems. For this reason, alongside with the level of complexity of performing MRCI-F12 calculations with extended active space, the $\Delta\mathrm{MRCI}_{\mathrm{dd}}$ correction is not incorporated in the composite scheme; the inclusion of higher order correlation seems to be "sufficient enough "at the time being. Instead, a revision of some of the experimental results is proposed, in order for better reference values that provide higher confidence for computational studies to be available in the future.

7.3.3 Further studies involving the 3dMLBE20 database

Since the completion of this investigation, additional research findings were published regarding the molecules comprising the 3dMLBE20 database. More specifically, Cheng *et al*., Fang *et al*., and Aoto *et al*., investigated the suitability of CCSD(T) calculations as benchmark calculations, and expressed the need for a re-examination of the experimental values for a subset of the molecular database, due to the fact that discrepancies between theoretically calculated values and theoretical ones were too high.[422–424] Fang *et al*. re-evaluated the experimental D^{0}_{0} values for the hydrides based on a proton transfer reaction (for more details see Reference 423) and reported "newly" evaluated values for experimental D^{0}_{0} for each molecule in the database. As shown in Table 7.8.

Similarly with before, the composite $\mathrm{D}^{0}_{0_{\mathrm{comp}}}$ values along with with the experimental D^{0}_{0} are plotted in Figure 7.3 in order to facilitate the comparison between the two. $\Delta\mathrm{D}^{0}_{0}$ is plotted as single points within the error margins associated with the respective experiment plotted as a pink region. Figure 7.3 strikingly demonstrates right away that the composite values are now well within the range of the error associated with the experiment, as well as within the ±3 kcal/mol threshold of "chemical accuracy" expected for TMs, for the majority of cases. This once again indicates that, as discussed earlier, there is need to re-evaluate the experimental information available in order to proceed to meaningful comparisons between experimental and computational data; a conclusion supported from both References 422 and 424 as well.

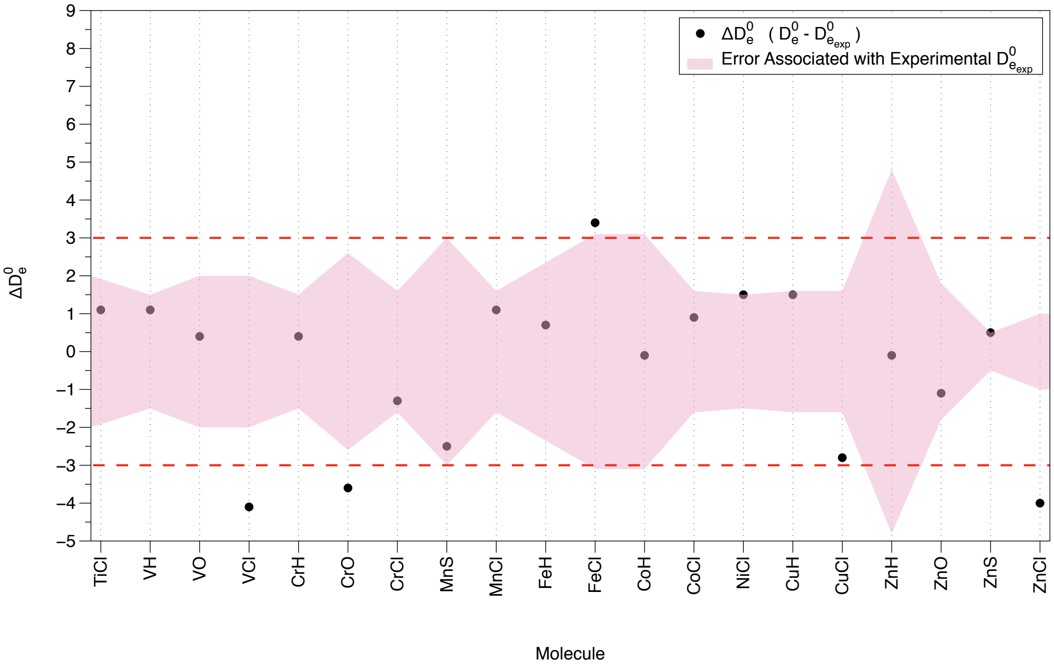


Figure 7.3: Difference in dissociation energies ΔD_0^0 (in kcal/mol) between the composite $D_{0_{comp}}^0$ and the experimental D_0^0 reported in Reference,[423] in presence of the experimental error associated with D_0^0.

Table 7.8: Comparison of experimental D_0^0 of Reference 423 and composite $D_{0_{\text{comp}}}^0$ dissociation energies in kcal/mol for molecules of the 3*d*MLBE20 database.

Molecule	Molecular State	D_0^0 (kcal/mol)	$D_{0_{\text{comp}}}^0$ (kcal/mol)
TiCl	$^4\Phi$	100.1 ± 2.0	101.2
VH	$^5\Delta$	53.7 ± 1.5	54.8
VO	$^4\Sigma^-$	149.5 ± 2.0	149.9
VCl	$^5\Delta$	101.9 ± 2.0	97.8
CrH	$^6\Sigma^+$	49.1 ± 1.5	49.5
CrO	$^5\Pi$	109.8 ± 2.6	106.2
CrCl	$^6\Sigma^+$	89.6 ± 1.6	88.3
MnS	$^6\Sigma^+$	69.7 ± 3.0	67.2
MnCl	$^7\Sigma^+$	80.2 ± 1.6	81.3
FeH	$^6\Delta$	37.0 ± 3.1	37.7
FeH	$^4\Delta$	37.0 ± 3.1	34.0
FeCl	$^6\Delta$	77.9 ± 1.6	81.3
CoH	$^3\Phi$	51.9 ± 1.5	51.8
CoCl	$^3\Phi$	79.9 ± 1.6	80.8
NiCl	$^2\Pi$	89.2 ± 1.6	90.7
CuH	$^1\Sigma^+$	60.3 ± 4.8	61.8
CuCl	$^1\Sigma^+$	89.6 ± 1.8	86.8
ZnH	$^2\Sigma^+$	19.5 ± 0.5	19.4
ZnO	$^1\Sigma^+$	37.1 ± 1.0	36.0
ZnS	$^1\Sigma^+$	48.4 ± 3.0	32.9
ZnCl	$^2\Sigma^+$	53.5 ± 1.0	49.5

7.3.4 Frozen core CCSD(T) and CCSD(T)-F12b basis set convergence

In addition to CCSD(T)-F12b calculations that were employed in order to accurately calculate dissociation (atomisation) energies, for the 3*d*MLBE20 dataset, conventional CCSD(T) calculations were performed to assess and compare their convergence to the CBS limit, and examine possible fortuitous error cancellations that could provide some guidelines regarding which methods can be used for larger systems (in which the composite treatment is not possible). To begin with, conventional CCSD(T) and explicitly correlated CCSD(T)-F12b calculations were performed for all systems, evaluating the frozen-core CBS limits. In order to obtain the CCSD(T)/CBS limit, the CCSD and (T) contributions need to be calculated separately, since explicit correlation in the CCSD(T)-F12b method is only included at the CCSD level. These were obtained via extrapolation[359,425] of conventional CCSD(T)/aug-cc-pVTZ and aug-cc-pVQZ, as well as aug-cc-pVQZ and aug-cc-pV5Z results, with $\ell_{\max} = n + 1$ for the transition metals, $E_n^{\text{corr}} = E_{\text{CBS}}^{\text{corr}} +$

$\frac{A}{(\ell_{\max}+\frac{1}{2})^4}$. Similarly, and as described earlier, the CCSD(T)-F12b energies were extrapolated to the CBS limit, using the extrapolation scheme described by Hill *et al.*,[384] as seen in equation 5.3.

Table 7.9: Basis set incompleteness errors (BSIE) of the frozen-core CCSD(T) and CCSD(T)-F12b atomisation energies (kcal/mol) for the 3dMLBE20 dataset (aug-cc-pV*n*Z has been shortened to aV*n*Z).

	Conventional CCSD(T)				CCSD(T)-F12b			$\text{CBS}^{\text{conv}}_{\text{Q5}}$	$\text{CBS}^{\text{F12}}_{\text{TQ}}$
Molecule	aVDZ	aVTZ	aVQZ	aV5Z	aVDZ	aVTZ	aVQZ		
TiCl	−6.66	−3.93	−0.92	−0.92	−1.33	−0.96	−0.40	101.45	101.49
VH	−2.46	−0.97	−0.16	−0.16	−0.42	−0.20	−0.06	56.40	56.38
VO	−11.43	−4.71	−1.04	−1.04	−1.43	−0.95	−0.36	149.06	149.09
VCl	−6.36	−3.75	−0.80	−0.80	−0.92	−0.80	−0.28	100.09	100.03
CrH	−2.56	−0.77	−0.19	−0.19	−0.14	−0.21	−0.05	50.23	50.30
CrO	−12.56	−4.57	−1.25	−1.25	−2.52	−1.21	−0.45	103.61	103.85
CrCl	−6.42	−3.73	−0.87	−0.87	−0.37	−0.89	−0.29	89.99	90.06
MnS	−11.30	−5.78	−1.39	−1.39	−2.10	−1.06	−0.45	67.81	67.93
MnCl	−5.95	−3.87	−0.89	−0.89	−0.93	−0.89	−0.30	84.85	84.94
FeH ($^6\Delta$)	−2.41	−0.80	−0.19	−0.19	−0.44	−0.14	−0.03	41.37	41.65
FeH ($^4\Delta$)	−8.83	−3.75	−1.07	−1.07	−4.37	−1.85	−0.57	34.65	35.11
FeCl	−6.29	−4.01	−0.91	−0.91	−0.94	−0.88	−0.29	84.71	84.97
CoH	−7.50	−2.90	−0.77	−0.77	−4.31	−1.56	−0.53	52.45	52.67
CoCl	−12.09	−6.30	−1.55	−1.55	−6.46	−2.45	−0.86	82.92	83.14
NiCl	−12.04	−6.47	−1.44	−1.44	−7.29	−2.32	−0.79	101.91	101.94
CuH	−2.02	−0.32	0.07	0.07	−0.40	0.02	0.01	62.28	62.17
CuCl	−5.44	−3.53	−0.61	−0.61	−1.19	−0.67	−0.23	89.19	88.95
ZnH	−1.85	−0.48	−0.05	−0.05	−0.31	0.07	0.04	23.32	23.34
ZnO	−8.29	−3.44	−0.77	−0.77	−2.54	−0.85	−0.32	38.47	38.54
ZnS	−8.32	−4.67	−0.83	−0.83	−2.12	−1.03	−0.34	36.45	36.21
ZnCl	−5.48	−3.73	−0.73	−0.73	−0.87	−0.69	−0.21	54.44	54.32
MSE	−6.96	−3.45	−1.47	−0.78	−1.97	−0.93	−0.32		
MUE	6.96	3.45	1.47	0.79	1.97	0.94	0.33		
σ	3.52	1.83	0.84	0.46	2.02	0.68	0.24		
RMSE	7.94	3.98	1.72	0.92	2.86	1.17	0.41		
|Max|	12.56	6.47	2.79	1.55	7.29	2.45	0.86		

Table 7.9 summarizes the convergence behaviour of the frozen-core atomisation energies calculated with conventional CCSD(T) and CCSD(T)-F12b relative to the reference CBS limit obtained with CCSD(T)-F12b/aug-cc-pVTZ and aug-cc-pVQZ basis sets, by displaying the basis set incompleteness error (BSIE) relative to the extrapolated complete basis sets (CBS) limit also shown in the estimated CBS extrapolated atomisation energies for both conventional methods

(denoted $\mathrm{CBS}^{\mathrm{conv}}_{\mathrm{Q5}}$) and explicitly correlated methods (denoted $\mathrm{CBS}^{\mathrm{F12}}_{\mathrm{TQ}}$).

Figure 7.4 is series of violin plots that depict the BSIE in atomisation energies for conventional CCSD(T) and CCSD(T)-F12b calculations, using the aug-cc-pV*n*Z basis sets. Each individual point on the violin plots, depicts the BSIE in the atomisation energy of each diatomic molecule of the 3*d*MLBE20 database, while the black triangle represents the mean signed error. The height of the violin plot represents the range of values, while the width represents the density of the points; the more points around a value, the wider the violin plot around the same point. Figure 7.4 clearly shows that explicitly correlated methods converge much quicker to the CBS limit. It is therefore established, that the use of explicitly correlated methods instead of conventional ones, such as CCSD(T)-F12b and CCSD(T), yields substantially more accurate results (of at least $n+1$ quality when a basis set of cardinal number n is used) at a smaller computational cost, and should therefore preferentially be used.

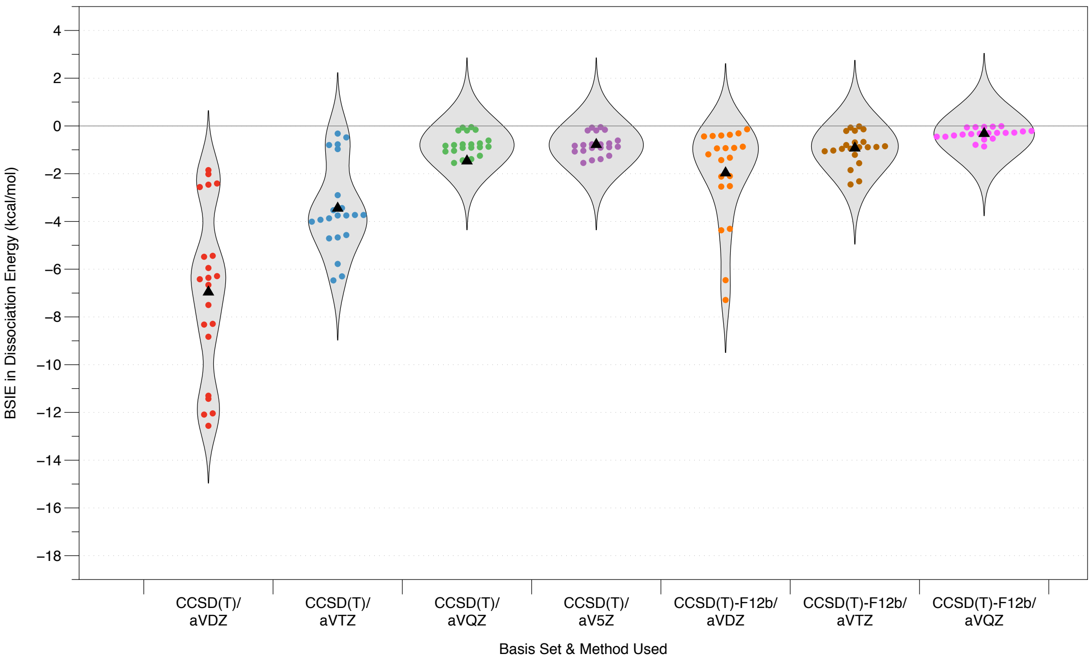


Figure 7.4: Violin plots depicting the BSIE error (kcal/mol) in the dissociation energy for the 3*d*MLBE20 test set in CCSD(T) and CCSD(T)-F12b calculations, using aV*n*Z (*n* = D - 5) basis sets.

As shown in Table 7.9, the conventional CCSD(T) atomisation energies converge slowly with respect to the basis set, with a mean unsigned error of 6.96 kcal/mol at the DZ level which decreases to 3.45, 1.47 and 0.79 at the TZ, QZ and 5Z level, respectively. On the other hand the CCSD(T)-F12b results exhibit a much faster convergence, indicated by the smaller BSIE values at all cardinal levels, a fact that is not surprising; the mean average error drops from 1.97 kcal/mol at the DZ level to 0.94 and 0.33 kcal/mol at the TZ and QZ levels, respectively. Already at the TZ level the mean unsigned error is only 0.94 kcal/mol achieving roughly the same convergence as that of the much more expensive CCSD(T)/aug-cc-pV5Z calculation. We can also see that both $\mathrm{CBS}^{\mathrm{conv}}_{\mathrm{Q5}}$ and $\mathrm{CBS}^{\mathrm{F12}}_{\mathrm{TQ}}$ estimates are in good agreement with each other, a fact that ensures that this accelerated convergence is not a result of some cancellation of error, and that as expected both CCSD(T) and CCSD(T)-F12b converge to the same limit.

A similar analysis to the one above can be performed for the equilibrium bond lengths of the 20 diatomics. In every case the sixth order polynomial fitting procedure mentioned earlier was used to evaluate the equilibrium bond-length, $\mathrm{R_e}$. Table 7.10 shows the equilibrium bond-lengths $\mathrm{R_e}$, calculated at the CCSD(T) and CCSD(T)-F12b levels of theory, as well as the respective CBS estimates.

Table 7.10: Equilibrium bond-lengths $\mathrm{R_e}$, and CBS estimates (in Å) for the molecules of the 3*d*MLBE20 database, calculated at the CCSD(T) and CCSD(T)-F12b levels of theory with the aV*n*Z basis sets for the 3dMLBE20 dataset (aug-cc-pV*n*Z has been shortened to aV*n*Z).

	Conventional CCSD(T)					CCSD(T)-F12b			
Molecule	aVDZ	aVTZ	aVQZ	aV5Z	$\mathrm{CBS}^{\mathrm{conv}}_{\mathrm{Q5}}$	aVDZ	aVTZ	aVQZ	$\mathrm{CBS}^{\mathrm{F12}}_{\mathrm{TQ}}$
TiCl	2.3258	2.3128	2.3108	2.3080	2.3053	2.3082	2.3076	2.3083	2.3083
VH	1.7191	1.7126	1.7093	1.7083	1.7075	1.7107	1.7089	1.7082	1.7079
VO	1.6107	1.6020	1.5987	1.5975	1.5967	1.6003	1.5989	1.5977	1.5974
VCl	2.2751	2.2595	2.2575	2.2550	2.2530	2.2565	2.2547	2.2552	2.2554
CrH	1.6745	1.6622	1.6592	1.6580	1.6567	1.6645	1.6584	1.6582	1.6577
CrO	1.6366	1.6283	1.6250	1.6238	1.6547	1.6232	1.6273	1.6243	1.6551
CrCl	2.2339	2.2096	2.2081	2.2056	2.2030	2.2108	2.2047	2.2054	2.2053
MnS	2.1170	2.0988	2.0928	2.0899	2.0870	2.0883	2.0881	2.0881	2.0880
MnCl	2.2720	2.2596	2.2563	2.2543	2.2523	2.2546	2.2538	2.2537	2.2535
FeH ($^6\Delta$)	1.6946	1.6883	1.6861	1.6853	1.6845	1.6875	1.6861	1.6851	1.6847
FeH ($^4\Delta$)	1.5722	1.5616	1.5597	1.5587	1.5577	1.5657	1.5610	1.5595	1.5588
FeCl	2.2069	2.1969	2.1926	2.1909	2.1892	2.1912	2.1908	2.1904	2.1900
CoH	1.5209	1.5182	1.5182	1.5182	1.5184	1.5142	1.5200	1.5197	1.5199
CoCl	2.0978	2.0920	2.0886	2.0876	2.0867	2.0645	2.0876	2.0879	2.0886
NiCl	2.0961	2.0860	2.0808	2.0792	2.0778	2.0804	2.0806	2.0796	2.0790
CuH	1.4923	1.4840	1.4829	1.4829	1.4830	1.4859	1.4849	1.4842	1.4839
CuCl	2.0925	2.0833	2.0770	2.0752	2.0736	2.0758	2.0771	2.0755	2.0747
ZnH	1.6107	1.6027	1.6003	1.6005	1.6009	1.6043	1.6029	1.6017	1.6012
ZnO	1.7297	1.7189	1.7138	1.7124	1.7112	1.7173	1.7135	1.7120	1.7116
ZnS	2.0751	2.0705	2.0620	2.0596	2.0571	2.0593	2.0610	2.0590	2.0581
ZnCl	2.1543	2.1493	2.1431	2.1406	2.1383	2.1394	2.1422	2.1407	2.1399

From Table 7.10 it can be seen that while in all cases $\mathrm{CBS}^{\mathrm{F12}}_{\mathrm{TQ}}$ estimates longer bond lengths than

CBS^{conv}_{Q5}, the average difference of 0.001 Å is not unreasonable. The accelerated convergence of CCSD(T)-F12b, is once again evident, and even more obvious for bond lengths, as the average bond length calculated at the CCSD(T)-F12b level of theory with the aug-cc-pVDZ basis set is roughly equivalent to that calculated using CCSD(T) and aug-cc-pV5Z.

Up to this point, the performance of the composite method with respect to experimental data as well as the convergence behavior of "simple" CCSD(T) and CCSD(T)-F12b calculations has been assessed. While it is clear that the composite method used produces accurate energetic and geometrical results, this has been focused on small transition-metal diatomics. However, it may not be possible to afford this procedure for large systems, especially when it comes to the more expensive corrections, such as ΔHO. In order to assess how a "simple" calculation reproduces the composite results, the difference between the composite atomisation energies $D^0_{0_{comp}}$ and the atomisation energies evaluated using CCSD(T)/aVnZ or CCSD(T)-F12b/aVnZ was calculated, and the difference $\Delta D^0_{0_{comp}}$ was plotted in a series of violin plots that can be seen in Figure 7.5.

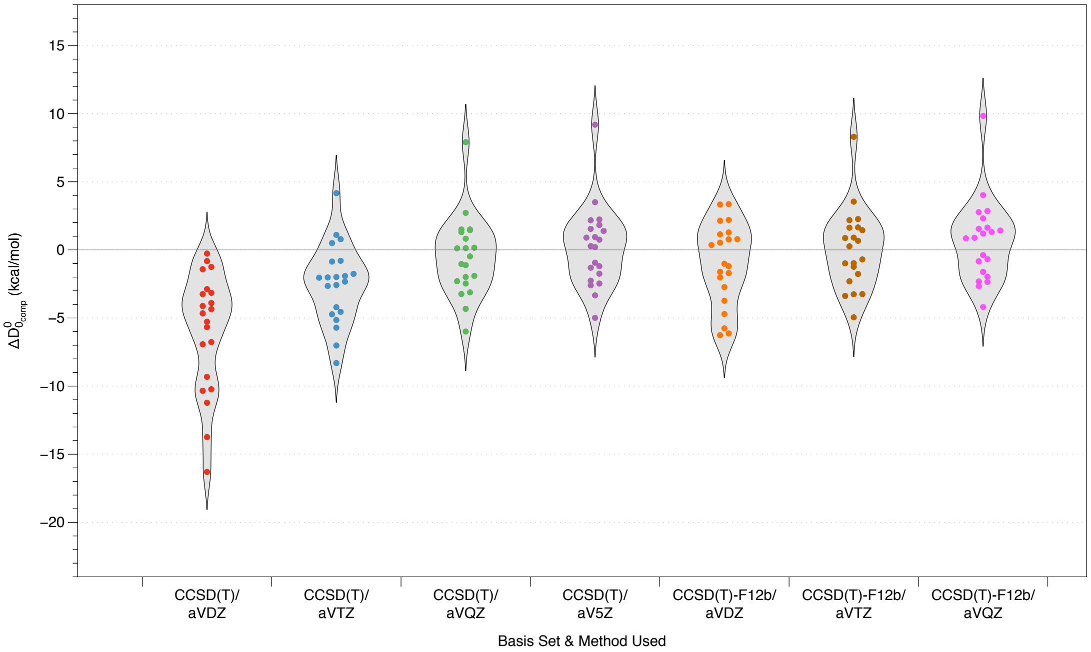


Figure 7.5: Violin plots depicting $\Delta D^0_{0_{comp}}$ for the 3dMLBE20 test set in CCSD(T) and CCSD(T)-F12b calculations.

Due to fortuitous error cancellations, if one is working on a system of such size that a composite technique is not applicable, the best alternative would be to perform a CCSD(T)-F12b calculation using the aVDZ basis sets. CCSD(T-F12b/aVDZ calculations produce a "well-controlled"$\Delta D^0_{0_{comp}}$ with a mean unsigned error of 2.51 kcal/mol and a maximum error of 6.26 kcal/mol, while the more expensive aVTZ only improves the mean unsigned error by 0.30 kcal/mol while the absolute max error actually increases by 2.04 kcal/mol. As can be seen in Figure 7.5, an outlier appears in

CCSD(T)/aVQZ, CCSD(T)/aV5Z, CCSD(T)-F12b/aVTZ and CCSD(T)-F12b/aVQZ. This point corresponds to NiCl, which is the molecule that has by far the biggest sum of corrections in the composite scheme (ΔCV + ΔDK + ΔHO + ΔSO $\approx$ 10.62 kcal/mol). While the magnitude of the corrections is evident in the above mentioned points, it is actually absent in the cases of CCSD(T)/aug-cc-pVDZ, CCSD(T)/aug-cc-pVTZ and CCSD(T)-F12b/aug-cc-pVDZ; this is of course due to fortuitous cancellation of error, between the composite corrections and the BSIE. The above findings therefore suggest that CCSD(T)-F12b calculations with aug-cc-pVDZ basis set should be utilized in lieu of potentiality of applying the composite technique in larger systems.

Finally, it is interesting to see how the present calculations (both "simple" and composite) compare with other types of calculations, such as density functional theory (DFT) calculations. In the recent paper by Xu *et al*. Kohn-Sham (KS) DFT calculation results were compared with coupled cluster calculation results.[368] The coupled cluster results were found to be comparable but not necessarily better than KS density functional calculations (when a wide set of choices of exchange correlation functionals was used), and the authors suggested that coupled cluster calculations should not be used to provide validated benchmarks for KS theory (assuming that the existing experimental data are accurate). Throughout this work, it has become apparent that the existing experimental results are often quite outdated with large error margins, and in certain cases deviate strongly from our "best" calculations, a fact that could suggest that some of the experimental data may not be reliable. Furthermore, it is important not to forget that in order to get chemically accurate results with coupled cluster methods, one should use a relatively large basis set, of at least triple-zeta quality, if not higher. Of course, this bottleneck has been shown to be bypassable by the use of explicitly correlated methods such as CCSD(T)-F12b, which achieves significantly smaller BSIE at the same cardinal level. Nonetheless, any future comparisons between the composite results and DFT calculations can be of interest, and thus, Table 7.11 provides data such as best composite energy values without spin-orbit corrections, as well as the values of our computed zero-point vibrational energy (ZPE) and thermal corrections, that can be directly used for comparisons with DFT calculations.

Table 7.11: Best composite energy excluding ΔSO (denoted $D^0_{0_{\text{comp}}}$XSO) as well as zero-point energy (ΔZPE) and molecular thermal corrections [$\Delta H(298-0)$] for diatomics of the the 3*d*MLBE20 database (aug-cc-pV*n*Z has been shortened to aV*n*Z). All values given in kcal/mol.

Molecule	$D^0_{0_{\text{comp}}}$XSO	ΔZPE	$\Delta H(298-0)$
TiCl	102.85	0.557	2.274
VH	57.62	2.324	2.076
VO	152.49	1.445	2.096
VCl	99.54	0.573	2.267
CrH	51.86	2.379	2.075
CrO	107.54	1.435	2.097
CrCl	89.71	0.577	2.266
MnS	68.46	0.686	2.224
MnCl	82.67	0.547	2.279
FeH ($^6\Delta$)	40.03	2.344	2.075
FeH ($^4\Delta$)	36.58	2.486	2.075
FeCl	82.58	0.578	2.265
CoH	54.68	2.660	2.074
CoCl	82.42	0.597	2.257
NiCl	94.02	0.580	2.264
CuH	64.50	2.664	2.074
CuCl	88.20	0.578	2.265
ZnH	21.75	2.310	2.076
ZnO	37.22	1.055	2.135
ZnS	34.15	0.658	2.234
ZnCl	50.89	0.561	2.272

7.4 Conclusions

In the present study, the modified FPD thermochemistry scheme of Bross *et al*. was used to calculate accurate atomisation energies for 3*d* transition metal containing systems. This modified scheme utilized the explicitly correlated CCSD(T)-F12b method, which was shown to produce smaller BSIE than CCSD(T) at the same cardinal level, thus achieving accelerated convergence to the CBS limit. Most of the composite calculated atomisation energies were found to be in relatively good agreement with the experimental values available, however in certain cases (VH, CoH, CrH and FeCl) the deviation is quite significant. These molecules deviate to such that is much larger than any conceivable error in this composite approach. For this reason, additional calculations were performed in order to examine whether multi-reference calculations are necessary. In most cases, the correction that accounted for their potential multi-reference nature did not seem to “correct” the obtained values (i.e. make them agree with experimental data). Furthermore, a series of five multi-reference diagnostics (T_1, D_1, C_0^2, %TAE_e[(T)] and %TAE_e[Q]) was calculated to examine which diagnostic (or combination of) provides a "foolproof" insight of multi-reference character. Unfortunately, each diagnostic suggested that a different subset of the 3*d*MLBE20 database required multi-reference treatment, often leaving the deviating cases in the single-reference subset; and therefore concluded that these deviations are most likely not due to a shortcoming of the composite method used, but that further experimental work is warranted in order to settle these issues. Finally, a comparison between composite and simple CCSD(T)-F12b calculated atomisation energies was carried out, through which a fortuitous cancellation of error was observed for the case of CCSD(T)-F12b calculations using the small aug-cc-pVDZ basis set, and thus we expect that a CCSD(T)-F12b/aug-cc-pVDZ calculation can potentially be a good starting point for transition metal systems of larger size that the composite method is impractical to use upon.

Chapter 8

Outlook and Future Work

This work aimed to ease and facilitate the way in which explicitly correlated calculations are performed on transition metal containing systems. It largely focused on the development of basis sets specifically designed for explicitly correlated methods [MP2-F12 and CCSD(T)-F12b].

In Chapter 5 auxiliary basis sets specifically matched to the correlation consistent cc-pV*n*Z-F12 and cc-pCV*n*Z-F12 orbital basis sets for the elements H-Ar were optimised, at the density-fitted second-order Møller-Plesset perturbation theory level of theory.[124,143,238,267] These sets were designed for use in explicitly correlated (F12) methods, which utilize density fitting for the evaluation of two-electron integrals. The development of these sets was an important first step towards the "goal" of efficient F12 calculations for bigger systems and the subsequent development of other orbital and auxiliary basis sets for explicit correlation, as they allowed us to perform explicitly correlated calculations in lighter systems (and thus exclude potential sources of error or ambiguity when developing other basis sets). Their development, furthermore, provided updated guidelines for the optimization of density fitting auxiliary basis sets for use with F12 methods for other elements.

In Chapter 6, orbital and auxiliary basis sets for the 4*d* transition metal elements Y-Pd were developed for use in explicitly correlated (F12) methods. The development of these sets is of great importance, as they allow the performance of F12 calculations within a well-defined environment; explicitly correlated calculations could be performed with non-F12-specific basis sets, however the convergence behaviour and the errors associated with these calculations would not be well-controlled. Orbital basis sets for standard frozen-core calculations as well as core-valence and diffuse augmented sets were developed, along with the corresponding auxiliary basis sets. Auxiliary basis sets for the density fitting of the evaluation of two-electron integrals were developed for both valence-only and core-valence sets, while, due to time concerns, auxiliary basis sets for the resolution-of-identity utilised in many-electron integrals were only developed for the matching frozen-core orbital basis sets. The development of the matching OPTRI sets for the core-valence cc-pCV*n*Z-PP-F12 could be a subject of future work.

Finally, Chapter 5 addresses an existing composite approach, tailored to explicitly-correlated methods, for 3*d* transition metal containing systems.[284] The chapter follows the analysis of the modified-FPD recipe, and evaluates composite spectroscopic constants, such as atomisation energies and equilibrium bond lengths, for a series of diatomic molecules of the 3*d*MLBE20 dataset, for which previous publications[368] suggested that CCSD(T) calculations were not of benchmark quality. The convergence of both conventional and explicitly correlated coupled cluster methods, CCSD(T) and CCSD(T)-F12b is examined, and the accelerated convergence associated with F12 methods is once again evident. The agreement between the calculated spectroscopical constants and the experimental values (in some cases revised) of the molecular set is good; thus, both CCSD(T) and CCSD(T)-F12b are shown to provide reliable results at the CBS limit. Furthermore, the composite approach provides us with a "minimal requirement" recipe in which the method/basis set combination that is more favored from fortuitous error cancellation is selected; this recipe can be utilised in bigger systems that contain 3*d* transition metal elements or in cases where computational resources are scarce. Future work could expand this protocol into 4*d* transition metal elements, by performing a similar analysis for a similar database of small diatomic 4*d*-containing systems.

Bibliography

[1] Dirac, P. A. M. *Proc. R. Soc. Lond. A Math Phys. Sci.* **,** **1929**, *123*, 714.

[2] Moore, G. E. *Electronics* **1965**, *38*, 1.

[3] Schrödinger, E. *Annalen der Physik.* **1926**, *79*, 361.

[4] Pauli, W. J. *Z. Physik* **1925**, *31*, 765.

[5] Born, M. *Proc. R. Soc. Lond. A* **1934**, *143*, 410.

[6] Christiansen, O.; Olsen, J.; Jørgensen, P.; Koch, H.; Malmqvist, P. øA. *Chem. Phys. Lett.* **1996**, *261*, 339.

[7] Pople, J. A.; S., B. J.; Seeger, R. *Int. J Quantum Chem. Symp.* **1976**, *1*, 10.

[8] Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

[9] Langhoff, S. R.; Davidson, E. R. *Int. J. Quantum Chem.* **1974**, *8*, 61.

[10] Meissner, L. *Chem. Phys. Lett.* **1988**, *146*, 204.

[11] Wlodzistaw, D.; Diercksen, G. H. F. *J. Chem. Phys.* **1994**, *101*, 3018.

[12] Shiozaki, T.; Knizia, G.; Werner, H.-J. *J. Chem. Phys.* **2011**, *134*, 034113.

[13] Johnson, E. R.; Dickson, R. M.; Becke, A. D. *J. Chem. Phys.* **2007**, *126*, 184104.

[14] Werner, H.-J.; Shiozaki, T. *Mol. Phys.* **2013**, *111*, 607.

[15] McWeeny, R. *Rev. Mod. Phys.* **1960**, *32*, 335.

[16] Hollett, J. W.; McKemmish, L. K.; Gill, P. M. W. *J. Chem. Phys.* **2011**, *134*, 114111.

[17] Löwdin, P.-O. *Adv. Chem. Rev.* **1959**, *22*, 207.

[18] Pople, J.; Binkley, J. *Mol. Phys.* **1975**, *29*, 599.

[19] Hollett, J. W.; McKemmish, L. K.; Gill, P. M. W. *J. Chem. Phys.* **2011**, *134*, 224103.

[20] Almlöf, J.; Taylor, P. R. *J. Chem. Phys.* **1987**, *86*, 4070.

[21] Widmark, P.-O.; Malmqvist, P. øA.; Roos, B. *Theor. Chim. Acta* **1990**, *77*, 291.

[22] Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007.

[23] Kendall, R. A.; Dunning, T. H.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796.

[24] Woon, D. E.; Dunning, T. H. *J. Chem. Phys.* **1995**, *103*, 4572.

[25] Kato, T. *Commun. Pure Appl. Math.* **1957**, *10*, 151.

[26] Hylleraas, E. A. *Z Phys.* **1928**, *32*, 469.

[27] Hylleraas, E. A. *Z. Phys.* **1930**, *65*, 209.

[28] Sinanoğlou, O. *J. Chem. Phys.* **1962**, *36*, 706.

[29] Szalewicz, K.; Jeziorski, B.; Monkhorst, H. J.; Zabolitzky, J. G. *Chem. Phys. Lett.* **1982**, *91*, 169.

[30] Szalewicz, K.; Zabolitzky, J. G.; Jeziorski, B.; Monkhorst, H. J. *J. Chem. Phys.* **1984**, *81*, 2723.

[31] Lester, W. A. J.; Krauss, M. *J. Chem. Phys.* **1964**, *41*, 1407.

[32] Boys, S. F.; Handy, N. C. *Proc. R. Soc. London, Ser. A* **1969**, *309*, 209.

[33] Boys, S. F.; Handy, N. C. *Proc. R. Soc. London, Ser. A* **1969**, *310*, 43.

[34] Boys, S. F. *Proc. R. Soc. London. Ser. A* **1960**, *258*, 402.

[35] Singer, K. *Proc. R. Soc. London. Ser. A* **1960**, *258*, 412.

[36] Szalewicz, K.; Jeziorski, B.; Monkhorst, H. J.; Zabolitzky, J. G. *J. Chem. Phys.* **1983**, *78*, 1420.

[37] Szalewicz, K.; Jeziorski, B.; Monkhorst, H. J.; Zabolitzky, J. G. *J. Chem. Phys.* **1983**, *79*, 5543.

[38] Jeziorski, B.; Monkhorst, H. J.; Szalewicz, K.; Zabolitzky, J. G. *J. Chem. Phys.* **1984**, *81*, 368.

[39] Karunakaran, K. M.; Christoffersen, R. E. *J. Chem. Phys.* **1975**, *62*, 1972.

[40] Kozlowski, P. M.; Adamowicz, L. *J. Chem. Phys.* **1991**, *95*, 6681.

[41] Nooijen, M.; Bartlett, R. J. *J. Chem. Phys.* **1998**, *109*, 8232.

[42] Handy, N. C. *Mol. Phys.* **1972**, *23*, 1.

[43] Ten-No, S. *Chem. Phys. Lett.* **2000**, *330*, 169.

[44] Hino, O.; Tanimura, Y.; Ten-No, S. *J. Chem. Phys.* **2001**, *115*, 7865.

[45] Kutzelnigg, W. *Theor. Chim. Acta* **1985**, *68*, 445.

[46] Klopper, W.; Kutzelnigg, W. *Chem. Phys. Lett.* **1987**, *134*, 17.

[47] Klopper, W.; Kutzelnigg, W. *J. Chem. Phys.* **1991**, *94*, 2020.

[48] Werner, H. J.; Adler, T. B.; Manby, F. R. *J. Chem. Phys.* **2007**, *126*, 164102.

[49] Tew, D. P.; Klopper, W. *J. Chem. Phys.* **2006**, *125*, 094302.

[50] Sinnokrot, M. O.; Valeev, E. F.; Sherrill, C. D. *J. Am. Chem. Soc.* **2002**, *124*, 10887.

[51] Schütz, M.; Klopper, W.; Lüthi, H. P.; Noga, J.; Vogtner, S. *Top. Curr. Chem.* **1999**, *203*, 21.

[52] Klopper, W.; Lüthi, H. P. *Chem. Phys. Lett.* **1996**, *262*, 546.

[53] Persson, B. J.; Taylor, P. R. *J. Chem. Phys.* **1996**, *105*, 5915.

[54] Persson, B. J.; Taylor, P. R. *Theor. Chem. Acc.* **1997**, *97*, 240.

[55] Samson, C. C. M.; Klopper, W.; Helgaker, T. *Comput. Phys. Commun.* **2002**, *149*, 1.

[56] Tew, D. P.; Klopper, W. *J. Chem. Phys.* **2005**, *123*, 074101.

[57] May, A. J.; Valeev, E. F.; Polly, R.; Manby, F. R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 2710.

[58] Klopper, W.; Kutzelnigg, W. *J. Phys. Chem.* **1990**, *94*, 5625.

[59] Klopper, W.; Samson, C. C. M. *J. Chem. Phys.* **2002**, *116*, 6397.

[60] Kong, L.; Bischoff, F. A.; Valeev, E. F. *Chem. Rev.* **2012**, *112*, 75.

[61] Valeev, E. F. *Chem. Phys. Lett.* **2004**, *395*, 190.

[62] Wind, P.; Klopper, W.; Helgaker, T. *Theor. Chim. Acta* **2002**, *107*, 173.

[63] Dahle, P.; Helgaker, T.; Jonsson, D.; Taylor, P. R. *Phys. Chem. Chem. Phys.* **2007**, *9*, 3112.

[64] Dahle, P.; Helgaker, T.; Jonsson, D.; Taylor, P. R. *Phys. Chem. Chem. Phys.* **2008**, *10*, 3377.

[65] Polly, R.; Werner, H.-J.; Dahle, P.; Taylor, P. R. *J. Chem. Phys.* **2006**, *124*, 234107.

[66] Werner, H.-J.; Knowles, P. J.; Knizia, G.; Manby, F. R.; Schütz, M.; *et. al*; *MOLPRO, version 2012.1, a package of ab initio programs*; 2012.

[67] Ten-No, S. *Chem. Phys. Lett.* **2004**, *398*, 56.

[68] Pack, R. T.; Brown, W. B. *J. Chem. Phys.* **1966**, *45*, 556.

[69] Köhn, A.; Richings, G.; Tew, D. *J. Chem. Phys.* **2008**, *129*, 201103.

[70] Shiozaki, T.; Kamiya, M.; Hirata, S.; Valeev, E. F. *J. Chem. Phys.* **2008**, *129*, 071101.

[71] Adler, T. B.; Knizia, G.; Werner, H. J. *J. Chem. Phys.* **2007**, *127*, 221106.

[72] Knizia, G.; Adler, T. B.; Werner, H. J. *J. Chem. Phys.* **2009**, *130*, 054104.

[73] Hättig, C.; Klopper, W.; Köhn, A.; Tew, D. P. *Chem. Rev.* **2012**, *112*, 4.

[74] Klopper, W.; Manby, F. R.; Ten-No, S.; Valeev, E. F. *Int. Rev. Phys. Chem.* **2006**, *25*, 427.

[75] Kutzelnigg, W.; Klopper, W. *J. Chem. Phys.* **1991**, *94*, 1985.

[76] May, A. J.; Manby, F. R. *J. Chem. Phys.* **2004**, *121*, 4479.

[77] Manby, F. R. *J. Chem. Phys.* **2003**, *119*, 4607.

[78] Dunlap, B. I. *Phys. Chem. Chem. Phys.* **2000**, *2*, 2113.

[79] Dunlap, B. *J. Mol. Struct. (THEOCHEM)* **2000**, *529*, 37.

[80] Baerends, E. J.; Felton, R. H.; Roos, P. *Chem. Phys.* **1973**, *71*, 3396.

[81] Dunlap, B. I.; Connolly, J. W. D.; Sabin, J. R. *J. Chem. Phys.* **1979**, *71*, 3396.

[82] Alsenoy, C. V. *J. Comput. Chem.* **1988**, *9*, 620.

[83] Vahtras, O.; Almlöf, J.; Feyereisen, M. *Chem. Phys. Lett.* **1993**, *213*, 514.

[84] Feyereisen, M.; Fitzgerald, G.; Komornicki, E. *Chem. Phys. Lett.* **1993**, *208*, 359.

[85] Bernholdt, D. E.; Harrison, R. J. *Chem. Phys. Lett.* **1996**, *250*, 447.

[86] Ten-No, S.; Iwata, S. *Chem. Phys. Lett.* **1995**, *240*, 578.

[87] Ten-No, S.; Iwata, S. *J. Chem. Phys.* **1996**, *105*, 3604.

[88] Rendell, A. P.; Lee, T. J. *J. Chem. Phys.* **1994**, *101*, 400.

[89] Jensen, F. In *Introduction to Computational Chemistry*, 2nd ed.; Wiley, Chichester, 2007.

[90] Clementi, E.; Davis, D. R. *J. Comput. Phys.* **1967**, *1*, 223.

[91] G., C.; Szczesniak, M. M. *Chem. Rev* **1994**, *94*, 1723.

[92] van Duijneveldt, F. B.; van Duijneveldt-van de Rijdt, J.; vanLenthe, J. *Chem. Rev.* **1994**, *94*, 1873.

[93] Boys, S.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.

[94] Morokuma, K.; Kitaura, K. In *Chemical Applications of Atomic and Molecular Electrostatic Potentials*; Plenum Press, New York, 1981.

[95] Almlöf, J.; Taylor, P. R. *J. Phys. Chem.* **1987**, *86*, 4070.

[96] Almlöf, J.; Helgaker, T.; Taylor, P. R. *J. Phys. Chem.* **1988**, *92*, 3029.

[97] Almlöf, J.; Taylor, P. R. *Adv. Quantum Chem.* **1991**, *22*, 301.

[98] Jankowski, K.; Becherer, R.; Scharf, P.; Schiffer, H.; Ahlrichs, R. *J. Chem. Phys.* **1985**, *82*, 1413.

[99] van Duijneveldt. F. B. In *IBM Research Report RJ*; San Jose, California, 1971; p 945.

[100] Bauschlicher Jr., C. W.; Taylor, P. R. *Theor. Chim. Acta* **1993**, *86*, 13.

[101] Bauschlicher Jr., C. W. *Theor. Chim. Acta* **1995**, *92*, 183.

[102] Widmark, P.-O.; Malmqvist, P. øA.; Roos, B. O. *Theor. Chim. Acta* **1990**, *77*, 291.

[103] Widmark, P.-O.; Persson, B. J.; Roos, B. O. *Theor. Chim. Acta* **1991**, *79*, 419.

[104] Pou-Amérgio, R.; Merchán, M.; Nebot-Gil, P.-O., I. Widmark; Roos, B. O. *Theor. Chim. Acta* **1995**, *92*, 149.

[105] Pierloot, K.; Dumez, B.; Widmark, P.-O.; Roos, B. O. *Theor. Chim. Acta* **1995**, *90*, 87.

[106] Roos, B. O.; Veryazov, V.; Widmark, P.-O. *Theor. Chem. Acc.* **2004**, *111*, 345.

[107] Roos, B.; Lindh, R.; Malmqvist, P.-øA.; Veryazov, V.; Widmark, P.-O. *Phys. Chem. A* **2005**, *109*, 6575.

[108] Roos, B.; Lindh, R.; Malmqvist, P.-øA.; Veryazov, V.; Widmark, P.-O.; Borin, A. C. *J. Phys. Chem. A* **2008**, *112*, 11431.

[109] Roos, B.; Lindh, R.; Malmqvist, P.-øA.; Veryazov, V.; Widmark, P.-O. *Phys. Chem. A* **2004**, *108*, 2851.

[110] Roos, B.; Lindh, R.; Malmqvist, P.-øA.; Veryazov, V.; Widmark, P.-O. *Chem. Phys. Lett.* **2005**, *409*, 295.

[111] Aquilante, F.; De Vico, L.; Ferré, N.; Ghigo, G.; Malmqvist, P.-øA.; Neogrády, P.; Pedersen, T. B.; Pitonak, M.; Reiher, M.; Roos, B. O.; Serrano-Andrés, L.; Urban, M.; Veryazov, R. *J. Comput. Chem.* **2010**, *31*, 224.

[112] Feller, D.; Peterson, K. A.; Hill, J. G. *J. Chem. Phys.* **2011**, *135*, 044102.

[113] Feller, D.; Peterson, K. A.; Crawford, T. D. *J. Chem. Phys.* **2006**, *124*, 054107.

[114] Prascher, B. P.; Woon, D. E.; Peterson, K. A.; Dunning, T. H.; Wilson, A. K. *Theor. Chem. Acc.* **2011**, *128*, 69.

[115] van Mourik, T.; Wilson, A. K.; Dunning, T. H. *J. Mol. Struct. (THEOCHEM)* **1996**, *388*, 339.

[116] Woon, D. E.; Dunning, T. H. *J. Chem. Phys.* **1994**, *100*, 2975.

[117] Woon, D. E.; Dunning, T. H. *J. Chem. Phys.* **1993**, *98*, 1358.

[118] van Mourik, T.; Dunning, T. H. *Int. J. Quantum Chem.* **2000**, *76*, 205.

[119] Wilson, K. A.; Peterson, K. A.; Woon, D. E.; Dunning, T. H. *J. Chem. Phys.* **1999**, *110*, 7667.

[120] Peterson, K. A. *Ann. Reports Comput. Chem.* **2007**, *3*, 195.

[121] Kendall, R. A.; Dunning Jr., T. H.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796.

[122] Peterson, K. A.; Dunning Jr., T. H. *J. Chem. Phys.* **2002**, *117*, 10548.

[123] DeYonker, N. J.; Peterson, K. A.; Wilson, A. K. *J. Phys. Chem. A* **2007**, *111*, 11383.

[124] Hill, J. G.; Mazumder, S.; Peterson, K. A. *J. Chem. Phys.* **2010**, *132*, 054108.

[125] Reiher, M.; Wolf, A. *J. Chem. Phys* **2004**, *121*, 2037.

[126] de Jong, W. A.; Harrison, R. J.; Dixon, D. A. *J. Chem. Phys.* **2001**, *114*, 48.

[127] Bergner, A.; Dolg, M.; Küchle, W.; Stoll, H.; Preuß, H. *Mol. Phys.* **1993**, *80*, 1431.

[128] Martin, J. M. L.; Sundermann, A. *J. Chem. Phys.* **2001**, *114*, 3408.

[129] Metz, B.; Stoll, H.; M., D. *J. Chem. Phys.* **2000**, *113*, 2563.

[130] Peterson, K. A. *J. Chem. Phys.* **2003**, *119*, 11099.

[131] Peterson, K. A.; Figgen, D.; Goll, E.; Stoll, H.; Dolg, M. *J. Chem. Phys.* **2003**, *119*, 11113.

[132] Peterson, K. A.; Yousaf, K. E. *J. Chem. Phys.* **2010**, *113*, 174116.

[133] Peterson, K. A.; Shepler, B. C.; Figgen, D.; Stoll, H. *J. Phys. Chem. A* **2006**, *110*, 13877.

[134] K. A. Peterson, K. A.; Shepler, B. C.; Figgen, D.; H., S. *J. Phys. Chem. A* **2006**, *110*, 13877.

[135] Dyall, K. G. *Theor. Chim. Acta* **1998**, *99*, 366.

[136] Dyall, K. G. *Theor. Chim. Acta* **1998**, *108*, 365.

[137] Dyall, K. G. *Theor. Chim. Acta* **2002**, *108*, 335.

[138] Dyall, K. G. *Theor. Chim. Acta* **2002**, *115*, 441.

[139] Dyall, K. G. *Theor. Chim. Acta* **2012**, *131*, 1217.

[140] Dyall, K. G. *Theor. Chim. Acta* **2012**, *131*, 1172.

[141] Hill, J. G. *J. Comp. Chem.* **2013**, *34*, 2168.

[142] Peterson, K. A.; Adler, T. B.; Werner, H.-J. *J. Chem. Phys.* **2008**, *128*, 084102.

[143] Hill, J. G.; Peterson, K. A. *Phys. Chem. Chem. Phys.* **2010**, *12*, 10460.

[144] Hill, J. G.; Peterson, K. A. *J. Chem. Phys.* **2014**, *141*, 094106.

[145] Press, W. H.; Teukolsky, S. A.; Vetterling, W. T.; Flannery, B. P. *Numerical Recipies in FORTRAN: The Art of Scientific Computing*, 2nd ed.; Cambridge University Press: Cambridge, 1192.

[146] Weigend, F. *Phys. Chem. Chem. Phys.* **2002**, *4285*, 4.

[147] Hättig, C. *Phys. Chem. Chem. Phys.* **2005**, *7*, 59.

[148] Jensen, F. *J. Chem. Phys.* **2001**, *115*, 9113.

[149] Jensen, F.; Helgaker, T. *J. Chem. Phys.* **2004**, *121*, 3463.

[150] Feller, D. *J. Chem. Phys.* **1992**, *96*, 6104.

[151] Halkier, A.; Helgaker, T.; Jørgensen, P.; Klopper, W.; Olsen, J. *Chem. Phys. Lett.* **1999**, *302*, 437.

[152] Dunning, T. H.; Peterson, K. A.; Wilson, K. A. *J. Chem. Phys.* **2001**, *114*, 9244.

[153] Peterson, K. A.; Dunning, T. H. *J. Chem. Phys.* **2002**, *117*, 10548.

[154] Pipek, J.; Mezey, P. G. *J. Chem. Phys.* **1989**, *90*, 4916.

[155] Flores, J. R. *J. Chem. Phys.* **1993**, *98*, 5642.

[156] Werner, H. J.; Manby, F. R. *J. Chem. Phys.* **2006**, *124*, 0545114.

[157] Hill, J. G.; Mazumder, S.; Peterson, K. A. *J. Chem. Phys.* **2010**, *132*, 054108.

[158] Prascher, B. P.; Woon, D. E.; Peterson, K. A.; Dunning, T. H.; Wilson, A. K. *Theor. Chem. Acc.* **2011**, *128*, 69.

[159] Iron, M. A.; Oren, M.; Martin, J. M. L. *Mol. Phys* **2003**, *101*, 1345.

[160] Vasiliu, M.; Li, S.; Peterson, K. A.; Feller, D.; Gole, J. L.; Dixon, D. A. *J. Phys. Chem. A* **2010**, *114*, 4272.

[161] Schwenke, D. W. *J. Chem. Phys.* **2005**, *122*, 014107.

[162] Hill, J. G.; Peterson, K. A.; Knizia, G.; Werner, H. J. *J. Chem. Phys.* **2009**, *131*, 194105.

[163] Adler, T. B.; Knizia, G.; J., W. H. *J. Chem. Phys.* **2007**, *127*, 221106.

[164] Hill, J. G.; Peterson, K. A. *J. Chem. Phys.* **2014**, *141*, 094106.

[165] Peterson, K. A.; Figgen, D.; Goll, E.; Stoll, H.; Gold, M. *J. Chem. Phys.* **2003**, *119*, 11113.

[166] Peterson, K. A.; Shelper, B. C.; Figgen, D.; Stoll, H. *J. Chem. Phys.* **2006**, *110*, 13877.

[167] Metz, B.; Schweizer, M.; Stoll, H.; Dolg, M.; Liu, W. *Theor. Chem. Acc.* **200**, *104*, 22.

[168] Metz, B.; Stoll, H.; Dolg, M. *J. Chem. Phys.* **2000**, *113*, 2563.

[169] Weigend, F. *J. Comp. Chem.* **2008**, *29*, 167.

[170] Peterson, K. A. *J. Chem. Phys.* **2003**, *119*, 11099.

[171] Peterson, K. A.; Shepler, B. C.; Figgen, D.; Stoll, H. *J Phys. Chem. A* **2006**, *110*, 13877.

[172] Peterson, K. A.; Wilson, A. K. *J. Phys. Chem. A* **2007**, *111*, 11383.

[173] Helgaker, T.; Klopper, W.; Koch, H.; Noga, J. *J. Chem. Phys.* **1997**, *106*, 9639.

[174] Halkier, A.; Helgaker, T.; Jørgensen, P.; Klopper, W.; Koch, H.; Olsen, J.; Wilson, A. K. *Chem. Phys. Lett.* **1998**, *286*, 243.

[175] Peterson, K. A.; Krause, C.; Stoll, H.; Hill, G. J.; Werner, H. J. *Mol. Phys.* **2011**, *109*, 2607.

[176] Peterson, K. A.; Yousaf, K. E. *J. Chem. Phys.* **2010**, *133*, 1434.

[177] Valeev, E. F. *Chem. Phys. Lett.* **2004**, *395*, 190.

[178] Yousaf, K. E.; Peterson, K. A. *J. Chem. Phys.* **2008**, *129*, 184108.

[179] Yousaf, K. E.; Peterson, K. A. *Chem. Phys. Lett.* **2009**, *476*, 303.

[180] Weigend, F.; Häser, M.; Patzelt, H.; Ahlrichs, R. *Chem. Phys. Lett.* **1998**, *294*, 193.

[181] Partridge, H. *J. Chem. Phys.* **1987**, *87*, 6643.

[182] Partridge, H. *J. Chem. Phys.* **1989**, *90*, 1043.

[183] Wilson, A. K.; Van Mourik, T.; Dunning, T. H. *J. Mol. Struct. (Theochem)* **1996**, *388*, 399.

[184] Van Mourik, T.; Dunning, T. H. *Int. J. Quantum Chem.* **2000**, *76*, 205.

[185] Petersson, G. A.; Zhong, S.; Montgomery, J. A.; Frisch, M. J. *J. Chem. Phys.* **2003**, *118*, 1101.

[186] Aquilante, F.; Lindh, T. B., R. Pedersen *J. Chem. Phys.* **2007**, *127*, 114107.

[187] Polly, R.; Werner, H. J.; Manby, F. R.; Knowles, P. J. *Mol. Phys.* **2004**, *8*, 102.

[188] Baerends, J.; Ellis, D. E.; Ros, P. *Chem. Phys.* **1973**, *2*, 41.

[189] Dunlap, B. I.; Connolly, J. W. D.; Sabin, J. R. *J. Chem. Phys.* **1979**, *71*, 3396.

[190] Hättig, C.; Weigend, F. *J. Chem. Phys.* **2000**, *113*, 5154.

[191] Weigend, F.; Köhn, A.; Hättig, C. *J. Chem. Phys.* **2002**, *116*, 3175.

[192] Weigend, F.; Häser *Theor. Chim. Acta* **1997**, *97*, 331.

[193] Hättig, C. *J. Chem. Phys.* **2003**, *118*, 7751.

[194] Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kölmel, C. *J. Chem. Phys.* **1989**, *162*, 165.

[195] Hill, J. G. *J. Comp. Chem.* **2013**, *34*, 2168.

[196] Hill, J. G.; Peterson, K. A. *J. Chem. Theory Comput.* **2012**, *8*, 518.

[197] Hill, J. G. *J. Chem. Phys.* **2011**, *135*, 044105.

[198] Hill, J. G.; Platts, J. A. *J. Chem. Theory Comput.* **2009**, *5*, 500.

[199] Hill, J. G.; Platts, J. A. *J. Chem. Phys.* **2008**, *128*, 044104.

[200] Nelder, J.; Mead, R. *Comput. J.* **1965**, *7*, 308.

[201] Pierloot, K. In *Computational Organometallic Chemistry*; Marcel Dekker Inc.: New York, 2001.

[202] Mathews, J. H.; Fink, K. K. *Numerical Methods Using Matlab*, 4th ed.; Prentice-Hall Inc., 2004; Chapter 8.

[203] Wright, M. In *Proceedings of the 1995 Dundee Biennial Conference in Numerical Analysis*; Griffiths, D. F.; Watson, G. A., Eds.; Addison Wesley Longman: Harlow, UK, 1996; p 191.

[204] Lagarias, J.; Reeds, J.; Wright, M.; Wright, P. *SIAM J. Optim.* **1998**, *9*, 112.

[205] Powell, M. J. D. *Mathematical Programming* **1973**, *4*, 193.

[206] McKinnon, K. I. M. *SIAM J Optimization* **1999**, *9*, 148.

[207] Zhongguo, K. Y. *Scientia Sinica* **1979**, 53.

[208] Zhongguo, K. Y. *Scientia Sinica* **1979**, 69.

[209] Kolda, T. G.; Lewis, R. M.; Torczon, V. *SIAM Rev.* **2003**, *45*, 385.

[210] Lewis, R. M.; Shepherd, A.; Torczon, V. *SIAM J. Sci. Comput.* **2007**, *29*, 2507.

[211] Deuflhard, P. In *Computational Mathematics*; Springer International, 2004; Vol. 35.

[212] Davidson, W. In *A.E.C. Research and Development Report, ANL-5990*.

[213] Fletcher, R.; Powell, M. *Comput. J* **1963**, *6*, 163.

[214] John, D. H.; Michael, C. Z. *Chem. Phys. Lett.* **1985**, *122*, 264.

[215] Werner, H.-J.; Knowles, P. J.; Knizia, G.; Manby, F. R.; Schütz, M.; Celani, P.; Korona, T.; Lindh, R.; Mitrushenkov, A.; Rauhut, G.; Shamasundar, K. R.; Adler, T. B.; Amos, R. D.; Bernhardsson, A.; Berning, A.; Cooper, D. L.; Deegan, M. J. O.; Dobbyn, A. J.; Eckert, F.; Goll, E.; Hampel, C.; Hesselmann, A.; Hetzer, G.; Hrenar, T.; Jansen, G.; Köppl, C.; Liu, Y.; Lloyd, A. W.; Mata, R. A.; May, A. J.; McNicholas, S. J.; Meyer, W.; Mura, M. E.; Nicklass, A.; O'Neill, D. P.; Palmieri, P.; Peng, D.; Pflüger, K.; Pitzer, R.; Reiher, M.; Shiozaki, T.; Stoll,

H.; Stone, A. J.; Tarroni, R.; Thorsteinsson, T.; Wang, M.; *MOLPRO, version 2012.1, a package of ab initio programs*.

[216] *TURBOMOLE V6.2 2010, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007; available from* `http://www.turbomole.com`.

[217] Hättig, C. *Phys. Chem. Chem. Phys.* **2008**, *7*, 59.

[218] Hättig, C.; Weigend, F. *J. Chem. Phys.* **2000**, *113*, 5154.

[219] Hättig, C. *J. Chem. Phys.* **2003**, *118*, 7751.

[220] Whitten, J. L. *J. Chem. Phys.* **1973**, *58*, 4496.

[221] Vahtras, O.; Almlöf, J. E.; Feyereisen, M. W. *Chem. Phys. Lett.* **1993**, *213*, 514.

[222] Kendall, R. A.; Frúchtl, H. A. *Theor. Chem. Acc.* **1997**, *97*, 158.

[223] Ten-No, S.; Manby, F. R. *J. Chem. Phys.* **2003**, *119*, 5358.

[224] Werner, H.-J.; Manby, F. R.; Knowles, P. J. *J. Chem. Phys.* **2003**, *118*, 8149.

[225] Manby, F. R. *J. Chem. Phys.* **2003**, *119*, 4607.

[226] Schütz, M.; Werner, H.-J.; Lindh, R.; Manby, F. R. *J. Chem. Phys.* **2004**, *121*, 737.

[227] Werner, H.-J.; Manby, F. *J. Chem. Phys.* **2006**, *124*, 054114.

[228] Feyereisen, M.; Fitzgerald, G.; Komornicki, A. *Chem. Phys. Lett.* **1993**, *208*, 359.

[229] Pedersen, T. B.; Aquilante, F.; Lindh, R. *Theor. Chem. Acc.* **2009**, *124*, 1.

[230] Aquilante, F.; Boman, L.; J., B.; Koch, H.; Lindh, R.; Sánchez deMerás, A.; Pedersen, T. B. In *Linear-Scaling Techniques in Computational Chemistry and Physics*; Zalešny, R.; Papadopoulos, M. G.; Mezey, P. G.; Leszczynski, J., Eds.; Springer: Berlin, 2011; Vol. 13, p 301.

[231] Aquilante, F.; Lindh, R.; Pedersen, T. B. *J. Chem. Phys.* **2007**, *127*, 114107.

[232] Weigend, F. *Phys. Chem. Chem. Phys.* **2002**, *4285*, 4.

[233] Weigend, F.; Furche, F.; Ahlrichs, R. *J. Chem. Phys.* **2003**, *119*, 12753.

[234] Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.

[235] Weigend, F. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057.

[236] Hellweg, A.; Hättig, C.; Höfener, S.; Klopper, W. *Theor. Chem. Acc.* **2007**, *117*, 587.

[237] Hill, J. G. *J. Chem. Phys.* **2011**, *135*, 044105.

[238] Peterson, K. A.; Adler, T.; Werner, H.-J. *J. Chem. Phys.* **2008**, *128*, 084102.

[239] Hättig, C.; Weigend, F. *J. Chem. Phys.* **2000**, *113*, 5154.

[240] Werner, H.-J.; Knowles, P. J.; Knizia, G.; Manby, F. R.; Schütz, M. *WIREs Comput Mol Sci* **2012**, *2*, 242–253.

[241] Hill, J. G.; Peterson, K. A. *J. Chem. Theory Comput.* **2012**, *8*, 518.

[242] Yousaf, K. E.; Peterson, K. A. *J. Chem. Phys.* **2008**, *129*, 184108.

[243] Yousaf, K. E.; Peterson, K. A. *Chem. Phys. Lett.* **2009**, *476*, 303.

[244] Valeev, E. F. *Chem. Phys. Lett.* **2004**, *395*, 190.

[245] Klopper, W.; Samson, C. C. M. *J. Chem. Phys.* **2002**, *116*, 6397.

[246] Werner, H.-J.; Adler, T. B.; Manby, F. R. *J. Chem. Phys.* **2007**, *126*, 164102.

[247] Weigend, F.; Köhn, A.; Hättig, C. *J. Chem. Phys.* **2002**, *116*, 3175.

[248] Hill, J. G.; Peterson, K. A.; Knizia, G.; Werner, H.-J. *J. Chem. Phys.* **2009**, *19*, 194105.

[249] Weigend, F. *J. Comp. Chem.* **2007**, *29*, 167.

[250] Schwenke, D. *J. Chem. Phys.* **2005**, *122*, 014107.

[251] Feller, D. *J. Comp. Chem.* **1996**, *17*, 1571.

[252] Schuchardt, K. L.; Didier, B. T.; Elsethagen, T.; Sun, L.; Gurumoorthi, V.; Chase, J.; Li, J.; Windus, T. L. *J. Chem. Inf. Model.* **2007**, *47*, 1045.

[253] Bauschlicher, C. W. *Theor. Chem. Acc.* **1999**, *103*, 141.

[254] Ricca, A.; Bauschlicher, C. W. *Theor. Chem. Acc.* **2001**, *106*, 314.

[255] Balabanov, B.; Peterson, K. A. *J. Chem. Phys.* **2005**, *123*, 064107.

[256] Balabanov, B.; Peterson, K. A. *J. Chem. Phys.* **2006**, *125*, 074110.

[257] Peterson, K. A.; Puzzarini, C. *Theor. Chem. Acc.* **2005**, *114*, 283.

[258] D. Figgen, A.; Rauhut, G.; Dolg, M.; Stoll, H. *Chem. Phys.* **2005**, *311*, 227.

[259] Peterson, K. A.; Figgen, D.; Dolg, M.; Stoll, H. *J. Chem. Phys.* **2007**, *126*, 124101.

[260] Figgen, D.; Peterson, K. A.; Stoll, H. *J. Chem. Phys.* **2008**, *128*, 034110.

[261] D. Figgen, A.; Peterson, K. A.; Dolg, M.; Stoll, H. *J. Chem. Phys.* **2009**, *130*, 164108.

[262] Werner, H.-J.; Adler, T. B.; Knizia, G.; Manby, F. R. In *Recent Progress in Coupled Cluster Methods: Theory and Applications*; Čársky P., P.; Paldus, J.; Pittner, J., Eds.; Springer: Berlin, 2010; p 573.

[263] DePrince, A. E.; Sherrill, C. D. *J. Chem. Theory Comput.* **2013**, *9*, 2687.

[264] Weigend, F.; Kattannek, M.; Ahlrichs, R. *J. Chem. Phys.* **2009**, *130*, 164106.

[265] Blaudeau, J.-P.; Brozell, S. R.; Matsika, S.; Zhang, Z.; Pitzer, R. M. *Int. J. Quantum Chem.* **2000**, *77*, 516.

[266] Hill, J. G.; Platts, J. A. *J. Chem. Phys.* **2008**, *128*, 044104.

[267] Kritikou, S.; Hill, J. G. *J. Chem. Theory Comput.* **2015**, *11*, 5269.

[268] Kohn, W.; Becke, A. D.; Parr, R. G. *J. Phys. Chem.* **1996**, *100*, 12974.

[269] Frenking, G.; Frohlich, N. *Chem. Rev.* **2000**, *100*, 717.

[270] Russo, T. V.; L., M. R.; Hay, P. J. *J. Chem. Phys.* **1994**, *101*, 7729.

[271] Siegbahn, P. E. M.; Blomberg, M. R. A. *Chem. Rev.* **2000**, *100*, 421.

[272] Zhao, Y.; Truhlar, D. G. *Acc. Chem. Res.* **2008**, *41*, 157.

[273] Pople, J. A.; Head-Gordon, M.; Fox, D. J.; Raghavachari, K.; Curtiss, L. A. *J. Chem. Phys* **1989**, *90*, 5622.

[274] Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.

[275] Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 7764.

[276] Curtiss, L. A.; Redfern, P. C.; Raghavachari, K. *J. Chem. Phys.* **2007**, *126*, 084108.

[277] Martin, J. M. L.; de Oliveira, G. *J. Chem. Phys.* **1999**, *115*, 1843.

[278] Boese, A. D.; Oren, M.; Atasoylu, O.; Martin, J. M. L.; Kállay, M.; Gauss, J. *J. Chem. Phys.* **2004**, *120*, 4129.

[279] Karton, A.; Rabinovich, E.; Martin, J. M. L.; Ruscic, B. *J. Chem. Phys.* **2006**, *125*, 144108.

[280] Nyden, M. R.; Petersson, G. A. *J. Chem. Phys.* **1981**, *75*, 1843.

[281] Montgomery Jr, J. A.; Ochterski, J. W.; Petersson, G. A. *J. Chem. Phys.* **1994**, *101*, 5900.

[282] Ochterski, J. W.; Petersson, G. A.; Montgomery Jr, J. A. *J. Chem. Phys.* **1996**, *104*, 2598.

[283] Wood, G. P. F.; Radom, L.; Petersson, G. A.; Barnes, E. C.; Frisch, M. J.; Montgomery Jr, J. A. *J. Chem. Phys.* **2006**, *125*, 094106.

[284] Feller, D.; Peterson, K. A.; Dixon, D. A. *J. Chem. Phys.* **2008**, *129*, 204105.

[285] Li, S.; Hennigan, J. M.; Dixon, D. A.; Peterson, K. A. *J. Phys. Chem. A* **2009**, *113*, 7861.

[286] DeYonker, N. J.; Peterson, K. A.; Steyl, G.; Wilson, A. K.; Cundari, T. R. *J. Phys. Chem. A* **2007**, *111*, 11269.

[287] Jiang, W.; DeYonker, N. J.; Determan, J. J.; Wilson, A. K. *J. Phys. Chem. A* **2012**, *116*, 870.

[288] East, A. L. L.; Allen, W. D.; Császár, A. G. In *Structure and Conformations of Non-Rigid Molecules*; Laane, J.; Dakkouri, M.; van der Veken, B.; O., K. H., Eds.; NATO ASI Series: Dordrecht, 1993; pp 343–373.

[289] Császár, A. G.; Allen, W. D.; Schaefer III, H. F. *J. Chem. Phys.* **1998**, *108*, 9751.

[290] Tajti, A.; Szalay, P. G.; Császár, A. G.; Kállay, M.; Gauss, J.; Valeev, E. F.; Flowers, B. A.; Vázquez, J.; Stanton, J. F. *J. Chem. Phys.* **2004**, *121*, 11599.

[291] Bross, D. H.; Hill, J. G.; Werner, H.-J.; Peterson, K. A. *J. Chem. Phys.* **2013**, *139*, 094302.

[292] Curtiss, L. A.; Jones, C.; Trucks, G. W.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys* **1990**, *93*, 2537.

[293] Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968.

[294] Curtiss, L. A.; Jones, C.; W., T. G.; Raghavachari, K.; A., P. J. *J. Chem. Phys.* **1990**, *92*, 2537.

[295] Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

[296] Kong, L.; Bischoff, F. A.; Valeev, E. F. *Chem. Rev.* **2012**, *112*, 75.

[297] Raghavachari, K.; Pople, J. A. *Int. J. Quantum Chem.* **1978**, *14*, 91.

[298] Raghavachari, K.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.

[299] Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1989**, *80*, 3265.

[300] Handy, N. C.; Knowles, P. J.; Sornasundrarn, K. *Theor. Chim. Acta* **1985**, *68*, 87.

[301] Raghavachari, K. *J. Chem. Phys.* **1985**, *82*, 4607.

[302] Nobes, R. H.; Pople, J. A.; Radom, L.; Handy, N. C.; Knowles, P. J. *J. Chem. Phys. Lett.* **1987**, *138*, 481.

[303] Pople, J. A.; Schlegel, H. B.; Krishnan, R.; Defrees, D. J.; Binkley, J. S.; Frisch, M. J.; Whiteside, R. A.; Hout, R. F.; Hehre, W. J. *Int. J. Quantum Chem. Symp.* **1981**, *15*, 269.

[304] Curtiss, L. A.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1993**, *98*, 1293.

[305] Bauschlicher Jr, C. W.; Partridge, H. *J. Chem. Phys.* **1995**, *103*, 1788.

[306] Smith, B. J.; Radom, L. *J. Phys. Chem.* **1995**, *99*, 6468.

[307] Curtiss, L. A.; Redfern, P. C.; Smith, B. J.; Radom, L. *J. Chem. Phys.* **1996**, *104*, 5148.

[308] Curtiss, L. A.; Redfern, P. C.; Raghavachari, K.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1999**, *110*, 4703.

[309] Baboul, A. G.; Curtiss, L. A.; Redfern, P. C.; Raghavachari, K. *J. Chem. Phys.* **1999**, *110*, 7650.

[310] Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Baboul, A. G.; Pople, J. A. *Chem. Phys. Lett.* **1999**, *314*, 101.

[311] Curtiss, L. A.; Redfern, P. C.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **2001**, *114*, 108.

[312] Henry, D. J.; Sullivan, M. B.; Radom, L. *J. Chem. Phys.* **2003**, *118*, 4849.

[313] Curtiss, L. A.; Redfern, P. C.; Raghavachari, K. *J. Chem. Phys.* **2007**, *127*, 124105.

[314] Gdanitz, R. J.; Ahlrichs, R. *Chem. Phys. Lett.* **1988**, *143*, 413.

[315] Barnes, E. C.; Petersson, G. A.; Montgomery, J. J. A.; Frisch, M. J.; Martin, J. M. L. *J. Chem. Theory Comput.* **2009**, *5*, 2687.

[316] Karton, A.; Rabinovich, E.; Martin, J. M. L.; Ruscic, B. *J. Chem. Phys.* **2006**, *125*, 144108.

[317] Mintz, B.; Chan, B.; Sullivan, M. B.; Buesgen, T.; Scott, A. P.; Kass, S. R.; Radom, L.; Wilson, A. K. *J. Phys. Chem. A* **2009**, *113*, 9501.

[318] Karton, A.; Taylor, P. R.; Martin, J. M. L. *J. Chem. Phys.* **127**, *064104*.

[319] Karton, A.; Martin, J. M. L. *J. Chem. Phys.* **2012**, *136*, 124114.

[320] Petersson, G. A.; Bennett, A.; Tensfeldt, T. G.; Al-Laham, M. A.; Shirley, W. A.; Mantzaris, J. *J. Chem. Phys.* **1988**, *89*, 2193.

[321] Petersson, G. A.; Al-Laham, M. A. *J. Chem. Phys.* **1991**, *94*, 6081.

[322] Petersson, G. A.; Tensfeldt, T. G.; Montgomery Jr, J. A. *J. Chem. Phys.* **1991**, *94*, 6091.

[323] Karton, A.; Daon, S.; Martin, J. M. L. *Chem. Phys. Lett.* **2010**, *210*, 165.

[324] Montgomery Jr, J. A.; Frisch, M. J.; Ochterski, J. W.; Petersson, G. A. *J. Chem. Phys.* **1999**, *110*, 2822.

[325] Mayer, P. M.; Parkinson, C. J.; Smith, D. M.; Radom, L. *J. Chem. Phys.* **1998**, *108*, 604.

[326] Feller, D.; Peterson, K. A.; Dixon, D. A. *Mol. Phys.* **2012**, *110*, 2381.

[327] Peterson, K. A.; Feller, D.; Dixon, D. A. *Theor. Chem. Acc.* **2012**, *131*, 1079.

[328] Feller, D.; Peterson, K. A.; Dixon, D. A. *Mol. Phys.* **2012**, *110*, 2381.

[329] Dixon, D. A.; Feller, D.; Peterson, K. A. *Annu. Rep. Comput. Chem.* **2012**, *8*, 1.

[330] Feller, D.; Peterson, K. A.; Ruscic, B. *Theor. Chem. Acc.* **2014**, *133*, 1407.

[331] Pollack, L.; Windus, T. L.; de Jong, W. A.; Dixon, D. A. *J. Phys. Chem. A* **2005**, *109*, 6934.

[332] Feller, D.; Peterson, K. A.; Crawford, T. D. *J. Chem. Phys.* **2006**, *124*, 054107.

[333] Douglas, M.; Kroll, N. M. *Ann. Phys.* **1974**, *82*, 89.

[334] Jansen, G.; A., H. B. *Phys. Rev. A* **1989**, *36*, 6016.

[335] de Jong, W. A.; Harrison, R. J.; Dixon, D. A. *J. Chem. Phys.* **2001**, *114*, 48.

[336] Dunham, J. L. *Phys. Rev.* **1932**, *41*, 713.

[337] Kutzelnigg, W. *Mol. Phys.* **1997**, *90*, 909.

[338] Werner, H.-J.; Knizia, G.; Adler, T. B.; Marchetti, O. *2010* **J. Phys. Chem.**, *224*, 493.

[339] D. P. Tew, D. P.; Hättig, C.; Bachorz, R. A.; Klopper, W. In *Recent Progress in Coupled Cluster Methods*; Cársky, P.; Paldus, J.; Pittner, J., Eds.; Springer: Dordrecht, 2010.

[340] Werner, H.-J.; Adler, T. B.; Knizia, G.; Manby, F. R. In *Recent Progress in Coupled Cluster Methods*; Cársky, P.; Paldus, J.; Pittner, J., Eds.; Springer: Dordrecht, 2010.

[341] Kong, L.; Bischoff, F. A.; Valeev, E. F. *Chem. Rev.* **2012**, *112*, 75.

[342] Hättig, C.; Klopper, W.; Köhn, A.; Tew, D. P. *Chem. Rev.* **2012**, *112*, 4.

[343] Knizia, G.; Adler, T. B.; Werner, H.-J. *J. Chem. Phys.* **2009**, *130*, 054104.

[344] Pfeiffer, F.; Rauhut, G.; Feller, D.; Peterson, K. A. *J. Chem. Phys.* **2013**, *138*, 044311.

[345] Kállay, M.; Rolik, Z.; Csontos, J.; Ladjánszki, I.; Szegedy, L.; Ladóczki, B.; Samu, G.; Petrov, K.; Farkas, M.; Nagy, P.; Mester, D.; Hégely, B.; *MRCC, a string-based quantum chemical program suite*; See also www.mrcc.hu.

[346] Rolik, Z.; Szegedy, L.; Ladjánszki, I.; Ladóczki, B.; Kállay, M. *J. Chem. Phys.* **2013**, *139*, 094105.

[347] Feller, D. *J. Chem. Phys.* **1992**, *96*, 6104.

[348] Peterson, K. A.; Woon, D. E.; Dunning Jr., T. H. *J. Chem. Phys.* **1994**, *100*, 7410.

[349] Kedrioza, G. S.; Pople, J. A.; Ratner, M. A.; Redfern, P. C.; Curtiss, L. A. *J. Chem. Phys.* **2001**, *115*, 718.

[350] DeYonker, N. J.; Grimes, T.; Yokel, S.; Dinescu, A.; Mintz, B.; Cundari, T. R.; Wilson, A. K. *J. Chem. Phys.* **2006**, *125*, 104111.

[351] DeYonker, N. J.; Peterson, K. A.; Steyl, A. K., G. Wilson; Cundari, T. R. *J. Phys. Chem. A* **2007**, *111*, 11269.

[352] DeYonker, N. J.; Williams, T. G.; Imel, A. E.; Cundari, T. R.; Wilson, A. K. *J. Chem. Phys.* **2009**, *131*, 024106.

[353] Mintz, B.; Williams, T. G.; Howard, L.; Wilson, A. K. *J. Chem. Phys.* **2009**, *130*, 234104.

[354] Prascher, B. P.; Lai, J. D.; Wilson, A. K. *J. Chem. Phys.* **2009**, *131*, 044130.

[355] Schütz, M. *J. Chem. Phys.* **2000**, *113*, 9986.

[356] Schütz, M.; Werner, H.-J. *Chem. Phys. Lett.* **2000**, *318*, 370.

[357] DeYonker, N. J.; Wilson, B. R.; Pierpont, A. W.; Cundari, T. R.; Wilson, A. K. *Mol. Phys.* **2009**, *107*, 1107.

[358] Valeev, E. F. *Chem. Phys. Lett.* **2004**, *395*, 190.

[359] Helgaker, T.; Klopper, W.; Koch, H.; Noga, J. *J. Chem. Phys.* **1997**, *106*, 9639.

[360] Bomble, Y. J.; Vázquez, J.; Kállay, M.; Michauk, C.; Szalay, P. G.; Császár, A. G.; Gauss, J.; Stanton, J. F. *J. Chem. Phys.* **2006**, *125*, 064108.

[361] Harding, M. E.; Vazquez, J.; Ruscic, B.; Wilson, A. K.; Gauss, J.; Stanton, J. F. *J. Chem. Phys.* **2008**, *138*, 114111.

[362] East, A. L. L.; Allen, W. D.; Császár, A. G. In *Structure and conformations of non-rigid molecules*; Laane, J.; van der Veken, B.; Overhammer, H., Eds.; Kluwer: Dordrecht, 1993.

[363] East, A. L. L.; Allen, W. D. *J. Chem. Phys.* **1993**, *99*, 4638.

[364] Császár, A. G.; Allen, W. D.; Schaefer III, H. F. *J. Chem. Phys.* **1998**, *108*, 9751.

[365] Schuurman, M. S.; Muir, S. R.; Allen, W. D.; Schaefer III, H. F. *J. Chem. Phys.* **2004**, *120*, 11586.

[366] East, A. L. L.; Johnson, C. S.; Allen, W. D. *J. Chem. Phys.* **1993**, *98*, 1299.

[367] Wolf, A.; Reiher, M.; A., H. B. *J. Chem. Phys.* **2002**, *117*, 9215.

[368] Xu, X.; Zhang, W.; Tang, M.; Truhlar, D. G. *J. Chem. Theory Comput.* **2015**, *11*, 2036.

[369] Knowles, P. J.; Hampel, C.; Werner, H.-J. *J. Chem. Phys.* **1993**, *99*, 5219.

[370] Knowles, P. J.; Hampel, C.; Werner, H.-J. *J. Chem. Phys.* **2000**, *112*, 3106.

[371] Dunning Jr., T. H.; Peterson, K. A.; Wilson, A. K. *J. Chem. Phys.* **2001**, *114*, 9244.

[372] Werner, H.-J.; Adler, T. B.; Manby, F. R. *J. Chem. Phys.* **2007**, *126*, 164102.

[373] Ten-no, S. *J. Chem. Phys.* **2004**, *121*, 117.

[374] Ten-no, S. *Chem. Phys. Lett.* **2004**, *398*, 56.

[375] Yousaf, K. E.; Peterson, K. A. *Chem. Phys. Lett.* **2009**, *476*, 303.

[376] Chandra, P.; Buenker, R. J. *J. Chem. Phys.* **1983**, *79*, 358.

[377] Chandra, P.; Buenker, R. J. *J. Chem. Phys.* **1983**, *79*, 366.

[378] Yungman, V. S. In *Thermal Constants of Substances*; Wiley: New York, 1999.

[379] Chase, J. M. W.; Davies, C. A.; Downey, J. J. R.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. *NIST-JANAF Tables J. Phys. Chem. Ref. Data, Monogr.* **1998**, *9*, 1.

[380] Jiang, W.; DeYonker, N. J.; Determan, J. J.; Wilson, A. K. *J. Phys. Chem. A* **2011**, *116*, 870.

[381] Werner, H.-J.; Knowles, P. J. *J. Chem. Phys.* **1988**, *89*, 5803.

[382] Knowles, P. J.; Werner, H.-J. *Chem. Phys. Lett.* **1988**, *145*, 514.

[383] Dunning Jr., T. H.; Botch, B. H.; Harrison, J. F. *J. Chem. Phys.* **1980**, *72*, 3419.

[384] Hill, J. G.; Peterson, K. A.; Knizia, G.; Werner, H.-J. *J. Chem. Phys.* **2009**, *131*, 194105.

[385] Feller, D.; Peterson, K. A.; Dixon, D. A. *J. Chem. Phys.* **2008**, *129*, 204105.

[386] Hughes, T.; Harvey, J.; Friesner, R. *Phys. Chem. Chem. Phys.* **2012**, *13*, 7724.

[387] Chan, B.; Karton, A.; Raghavachari, K.; Radom, L. *J. Chem. Theory Comput.* **2012**, *8*, 3159.

[388] Peterson, K. A.; Krause, C.; Stoll, H.; Hill, J. G.; Werner, H.-J. *Mol. Phys.* **2011**, *109*, 2607.

[389] Hildenbrand, D. L. *J. Chem. Phys.* **2009**, *113*, 1472.

[390] Chen, Y.; Clemmer, D. E.; Armentrout, P. B. *J. Chem. Phys.* **1993**, *98*, 4929.

[391] Balducci, G.; Gigli, G.; Guido, M. *J. Chem. Phys.* **1983**, *79*, 5616.

[392] Hildenbrand, D. L.; Lau, K. H.; Perez-Mariano, J.; Sanjurjo, A. J. *J. Phys. Chem. A* **2008**, *112*, 9978.

[393] Ebbinghaus, B. B. *Combustion and Flame* **1993**, *93*, 119.

[394] Hildenbrand, D. L. *J. Chem. Phys.* **1995**, *103*, 2634.

[395] Schultz, R. H.; Armentrout, P. B. *J. Chem. Phys.* **1991**, *94*, 2262.

[396] Fisher, E. R.; Armentrout, P. B. *J. Phys. Chem.* **1990**, *94*, 1674.

[397] Seto, J. Y.; Morbi, Z.; Charron, F.; Lee, S. K.; Bernath, P. F.; Le Roy, R. J. *J. Chem. Phys.* **1999**, *110*, 11756.

[398] Chase, J. M. W.; Davies, C. A.; Downey, J. J. R.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. In *NIST - JANAF Tables (4th ed.)*; J. Phys. Chem. Ref. Data, Mono. 9, Suppl. 1 ed., 1998.

[399] Von Szentpály, L. *J. Phys. Chem. A* **2008**, *112*, 12695.

[400] Jiang, W.; DeYonker, N. J.; Wilson, A. K. *J. Chem. Theory Comput.* **2012**, *8*, 460.

[401] Miller, A. E. S.; Miller, T. M.; Morris, R. A.; Viggiano, A. A.; Vandoren, J. M.; Paulson, J. F. *Int. J. Mass Spectrom. Ion Process.* **2005**, *123*, 205.

[402] Tanaka, K.; Sekiya, M.; Yoshimine, M. *J. Chem. Phys.* **2001**, *115*, 4558.

[403] DeYonker, N. J.; Allen, W. D. *J. Chem. Phys.* **2012**, *137*, 234303.

[404] Janssen, C. L.; Nielsen, I. M. B. *Chem. Phys. Lett.* **1998**, *423*, 37.

[405] Lee, T. J. *Chem. Phys. Lett.* **2003**, *372*, 362.

[406] Lee, T. J.; Taylor, P. R. *Int. J. Quantum Chem.* **1989**, *36*, 199.

[407] Lee, T. J.; Rice, J. E.; Scuseria, G. E.; Schaefer III, H. F. *Theor. Chim. Acta* **1989**, *75*, 87.

[408] Langhoff, S. R.; Bauschlicher, C. W. *Annu. Rev. Phys. Chem.* **1988**, *39*, 181.

[409] Leininger, M. L.; Nielsen, I. M. B.; Crawford, T. D.; Janssen, C. L. *Chem. Phys. Lett.* **2000**, *338*, 431.

[410] Karton, A.; Rabinovich, E.; Martin, J. M. L.; Ruscic, B. *J. Chem. Phys.* **2006**, *125*, 144108.

[411] Karton, A.; Daon, S.; Martin, J. M. L. *Chem. Phys. Lett.* **2011**, *510*, 165.

[412] Moore, C. E. In *Atomic energy levels, circular no. 467*; U.S. National Bureau of Standards: Washington, DC, 1949.

[413] Cramer, C. J.; Truhlar, D. G. *Phys. Chem. Chem. Phys.* **2009**, *11*, 10757.

[414] Silverstone, H. J.; Sinanoglu, O. *J. Chem. Phys.* **1966**, *44*, 1899.

[415] Schmidt, M. W.; Gordon, M. S. *Annu. Rev. Phys. Chem.* **1998**, *49*, 233.

[416] Roos, B. O.; Andersson, K.; Fulscher, M. P.; Malmqvist, P. øA.; Serrano-Andres, L.; Pierloot, K.; Merchan, M. *Adv. Chem. Phys.* **1996**, *93*, 219.

[417] Siegbahn, P. E. M. *Adv. Chem. Phys.* **1996**, *93*, 333.

[418] Li, X.; Paldus, J. *J. Chem. Phys.* **2007**, *126*, 234303.

[419] Langhoff, S. R.; Davidson, E. R. *Int. J. Quantum Chem.* **1974**, *8*, 61.

[420] Sears, J. S.; Sherrill, C. D. *J. Phys. Chem. A* **2008**, *112*, 6741.

[421] Sears, J. S.; Sherrill, C. D. *J. Phys. Chem. A* **2008**, *112*, 3466.

[422] Aoto, Y. A.; de Lima Batista, A. P.; Köhn, A.; de Oliveira-Filho, A. G. S. *J. Chem. Theory Comput.* **,** **2017**, *13*, 5291.

[423] Zongtang Fang, Z.; Vasiliu, M.; Peterson, K. A.; Dixon, D. A. *J. Chem. Theory Comput.* **2017**, *13*, 1057.

[424] Cheng, L.; Gauss, J.; Ruscic, B.; Armentrout, P. B.; Stanton, J. F. *J. Chem. Theory Comput.* **,** **2017**, *13*, 1044.

[425] Halkier, A.; Helgaker, T.; Jørgensen, P.; Klopper, W.; Koch, H.; Olsen, J.; Wilson, A. *Chem. Phys. Lett.* **1998**, *286*, 243.

Appendix A

List of Abbreviations

ANO: Atomic natural orbitals

AO: Atomic orbital

BO: Born-Oppenheimer

BSIE: Basis set incompleteness error

BSSE: Basis set superposition error

CABS: Complimentary auxiliary basis set

CASSCF Complete active space self consistent field

CBS: Complete basis bet

cc: correlation consistent

CC: Coupled cluster

CCSD(T): Coupled cluster with single, double, and perturbative triple excitations

CI: Configuration interaction

CISD: Configuration interaction with single, and double excitations

DFT: Density functional theory

ECP: Effective core potential

HF: Hartree-Fock

icMRCI: Internally-contracted Multi Reference Configuration Interaction

KS: Kohn-Sham

LCAO: Linear combination of atomic orbital

MCSCF: Multi-Configurational Self-Consistent field

MO: Molecular orbital

MP$_n$: n^{th} order Møller-Plesset Perturbation theory

pce: Per correlated electron

PES: Potential energy surface

ppm: Part per million

PT: Perturbation theory

QISD: Quadratic configuration interaction with single, and double excitations

QISD(T): Quadratic configuration interactions with single, double, and perturbative triple excitations

RHF: Restricted Hartree-Fock

SCF: Self-consistent field

TM: Transition metal

UHF: Unrestricted Hartree-Fock

Appendix B

Supplementary Information for Chapter 4:

Basics of unconstrained optimisation

B.1 Mathematical Set Notation

- $\in$ belongs in
- $\notin$ does not belong in
- $\exists$ there exists
- $\forall$ for all
- $\mathbb{R}$ real number set
- $X \setminus Y$ a set that is made by subtracting the elements of set Y from set X.

Appendix C

Supplementary Information for Chapter 5:

Auxiliary basis sets for density fitting in explicitly correlated calculations: The atoms H-Ar.

C.1 MP2Fit Auxiliary basis sets

All auxiliary basis sets are provided in molpro format.

C.1.1 cc-pVDZ-F12/MP2Fit

```
!H cc-pVDZ-F12/MP2Fit
s, H, 18.16, 4.48346, 1.46001, 0.598208, 0.261817, 0.134824
p, H, 5.40776, 1.63382, 0.715305, 0.428532
d, H, 2.07531, 0.597566
f, H, 0.548776

!He cc-pVDZ-F12/MP2Fit
s, He, 26.5905, 5.7116, 1.49801, 1.01539, 0.424143, 0.200012
p, He, 6.19208, 1.82496, 0.776876, 0.525522
d, He, 3.36159, 1.1907
f, He, 2.00066

!Li cc-pVDZ-F12/MP2Fit
s, Li, 129.859, 24.2797, 6.5529, 2.73433, 0.990997, 0.327161, 0.140162, 0.048789, 0.026635
p, Li, 33.9686, 6.43836, 2.04092, 0.664442, 0.327296, 0.168976, 0.093781, 0.054567
d, Li, 21.5929, 4.9576, 2.32007, 0.630444, 0.207368, 0.11385, 0.074406
f, Li, 1.20941, 0.361572, 0.153652
g, Li, 0.661278, 0.235703

!Be cc-pVDZ-F12/MP2Fit
s, Be, 153.184, 29.5781, 7.03047, 3.89133, 1.00588, 0.404077, 0.215952, 0.0847937, 0.0619588
p, Be, 36.5531, 8.29802, 2.7645, 1.66691, 0.574087, 0.252809, 0.11263, 0.0596529
d, Be, 24.8649, 5.92845, 2.47263, 0.852982, 0.434353, 0.214859, 0.140997
f, Be, 1.45228, 0.608683, 0.305491
g, Be, 0.940201, 0.431216

!B cc-pVDZ-F12/MP2Fit
s, B, 183.02, 35.7197, 7.6251, 4.01552, 1.37543, 0.72854, 0.366728, 0.161018, 0.107434
p, B, 41.0144, 8.87911, 2.88213, 1.79173, 0.972442, 0.416723, 0.193673, 0.097493
d, B, 29.8454, 6.40033, 2.90012, 1.07529, 0.462123, 0.284352, 0.170965
f, B, 1.5125, 0.626316, 0.35377
g, B, 0.973295, 0.470714

!C cc-pVDZ-F12/MP2Fit
s, C, 217.147, 45.4454, 8.77756, 4.70211, 1.52151, 0.831642, 0.549314, 0.292388, 0.139793
p, C, 44.8091, 12.6825, 3.9777, 1.87719, 1.00621, 0.610948, 0.288406, 0.143925
d, C, 33.5616, 6.96843, 2.97989, 1.37487, 0.668843, 0.402303, 0.17822
f, C, 2.53822, 1.31916, 0.524912
g, C, 1.82984, 0.832131

!N cc-pVDZ-F12/MP2Fit
s, N, 259.981, 54.8864, 10.8078, 5.91761, 1.90228, 1.02205, 0.687885, 0.367479, 0.167791
p, N, 50.914, 16.3633, 5.81529, 2.46172, 1.06747, 0.685846, 0.352192, 0.176597
d, N, 39.2239, 8.71041, 3.23731, 1.80636, 0.856823, 0.477301, 0.216833
f, N, 3.19647, 1.66879, 0.736831
g, N, 2.3096, 1.10888

!O cc-pVDZ-F12/MP2Fit
s, O, 310.683, 65.6513, 12.8281, 7.22646, 2.42415, 1.26969, 0.797102, 0.371911, 0.171698
```

p, O, 60.9193, 20.1036, 7.73817, 3.14567, 1.39683, 0.813556, 0.434827, 0.219358
d, O, 44.5431, 11.3278, 3.83573, 2.10467, 1.0171, 0.503405, 0.221001
f, O, 4.21329, 2.06298, 0.853697
g, O, 2.94821, 1.32709

!F cc-pVDZ-F12/MP2Fit
s, F, 372.389, 78.1815, 15.3232, 9.10981, 3.11276, 1.60512, 1.01805, 0.47221, 0.211241
p, F, 73.5568, 24.3347, 9.89563, 3.98417, 1.85467, 0.993959, 0.531681, 0.271275
d, F, 51.6512, 14.2244, 4.91705, 2.57525, 1.27964, 0.634557, 0.271273
f, F, 5.46977, 2.67877, 1.05618
g, F, 3.82783, 1.68204

!Ne cc-pVDZ-F12/MP2Fit
s, Ne, 443.974, 93.6263, 18.4209, 11.6551, 3.93529, 1.99865, 1.25782, 0.575134, 0.257276
p, Ne, 90.9531, 29.0911, 12.9485, 4.82982, 2.52853, 1.19118, 0.699103, 0.350337
d, Ne, 59.3, 17.2653, 6.18805, 3.48209, 1.66822, 0.799295, 0.328864
f, Ne, 7.28479, 3.69564, 1.37008
g, Ne, 5.18864, 2.25019

!Na cc-pVDZ-F12/MP2Fit
s, Na, 150.842, 48.8654, 28.1129, 8.41625, 4.51979, 3.43744, 1.01874, 0.435117, 0.25864, 0.105036, 0.049949, 0.03949
p, Na, 58.3642, 13.3584, 5.31526, 1.6879, 0.982276, 0.203713, 0.176943, 0.144287, 0.067728, 0.034798
d, Na, 26.5895, 6.07994, 1.97949, 0.850431, 0.577881, 0.304273, 0.126958, 0.061531, 0.040662
f, Na, 4.77959, 1.82168, 0.567264, 0.188754, 0.048689
g, Na, 0.586387, 0.191732

!Mg cc-pVDZ-F12/MP2Fit
s, Mg, 169.575, 71.223, 44.0817, 16.1557, 7.51175, 3.62217, 1.14724, 0.482898, 0.293586, 0.115543, 0.058903, 0.047294
p, Mg, 60.5553, 14.014, 6.12886, 1.78147, 1.02558, 0.213058, 0.190875, 0.162848, 0.082037, 0.0408
d, Mg, 27.4747, 9.48642, 2.7276, 1.43183, 0.818005, 0.314616, 0.152786, 0.079241, 0.052509
f, Mg, 5.08676, 1.97623, 0.671176, 0.219246, 0.089569
g, Mg, 0.65824, 0.383605

!Al cc-pVDZ-F12/MP2Fit
s, Al, 197.159, 82.5218, 50.5683, 16.5265, 8.01945, 3.76275, 1.36806, 0.533895, 0.323896, 0.172755, 0.0817025, 0.0596359
p, Al, 80.6056, 14.1318, 6.15226, 2.59034, 1.27001, 0.426108, 0.331364, 0.241031, 0.116562, 0.0593975
d, Al, 29.6493, 10.2344, 3.54767, 2.14277, 1.24307, 0.572871, 0.246089, 0.105905, 0.0624519
f, Al, 5.14226, 1.99476, 0.672944, 0.256582, 0.124926
g, Al, 0.715417, 0.415531

!Si cc-pVDZ-F12/MP2Fit
s, Si, 234.629, 98.6616, 60.254, 18.4652, 8.87467, 3.90268, 1.58547, 0.747467, 0.486927, 0.297793, 0.129412, 0.077359
p, Si, 100.604, 14.8254, 6.67116, 2.8376, 1.51247, 0.556258, 0.413636, 0.278908, 0.148215, 0.081664
d, Si, 30.6129, 11.0334, 4.34231, 2.87745, 1.62714, 0.727352, 0.348525, 0.173358, 0.091721
f, Si, 7.184, 3.07915, 0.792716, 0.353952, 0.126097
g, Si, 1.04397, 0.422528

!P cc-pVDZ-F12/MP2Fit
s, P, 282.002, 123.69, 78.0226, 26.9303, 9.87371, 4.66967, 2.02255, 1.05181, 0.598048, 0.342959, 0.167153, 0.100532
p, P, 118.149, 17.0626, 8.17647, 3.37399, 1.82049, 0.727827, 0.501774, 0.336455, 0.180944, 0.097019
d, P, 35.003, 12.3305, 5.55788, 4.03355, 2.34774, 0.899945, 0.432382, 0.205774, 0.119727
f, P, 9.72041, 3.82635, 1.01659, 0.44459, 0.156961
g, P, 1.30428, 0.52833

!S cc-pVDZ-F12/MP2Fit
s, S, 337.801, 147.798, 92.6888, 30.7475, 12.4717, 6.30354, 2.75699, 1.30722, 0.718982, 0.413111, 0.188309, 0.105993
p, S, 138.211, 18.1764, 9.04937, 3.98074, 2.21244, 0.887146, 0.601335, 0.39587, 0.221916, 0.121098

```
d, S, 48.2767, 14.6924, 7.55743, 5.60839, 3.39973, 1.08115, 0.495036, 0.239571, 0.129744
f, S, 13.0094, 4.41724, 1.22632, 0.49078, 0.178598
g, S, 1.47238, 0.592124

!Cl cc-pVDZ-F12/MP2Fit
s, Cl, 405.272, 177.317, 111.14, 36.7363, 14.9949, 7.61587, 3.3496, 1.5956, 0.885288, 0.507094, 0.226849, 0.126808
p, Cl, 159.047, 20.522, 10.6517, 4.76146, 2.6618, 1.07022, 0.723256, 0.474725, 0.266574, 0.145864
d, Cl, 60.3076, 17.6675, 9.11981, 6.76766, 4.10419, 1.35573, 0.608973, 0.293974, 0.155661
f, Cl, 17.4333, 5.77144, 1.53591, 0.602619, 0.216451
g, Cl, 1.86493, 0.722323

!Ar cc-pVDZ-F12/MP2Fit
s, Ar, 486.458, 212.85, 133.447, 44.1076, 17.9377, 9.07789, 3.99894, 1.92069, 1.06882, 0.6136, 0.272653, 0.150717
p, Ar, 176.324, 22.4035, 12.4459, 5.68228, 3.21147, 1.30719, 0.877323, 0.571215, 0.320914, 0.176321
d, Ar, 74.3936, 21.5888, 11.0604, 7.96485, 4.94733, 1.61418, 0.738718, 0.349273, 0.186193
f, Ar, 21.2841, 7.31451, 1.83851, 0.710271, 0.297919
g, Ar, 2.27932, 0.920008
```

C.1.2 cc-pVTZ-F12/MP2Fit

```
!H cc-pVTZ-F12/MP2Fit
s, H, 25.6037, 5.30727, 2.03616, 1.23408, 0.687196, 0.362326, 0.207115
p, H, 6.58644, 2.53328, 1.7989, 0.765088, 0.350096
d, H, 2.2634, 0.751248, 0.262469
f, H, 1.7793, 0.873392
g, H, 1.18632

!He cc-pVTZ-F12/MP2Fit
s, He, 44.0428, 9.49713, 2.66028, 1.56784, 0.847025, 0.439706, 0.245193
p, He, 9.45825, 4.27609, 2.00522, 0.80446, 0.481563
d, He, 2.62272, 1.05717, 0.320944
f, He, 3.33026, 1.16498
g, He, 1.96969

!Li cc-pVTZ-F12/MP2Fit
s, Li, 131.043, 66.8228, 33.5302, 8.39902, 3.82787, 1.03622, 0.641357, 0.298372, 0.143074, 0.080861, 0.0467
p, Li, 73.8515, 25.1686, 7.64038, 2.75996, 1.19016, 0.505493, 0.323201, 0.158404, 0.084796, 0.058504
d, Li, 17.2124, 6.21454, 2.89276, 1.69446, 0.801421, 0.370596, 0.272083, 0.159245, 0.092445
f, Li, 2.48611, 0.548262, 0.27885, 0.193408, 0.110138
g, Li, 1.16749, 0.391003, 0.232232, 0.14595
h, Li, 0.301336

!Be cc-pVTZ-F12/MP2Fit
s, Be, 138.675, 71.4167, 41.7384, 9.01262, 4.11543, 1.55017, 0.778095, 0.420978, 0.179518, 0.113803, 0.060719
p, Be, 78.2949, 26.5503, 10.1508, 3.74356, 2.08598, 1.21451, 0.430516, 0.192438, 0.125338, 0.074288
d, Be, 17.869, 8.04385, 3.5569, 2.08265, 1.16233, 0.621355, 0.323667, 0.169624, 0.096212
f, Be, 2.84997, 1.49015, 0.640523, 0.427057, 0.214965
g, Be, 2.0608, 0.976972, 0.523011, 0.302989
h, Be, 0.714819

!B cc-pVTZ-F12/MP2Fit
s, B, 142.025, 84.076, 49.1799, 9.45743, 4.87784, 1.84633, 0.953913, 0.520833, 0.290793, 0.190906, 0.086439
p, B, 92.2378, 31.1964, 11.0498, 4.66903, 2.64295, 1.41867, 0.775417, 0.319368, 0.187611, 0.09654
d, B, 18.0693, 9.46291, 4.1846, 2.45014, 1.36758, 0.736527, 0.383021, 0.198467, 0.107787
f, B, 3.37219, 1.77008, 0.793909, 0.595184, 0.282287
```

```
g, B, 2.09748, 1.04358, 0.714451, 0.431797
h, B, 0.863476

!C cc-pVTZ-F12/MP2Fit
s, C, 168.355, 99.7838, 59.2534, 11.1925, 5.68001, 2.18753, 1.17791, 0.622947, 0.338525, 0.222238, 0.089462
p, C, 108.813, 36.6964, 13.4913, 6.07901, 3.46455, 1.74396, 1.1005, 0.481041, 0.295699, 0.128109
d, C, 21.2899, 11.1533, 5.00195, 2.9575, 1.57749, 0.90589, 0.519288, 0.226261, 0.123832
f, C, 4.0231, 2.22241, 1.19163, 0.611226, 0.331026
g, C, 2.4676, 1.23074, 0.83538, 0.475321
h, C, 1.01397

!N cc-pVTZ-F12/MP2Fit
s, N, 211.98, 116.178, 69.4941, 13.9118, 6.78281, 3.40889, 1.42452, 0.831518, 0.464518, 0.283887, 0.123681
p, N, 130.569, 39.1519, 18.9976, 7.12225, 4.88776, 2.03516, 1.48619, 0.655786, 0.40446, 0.171781
d, N, 24.9581, 12.1317, 5.75036, 3.77248, 1.71172, 0.9939, 0.603329, 0.296834, 0.15222
f, N, 6.61621, 3.45706, 1.76319, 0.833167, 0.516166
g, N, 3.6705, 1.87073, 0.916455, 0.576257
h, N, 1.30937

!O cc-pVTZ-F12/MP2Fit
s, O, 257.015, 138.152, 82.6271, 16.2796, 8.7611, 4.61335, 1.8295, 1.03048, 0.5607, 0.33932, 0.148602
p, O, 157.232, 46.2254, 22.6748, 8.64256, 5.91936, 2.41398, 1.75615, 0.802688, 0.498143, 0.206938
d, O, 31.3118, 14.377, 6.83353, 4.46612, 2.08928, 1.1997, 0.724484, 0.356466, 0.182784
f, O, 8.14069, 4.18098, 1.9692, 1.02479, 0.615929
g, O, 4.50994, 2.17924, 1.09474, 0.696074
h, O, 1.54457

!F cc-pVTZ-F12/MP2Fit
s, F, 330.369, 162.53, 99.1351, 20.2944, 12.046, 6.00412, 2.29572, 1.32889, 0.704804, 0.415121, 0.180122
p, F, 191.333, 52.2816, 26.3259, 10.7143, 7.51937, 2.95856, 2.09757, 0.993256, 0.620646, 0.252891
d, F, 44.473, 17.6356, 8.28567, 4.97942, 2.4165, 1.46355, 0.867457, 0.430555, 0.220627
f, F, 10.2702, 5.26037, 2.71923, 1.63096, 0.797452
g, F, 6.65693, 3.49307, 1.52646, 0.868292
h, F, 2.30912

!Ne cc-pVTZ-F12/MP2Fit
s, Ne, 423.233, 191.668, 119.14, 25.1636, 15.763, 7.34955, 2.85558, 1.71071, 0.888151, 0.510515, 0.21958
p, Ne, 231.249, 61.6186, 31.3748, 13.2785, 9.57232, 3.55076, 2.49145, 1.18733, 0.75116, 0.30719
d, Ne, 56.3488, 23.2452, 10.4938, 6.03393, 3.30537, 1.78804, 1.03419, 0.524692, 0.268117
f, Ne, 13.3726, 6.83653, 3.74064, 1.96383, 1.0398
g, Ne, 9.69316, 5.30903, 1.9621, 1.124
h, Ne, 3.22752

!Na cc-pVTZ-F12/MP2Fit
s, Na, 151.741, 91.0356, 57.0133, 22.2774, 13.9409, 8.72218, 3.47704, 1.10139, 0.632803, 0.275752, 0.133735, 0.077423, 0.051002, 0.032244
p, Na, 185.978, 95.6529, 34.1413, 11.9279, 5.08181, 1.68964, 0.975595, 0.37302, 0.261251, 0.106668, 0.06222, 0.044304
d, Na, 39.3859, 12.6543, 6.55753, 4.34205, 2.21631, 1.18246, 0.513175, 0.214048, 0.136202, 0.093428, 0.060933
f, Na, 8.37033, 3.24071, 1.76177, 0.709361, 0.388671, 0.135512, 0.090178
g, Na, 1.38179, 0.502073, 0.200578, 0.110882
h, Na, 0.31734

!Mg cc-pVTZ-F12/MP2Fit
s, Mg, 174.661, 104.679, 65.8466, 26.004, 16.1262, 10.0166, 3.64271, 1.35666, 0.910106, 0.323555, 0.151613, 0.113451, 0.068598, 0.037
p, Mg, 209.436, 109.755, 36.72, 12.9172, 7.91979, 3.32069, 2.17083, 0.850849, 0.386967, 0.191159, 0.105752, 0.061666
d, Mg, 59.5326, 19.9849, 8.46618, 4.6157, 3.10069, 2.01919, 0.682638, 0.433019, 0.236048, 0.106506, 0.076582
f, Mg, 11.3559, 4.30484, 2.34518, 0.894397, 0.62126, 0.304375, 0.162652
g, Mg, 1.44828, 0.745421, 0.434851, 0.222502
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h, Mg, 0.56934

!Al cc-pVTZ-F12/MP2Fit
s, Al, 209.631, 125.217, 78.5609, 30.5634, 18.4769, 10.586, 4.21874, 1.82152, 1.25999, 0.41852, 0.214605, 0.152548, 0.0788303, 0.0442385
p, Al, 250.746, 134.137, 37.2981, 13.8676, 10.7721, 4.4355, 2.34943, 0.851718, 0.45911, 0.217712, 0.112704, 0.0673772
d, Al, 70.2329, 23.438, 10.1462, 5.33969, 3.59928, 2.26394, 0.684913, 0.493861, 0.288286, 0.141763, 0.0996255
f, Al, 12.8347, 5.45694, 2.53308, 1.00675, 0.702497, 0.356328, 0.17423
g, Al, 2.38274, 0.824758, 0.518775, 0.248907
h, Al, 0.654113

!Si cc-pVTZ-F12/MP2Fit
s, Si, 260.655, 154.661, 96.5095, 36.105, 20.1317, 10.9815, 5.06089, 1.96111, 1.44989, 0.573769, 0.333657, 0.244557, 0.091881, 0.050325
p, Si, 313.023, 174.015, 41.1652, 15.1754, 11.5179, 5.53619, 2.5295, 1.27025, 0.616037, 0.286383, 0.182528, 0.088566
d, Si, 86.2496, 29.1525, 11.821, 7.0876, 3.88214, 2.98304, 1.14103, 0.559672, 0.303837, 0.155682, 0.101346
f, Si, 14.904, 6.94572, 3.75668, 1.46064, 0.809717, 0.378543, 0.224704
g, Si, 2.95031, 0.995848, 0.647712, 0.331931
h, Si, 0.803133

!P cc-pVTZ-F12/MP2Fit
s, P, 325.168, 192.702, 120.126, 44.4734, 24.2296, 12.8798, 5.8019, 2.30929, 1.76423, 0.754891, 0.439062, 0.326912, 0.131915, 0.067733
p, P, 392.835, 220.958, 49.0892, 16.4796, 12.8597, 6.93664, 3.29414, 1.59082, 0.810867, 0.368415, 0.239418, 0.112219
d, P, 107.043, 36.9132, 14.557, 8.70637, 4.72063, 3.65215, 1.6096, 0.760552, 0.386451, 0.194242, 0.113672
f, P, 18.0587, 8.70872, 4.73234, 1.92281, 0.981036, 0.471428, 0.283448
g, P, 3.68313, 1.20124, 0.820241, 0.409127
h, P, 0.992624

!S cc-pVTZ-F12/MP2Fit
s, S, 389.937, 230.81, 143.872, 52.8441, 28.2988, 14.9302, 6.67138, 2.65194, 2.05728, 0.948349, 0.550898, 0.40119, 0.156727, 0.08219
p, S, 471.41, 264.789, 58.6446, 18.3977, 14.1844, 7.68424, 3.81318, 1.8962, 0.922498, 0.506795, 0.290062, 0.125122
d, S, 127.539, 44.2063, 16.9343, 9.99542, 5.0875, 3.90458, 2.06894, 0.935929, 0.452906, 0.243643, 0.119922
f, S, 21.2046, 10.3929, 5.80511, 2.43328, 1.13188, 0.635801, 0.360427
g, S, 4.43259, 1.4537, 0.941903, 0.450139
h, S, 1.17015

!Cl cc-pVTZ-F12/MP2Fit
s, Cl, 487.448, 288.469, 179.802, 65.8909, 35.1411, 18.5335, 8.24656, 3.26896, 2.53705, 1.20271, 0.694107, 0.498091, 0.192972, 0.10309
p, Cl, 589.246, 330.868, 73.1692, 22.2357, 17.0269, 9.11613, 4.44889, 2.18607, 1.09144, 0.652911, 0.342464, 0.154034
d, Cl, 158.959, 55.2701, 20.7653, 12.2882, 6.0831, 4.62497, 2.48036, 1.05691, 0.542545, 0.296088, 0.141668
f, Cl, 26.0818, 13.0533, 7.31785, 2.92395, 1.2988, 0.797471, 0.421228
g, Cl, 5.53484, 1.80342, 1.15409, 0.543752
h, Cl, 1.44267

!Ar cc-pVTZ-F12/MP2Fit
s, Ar, 585.002, 346.148, 215.743, 79.0037, 42.0776, 22.1688, 9.82728, 3.8859, 3.02427, 1.4536, 0.835812, 0.594914, 0.230064, 0.123978
p, Ar, 707.088, 396.941, 87.7398, 26.1585, 19.9149, 10.5297, 5.15425, 2.5799, 1.26973, 0.791981, 0.412032, 0.18623
d, Ar, 190.701, 66.3391, 24.8312, 14.7401, 7.26683, 5.51436, 2.9683, 1.30158, 0.630887, 0.338825, 0.166419
f, Ar, 30.9178, 15.6556, 8.87733, 3.67579, 1.57283, 0.931294, 0.503711
g, Ar, 6.61806, 2.06902, 1.41026, 0.658444
h, Ar, 1.70818

C.1.3 cc-pVQZ-F12/MP2Fit

!H cc-pVQZ-F12/MP2Fit
s, H, 97.1313, 18.9366, 5.43323, 1.93823, 1.27324, 0.686296, 0.33445, 0.142999
p, H, 10.7919, 3.94392, 1.73729, 0.723821, 0.357907, 0.176046

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d, H, 3.83163, 1.54855, 0.669395, 0.427949
f, H, 3.88063, 1.53882, 0.706655
g, H, 3.07132, 0.898362
h, H, 0.807491

!He cc-pVQZ-F12/MP2Fit
s, He, 109.987, 20.4003, 5.73172, 2.57906, 1.77807, 0.890023, 0.394219, 0.160173
p, He, 11.4948, 4.89228, 3.0669, 1.54383, 0.637878, 0.203734
d, He, 4.26867, 1.593, 0.735843, 0.470762
f, He, 4.0107, 1.81127, 1.02067
g, He, 2.69527, 1.35967
h, He, 0.957169

!Li cc-pVQZ-F12/MP2Fit
s, Li, 247.539, 97.2227, 36.7823, 23.8749, 8.59491, 5.0367, 1.87198, 0.934954, 0.491253, 0.185091, 0.121094, 0.053158, 0.035233
p, Li, 161.77, 38.7482, 23.0401, 9.34667, 3.69504, 1.85061, 0.89398, 0.392764, 0.254568, 0.121666, 0.075014, 0.035981
d, Li, 29.2769, 11.3903, 4.45344, 2.77977, 1.72354, 0.666425, 0.403439, 0.240771, 0.153354, 0.100445, 0.067188
f, Li, 22.6168, 8.63188, 1.75844, 0.590496, 0.291101, 0.169955, 0.102032
g, Li, 13.6364, 4.75972, 0.564294, 0.289469, 0.177398, 0.122535
h, Li, 0.40416, 0.226608, 0.147437
i, Li, 0.302632


!Be cc-pVQZ-F12/MP2Fit
s, Be, 379.597, 149.724, 56.0508, 35.3148, 13.0506, 7.68588, 2.32778, 0.96402, 0.618831, 0.336446, 0.184112, 0.093104, 0.054258
p, Be, 250.523, 60.6108, 37.5086, 14.2057, 8.48671, 2.68532, 1.41676, 0.516424, 0.306638, 0.174713, 0.107856, 0.053437
d, Be, 45.0471, 17.5905, 6.86666, 4.28752, 2.68019, 1.03753, 0.620497, 0.378386, 0.249364, 0.130681, 0.082559
f, Be, 35.1518, 13.6713, 3.98057, 1.13488, 0.591749, 0.324402, 0.181127
g, Be, 20.5958, 8.01645, 2.06569, 1.05502, 0.461945, 0.238428
h, Be, 1.47626, 0.698113, 0.331875
i, Be, 1.01518

!B cc-pVQZ-F12/MP2Fit
s, B, 455.99, 179.82, 67.2298, 42.358, 15.6131, 9.18291, 2.91182, 1.44232, 0.887097, 0.508854, 0.298696, 0.164159, 0.088337
p, B, 300.367, 71.4858, 44.3165, 14.9567, 8.59507, 3.14189, 2.19072, 0.91506, 0.484663, 0.25901, 0.135088, 0.065608
d, B, 54.1154, 21.1497, 8.2538, 5.13861, 3.17512, 1.24285, 0.782607, 0.489295, 0.306296, 0.192543, 0.120272
f, B, 40.7688, 14.6105, 4.38693, 1.37397, 0.763788, 0.563311, 0.267449
g, B, 23.967, 8.47802, 2.26188, 1.17199, 0.52915, 0.381765
h, B, 3.10142, 1.25063, 0.495643
i, B, 1.96944

!C cc-pVQZ-F12/MP2Fit
s, C, 569.47, 223.299, 82.4874, 51.4324, 17.5607, 9.56023, 3.6878, 2.16313, 1.15462, 0.536675, 0.318395, 0.195726, 0.101885
p, C, 375.404, 88.3745, 55.037, 16.474, 9.45025, 3.90821, 2.24318, 1.31241, 0.750258, 0.375419, 0.166527, 0.076823
d, C, 67.6546, 26.6284, 10.2011, 6.44869, 4.22472, 1.8171, 0.995613, 0.597275, 0.392952, 0.253765, 0.152644
f, C, 47.8132, 16.4652, 5.17995, 1.87455, 1.22165, 0.741621, 0.394124
g, C, 29.1116, 11.3891, 2.41226, 1.49539, 0.796805, 0.412938
h, C, 3.91002, 1.6749, 0.700009
i, C, 2.55908

!N cc-pVQZ-F12/MP2Fit
s, N, 711.887, 278.49, 102.854, 63.9447, 21.4569, 11.3967, 4.42835, 2.79684, 1.63927, 0.767091, 0.427709, 0.249006, 0.146657
p, N, 469.718, 111.034, 69.2215, 21.3743, 11.5798, 4.30713, 3.29075, 1.74176, 0.9667, 0.528831, 0.220756, 0.107094
d, N, 84.5515, 33.201, 12.6433, 7.93687, 5.2027, 2.34578, 1.27267, 0.752362, 0.4906, 0.315851, 0.190401
f, N, 58.7867, 18.6645, 7.87757, 3.08855, 1.5097, 0.905341, 0.540268
g, N, 36.1606, 13.5113, 3.72863, 1.78856, 1.01857, 0.636226
h, N, 4.87443, 2.0462, 0.805313
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i, N, 3.15817

!O cc-pVQZ-F12/MP2Fit
s, O, 854.518, 333.611, 123.305, 76.4596, 25.2683, 13.1026, 5.06485, 3.31659, 2.03608, 0.964241, 0.510577, 0.283063, 0.165336
p, O, 562.868, 132.89, 82.2166, 25.6218, 14.0625, 5.25475, 3.83842, 1.9395, 1.1235, 0.645728, 0.296883, 0.128811
d, O, 101.344, 39.7515, 14.9408, 9.1988, 6.06667, 3.0591, 1.61407, 0.909019, 0.57884, 0.367978, 0.220661
f, O, 70.4335, 21.9362, 9.78548, 4.22193, 1.8678, 1.06325, 0.649027
g, O, 43.1154, 15.2621, 5.15058, 2.16374, 1.22893, 0.732714
h, O, 4.90438, 2.3047, 0.94108
i, O, 3.36201

!F cc-pVQZ-F12/MP2Fit
s, F, 1025.54, 400.301, 147.974, 91.7416, 30.3031, 15.7041, 6.06029, 3.97157, 2.45137, 1.17042, 0.618504, 0.341362, 0.198832
p, F, 675.195, 159.477, 98.4183, 30.7688, 16.9885, 6.45525, 4.69932, 2.35213, 1.35515, 0.776462, 0.346035, 0.161362
d, F, 121.613, 47.6935, 17.9218, 11.0201, 7.25914, 3.69039, 1.944, 1.09093, 0.695091, 0.442027, 0.265098
f, F, 84.3618, 23.4368, 11.4895, 5.22265, 2.38578, 1.26471, 0.756035
g, F, 51.6519, 17.8377, 6.55749, 2.79504, 1.4765, 0.885605
h, F, 5.70816, 2.98747, 1.23298
i, F, 4.12952

!Ne cc-pVQZ-F12/MP2Fit
s, Ne, 1235.58, 478.886, 178.236, 109.707, 35.1986, 18.7794, 7.41636, 4.77763, 3.10135, 1.55934, 0.795844, 0.366685, 0.204234
p, Ne, 800.852, 189.793, 110.152, 37.1373, 21.4937, 9.12155, 5.40976, 2.88384, 1.71538, 1.04155, 0.548448, 0.293597
d, Ne, 146.12, 55.2378, 22.4352, 13.2356, 8.24782, 4.63014, 2.50397, 1.32218, 0.817142, 0.474259, 0.278092
f, Ne, 95.8758, 18.2633, 9.14316, 5.24627, 2.9366, 1.51991, 0.8651
g, Ne, 67.3221, 18.879, 8.89912, 4.71261, 2.72426, 1.28005
h, Ne, 7.49088, 4.49499, 1.59479
i, Ne, 5.80271

!Na cc-pVQZ-F12/MP2Fit
s, Na, 173.773, 97.1298, 59.6982, 36.96, 14.9229, 8.94473, 5.55914, 3.41909, 2.16589, 1.34533, 0.789385, 0.395384, 0.198989, 0.108334, 0.059155, 0.039855
p, Na, 101.567, 62.5508, 39.3119, 15.1024, 9.31941, 5.57815, 2.36049, 1.47407, 0.754092, 0.312899, 0.19243, 0.116163, 0.080019, 0.057069
d, Na, 46.4078, 28.998, 17.9945, 6.94725, 4.24316, 2.58467, 1.58565, 0.943046, 0.568246, 0.318839, 0.173342, 0.101838, 0.066047
f, Na, 34.1078, 13.2134, 6.50563, 2.77945, 1.02894, 0.440984, 0.226966, 0.148672, 0.100215
g, Na, 19.0507, 1.49571, 0.595122, 0.313043, 0.200595, 0.119396
h, Na, 0.758194, 0.245161, 0.151957
i, Na, 0.193013

!Mg cc-pVQZ-F12/MP2Fit
s, Mg, 188.743, 113.033, 71.4844, 45.0437, 17.3966, 10.8604, 6.73101, 4.1028, 2.53007, 1.53699, 0.86027, 0.47455, 0.255938, 0.122754, 0.076738, 0.052117
p, Mg, 127.822, 76.5923, 46.1709, 18.8425, 11.282, 5.91129, 3.0992, 1.64922, 0.915004, 0.426434, 0.231041, 0.129227, 0.083787, 0.060793
d, Mg, 59.3494, 35.5838, 22.3912, 8.65573, 5.37662, 3.34577, 2.09372, 1.30176, 0.711941, 0.485794, 0.284825, 0.170145, 0.105949
f, Mg, 42.8945, 16.6446, 8.55634, 3.72889, 1.44744, 0.548064, 0.356327, 0.252958, 0.142452
g, Mg, 23.9824, 2.26347, 0.906584, 0.683377, 0.354597, 0.185341
h, Mg, 1.43249, 0.492264, 0.112649
i, Mg, 0.235485

!Al cc-pVQZ-F12/MP2Fit
s, Al, 247.07, 147.32, 92.7288, 58.1873, 22.2512, 13.7934, 8.48907, 5.11355, 3.08404, 1.79063, 0.927452, 0.506493, 0.311633, 0.17697, 0.108744, 0.067634
p, Al, 165.491, 99.1535, 59.6135, 23.772, 14.1088, 7.24786, 3.49221, 1.75246, 0.923367, 0.556073, 0.348507, 0.178035, 0.104427, 0.074838
d, Al, 76.1638, 45.8508, 28.6854, 11.0088, 6.82273, 4.21805, 2.5999, 1.56342, 0.778502, 0.617949, 0.332778, 0.17672, 0.109874
f, Al, 55.2732, 21.0251, 10.6506, 4.02204, 1.60892, 0.922941, 0.423908, 0.324905, 0.184422
g, Al, 30.2691, 5.96456, 0.913143, 0.718785, 0.447587, 0.224297
h, Al, 1.99917, 0.515763, 0.233715

i, Al, 0.347191

!Si cc-pVQZ-F12/MP2Fit
s, Si, 309.781, 184.303, 115.981, 72.7806, 27.8307, 17.2527, 10.6221, 6.39754, 3.85112, 2.21845, 1.16093, 0.684132, 0.45176, 0.250109, 0.147158, 0.101872
p, Si, 206.967, 123.967, 74.5151, 29.7024, 17.6404, 9.00015, 4.28678, 2.14919, 1.12237, 0.670739, 0.436059, 0.237421, 0.135031, 0.095608
d, Si, 95.1439, 57.2064, 35.7376, 13.5937, 8.37144, 5.09052, 3.06537, 1.74546, 0.822635, 0.643418, 0.351525, 0.215399, 0.117988
f, Si, 68.8711, 25.8502, 13.0865, 4.39708, 1.8263, 1.33486, 0.58974, 0.36815, 0.223009
g, Si, 34.2722, 6.46402, 1.28262, 0.778607, 0.482898, 0.27244
h, Si, 2.42715, 0.766207, 0.332845
i, Si, 0.505003

!P cc-pVQZ-F12/MP2Fit
s, P, 388.374, 230.58, 144.99, 91.0002, 34.7905, 21.5598, 13.2532, 7.08526, 4.17304, 2.3414, 1.22402, 0.740592, 0.493097, 0.280405, 0.165822, 0.116458
p, P, 258.926, 154.945, 93.1316, 37.1501, 22.0124, 11.0202, 5.10368, 2.54332, 1.34981, 0.817845, 0.543158, 0.303816, 0.170271, 0.119444
d, P, 118.918, 71.4724, 44.61, 16.9146, 10.3953, 5.28724, 3.12316, 1.78946, 1.02138, 0.653087, 0.36123, 0.226541, 0.127816
f, P, 85.4289, 30.5563, 16.4849, 6.20671, 2.70608, 1.74148, 0.755702, 0.483449, 0.288749
g, P, 42.8153, 7.2603, 1.72008, 0.896445, 0.53651, 0.321239
h, P, 2.94247, 0.932995, 0.412138
i, P, 0.620099

!S cc-pVQZ-F12/MP2Fit
s, S, 494.242, 289.363, 180.703, 112.636, 41.7352, 25.0339, 14.4893, 7.7342, 4.2249, 2.58963, 1.4132, 0.851517, 0.538755, 0.291012, 0.175018, 0.119624
p, S, 325.33, 192.696, 115.983, 44.8118, 24.1839, 11.4693, 5.32445, 2.85995, 1.70735, 1.08663, 0.702843, 0.395637, 0.22016, 0.127659
d, S, 148.125, 88.2033, 54.2435, 23.5069, 11.7223, 6.27544, 3.24879, 1.87925, 1.09554, 0.711915, 0.381, 0.239566, 0.129273
f, S, 104.691, 30.9005, 18.6414, 7.76167, 3.91388, 1.83362, 0.960051, 0.557681, 0.338062
g, S, 51.2149, 10.7927, 3.98805, 1.13187, 0.692512, 0.406131
h, S, 3.38521, 1.14262, 0.499441
i, S, 0.755427

!Cl cc-pVQZ-F12/MP2Fit
s, Cl, 563.363, 332.981, 209.261, 131.298, 49.9402, 30.8222, 18.8288, 9.86342, 5.6603, 3.15366, 1.74207, 1.09349, 0.703229, 0.349669, 0.185882, 0.126094
p, Cl, 373.778, 221.902, 133.355, 51.7518, 28.9827, 13.7962, 6.37378, 3.42832, 2.01389, 1.2537, 0.820267, 0.453891, 0.248097, 0.166978
d, Cl, 171.652, 103.092, 64.3071, 24.4785, 14.8499, 7.32097, 4.21317, 2.46829, 1.51689, 0.947582, 0.433063, 0.247967, 0.14637
f, Cl, 122.345, 40.9668, 23.6729, 10.0802, 4.6169, 2.22258, 1.14402, 0.636703, 0.389312
g, Cl, 55.5886, 11.7494, 5.0503, 1.32773, 0.891484, 0.509537
h, Cl, 3.76861, 1.33756, 0.594469
i, Cl, 0.891705

!Ar cc-pVQZ-F12/MP2Fit
s, Ar, 704.77, 416.329, 261.572, 164.099, 62.31, 38.4258, 23.4236, 12.167, 6.91398, 3.85276, 2.17073, 1.37845, 0.879038, 0.422921, 0.221579, 0.149881
p, Ar, 467.212, 276.381, 166.128, 63.5926, 34.68, 16.4913, 7.78497, 4.30311, 2.57959, 1.61037, 1.04125, 0.572313, 0.309624, 0.201853
d, Ar, 214.571, 128.857, 80.316, 30.6194, 18.4984, 9.08916, 5.23374, 3.08726, 1.90097, 1.16714, 0.524792, 0.295914, 0.176141
f, Ar, 152.902, 51.0475, 29.553, 13.1013, 5.97135, 2.62078, 1.42428, 0.794236, 0.473154
g, Ar, 69.0356, 15.9427, 7.09185, 1.69961, 1.02967, 0.59739
h, Ar, 4.17522, 1.91677, 0.768806
i, Ar, 1.21393

C.1.4 cc-pCVDZ-F12/MP2Fit

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!H cc-pVDZ-F12/MP2Fit
s, H, 18.16, 4.48346, 1.46001, 0.598208, 0.261817, 0.134824
p, H, 5.40776, 1.63382, 0.715305, 0.428532
d, H, 2.07531, 0.597566
f, H, 0.548776

!He cc-pVDZ-F12/MP2Fit
s, He, 26.5905, 5.7116, 1.49801, 1.01539, 0.424143, 0.200012
p, He, 6.19208, 1.82496, 0.776876, 0.525522
d, He, 3.36159, 1.1907
f, He, 2.00066

!Li cc-pCVDZ-F12/MP2Fit
s, Li, 128.005, 63.9903, 25.2815, 8.87182, 5.93023, 2.58568, 1.14734, 0.40494, 0.194574, 0.07753, 0.031241
p, Li, 31.7333, 8.01626, 4.56923, 2.27507, 1.10388, 0.55929, 0.233693, 0.104053, 0.06269, 0.020156
d, Li, 20.8282, 9.20651, 5.28528, 2.4656, 0.757139, 0.311696, 0.185166, 0.092317
f, Li, 1.36631, 0.485795, 0.240241
g, Li, 0.814707, 0.341625

!Be cc-pCVDZ-F12/MP2Fit
s, Be, 153.478, 81.4175, 28.9489, 12.4301, 6.00361, 3.29907, 1.15351, 0.457855, 0.232155, 0.089841, 0.064731
p, Be, 38.405, 12.6484, 7.3488, 3.01922, 1.64202, 0.59044, 0.256342, 0.112876, 0.066234, 0.0352
d, Be, 24.8649, 11.5081, 5.92845, 2.67334, 0.902982, 0.434277, 0.217267, 0.140152
f, Be, 1.5537, 0.626214, 0.307171
g, Be, 0.986381, 0.438583

!B cc-pCVDZ-F12/MP2Fit
s, B, 194.325, 101.602, 38.5708, 16.3907, 6.89924, 3.49631, 2.04455, 0.749637, 0.450771, 0.186504, 0.104061
p, B, 42.4657, 17.1188, 7.40528, 4.3457, 1.97432, 1.03319, 0.429791, 0.204947, 0.0988322, 0.0440192
d, B, 29.846, 14.3839, 6.37699, 2.92937, 1.07174, 0.460701, 0.287417, 0.172196
f, B, 1.72197, 0.866609, 0.396083
g, B, 1.22159, 0.585875

!C cc-pCVDZ-F12/MP2Fit
s, C, 248.165, 127.532, 47.4401, 21.1755, 8.55856, 4.13104, 2.33435, 0.973964, 0.641752, 0.290936, 0.141191
p, C, 52.6731, 22.7497, 9.71424, 4.42331, 2.13586, 1.17504, 0.687166, 0.297741, 0.145785, 0.055077
d, C, 33.316, 17.381, 7.10212, 3.50772, 1.42318, 0.746712, 0.436116, 0.184213
f, C, 2.58204, 1.32991, 0.524378
g, C, 1.85308, 0.835091

!N cc-pCVDZ-F12/MP2Fit
s, N, 314.069, 166.042, 60.9217, 26.039, 10.6107, 5.48529, 3.06732, 1.10468, 0.748178, 0.377477, 0.174635
p, N, 72.7477, 31.3651, 13.864, 5.75571, 2.63571, 1.28771, 0.717551, 0.358264, 0.178195, 0.068563
d, N, 39.3708, 21.8547, 7.3794, 3.89211, 2.00148, 0.94169, 0.504888, 0.216515
f, N, 3.33351, 1.71108, 0.742421
g, N, 2.38828, 1.12709

!O cc-pCVDZ-F12/MP2Fit
s, O, 371.326, 198.636, 71.8416, 33.7731, 11.9788, 5.74645, 3.55787, 1.36802, 0.960771, 0.407596, 0.183832
p, O, 92.5168, 39.7721, 17.9856, 7.52184, 3.25011, 1.46456, 0.818059, 0.438653, 0.220753, 0.085393
d, O, 45.4336, 25.9105, 8.70722, 4.18511, 2.1132, 1.06429, 0.514104, 0.230656
f, O, 4.28966, 2.08739, 0.855449
g, O, 2.99236, 1.33628
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!F cc-pCVDZ-F12/MP2Fit
s, F, 419.982, 242.863, 85.341, 41.5414, 15.0987, 8.95066, 4.45941, 2.56407, 1.12908, 0.508417, 0.216752
p, F, 111.861, 47.201, 22.8681, 9.72925, 4.11648, 1.91415, 1.00136, 0.534873, 0.272355, 0.102468
d, F, 54.5522, 32.8438, 12.335, 4.74621, 2.64178, 1.31127, 0.640936, 0.271604
f, F, 5.53146, 2.69337, 1.05759
g, F, 3.85982, 1.68774

!Ne cc-pCVDZ-F12/MP2Fit
s, Ne, 512.752, 297.675, 106.744, 46.7672, 18.1744, 11.4541, 5.04744, 2.90138, 1.34041, 0.603648, 0.262427
p, Ne, 134.034, 55.2965, 27.7261, 12.4828, 4.95457, 2.5881, 1.19261, 0.70789, 0.35178, 0.124215
d, Ne, 64.9608, 41.3932, 15.4439, 6.14264, 3.60227, 1.71056, 0.803719, 0.330853
f, Ne, 7.34485, 3.71622, 1.37168
g, Ne, 5.22447, 2.25776

!Na cc-pCVDZ-F12/MP2Fit
s, Na, 251.121, 104.24, 53.7495, 29.8752, 14.083, 8.22715, 4.18389, 3.20169, 1.1088, 0.448055, 0.261396, 0.10508, 0.0499335, 0.0394697
p, Na, 104.414, 25.7106, 12.0721, 6.81517, 3.80043, 1.9778, 0.978157, 0.382626, 0.229243, 0.121239, 0.0710956, 0.0361144
d, Na, 46.9562, 15.4191, 6.14411, 2.12391, 1.12989, 0.641291, 0.228283, 0.139529, 0.0663984, 0.0419816
f, Na, 12.009, 6.17373, 1.99787, 0.707999, 0.223577, 0.0497831
g, Na, 0.397859, 0.1055

!Mg cc-pCVDZ-F12/MP2Fit
s, Mg, 278.658, 140.698, 75.6014, 44.6508, 23.328, 14.6495, 5.75842, 3.61086, 1.7224, 0.574666, 0.303298, 0.120287, 0.062186, 0.047764
p, Mg, 135.733, 40.151, 18.681, 8.84139, 4.75814, 2.26731, 1.1061, 0.45233, 0.237792, 0.16554, 0.081685, 0.04157
d, Mg, 51.0761, 15.9983, 8.2111, 4.05608, 2.24697, 0.941292, 0.309711, 0.168926, 0.091746, 0.056029
f, Mg, 14.9066, 7.90925, 2.95382, 1.03912, 0.251757, 0.072507
g, Mg, 0.511473, 0.135108

!Al cc-pCVDZ-F12/MP2Fit
s, Al, 303.865, 155.864, 88.3486, 49.4066, 25.9379, 15.6942, 6.64983, 4.39534, 2.21701, 0.69563, 0.410074, 0.237577, 0.108642, 0.073192
p, Al, 156.61, 44.6477, 25.7599, 10.4447, 5.16807, 3.02241, 1.27511, 0.492513, 0.339512, 0.247939, 0.119471, 0.060635
d, Al, 57.5571, 19.4207, 10.9978, 4.89915, 2.83299, 1.36009, 0.544667, 0.256236, 0.112731, 0.063685
f, Al, 21.7021, 11.2857, 4.16056, 1.56658, 0.564088, 0.227858
g, Al, 0.940049, 0.358514

!Si cc-pCVDZ-F12/MP2Fit
s, Si, 346.738, 193.931, 110.22, 63.599, 38.4727, 16.7179, 8.59852, 4.785, 2.31327, 0.903351, 0.54523, 0.31186, 0.128986, 0.076293
p, Si, 183.802, 56.0636, 32.718, 12.9466, 5.47445, 3.67235, 1.51852, 0.56094, 0.420032, 0.285221, 0.150123, 0.083148
d, Si, 68.1573, 24.1321, 14.0852, 5.69856, 3.45694, 1.71799, 0.740492, 0.348319, 0.173996, 0.091534
f, Si, 27.1973, 14.4558, 5.57031, 2.27302, 0.807199, 0.31343
g, Si, 1.35454, 0.502991

!P cc-pCVDZ-F12/MP2Fit
s, P, 451.759, 242.577, 140.53, 82.6579, 41.4043, 23.9696, 9.89962, 5.75221, 2.7196, 1.23322, 0.646769, 0.359386, 0.167331, 0.097449
p, P, 226.789, 74.2066, 46.8059, 16.2999, 6.18202, 4.89984, 1.5889, 0.73929, 0.50971, 0.34689, 0.186511, 0.100799
d, P, 77.1627, 26.729, 17.7616, 6.62443, 4.25184, 1.87363, 0.88857, 0.439058, 0.212229, 0.120252
f, P, 28.9373, 15.7338, 6.95581, 3.03996, 1.02119, 0.395045
g, P, 1.76193, 0.63515

!S cc-pCVDZ-F12/MP2Fit
s, S, 494.133, 348.616, 162.419, 97.8207, 46.9261, 30.5772, 12.3877, 6.71654, 3.28511, 1.53503, 0.762721, 0.409851, 0.187494, 0.105964
p, S, 250.958, 89.8473, 56.6528, 19.1538, 7.62027, 5.1881, 2.02495, 0.886007, 0.62375, 0.41212, 0.226213, 0.124002
d, S, 83.1412, 28.9124, 19.6107, 7.53582, 5.03622, 2.3026, 1.05028, 0.504094, 0.24226, 0.128391
f, S, 35.5545, 16.4184, 8.48306, 3.82648, 1.20807, 0.463072
g, S, 2.15004, 0.747946

!Cl cc-pCVDZ-F12/MP2Fit
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s, Cl, 520.526, 420.11, 194.703, 116.823, 55.6758, 36.1925, 14.6397, 7.80731, 4.0683, 2.02414, 0.947071, 0.489773, 0.228451, 0.127775
p, Cl, 349.74, 94.8808, 62.8571, 19.9202, 9.77085, 6.31948, 2.74132, 1.16236, 0.749128, 0.475293, 0.268615, 0.148966
d, Cl, 91.9421, 31.9004, 20.3957, 8.83361, 5.91704, 2.86448, 1.30329, 0.62527, 0.29586, 0.154674
f, Cl, 40.8779, 17.7517, 10.4815, 4.45566, 1.51472, 0.565154
g, Cl, 2.5979, 0.92523

!Ar cc-pCVDZ-F12/MP2Fit
s, Ar, 573.197, 463.272, 227.234, 137.132, 66.1354, 42.606, 15.9398, 8.72036, 4.99942, 2.69569, 1.15171, 0.565111, 0.281332, 0.154009
p, Ar, 373.496, 108.81, 75.1307, 24.5127, 11.6374, 7.24674, 3.42066, 1.44798, 0.928538, 0.583972, 0.325969, 0.17948
d, Ar, 106.848, 36.7073, 22.7301, 10.2146, 6.84649, 3.77127, 1.59129, 0.740902, 0.352696, 0.186201
f, Ar, 48.6495, 19.831, 11.5154, 4.55077, 1.82494, 0.65388
g, Ar, 2.88182, 1.09238

C.1.5 cc-pCVTZ-F12/MP2Fit

!H cc-pVTZ-F12/MP2Fit
s, H, 25.6037, 5.30727, 2.03616, 1.23408, 0.687196, 0.362326, 0.207115
p, H, 6.58644, 2.53328, 1.7989, 0.765088, 0.350096
d, H, 2.2634, 0.751248, 0.262469
f, H, 1.7793, 0.873392
g, H, 1.18632

!He cc-pVTZ-F12/MP2Fit
s, He, 44.0428, 9.49713, 2.66028, 1.56784, 0.847025, 0.439706, 0.245193
p, He, 9.45825, 4.27609, 2.00522, 0.80446, 0.481563
d, He, 2.62272, 1.05717, 0.320944
f, He, 3.33026, 1.16498
g, He, 1.96969

!Li cc-pCVTZ-F12/MP2Fit
s, Li, 131.481, 90, 66.668, 33.6516, 17.3125, 8.93313, 3.78585, 1.00984, 0.705334, 0.386401, 0.152329, 0.101861, 0.052178
p, Li, 74.2474, 38.2806, 25.5102, 14.9534, 9.96977, 3.65951, 2.014, 1.05427, 0.417796, 0.179358, 0.109342, 0.072081
d, Li, 17.3135, 10.9951, 6.38797, 3.06901, 1.94057, 1.06015, 0.583716, 0.2761, 0.165329, 0.092556
f, Li, 2.71975, 1.34209, 0.6554, 0.355216, 0.215449, 0.115118
g, Li, 1.91054, 0.937874, 0.482502, 0.276642
h, Li, 0.672701

!Be cc-pCVTZ-F12/MP2Fit
s, Be, 138.675, 98.2134, 71.4167, 41.7384, 18.2154, 9.01259, 4.11541, 1.55017, 0.778096, 0.420979, 0.179518, 0.113803, 0.060719
p, Be, 78.2949, 41.0215, 26.5503, 17.3265, 10.1508, 3.74356, 2.08598, 1.21451, 0.430516, 0.192438, 0.125338, 0.074288
d, Be, 17.869, 11.2036, 8.04385, 3.5569, 2.08265, 1.16233, 0.621355, 0.323667, 0.169624, 0.096212
f, Be, 2.84997, 1.49015, 0.956213, 0.640523, 0.427057, 0.214965
g, Be, 2.0608, 0.976972, 0.639029, 0.371066
h, Be, 0.790135

!B cc-pCVTZ-F12/MP2Fit
s, B, 143.95, 101.931, 84.6216, 49.1834, 19.7649, 9.51322, 4.89458, 1.85818, 0.958709, 0.522024, 0.290789, 0.190623, 0.086559
p, B, 92.2384, 51.6982, 31.1965, 20.3238, 11.0268, 4.66322, 2.63959, 1.41867, 0.773991, 0.319468, 0.187192, 0.096283
d, B, 18.8717, 12.4449, 9.57956, 4.20943, 2.45589, 1.3721, 0.736272, 0.382347, 0.198467, 0.107787
f, B, 4.38486, 3.4185, 1.70308, 0.855842, 0.603335, 0.306451
g, B, 2.1002, 1.04275, 0.714461, 0.43302
h, B, 0.863138

!C cc-pCVTZ-F12/MP2Fit

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s, C, 186.668, 143.247, 118.784, 57.1235, 21.1714, 11.6244, 6.00683, 2.5362, 1.35116, 0.694698, 0.363731, 0.230872, 0.09187
p, C, 109.937, 59.526, 36.7464, 25.1884, 13.4249, 6.05866, 3.4088, 1.72075, 1.09303, 0.478749, 0.288926, 0.126994
d, C, 39.3695, 19.3498, 13.1991, 5.54165, 3.073, 1.60185, 0.952544, 0.521385, 0.229888, 0.124163
f, C, 14.0507, 4.02228, 2.26136, 1.178, 0.672267, 0.372196
g, C, 2.46773, 1.23847, 0.835974, 0.474554
h, C, 1.01751

!N cc-pCVTZ-F12/MP2Fit
s, N, 227.731, 172.001, 120.221, 70.0464, 23.7666, 13.9116, 6.81485, 3.44985, 1.44075, 0.836601, 0.465548, 0.284146, 0.123754
p, N, 130.942, 66.7842, 39.1564, 27.9886, 15.0393, 7.12272, 4.88753, 2.03288, 1.48494, 0.655407, 0.404268, 0.171767
d, N, 48.0432, 27.1004, 15.03, 6.40428, 4.12224, 1.79146, 1.01462, 0.608892, 0.297996, 0.152547
f, N, 17.8272, 6.59171, 3.4742, 1.76998, 0.833805, 0.516167
g, N, 3.67077, 1.87079, 0.91645, 0.576252
h, N, 1.30939

!O cc-pCVTZ-F12/MP2Fit
s, O, 518.699, 291.591, 191.129, 83.7046, 26.4931, 15.4289, 8.42512, 4.57266, 1.93583, 1.10178, 0.581937, 0.342467, 0.14938
p, O, 164.913, 72.5649, 46.303, 31.624, 15.4864, 8.63263, 5.88602, 2.3896, 1.74466, 0.80733, 0.49745, 0.206299
d, O, 72.8883, 28.0951, 19.5807, 8.03157, 4.77435, 2.47884, 1.72109, 0.821363, 0.396229, 0.190972
f, O, 21.8097, 7.87986, 4.48349, 2.07003, 1.02273, 0.610994
g, O, 4.52401, 2.20649, 1.09385, 0.69699
h, O, 1.55357

!F cc-pCVTZ-F12/MP2Fit
s, F, 758.623, 363.463, 225.956, 100.66, 34.459, 18.8917, 11.3782, 5.87709, 2.52451, 1.50695, 0.768447, 0.431946, 0.182736
p, F, 187.888, 90.0181, 52.2524, 33.3339, 18.4936, 10.6879, 7.47881, 2.95528, 2.10026, 1.00025, 0.619185, 0.253491
d, F, 106.519, 36.393, 21.3044, 8.82008, 5.36143, 2.64656, 1.92411, 0.874462, 0.434724, 0.222117
f, F, 26.5076, 10.2336, 5.33808, 2.77285, 1.55357, 0.790585
g, F, 6.84435, 3.52192, 1.54213, 0.877144
h, F, 2.33051

!Ne cc-pCVTZ-F12/MP2Fit
s, Ne, 827.074, 381.044, 237.905, 123.168, 46.661, 24.3549, 15.3785, 7.38549, 3.06308, 1.86422, 0.943498, 0.524206, 0.222179
p, Ne, 205.222, 94.4548, 57.0581, 37.4161, 22.8353, 13.4463, 9.63448, 3.56158, 2.50225, 1.1919, 0.751438, 0.308003
d, Ne, 124.563, 48.6247, 25.0227, 10.7194, 6.27407, 3.51841, 2.08039, 1.04237, 0.529352, 0.269902
f, Ne, 36.8296, 11.5945, 6.50838, 3.52327, 1.93701, 1.02925
g, Ne, 9.82938, 5.35272, 1.99182, 1.15647
h, Ne, 3.26522

!Na cc-pCVTZ-F12/MP2Fit
s, Na, 320.717, 211.354, 150.641, 89.4112, 56.383, 21.8863, 13.0608, 8.22261, 3.75566, 1.54389, 0.913341, 0.338011, 0.123976, 0.081416, 0.050381, 0.030159
p, Na, 183.883, 138.586, 93.518, 62.2023, 30.8845, 9.07852, 5.38097, 2.62559, 1.4493, 0.62545, 0.310728, 0.136456, 0.083635, 0.049384
d, Na, 47.0803, 24.061, 13.7963, 7.03432, 4.24601, 2.6079, 1.49789, 0.674053, 0.396821, 0.206472, 0.095789, 0.051043
f, Na, 15.2077, 7.22033, 4.64087, 2.1539, 0.860178, 0.549811, 0.189043, 0.100807
g, Na, 11.3307, 6.01307, 0.842217, 0.374657, 0.209358
h, Na, 0.280067

!Mg cc-pCVTZ-F12/MP2Fit
s, Mg, 371.285, 245.935, 175.324, 104.471, 65.4297, 22.6809, 14.2844, 8.88798, 3.95969, 1.66615, 0.914221, 0.393675, 0.155203, 0.116511, 0.069832, 0.038024
p, Mg, 209.483, 159.814, 109.872, 68.3186, 32.5197, 10.1537, 7.65831, 3.48748, 1.86316, 0.922079, 0.38342, 0.190853, 0.10689, 0.061616
d, Mg, 60.7411, 33.4814, 19.8067, 8.4371, 4.80695, 3.12088, 1.9588, 0.690362, 0.418679, 0.229722, 0.112681, 0.07775
f, Mg, 19.0976, 9.42526, 5.56722, 2.47522, 1.008, 0.651364, 0.306497, 0.163073
g, Mg, 13.4164, 7.24379, 1.57957, 0.446812, 0.223565
h, Mg, 0.316056
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!Al cc-pCVTZ-F12/MP2Fit
s, Al, 438.604, 289.706, 204.925, 120.127, 73.0857, 23.2015, 14.9139, 8.96243, 4.12516, 1.85703, 1.31634, 0.447076, 0.252478, 0.179976, 0.086069, 0.046278
p, Al, 246.424, 182.258, 123.159, 69.2851, 33.259, 11.2036, 7.99069, 3.70571, 1.91823, 0.939785, 0.440549, 0.224377, 0.116268, 0.069584
d, Al, 95.8335, 35.0255, 26.0739, 13.3027, 6.52577, 3.65734, 1.98319, 0.742388, 0.476169, 0.275271, 0.145653, 0.087963
f, Al, 22.2259, 10.9441, 5.93427, 2.63635, 1.2173, 0.657002, 0.350238, 0.176113
g, Al, 15.9, 8.63915, 1.84943, 0.639598, 0.250548
h, Al, 0.400313
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!Si cc-pCVTZ-F12/MP2Fit
s, Si, 550.881, 364.679, 259.192, 152.241, 93.7439, 30.1229, 16.0826, 9.79275, 4.77073, 1.8767, 1.44193, 0.606524, 0.350968, 0.255268, 0.091817, 0.0487
p, Si, 314.457, 242.782, 172.308, 103.894, 39.1677, 14.0853, 8.77368, 4.51295, 2.32093, 1.21767, 0.603832, 0.311539, 0.192444, 0.089827
d, Si, 129.491, 39.8165, 27.0094, 17.7765, 7.72919, 3.7759, 2.6515, 1.15603, 0.578492, 0.292319, 0.166651, 0.094079
f, Si, 29.2361, 14.1959, 7.99541, 3.36012, 1.59332, 0.844059, 0.473548, 0.246229
g, Si, 18.6204, 10.3001, 2.41907, 0.863283, 0.346839
h, Si, 0.547193
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!P cc-pCVTZ-F12/MP2Fit
s, P, 679.882, 451.658, 321.012, 188.55, 115.535, 36.3976, 20.3637, 12.8009, 6.26965, 2.3314, 1.79178, 0.805827, 0.46824, 0.344005, 0.133685, 0.068484
p, P, 387.849, 299.35, 213.174, 123.453, 41.3099, 17.2051, 12.6713, 6.26241, 3.2011, 1.53427, 0.75885, 0.428737, 0.247366, 0.118202
d, P, 142.655, 48.4518, 33.6077, 26.3615, 9.16844, 4.87596, 3.5293, 1.58618, 0.78524, 0.399602, 0.197931, 0.111203
f, P, 40.1276, 21.71, 10.786, 4.41468, 2.08854, 0.970243, 0.591895, 0.320693
g, P, 19.9248, 11.4338, 2.99018, 1.05377, 0.422121
h, P, 0.666947
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s, S, 817.683, 543.551, 386.332, 226.517, 139.216, 44.6255, 24.555, 15.2912, 7.53371, 2.75854, 2.13724, 1.01248, 0.58393, 0.418692, 0.1589, 0.083405
p, S, 456.773, 349.663, 246.11, 136.179, 46.8151, 19.9684, 13.9786, 6.78198, 3.71366, 1.87396, 0.914277, 0.519684, 0.288959, 0.126393
d, S, 173.065, 55.0726, 39.0245, 28.5672, 11.1928, 5.28397, 3.79113, 2.09382, 0.949, 0.459891, 0.243666, 0.118099
f, S, 53.3131, 26.192, 14.1516, 5.54866, 2.74376, 1.09063, 0.654507, 0.35945
g, S, 23.6052, 13.5963, 3.52528, 1.14904, 0.474574
h, S, 0.738448
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!Cl cc-pCVTZ-F12/MP2Fit
s, Cl, 1026.77, 683.269, 486.963, 286.476, 176.701, 60.5467, 34.0558, 19.7683, 8.98904, 3.47015, 2.68724, 1.30504, 0.737468, 0.514331, 0.193868, 0.104354
p, Cl, 563.399, 430.08, 300.198, 161.44, 48.627, 23.1445, 16.9502, 8.5243, 4.44567, 2.17667, 1.09339, 0.668637, 0.339318, 0.156244
d, Cl, 195.391, 77.9269, 49.8933, 30.295, 13.6642, 6.29233, 4.52286, 2.4859, 1.06707, 0.55019, 0.300789, 0.138466
f, Cl, 63.1086, 31.9174, 16.6314, 6.90788, 3.22488, 1.28178, 0.958814, 0.435698
g, Cl, 26.613, 15.5171, 3.95186, 1.34536, 0.560533
h, Cl, 0.8684
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!Ar cc-pCVTZ-F12/MP2Fit
s, Ar, 1224.71, 815.352, 584.009, 343.947, 212.575, 74.5349, 41.3371, 22.8072, 10.3533, 4.09171, 3.17545, 1.54086, 0.867309, 0.601652, 0.228233, 0.124612
p, Ar, 674.194, 513.73, 356.852, 188.589, 50.0688, 27.0315, 20.5529, 10.1443, 5.09811, 2.5907, 1.27927, 0.813491, 0.408196, 0.18851
d, Ar, 216.623, 96.7693, 62.0668, 32.0317, 16.012, 7.68618, 5.42386, 2.81245, 1.32769, 0.653138, 0.331974, 0.163064
f, Ar, 75.7535, 36.8493, 19.5686, 8.54943, 3.91583, 1.57928, 0.985487, 0.508212
g, Ar, 29.2736, 17.0177, 4.73969, 1.76971, 0.693386
h, Ar, 1.10774
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C.1.6 cc-pCVQZ-F12/MP2Fit

!H cc-pVQZ-F12/MP2Fit
s, H, 97.1313, 18.9366, 5.43323, 1.93823, 1.27324, 0.686296, 0.33445, 0.142999
p, H, 10.7919, 3.94392, 1.73729, 0.723821, 0.357907, 0.176046
d, H, 3.83163, 1.54855, 0.669395, 0.427949
f, H, 3.88063, 1.53882, 0.706655
g, H, 3.07132, 0.898362
h, H, 0.807491

!He cc-pVQZ-F12/MP2Fit
s, He, 109.987, 20.4003, 5.73172, 2.57906, 1.77807, 0.890023, 0.394219, 0.160173
p, He, 11.4948, 4.89228, 3.0669, 1.54383, 0.637878, 0.203734
d, He, 4.26867, 1.593, 0.735843, 0.470762
f, He, 4.0107, 1.81127, 1.02067
g, He, 2.69527, 1.35967
h, He, 0.957169

!Li cc-pCVQZ-F12/MP2Fit
s, Li, 306.663, 225.24, 102.395, 67.1944, 37.1793, 23.1432, 12.095, 8.00005, 4.99733, 2.06363, 0.968677, 0.546055, 0.25664, 0.126899, 0.051574, 0.034475
p, Li, 160.587, 109.401, 60.1767, 41.2572, 29.5093, 18.009, 7.03748, 3.07098, 2.09563, 1.03555, 0.401504, 0.237836, 0.109397, 0.077183, 0.043369
d, Li, 42.0079, 27.9486, 17.5564, 8.36993, 5.70837, 3.08147, 1.81139, 0.681013, 0.406074, 0.245931, 0.154202, 0.09828, 0.060905
f, Li, 60.1988, 38.8582, 22.4114, 8.46543, 2.07439, 0.690366, 0.262971, 0.173782, 0.106309
g, Li, 15.1795, 8.86639, 5.07703, 1.30063, 0.574046, 0.234405, 0.15202
h, Li, 1.28485, 0.432037, 0.183412
i, Li, 0.745052

!Be cc-pCVQZ-F12/MP2Fit
s, Be, 379.051, 263.296, 148.21, 101.258, 77.9795, 54.7006, 33.6894, 9.89173, 5.79438, 2.33956, 1.00345, 0.654531, 0.357292, 0.191531, 0.09469, 0.054669
p, Be, 249.2, 172.409, 95.5701, 77.3902, 59.2103, 35.9445, 13.6555, 6.56053, 2.87429, 1.34815, 0.515317, 0.356935, 0.219282, 0.112184, 0.095056
d, Be, 66.8493, 44.5183, 29.7851, 15.0519, 7.63335, 4.47281, 2.72029, 1.05875, 0.625703, 0.382559, 0.249575, 0.131646, 0.082776
f, Be, 95.6042, 59.7526, 35.1367, 13.6369, 3.82588, 1.17966, 0.595041, 0.323553, 0.183148
g, Be, 20.5963, 14.3067, 8.01718, 2.06526, 1.0543, 0.462799, 0.239338
h, Be, 2.03455, 0.737801, 0.34926
i, Be, 1.22519

!B cc-pCVQZ-F12/MP2Fit
s, B, 456.071, 317.896, 179.671, 123.326, 95.1806, 67.0553, 42.1631, 15.0165, 8.85171, 3.0199, 1.49439, 0.904305, 0.512383, 0.300036, 0.164968, 0.08882
p, B, 297.746, 204.863, 111.512, 90.2868, 69.0651, 40.4769, 15.3317, 7.21548, 3.44954, 2.35816, 0.940566, 0.497153, 0.264642, 0.134942, 0.115179
d, B, 81.0333, 54.084, 37.1109, 20.1012, 8.35117, 5.15786, 3.14718, 1.23722, 0.783675, 0.490345, 0.306431, 0.192551, 0.120307
f, B, 110.862, 69.2889, 40.7237, 14.5418, 3.83192, 1.40172, 0.777138, 0.559453, 0.267687
g, B, 23.9156, 16.1416, 8.35772, 2.27503, 1.16604, 0.525831, 0.375986
h, B, 3.09178, 1.24935, 0.495313
i, B, 1.96538

!C cc-pCVQZ-F12/MP2Fit
s, C, 569.074, 395.898, 222.779, 152.422, 117.235, 82.047, 50.9342, 17.4095, 9.68742, 3.93865, 2.33159, 1.22992, 0.56026, 0.325931, 0.196281, 0.11734
p, C, 370.699, 254.304, 136.538, 110.347, 84.1569, 47.371, 15.5509, 9.29137, 3.66126, 2.81512, 1.44265, 0.745192, 0.403884, 0.173905, 0.148129
d, C, 101.43, 67.6526, 46.9092, 26.1658, 10.2566, 6.44951, 4.1878, 1.79992, 0.997135, 0.599696, 0.394047, 0.253253, 0.152409
f, C, 130.357, 81.474, 47.8143, 16.8945, 5.25637, 1.87723, 1.30109, 0.74784, 0.395788
g, C, 29.0516, 20.1533, 11.2549, 2.49504, 1.50872, 0.796255, 0.417039
h, C, 3.95757, 1.66528, 0.695604
i, C, 2.56719

!N cc-pCVQZ-F12/MP2Fit
s, N, 709.091, 492.462, 275.585, 187.896, 143.846, 99.7961, 60.5536, 20.8156, 11.3433, 4.71784, 3.10054, 1.80948, 0.802881, 0.435213, 0.250041, 0.147058
p, N, 467.225, 321.495, 174.62, 141.59, 108.56, 64.1946, 20.4911, 11.5214, 4.38457, 3.3136, 1.74265, 0.980946, 0.541545, 0.223848, 0.188887
d, N, 126.053, 82.7574, 59.2898, 35.8222, 13.2022, 7.96801, 5.18031, 2.41145, 1.29266, 0.754763, 0.490996, 0.31671, 0.190819
f, N, 154.862, 96.7886, 54.3936, 21.7417, 8.19775, 3.09064, 1.49153, 0.876153, 0.53142
g, N, 36.0138, 24.5986, 13.1835, 3.75467, 1.79288, 1.05232, 0.636353
h, N, 4.60059, 2.04041, 0.805463
i, N, 3.06384

!O cc-pCVQZ-F12/MP2Fit
s, O, 847.802, 587.329, 326.274, 221.332, 168.351, 115.348, 67.4853, 23.6369, 13.3029, 5.52599, 3.70668, 2.25598, 1.01899, 0.517154, 0.277579, 0.161041
p, O, 560.719, 385.832, 210.165, 170.423, 130.657, 77.9767, 25.7887, 14.2289, 5.56867, 3.99321, 2.0031, 1.17848, 0.670504, 0.283875, 0.235534
d, O, 148.725, 94.4956, 70.2872, 46.0556, 17.2204, 9.61516, 6.09219, 3.13405, 1.64222, 0.912084, 0.575486, 0.362431, 0.216526
f, O, 180.881, 113.051, 60.6253, 27.6807, 10.3077, 4.21226, 1.87735, 1.06164, 0.654039
g, O, 42.9906, 28.9818, 14.9728, 5.02071, 2.15729, 1.23506, 0.733178
h, O, 4.62532, 2.26553, 0.937497
i, O, 3.2371

!F cc-pCVQZ-F12/MP2Fit
s, F, 1020.95, 706.341, 392.58, 266.266, 202.753, 139.16, 81.5188, 28.0066, 15.7878, 6.47301, 4.32156, 2.67588, 1.24782, 0.633507, 0.338889, 0.195834
p, F, 673.316, 463.419, 252.984, 187.11, 138.303, 85.8945, 31.3798, 17.287, 6.80095, 4.82051, 2.38419, 1.39501, 0.805277, 0.342453, 0.283907
d, F, 178.143, 112.676, 74.5706, 48.4595, 20.6034, 11.526, 7.26091, 3.86552, 1.99894, 1.096, 0.69422, 0.438762, 0.262363
f, F, 187.877, 119.424, 65.2186, 30.3373, 11.8412, 5.18439, 2.41618, 1.2653, 0.761531
g, F, 51.5421, 34.5872, 15.6196, 6.40589, 2.78491, 1.47572, 0.896142
h, F, 5.43814, 2.92742, 1.2308
i, F, 3.98995

!Ne cc-pCVQZ-F12/MP2Fit
s, Ne, 1231.86, 846.786, 466.2, 314.989, 238.784, 162.402, 91.7744, 32.4636, 20.2867, 8.77208, 5.59065, 3.37413, 1.63925, 0.796046, 0.388453, 0.219935
p, Ne, 799.05, 549.515, 299.247, 202.289, 154.286, 91.3177, 37.4763, 20.2056, 9.28373, 5.73625, 3.02842, 1.76273, 1.09196, 0.544012, 0.35167
d, Ne, 206.371, 116.559, 78.6087, 52.4694, 21.6459, 14.8523, 8.60408, 4.93263, 2.60422, 1.33145, 0.818882, 0.503707, 0.297045
f, Ne, 194.112, 121.516, 62.7871, 18.1216, 11.6712, 5.75641, 3.25736, 1.55971, 0.896654
g, Ne, 67.272, 42.2221, 16.0327, 8.15844, 4.4269, 2.66581, 1.2556
h, Ne, 7.46678, 4.49797, 1.59464
i, Ne, 5.79529

!Na cc-pCVQZ-F12/MP2Fit
s, Na, 264.242, 163.507, 128.831, 94.271, 58.6477, 36.7909, 14.187, 8.86067, 5.5139, 3.41623, 2.14632, 1.34005, 0.798591, 0.397937, 0.209636, 0.10978, 0.0598127, 0.049876
p, Na, 255.814, 159.786, 99.8351, 61.4213, 38.1688, 14.9236, 8.99553, 5.34465, 2.45228, 1.55948, 0.822524, 0.377755, 0.205399, 0.116067, 0.0752051, 0.054828
d, Na, 73.1515, 45.5087, 28.2409, 17.5148, 6.99222, 4.30942, 2.68445, 1.68509, 1.04376, 0.658894, 0.409255, 0.25406, 0.15895, 0.10028
f, Na, 32.9547, 23.0342, 9.71285, 5.73765, 2.65359, 1.04798, 0.551453, 0.271788, 0.159196, 0.110812
g, Na, 14.3535, 6.54277, 2.59182, 1.05799, 0.644382, 0.334375, 0.149837
h, Na, 1.14051, 0.435721, 0.124831
i, Na, 0.704941

!Mg cc-pCVQZ-F12/MP2Fit
s, Mg, 313.652, 192.68, 153.442, 114.452, 72.0684, 45.3409, 17.4298, 10.8632, 6.73541, 4.10999, 2.53358, 1.53743, 0.86025, 0.474262, 0.255342, 0.12198, 0.0761116, 0.0516539
p, Mg, 327.497, 204.69, 127.904, 76.6025, 46.1415, 18.8718, 11.2936, 5.88155, 3.08439, 1.64881, 0.912858, 0.424843, 0.231766, 0.129549, 0.0835033, 0.0603185

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d, Mg, 95.3203, 59.2444, 35.596, 22.3052, 8.6979, 5.37785, 3.34642, 2.09405, 1.30175, 0.711911, 0.485676, 0.284549, 0.169979, 0.105921
f, Mg, 41.6466, 29.0006, 13.565, 7.63514, 3.04004, 1.48477, 0.55156, 0.369822, 0.259097, 0.140589
g, Mg, 18.0123, 8.24691, 3.42207, 1.14044, 0.789709, 0.359125, 0.185726
h, Mg, 1.59445, 0.516523, 0.129131
i, Mg, 0.907508

!Al cc-pCVQZ-F12/MP2Fit
s, Al, 417.266, 248.797, 187.26, 133.935, 88.0056, 54.3346, 22.2665, 13.7897, 8.48704, 5.11326, 3.08142, 1.78604, 0.922627, 0.50443, 0.311746, 0.17767, 0.108842, 0.067367
p, Al, 422.734, 264.031, 164.436, 98.352, 58.3787, 21.2004, 12.1907, 6.26067, 3.36749, 1.77299, 0.940718, 0.567987, 0.356434, 0.180073, 0.104399, 0.074663
d, Al, 121.115, 75.7094, 45.0603, 28.186, 11.4614, 6.87615, 4.22499, 2.60335, 1.56381, 0.798888, 0.518391, 0.332045, 0.174568, 0.110021
f, Al, 54.9223, 36.7869, 21.8735, 8.82059, 3.57757, 1.69297, 0.92158, 0.418689, 0.32733, 0.196138
g, Al, 24.1784, 10.3924, 3.51558, 1.46145, 0.831981, 0.498465, 0.233528
h, Al, 1.60438, 0.520165, 0.233053
i, Al, 0.913533

!Si cc-pCVQZ-F12/MP2Fit
s, Si, 503.028, 312.401, 248.734, 185.252, 116.407, 73.0162, 27.8689, 17.2564, 10.6204, 6.3954, 3.84495, 2.21241, 1.15632, 0.683313, 0.454012, 0.252101, 0.146076, 0.099332
p, Si, 529.442, 330.928, 206.421, 123.513, 73.6974, 27.4852, 15.8885, 8.04338, 4.13015, 2.19253, 1.14006, 0.676144, 0.440793, 0.240834, 0.135128, 0.095642
d, Si, 150.319, 93.5338, 55.216, 33.852, 15.1866, 8.88153, 5.13385, 3.05726, 1.76476, 0.833235, 0.643173, 0.344903, 0.208393, 0.116811
f, Si, 68.3761, 42.8482, 27.459, 11.1299, 4.61719, 1.98552, 1.39212, 0.573857, 0.360796, 0.233525
g, Si, 25.9065, 11.9815, 3.91501, 1.61534, 0.867614, 0.543107, 0.307531
h, Si, 2.21149, 0.770237, 0.330231
i, Si, 1.30513

!P cc-pCVQZ-F12/MP2Fit
s, P, 635.522, 392.392, 293.207, 211.46, 145.345, 84.2047, 34.7869, 21.5278, 13.2426, 7.09308, 4.17658, 2.34136, 1.22236, 0.740547, 0.494715, 0.282743, 0.165359, 0.114155
p, P, 663.48, 413.766, 258.57, 154.273, 92.6549, 37.4251, 22.1546, 10.754, 5.008, 2.57169, 1.35763, 0.816448, 0.544001, 0.306216, 0.17022, 0.119266
d, P, 184.251, 116.253, 67.6115, 37.9975, 17.8546, 11.5051, 5.48138, 3.19173, 1.79651, 1.05396, 0.688624, 0.361674, 0.213456, 0.129512
f, P, 85.0385, 46.7172, 29.1232, 13.9501, 6.28107, 2.91427, 1.71052, 0.742988, 0.48438, 0.288387
g, P, 28.1097, 14.153, 4.54064, 1.89663, 0.897687, 0.595091, 0.333673
h, P, 2.72821, 0.931994, 0.411432
i, P, 1.59458

!S cc-pCVQZ-F12/MP2Fit
s, S, 795.993, 496.001, 392.885, 289.968, 180.961, 112.818, 41.7271, 24.9241, 14.3962, 7.71639, 4.21815, 2.58146, 1.4141, 0.852977, 0.535786, 0.302617, 0.166059, 0.125629
p, S, 832.204, 519.46, 324.452, 191.51, 115.181, 41.1009, 25.4353, 11.9184, 5.78249, 2.95096, 1.73668, 1.10327, 0.710655, 0.398967, 0.221675, 0.141512
d, S, 235.425, 146.64, 85.8943, 51.2962, 22.4874, 13.1516, 6.73529, 3.36326, 1.89709, 1.10055, 0.714084, 0.37693, 0.227073, 0.152419
f, S, 106.72, 57.0505, 31.378, 17.3875, 7.60933, 4.05579, 1.85379, 0.950449, 0.555705, 0.339686
g, S, 47.7885, 21.4901, 8.00304, 4.04642, 1.47095, 0.986748, 0.456353
h, S, 3.24748, 1.14201, 0.499109
i, S, 1.92579

!Cl cc-pCVQZ-F12/MP2Fit
s, Cl, 904.261, 564.275, 448.778, 333.323, 209.389, 131.365, 49.8942, 30.7699, 18.8004, 9.85054, 5.63599, 3.13523, 1.74042, 1.09756, 0.706331, 0.348795, 0.184203, 0.152092
p, Cl, 955.681, 596.872, 372.661, 220.762, 132.328, 47.8502, 26.8165, 13.445, 6.65141, 3.50644, 2.0475, 1.2736, 0.829739, 0.457886, 0.249447, 0.166672
d, Cl, 273.548, 170.731, 102.191, 63.1187, 24.9198, 15.6185, 7.42805, 4.22467, 2.47078, 1.52054, 0.950984, 0.432959, 0.246418, 0.174798
f, Cl, 123.137, 76.1948, 40.4041, 22.1378, 9.13559, 4.85377, 2.17529, 1.11336, 0.638099, 0.398895
g, Cl, 52.969, 25.1971, 9.6949, 5.09471, 1.56563, 1.13183, 0.531359
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h, Cl, 3.78833, 1.33908, 0.583813
i, Cl, 2.2523

!Ar cc-pCVQZ-F12/MP2Fit
s, Ar, 1129.85, 705.472, 561.024, 416.595, 261.692, 164.153, 62.2788, 38.3926, 23.39, 12.109, 6.85644, 3.82292, 2.17075, 1.38583, 0.883183, 0.42136, 0.219907, 0.18461
p, Ar, 1193.6, 745.04, 464.497, 273.738, 163.183, 56.5251, 27.6855, 15.5434, 8.07681, 4.42744, 2.65781, 1.66304, 1.06595, 0.581128, 0.312321, 0.200565
d, Ar, 342.765, 214.169, 128.482, 79.8187, 29.9682, 18.5727, 9.15829, 5.24017, 3.09151, 1.9052, 1.1703, 0.525264, 0.293839, 0.194652
f, Ar, 153.374, 97.5562, 51.0917, 28.0551, 11.3836, 6.32247, 2.62822, 1.4281, 0.794789, 0.47427
g, Ar, 61.5502, 31.3291, 12.6787, 6.80731, 1.77498, 1.15926, 0.633581
h, Ar, 5.15597, 1.91923, 0.773032
i, Ar, 3.14571

C.2 Additional Figures

To furthermore assess the performance of the new ABSs with existing sets, we compared the statistical behavior (MAE and σ) of the new sets to those of existing sets. To do so, normalized Gaussian distributions of the DF errors for a number of ABSs when used with the cc-pVnZ-F12 (Figures C.1 - C.3) and cc-pCVnZ-F12 OBS were plot (Figures C.4 - C.6). In addition, Table C.1 shows the size of the ABSs used in the figures below, in order to assess the performance of all new sets with regards to their size, per cardinal number.

Figure C.1 illustrates that the new cc-pVDZ-F12/MP2Fit outperforms the similar-sized aug-cc-pVTZ/MP2Fit, indicated by a lower MAE (central position of the Gaussian displaced to the left) and a much lower standard deviation σ as indicated by the width of the respective gaussians. Following the similar analysis, Figure C.2 shows that cc-pVTZ-F12/MP2Fit has similar error statistics with the much larger aug-cc-pwCVTZ/MP2Fit set, while figure VIII points out the cc-pVQZ-F12/MP2Fit set performs slightly better than aug-cc-pV5Z/MP2Fit while mainting a similar size. For the core-valence sets, Figures C.4 - C.6 show that cc-pCVDZ-F12/MP2Fit significantly outperforms the same-size aug-cc-pwCVTZ/MP2Fit, cc-pCVTZ-F12/MP2Fit has a similar MAE but better standard deviation than the larger aug-cc-pwCVQZ/MP2Fit, while cc-pCVQZ-F12/MP2Fit outperforms the much larger aug-cc-pwCV5Z-F12/MP2Fit. The above results show that the new sets achieve at least similar and usually better error statistics, while being smaller and thus more flexible.

The authors would like to acknowledge the use of the EPSRC UK National Service for Computational Chemistry Software (NSCCS) at Imperial College London in carrying out this work.

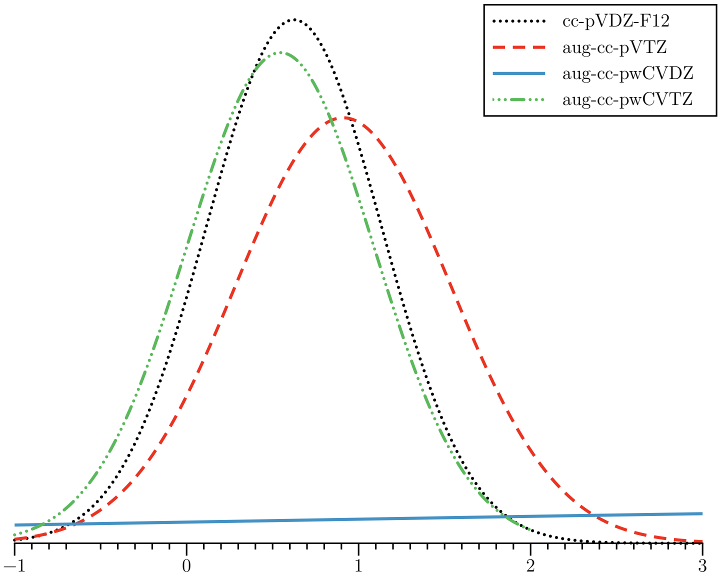

Figure C.1: Normalized Gaussian distributions of the ΔDF error in MP2 correlation energy for a test set of molecules that include elements H-Ar, at the cc-pVDZ-F12 level.

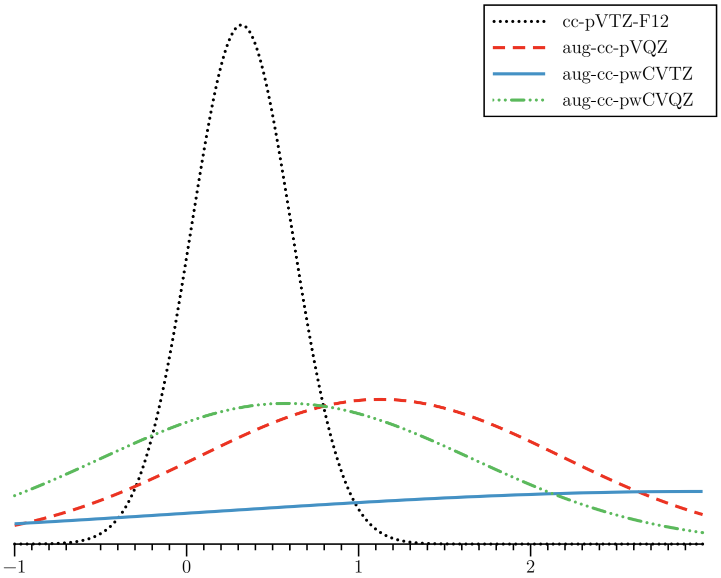

Figure C.2: Normalized Gaussian distributions of the ΔDF error in MP2 correlation energy for a test set of molecules that include elements H-Ar, at the cc-pVTZ-F12 level.

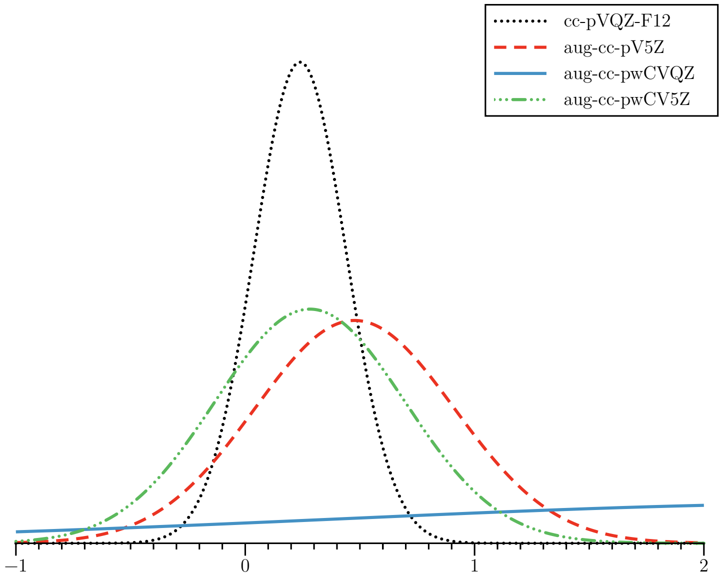

Figure C.3: Normalized Gaussian distributions of the ΔDF error in MP2 correlation energy for a test set of molecules that include elements H-Ar, at the cc-pVQZ-F12 level.

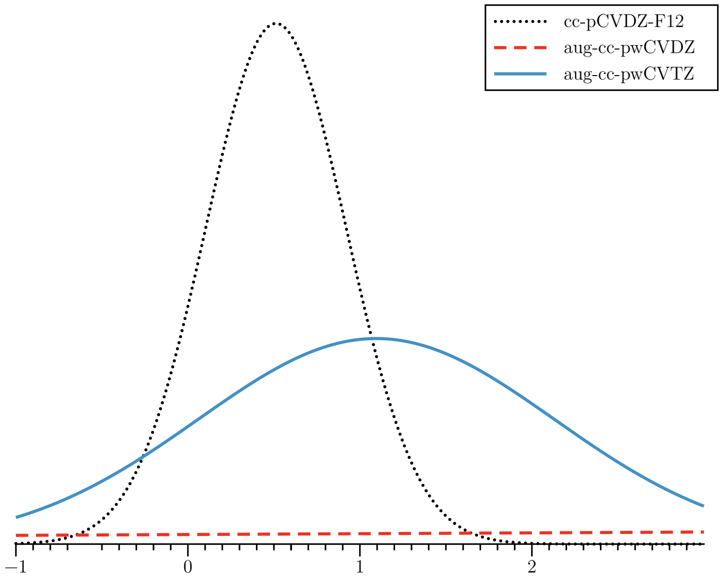

Figure C.4: Normalized Gaussian distributions of the ΔDF error in MP2 core-valence correlation energy for a test set of molecules that include elements H-Ar, at the cc-pCVDZ-F12 level.

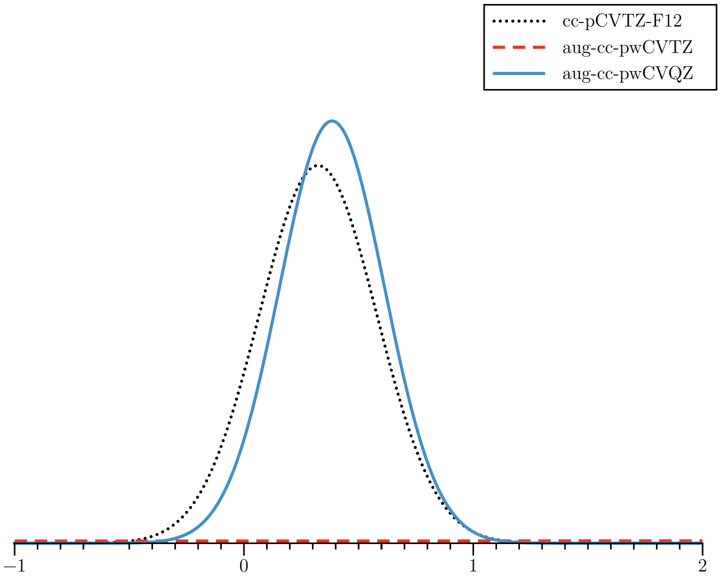

Figure C.5: Normalized Gaussian distributions of the ΔDF error in MP2 core-valence correlation energy for a test set of molecules that include elements H-Ar, at the cc-pCVTZ-F12 level.

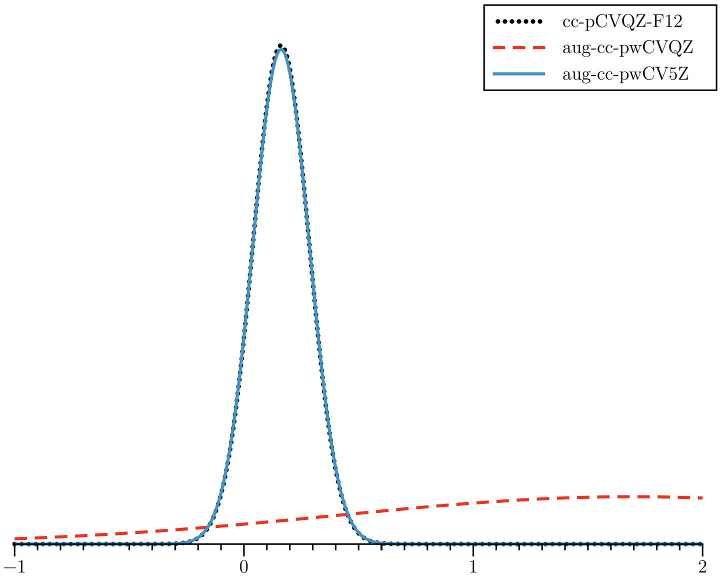

Figure C.6: Normalized Gaussian distributions of the ΔDF error in MP2 core-valence correlation energy for a test set of molecules that include elements H-Ar, at the cc-pCVQZ-F12 level.

Table C.1: Number of functions of new and existing MP2Fit auxiliary basis sets (assuming spherical orbitals)

ABS	Elements	Number of ABS functions
cc-pVDZ-F12/MP2Fit	H-He	35
	Li-Ne	107
	Na-Ar	140
cc-pVTZ-F12//MP2Fit	H-He	60
	Li-Ne	168
	Na-Ar	201
cc-pVQZ-F12/MP2Fit	H-He	96
	Li-Ne	253
	Na-Ar	286
cc-pCVDZ-F12/MP2Fit	Li-Ne	120
	Na-Ar	160
cc-pCVTZ-F12/MP2Fit	Li-Ne	188
	Na-Ar	230
cc-pCVQZ-F12/MP2Fit	Li-Ne	298
	Na-Ar	315
aug-cc-pVDZ/MP2Fit	H	23
	He	13
	Li-Ne	72
	Na-Ar	92
aug-cc-pVTZ/MP2Fit	H	46
	He	36
	Li-Ne	106
	Na-Ar	147
aug-cc-pVQZ/MP2Fit	H	80
	He	62
	Li-Ne	168
	Na-Ar	194
aug-cc-pV5Z/MP2Fit	H	127
	He	127
	Li-Ne	242
	Na-Ar	279
aug-cc-pwCVDZ/MP2Fit	Li-Ne	86
	Na-Ar	133
aug-cc-pwCVTZ/MP2Fit	Li-Ne	136
	Na-Ar	201
aug-cc-pwCVQZ/MP2Fit	Li-Ne	222
	Na-Ar	295
aug-cc-pwCV5Z/MP2Fit	Li-Ne	328
	Na-Ar	411

Appendix D

Supplementary Information for Chapter 6:

Basis Sets for explicitly correlated calculations: The atoms Y-Pd.

D.1 Orbital basis sets

All orbital basis sets are provided in molpro format.

D.1.1 cc-pVDZ-PP-F12

```
!Y cc-pVDZ-PP-F12
s, Y, 1.215550E+02, 1.335080E+01, 8.343040E+00, 5.212620E+00, 2.848220E+00, 7.360920E-01, 3.395250E-01, 8.500000E-02, 4.571900E-02, 2.177500E-02;
c, 1.10, 3.990000E-04, -3.737400E-02, 2.104080E-01, -1.742590E-01, -4.490590E-01, 7.515460E-01, 5.039130E-01, 3.819000E-02, -1.681900E-02, 5.199000E-03;
c, 1.10, -1.380000E-04, 1.265500E-02, -7.257700E-02, 6.894600E-02, 1.410760E-01, -3.097690E-01, -3.640910E-01, 3.089760E-01, 6.183900E-01, 2.694800E-01;
c, 1.10, 0.000202, -0.005459, -0.024633, -0.033332, 0.389816, -1.018775, -0.030205, 2.753454, -1.825975, -0.494858;
c, 1.10, -0.001217, 0.02234, -0.109196, -0.008341, 0.671286, -2.760323, 2.77312, 0.590809, -3.3291, 2.327642;
c, 10.10, 1.000000E+00;
s, Y, 1.040000E-02;
p, Y, 1.570570E+01, 9.814340E+00, 3.951520E+00, 1.028730E+00, 5.203410E-01, 2.628060E-01, 1.191270E-01, 5.326300E-02, 2.338400E-02;
c, 1.9, -1.008000E-03, 1.845100E-02, -1.533130E-01, 3.882870E-01, 4.715490E-01, 2.442250E-01, 3.745500E-02, 9.170000E-04, 5.430000E-04;
c, 1.9, -1.460000E-04, -4.538000E-03, 4.661300E-02, -1.376680E-01, -1.888270E-01, -1.161280E-01, 3.231850E-01, 6.065240E-01, 2.419670E-01;
c, 1.9, -0.000266, -0.005748, 0.059726, -0.172697, -0.248414, -0.166389, 0.559808, 0.590163, 0.047867;
c, 1.9, 0.002523, -0.016889, 0.124317, -0.381136, -0.870203, 1.1357, 0.859968, -1.082673, -0.135029;
c, 9.9, 1.000000E+00;
p, Y, 1.030000E-02;
d, Y, 1.585350E+01, 5.081830E+00, 1.450950E+00, 6.892770E-01, 3.133420E-01, 1.383830E-01, 5.955500E-02, 2.450300E-02;
c, 1.8, 9.920000E-04, -5.234000E-03, 8.678900E-02, 2.297090E-01, 3.256070E-01, 3.432860E-01, 2.503880E-01, 7.727600E-02;
c, 1.8, -0.001139, 0.006041, -0.124843, -0.333758, -0.379911, 0.17134, 0.61609, 0.204771;
c, 1.8, 0.001367, -0.007516, 0.173784, 0.550371, -0.069211, -0.985771, 0.36704, 0.587747;
c, 8.8, 1.000000E+00;
d, Y, 1.010000E-02;
f, Y, 0.438066, 0.116542;

!Zr cc-pVDZ-PP-F12
s, Zr, 1.368260E+02, 1.451280E+01, 9.069810E+00, 5.666400E+00, 3.113190E+00, 8.234820E-01, 3.811930E-01, 9.779200E-02, 5.083900E-02, 2.369300E-02;
c, 1.10, 4.090000E-04, -3.851700E-02, 2.158150E-01, -1.733400E-01, -4.700670E-01, 7.634610E-01, 5.037400E-01, 3.785900E-02, -1.539000E-02, 4.804000E-03;
c, 1.10, -1.420000E-04, 1.314500E-02, -7.534100E-02, 6.997800E-02, 1.504360E-01, -3.253820E-01, -3.567120E-01, 3.070140E-01, 6.239180E-01, 2.680050E-01;
c, 1.10, 0.000278, -0.009060, -0.017385, -0.056478, 0.463722, -1.229328, 0.170601, 2.604994, -1.824965, -0.390928;
c, 1.10, -0.002769, 0.085123, -0.329796, 0.268501, 0.586346, -3.077496, 3.340782, -0.558668, -1.996079, 1.833570;
c, 10.10, 1.000000E+00;
s, Zr, 1.100000E-02;
p, Zr, 1.741190E+01, 1.087990E+01, 4.328040E+00, 1.138640E+00, 5.758550E-01, 2.886700E-01, 1.280140E-01, 5.529000E-02, 2.361300E-02;
c, 1.9, -1.183000E-03, 1.917400E-02, -1.600700E-01, 4.057620E-01, 4.736200E-01, 2.319610E-01, 3.266200E-02, 6.340000E-04, 3.910000E-04;
c, 1.9, -1.340000E-04, -4.609000E-03, 4.818900E-02, -1.454840E-01, -1.898740E-01, -7.781400E-02, 3.319510E-01, 5.837920E-01, 2.468610E-01;
c, 1.9, -0.000271, -0.006390, 0.067595, -0.199853, -0.284930, -0.097245, 0.650866, 0.499489, 0.021642;
c, 1.9, 0.003226, -0.018832, 0.135472, -0.454012, -0.800296, 1.278091, 0.602365, -1.057289, -0.080795;
c, 9.9, 1.000000E+00;
p, Zr, 1.010000E-02;
d, Zr, 1.807320E+01, 5.219590E+00, 1.699850E+00, 8.363230E-01, 3.933540E-01, 1.788240E-01, 7.827500E-02, 3.224800E-02;
c, 1.8, 1.141000E-03, -8.281000E-03, 9.337700E-02, 2.509730E-01, 3.439070E-01, 3.298380E-01, 2.121770E-01, 5.859000E-02;
c, 1.8, -0.001129, 0.008331, -0.111513, -0.299284, -0.334845, 0.111229, 0.571392, 0.339706;
c, 1.8, 0.001089, -0.009250, 0.182316, 0.473318, 0.056017, -0.854440, -0.050623, 0.811626;
c, 8.8, 1.000000E+00;
```

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d, Zr, 1.330000E-02;
f, Zr, 0.657022, 0.177437;

!Nb cc-pVDZ-PP-F12
s, Nb, 1.530710E+02, 1.563630E+01, 9.772180E+00, 6.105440E+00, 3.390900E+00, 9.116760E-01, 4.221390E-01, 1.090790E-01, 5.562400E-02, 2.552400E-02;
c, 1.10, 4.270000E-04, -3.983400E-02, 2.232090E-01, -1.760000E-01, -4.860610E-01, 7.744000E-01, 5.027280E-01, 3.740300E-02, -1.464500E-02, 4.588000E-03;
c, 1.10, -1.480000E-04, 1.359700E-02, -7.819000E-02, 7.183800E-02, 1.563340E-01, -3.360430E-01, -3.472660E-01, 3.058060E-01, 6.211110E-01, 2.714220E-01;
c, 1.10, 0.00044, -0.016989, 0.006401, -0.098276, 0.523419, -1.34261, 0.288912, 2.462278, -1.731197, -0.384551;
c, 1.10, -0.004938, 0.17052, -0.62012, 0.638649, 0.411246, -3.148421, 3.523551, -0.978869, -1.471598, 1.613443;
c, 10.10, 1.000000E+00;
s, Nb, 1.170000E-02;
p, Nb, 1.887130E+01, 1.179290E+01, 4.715290E+00, 1.255300E+00, 6.350230E-01, 3.175950E-01, 1.410540E-01, 6.049400E-02, 2.563000E-02;
c, 1.9, -1.383000E-03, 2.071000E-02, -1.677060E-01, 4.181250E-01, 4.741640E-01, 2.237340E-01, 3.068900E-02, 6.280000E-04, 3.150000E-04;
c, 1.9, -1.020000E-04, -5.079000E-03, 5.132100E-02, -1.541440E-01, -1.927810E-01, -6.314700E-02, 3.412080E-01, 5.757850E-01, 2.428800E-01;
c, 1.9, -0.00021, -0.007439, 0.075853, -0.226861, -0.30774, -0.039583, 0.674512, 0.453857, 0.018026;
c, 1.9, 0.002791, -0.019272, 0.146631, -0.531006, -0.701985, 1.313725, 0.480003, -1.033874, -0.070944;
c, 9.9, 1.000000E+00;
p, Nb, 1.090000E-02;
d, Nb, 2.089850E+01, 5.601340E+00, 1.938050E+00, 9.775120E-01, 4.697960E-01, 2.179050E-01, 9.691700E-02, 4.035600E-02;
c, 1.8, 1.239000E-03, -9.137000E-03, 9.741800E-02, 2.640250E-01, 3.520390E-01, 3.189190E-01, 1.905900E-01, 4.872700E-02;
c, 1.8, -0.001275, 0.009442, -0.123791, -0.324681, -0.320145, 0.156172, 0.563642, 0.315979;
c, 1.8, 0.001464, -0.011899, 0.234277, 0.528187, -0.098693, -0.875487, 0.123318, 0.71165;
c, 8.8, 1.000000E+00;
d, Nb, 1.680000E-02;
f, Nb, 0.872393, 0.238530;

!Mo cc-pVDZ-PP-F12
s, Mo, 1.700690E+02, 1.673380E+01, 1.045870E+01, 6.534340E+00, 3.679350E+00, 1.001920E+00, 4.631400E-01, 1.187270E-01, 5.951400E-02, 2.703900E-02;
c, 1.10, 4.530000E-04, -4.138000E-02, 2.326990E-01, -1.825190E-01, -4.983180E-01, 7.853790E-01, 5.013700E-01, 3.582900E-02, -1.403700E-02, 4.276000E-03;
c, 1.10, -1.560000E-04, 1.399200E-02, -8.096300E-02, 7.445400E-02, 1.588830E-01, -3.414150E-01, -3.366740E-01, 3.095560E-01, 6.149970E-01, 2.713550E-01;
c, 1.10, 0.000499, -0.019907, 0.013219, -0.113935, 0.549784, -1.383369, 0.349221, 2.319466, -1.591676, -0.421122;
c, 1.10, -0.005393, 0.196021, -0.722018, 0.783385, 0.34952, -3.189942, 3.583307, -1.133227, -1.232403, 1.493237;
c, 10.10, 1.000000E+00;
s, Mo, 1.230000E-02;
p, Mo, 2.030800E+01, 1.269070E+01, 5.119500E+00, 1.377830E+00, 6.968240E-01, 3.473670E-01, 1.528190E-01, 6.504900E-02, 2.733900E-02;
c, 1.9, -1.514000E-03, 2.216800E-02, -1.743690E-01, 4.279430E-01, 4.753060E-01, 2.174030E-01, 2.852400E-02, 4.610000E-04, 3.060000E-04;
c, 1.9, -8.300000E-05, -5.447000E-03, 5.320300E-02, -1.581500E-01, -1.918290E-01, -5.244900E-02, 3.447620E-01, 5.699340E-01, 2.420080E-01;
c, 1.9, -0.000169, -0.008387, 0.082481, -0.247272, -0.324684, 0.015956, 0.683036, 0.417834, 0.017267;
c, 1.9, 0.001652, -0.018677, 0.15689, -0.599832, -0.622281, 1.359233, 0.351888, -0.999922, -0.054939;
c, 9.9, 1.000000E+00;
p, Mo, 1.150000E-02;
d, Mo, 2.260320E+01, 6.339140E+00, 2.177630E+00, 1.107000E+00, 5.353720E-01, 2.489800E-01, 1.104090E-01, 4.537700E-02;
c, 1.8, 1.306000E-03, -1.243800E-02, 1.035120E-01, 2.776610E-01, 3.588570E-01, 3.092260E-01, 1.740360E-01, 4.269800E-02;
c, 1.8, -0.001231, 0.012107, -0.115324, -0.316715, -0.297884, 0.16358, 0.54045, 0.357338;
c, 1.8, 0.001592, -0.018131, 0.258039, 0.520842, -0.12153, -0.812424, 0.041985, 0.736926;
c, 8.8, 1.000000E+00;
d, Mo, 1.860000E-02;
f, Mo, 0.306918, 1.116500

!Tc cc-pVDZ-PP-F12
s, Tc, 1.885090E+02, 1.780800E+01, 1.113100E+01, 6.954830E+00, 3.976400E+00, 1.093810E+00, 5.040080E-01, 1.272060E-01, 6.304700E-02,
```

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2.840800E-02;
c, 1.10, 4.850000E-04, -4.306600E-02, 2.441460E-01, -1.935770E-01, -5.059760E-01, 7.962750E-01, 4.985920E-01, 3.414600E-02, -1.299100E-02,
4.184000E-03;
c, 1.10, -1.640000E-04, 1.434600E-02, -8.374100E-02, 7.842800E-02, 1.569650E-01, -3.397950E-01, -3.239530E-01, 3.005360E-01, 6.094500E-01,
2.799160E-01;
c, 10.10, 1.000000E+00;
c, 1.10, 0.000658, -0.02949, 0.044493, -0.167566, 0.603497, -1.43773, 0.411672, 2.215836, -1.496613, -0.435643;
c, 1.10, -0.002441, 0.095036, -0.387603, 0.403361, 0.371126, -2.296074, 2.252037, 0.782609, -3.365703, 2.368472;
s, Tc, 1.280000E-02;
p, Tc, 2.164440E+01, 1.352680E+01, 5.542660E+00, 1.506110E+00, 7.616800E-01, 3.783660E-01, 1.635880E-01, 6.894100E-02, 2.867400E-02;
c, 1.9, -1.559000E-03, 2.370900E-02, -1.803710E-01, 4.355170E-01, 4.764540E-01, 2.128830E-01, 2.664300E-02, 1.880000E-04, 3.260000E-04;
c, 1.9, -9.600000E-05, -5.722000E-03, 5.394400E-02, -1.582580E-01, -1.873640E-01, -4.484600E-02, 3.427490E-01, 5.657040E-01, 2.454980E-01;
c, 1.9, -0.000278, -0.00925, 0.089333, -0.269572, -0.340806, 0.077042, 0.689067, 0.379664, 0.014777;
c, 1.9, 0.00051, -0.018416, 0.167242, -0.665936, -0.546456, 1.408708, 0.206838, -0.951805, -0.040152;
c, 9.9, 1.000000E+00;
p, Tc, 1.190000E-02;
d, Tc, 2.538280E+01, 6.985380E+00, 2.412170E+00, 1.241770E+00, 6.052420E-01, 2.828290E-01, 1.255600E-01, 5.148500E-02;
c, 1.8, 1.339000E-03, -1.328100E-02, 1.080380E-01, 2.860310E-01, 3.608340E-01, 3.011930E-01, 1.650010E-01, 4.042500E-02;
c, 1.8, -0.001296, 0.013245, -0.120612, -0.340102, -0.28903, 0.209852, 0.56057, 0.30187;
c, 1.8, 0.001969, -0.022368, 0.305719, 0.577539, -0.295248, -0.823245, 0.270203, 0.592692;
c, 8.8, 1.000000E+00;
d, Tc, 2.110000E-02;
f, Tc, 0.333888, 1.266270;

!Ru cc-pVDZ-PP-F12
s, Ru, 2.082500E+02, 1.884710E+01, 1.178180E+01, 7.361950E+00, 4.277710E+00, 1.191070E+00, 5.485680E-01, 1.386940E-01, 6.765100E-02,
3.014100E-02;
c, 1.10, 5.230000E-04, -4.491300E-02, 2.576260E-01, -2.091300E-01, -5.106620E-01, 8.032470E-01, 4.984140E-01, 3.376600E-02, -1.209400E-02,
4.197000E-03;
c, 1.10, -1.750000E-04, 1.480300E-02, -8.752700E-02, 8.428200E-02, 1.549110E-01, -3.381410E-01, -3.160050E-01, 2.835260E-01, 6.092730E-01,
2.932010E-01;
c, 1.10, 0.000394, -0.020885, 0.011286, -0.134516, 0.613718, -1.500395, 0.473209, 2.127158, -1.421879, -0.432682;
c, 1.10, -0.003971, 0.160332, -0.633022, 0.687576, 0.427069, -3.214260, 3.568551, -1.175975, -1.125964, 1.432979;
c, 10.10, 1.000000
s, Ru, 1.340000E-02;
p, Ru, 2.277530E+01, 1.423400E+01, 5.987550E+00, 1.639240E+00, 8.278800E-01, 4.090100E-01, 1.718770E-01, 7.127100E-02, 2.922600E-02;
c, 1.9, -1.544000E-03, 2.577100E-02, -1.865980E-01, 4.427740E-01, 4.781510E-01, 2.083690E-01, 2.463500E-02, -2.190000E-04, 3.700000E-04;
c, 1.9, -1.480000E-04, -9.174000E-03, 8.137400E-02, -2.361250E-01, -2.943330E-01, 1.509800E-02, 6.560890E-01, 4.389440E-01, 1.816800E-02;
c, 1.9, -0.000358, -0.010825, 0.099246, -0.301294, -0.369041, 0.168038, 0.705934, 0.313602, 0.009083;
c, 1.9, 0.000345, -0.020720, 0.180233, -0.738149, -0.461626, 1.484084, -0.007921, -0.884623, -0.010899;
c, 9.9, 1.000000
p, Ru, 1.200000E-02;
d, Ru, 2.588380E+01, 7.592550E+00, 2.712930E+00, 1.397080E+00, 6.825650E-01, 3.193780E-01, 1.417810E-01, 5.801700E-02;
c, 1.8, 1.523000E-03, -1.816200E-02, 1.096910E-01, 2.915970E-01, 3.620440E-01, 2.975140E-01, 1.610370E-01, 3.897000E-02;
c, 1.8, -0.001546, 0.019269, -0.130688, -0.369171, -0.271534, 0.252098, 0.548800, 0.274524;
c, 1.8, 0.002631, -0.033274, 0.299483, 0.608895, -0.370795, -0.797920, 0.329762, 0.571476;
c, 8.8, 1.000000
d, Ru, 2.370000E-02;
f, Ru, 1.544488, 0.398128;

!Rh cc-pVDZ-PP-F12
s, Rh, 2.289320E+02, 1.990870E+01, 1.244680E+01, 7.778210E+00, 4.580060E+00, 1.290680E+00, 5.934140E-01, 1.491580E-01, 7.195300E-02,
3.175200E-02;
c, 1.10, 5.680000E-04, -4.680300E-02, 2.723670E-01, -2.301680E-01, -5.095540E-01, 8.098500E-01, 4.978760E-01, 3.315400E-02, -1.151300E-02,
4.206000E-03;
c, 1.10, -1.860000E-04, 1.518000E-02, -9.113000E-02, 9.119900E-02, 1.503790E-01, -3.344630E-01, -3.074430E-01, 2.695540E-01, 6.048640E-01,
3.070670E-01;
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c, 1.10, 0.000311, -0.01958, 0.004751, -0.129825, 0.614754, -1.478033, 0.460452, 1.992395, -1.193214, -0.537879;
c, 1.10, -0.002843, 0.112088, -0.468617, 0.455369, 0.571321, -3.149643, 3.353112, -0.744556, -1.575198, 1.585372;
c, 10.10, 1.000000E+00;
s, Rh, 1.400000E-02;
p, Rh, 2.421170E+01, 1.513310E+01, 6.447200E+00, 1.777760E+00, 8.990200E-01, 4.445220E-01, 1.886740E-01, 7.851400E-02, 3.219500E-02;
c, 1.9, -1.579000E-03, 2.719800E-02, -1.914630E-01, 4.476580E-01, 4.777240E-01, 2.058190E-01, 2.435200E-02, -5.800000E-05, 3.330000E-04;
c, 1.9, -1.320000E-04, -6.532000E-03, 5.644500E-02, -1.610630E-01, -1.842580E-01, -3.361000E-02, 3.445440E-01, 5.595730E-01, 2.467510E-01;
c, 1.9, -0.000122, -0.012728, 0.108665, -0.333076, -0.37623, 0.217222, 0.688442, 0.299196, 0.011732;
c, 1.9, 0.001003, -0.024122, 0.192722, -0.799952, -0.375139, 1.482737, -0.078886, -0.852145, -0.022004;
c, 9.9, 1.000000E+00;
p, Rh, 1.320000E-02;
d, Rh, 2.949980E+01, 7.404370E+00, 3.059590E+00, 1.582050E+00, 7.748340E-01, 3.630560E-01, 1.610470E-01, 6.562000E-02;
c, 1.8, 1.677000E-03, -1.843900E-02, 1.050760E-01, 2.937700E-01, 3.641780E-01, 2.972650E-01, 1.599580E-01, 3.867900E-02;
c, 1.8, -0.001787, 0.020316, -0.132675, -0.383604, -0.261824, 0.264271, 0.539346, 0.271947;
c, 1.8, 0.003085, -0.035711, 0.286338, 0.630244, -0.387408, -0.79348, 0.341782, 0.572018;
c, 8.8, 1.000000E+00;
d, Rh, 2.670000E-02;
f, Rh, 1.938236, 0.467566;

!Pd cc-pVDZ-PP-F12
s, Pd, 2.472020E+02, 2.079370E+01, 1.300190E+01, 8.125620E+00, 4.888420E+00, 1.392060E+00, 6.383820E-01, 1.588280E-01, 7.579300E-02, 3.318400E-02;
c, 1.10, 6.240000E-04, -5.019800E-02, 2.962420E-01, -2.640150E-01, -5.037150E-01, 8.177430E-01, 4.964090E-01, 3.231800E-02, -1.102300E-02, 4.217000E-03;
c, 1.10, -2.000000E-04, 1.586700E-02, -9.687000E-02, 1.017160E-01, 1.434910E-01, -3.291740E-01, -2.996310E-01, 2.591500E-01, 5.993290E-01, 3.186520E-01;
c, 1.10, 0.000144, -0.016787, -0.003892, -0.137673, 0.64008, -1.483671, 0.461522, 1.892092, -1.025108, -0.598172;
c, 1.10, -0.002055, 0.075915, -0.336622, 0.247934, 0.698326, -3.019637, 3.069089, -0.281503, -2.057002, 1.759608;
c, 10.10, 1.000000E+00;
s, Pd, 1.450000E-02;
p, Pd, 2.488240E+01, 1.555170E+01, 6.923430E+00, 1.922860E+00, 9.711910E-01, 4.769190E-01, 1.938660E-01, 7.879200E-02, 3.165300E-02;
c, 1.9, -1.722000E-03, 3.153400E-02, -2.010620E-01, 4.525720E-01, 4.799470E-01, 2.040450E-01, 2.251700E-02, -6.140000E-04, 4.090000E-04;
c, 1.9, -2.120000E-04, -6.801000E-03, 5.398800E-02, -1.486710E-01, -1.667440E-01, -3.472600E-02, 3.263210E-01, 5.599760E-01, 2.643670E-01;
c, 1.9, -0.000663, -0.01554, 0.126776, -0.393528, -0.411615, 0.384806, 0.665642, 0.177641, 0.007242;
c, 1.9, 0.001856, -0.031032, 0.214604, -0.918703, -0.171037, 1.485386, -0.370775, -0.734498, 0.001632;
c, 9.9, 1.000000E+00;
p, Pd, 1.270000E-02;
d, Pd, 2.902040E+01, 6.411490E+00, 3.997360E+00, 1.887420E+00, 9.132080E-01, 4.256750E-01, 1.877270E-01, 7.579000E-02;
c, 1.8, 2.172000E-03, -4.795800E-02, 1.033430E-01, 2.932100E-01, 3.716870E-01, 3.064560E-01, 1.666290E-01, 4.106300E-02;
c, 1.8, -0.002442, 0.057813, -0.137266, -0.422404, -0.284325, 0.283976, 0.529446, 0.256741;
c, 1.8, 0.003816, -0.09517, 0.252292, 0.675294, -0.330274, -0.809732, 0.306929, 0.625382;
c, 8.8, 1.000000E+00;
d, Pd, 3.060000E-02;
f, Pd, 2.417292, 0.529142;
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D.1.2 cc-pVTZ-PP-F12

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!Y cc-pVTZ-PP-F12
s, Y, 5.177130E+03, 8.037880E+02, 1.768550E+02, 2.470940E+01, 1.543110E+01, 9.637060E+00, 3.655690E+00, 2.188790E+00, 9.669010E-01, 5.203350E-01, 2.687380E-01, 9.343100E-02, 4.427800E-02, 2.058600E-02;
c, 1.14, 6.000000E-06, 4.200000E-05, 1.850000E-04, 6.856000E-03, -5.141000E-02, 1.537220E-01, -3.427500E-01, -2.814160E-01, 4.317850E-01, 6.443500E-01, 2.560410E-01, 1.421600E-02, -8.570000E-04, 1.322000E-03;
c, 1.14, -2.000000E-06, -1.300000E-05, -6.300000E-05, -2.034000E-03, 1.568900E-02, -4.870300E-02, 1.209540E-01, 8.579500E-02, -1.647410E-01, -3.133730E-01, -2.505130E-01, 3.309260E-01, 6.689400E-01, 2.304090E-01;
c, 1.14, 0.000004, -0.000061, 0.00002, -0.008106, 0.043476, -0.108126, 0.278177, 0.053377, -0.129956, -1.291926, 0.57062, 2.055829, -1.162428,
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-0.599109
c, 1.14, -0.000048, 0.000127, -0.000585, 0.00035, 0.027479, -0.120737, 0.382173, 0.178348, -0.653718, -2.353402, 3.909156, -1.154712, -1.869095,
1.827747
c, 1.14, -0.000353, 0.001431, -0.00455, 0.099051, -0.289929, 0.263855, -0.357753, 1.627814, -3.97209, 2.047772, 2.704843, -6.44642, 7.049668,
-3.063988
c, 14.14, 1.000000E+00;
s, Y, 9.600000E-03;
p, Y, 1.074110E+02, 7.825370E+00, 4.889640E+00, 2.634670E+00, 1.290640E+00, 6.865630E-01, 3.642540E-01, 1.880790E-01, 9.064700E-02,
4.339300E-02, 2.034000E-02;
c, 1.11, 9.100000E-05, 4.127300E-02, -1.207510E-01, -9.130900E-02, 2.467110E-01, 4.542820E-01, 3.496890E-01, 1.146010E-01, 1.095500E-02,
1.613000E-03, -6.000000E-06;
c, 1.11, -3.000000E-05, -1.282000E-02, 3.891800E-02, 2.621700E-02, -8.505300E-02, -1.644870E-01, -1.767940E-01, 3.906100E-02, 4.379790E-01,
5.157770E-01, 1.527620E-01;
c, 1.11, -0.000039, -0.01627, 0.049061, 0.035306, -0.110046, -0.204525, -0.254978, 0.094509, 0.670929, 0.380375, 0.019995
c, 1.11, -0.000003, -0.034106, 0.101788, 0.067831, -0.206864, -0.719908, -0.102026, 1.529972, -0.092019, -0.864816, -0.043533
c, 1.11, -0.000086, -0.051308, 0.15981, 0.111308, -0.481858, -1.618528, 2.962499, -0.537254, -1.913963, 1.340141, 0.125845
c, 11.11, 1.000000E+00;
p, Y, 9.500000E-03;
d, Y, 4.447070E+01, 1.222600E+01, 5.014590E+00, 1.665760E+00, 8.894000E-01, 4.492320E-01, 2.178540E-01, 1.023240E-01, 4.684000E-02,
2.059400E-02;
c, 1.10, 1.300000E-04, 1.245000E-03, -6.418000E-03, 5.152400E-02, 1.608100E-01, 2.592560E-01, 3.131190E-01, 2.970510E-01, 1.865630E-01,
4.596000E-02;
c, 1.10, -0.000186, -0.001583, 0.008224, -0.077074, -0.227683, -0.375791, -0.180837, 0.393034, 0.50354, 0.113022
c, 1.10, 0.000154, 0.002278, -0.011393, 0.096759, 0.37161, 0.417213, -0.669102, -0.615468, 0.668319, 0.350459
c, 1.10, -0.001514, 0.00309, -0.000104, -0.089066, -0.898614, 0.471007, 1.281507, -1.558363, 0.240058, 0.583139
c, 10.10, 1.000000E+00;
d, Y, 9.100000E-03;
f, Y, 0.938823, 0.264213, 0.085714
g, Y, 0.457297, 0.143944


!Zr cc-pVTZ-PP-F12
s, Zr, 5.675240E+03, 8.631340E+02, 1.903400E+02, 2.690900E+01, 1.680390E+01, 1.049570E+01, 3.931680E+00, 2.406530E+00, 1.056280E+00,
5.710270E-01, 2.958580E-01, 1.043250E-01, 4.856300E-02, 2.235600E-02;
c, 1.14, 6.000000E-06, 4.600000E-05, 1.980000E-04, 7.057000E-03, -5.304900E-02, 1.577920E-01, -3.577070E-01, -2.830480E-01, 4.624190E-01,
6.391000E-01, 2.418360E-01, 1.361400E-02, -7.280000E-04, 1.189000E-03;
c, 1.14, -2.000000E-06, -1.500000E-05, -6.800000E-05, -2.135000E-03, 1.646500E-02, -5.081000E-02, 1.293950E-01, 8.582500E-02, -1.802650E-01,
-3.258040E-01, -2.273070E-01, 3.456950E-01, 6.582420E-01, 2.259630E-01;
c, 1.14, 0.000005, -0.000074, 0.000022, -0.009156, 0.049112, -0.121954, 0.325018, 0.056044, -0.208793, -1.459935, 0.921776, 1.858515, -1.229171,
-0.477992
c, 1.14, -0.000094, 0.000311, -0.001158, 0.011477, -0.004571, -0.091653, 0.357571, 0.34239, -1.252777, -1.737999, 4.016129, -2.053872, -0.872332,
1.436767
c, 1.14, -0.000356, 0.001441, -0.0047, 0.09978, -0.288496, 0.244086, -0.302131, 1.834897, -5.714581, 5.540954, -0.312634, -4.480546, 5.7936, -
2.775522
c, 14.14, 1.000000E+00;
s, Zr, 1.030000E-02;
p, Zr, 1.226140E+02, 8.601760E+00, 5.375670E+00, 2.873260E+00, 1.431480E+00, 7.585420E-01, 3.983330E-01, 2.005520E-01, 9.426300E-02,
4.397300E-02, 2.024600E-02;
c, 1.11, 8.900000E-05, 4.318900E-02, -1.256900E-01, -9.845300E-02, 2.616530E-01, 4.684370E-01, 3.431180E-01, 1.015390E-01, 7.775000E-03,
1.468000E-03, -1.310000E-04;
c, 1.11, -2.900000E-05, -1.329200E-02, 4.026100E-02, 2.784200E-02, -9.002800E-02, -1.740550E-01, -1.576400E-01, 8.132800E-02, 4.341340E-01,
4.929950E-01, 1.520090E-01;
c, 1.11, -0.000039, -0.018783, 0.056514, 0.041589, -0.130112, -0.245527, -0.256485, 0.232923, 0.688611, 0.272127, 0.007375
c, 1.11, 0.000024, -0.03836, 0.11498, 0.067734, -0.238656, -0.779337, 0.137066, 1.482464, -0.390287, -0.735729, -0.017207
c, 1.11, -0.000069, -0.056109, 0.172314, 0.176225, -0.817504, -1.156575, 2.91158, -1.056247, -1.421402, 1.301555, 0.036931
c, 11.11, 1.000000E+00;
p, Zr, 9.300000E-03;
d, Zr, 4.864310E+01, 1.358350E+01, 5.394530E+00, 1.863000E+00, 1.007920E+00, 5.198200E-01, 2.594550E-01, 1.255900E-01, 5.893200E-02,
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2.622900E-02;
c, 1.10, 1.600000E-04, 1.513000E-03, -9.133000E-03, 6.386900E-02, 1.893790E-01, 2.877480E-01, 3.152610E-01, 2.608760E-01, 1.415580E-01,
3.083200E-02;
c, 1.10, -0.000204, -0.00165, 0.010191, -0.083711, -0.237777, -0.350698, -0.110014, 0.369867, 0.487825, 0.173269
c, 1.10, 0.000301, 0.001936, -0.012565, 0.129514, 0.362574, 0.306264, -0.527782, -0.617773, 0.443537, 0.544729
c, 1.10, -0.000887, -0.000822, 0.014114, -0.199882, -0.766917, 0.442286, 1.156101, -1.114311, -0.330849, 0.826964
c, 10.10, 1.000000E+00;
d, Zr, 1.170000E-02;
f, Zr, 1.405678, 0.396367, 0.128964
g, Zr, 0.607773, 0.194614

!Nb cc-pVTZ-PP-F12
s, Nb, 5.729360E+03, 8.987570E+02, 2.031540E+02, 2.908210E+01, 1.815960E+01, 1.134200E+01, 4.224540E+00, 2.638170E+00, 1.150990E+00,
6.250000E-01, 3.244810E-01, 1.141370E-01, 5.242300E-02, 2.390400E-02;
c, 1.14, 8.000000E-06, 5.200000E-05, 2.160000E-04, 7.396000E-03, -5.525100E-02, 1.632580E-01, -3.721490E-01, -2.827570E-01, 4.840580E-01,
6.333390E-01, 2.343950E-01, 1.324600E-02, -7.750000E-04, 1.138000E-03;
c, 1.14, -3.000000E-06, -1.700000E-05, -7.500000E-05, -2.252000E-03, 1.724200E-02, -5.286300E-02, 1.363550E-01, 8.454100E-02, -1.912600E-01,
-3.296300E-01, -2.097360E-01, 3.537950E-01, 6.495660E-01, 2.230370E-01;
c, 1.14, 0.000009, -0.000102, 0.000065, -0.010654, 0.055053, -0.133014, 0.357541, 0.049344, -0.256141, -1.514658, 1.086488, 1.724257, -1.220764,
-0.436103
c, 1.14, -0.000132, 0.000446, -0.001591, 0.018991, -0.02491, -0.078005, 0.359054, 0.452024, -1.706153, -1.275341, 4.025672, -2.539368, -0.285362,
1.185084
c, 1.14, -0.000337, 0.00133, -0.004462, 0.09184, -0.259338, 0.190008, -0.174843, 1.917658, -7.141763, 8.429109, -2.846465, -2.760189, 4.635096,
-2.455319
c, 14.14, 1.000000E+00;
s, Nb, 1.090000E-02;
p, Nb, 1.384600E+02, 9.312380E+00, 5.820150E+00, 3.058960E+00, 1.590270E+00, 8.361380E-01, 4.360320E-01, 2.167160E-01, 1.018830E-01,
4.738700E-02, 2.174800E-02;
c, 1.11, 8.700000E-05, 4.608500E-02, -1.347720E-01, -1.053350E-01, 2.747760E-01, 4.792360E-01, 3.375730E-01, 9.415800E-02, 6.233000E-03,
1.469000E-03, -1.870000E-04;
c, 1.11, -2.900000E-05, -1.438600E-02, 4.381300E-02, 3.028700E-02, -9.630900E-02, -1.837030E-01, -1.496950E-01, 1.031560E-01, 4.396420E-01,
4.785870E-01, 1.452610E-01;
c, 1.11, -0.000039, -0.02137, 0.06477, 0.046926, -0.146161, -0.279494, -0.236595, 0.30512, 0.667685, 0.231227, 0.006332
c, 1.11, 0.000017, -0.042335, 0.128828, 0.072854, -0.273566, -0.826158, 0.326571, 1.393085, -0.513294, -0.668632, -0.013841
c, 1.11, -0.00002, -0.064431, 0.200749, 0.189574, -0.954516, -0.965464, 2.930836, -1.36921, -1.150249, 1.265704, 0.0033
c, 11.11, 1.000000E+00;
p, Nb, 1.000000E-02;
d, Nb, 5.552430E+01, 1.584300E+01, 5.792060E+00, 2.177680E+00, 1.220900E+00, 6.445770E-01, 3.278110E-01, 1.609180E-01, 7.613100E-02,
3.391100E-02;
c, 1.10, 1.800000E-04, 1.565000E-03, -1.003600E-02, 5.851800E-02, 1.897930E-01, 2.945090E-01, 3.174790E-01, 2.524380E-01, 1.316200E-01,
2.799600E-02;
c, 1.10, -0.000217, -0.00169, 0.011005, -0.076727, -0.233244, -0.342938, -0.121789, 0.334395, 0.502004, 0.202853
c, 1.10, 0.000342, 0.00235, -0.015785, 0.140641, 0.40976, 0.313146, -0.583717, -0.613474, 0.451645, 0.51626
c, 1.10, -0.001068, -0.001157, 0.017771, -0.245347, -0.760142, 0.514699, 1.134331, -1.160223, -0.308984, 0.829126
c, 10.10, 1.000000E+00;
d, Nb, 1.510000E-02;
f, Nb, 2.119022, 0.566675, 0.181479
g, Nb, 0.808382, 0.262449

!Mo cc-pVTZ-PP-F12
s, Mo, 6.711230E+03, 9.882620E+02, 2.162910E+02, 3.116170E+01, 1.946540E+01, 1.216030E+01, 4.517100E+00, 2.820320E+00, 1.260280E+00,
6.800130E-01, 3.514060E-01, 1.247460E-01, 5.668700E-02, 2.556900E-02;
c, 1.14, 8.000000E-06, 5.900000E-05, 2.440000E-04, 7.751000E-03, -5.775000E-02, 1.702780E-01, -3.983930E-01, -2.761780E-01, 5.039470E-01,
6.368170E-01, 2.246810E-01, 1.201300E-02, -7.040000E-04, 9.450000E-04;
c, 1.14, -3.000000E-06, -1.900000E-05, -8.400000E-05, -2.328000E-03, 1.783400E-02, -5.469700E-02, 1.452280E-01, 8.058100E-02, -1.986470E-01,
-3.318030E-01, -1.945790E-01, 3.483100E-01, 6.441110E-01, 2.303200E-01;
c, 1.14, 0.000006, -0.000098, 0.000043, -0.011208, 0.057492, -0.138485, 0.377366, 0.051198, -0.322108, -1.443255, 1.088486, 1.625088, -1.103985,
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c, 1.14, -0.000157, 0.000676, -0.003177, 0.073731, -0.201464, 0.107905, 0.045632, 1.787159, -7.557456, 9.441689, -3.895245, -1.944682, 3.996145, -2.222969
c, 14.14, 1.000000E+00;
s, Mo, 1.150000E-02;
p, Mo, 1.529580E+02, 1.004540E+01, 6.278690E+00, 3.252900E+00, 1.756190E+00, 9.164400E-01, 4.752100E-01, 2.340410E-01, 1.099870E-01, 5.090000E-02, 2.319800E-02;
c, 1.11, 8.900000E-05, 4.865800E-02, -1.429160E-01, -1.119240E-01, 2.872550E-01, 4.882670E-01, 3.325040E-01, 8.794500E-02, 5.137000E-03, 1.469000E-03, -2.090000E-04;
c, 1.11, -3.000000E-05, -1.511800E-02, 4.623700E-02, 3.216100E-02, -1.003680E-01, -1.878280E-01, -1.412290E-01, 1.129270E-01, 4.365490E-01, 4.735680E-01, 1.457880E-01;
c, 1.11, -0.000039, -0.023432, 0.071368, 0.051749, -0.159389, -0.305038, -0.20949, 0.347197, 0.642104, 0.214223, 0.006692
c, 1.11, -0.000003, -0.04546, 0.139671, 0.088855, -0.33194, -0.841033, 0.477726, 1.2959, -0.58288, -0.615162, -0.011913
c, 1.11, -0.000246, -0.059979, 0.193334, 0.285126, -1.242715, -0.620363, 2.865162, -1.685448, -0.801957, 1.142574, -0.001398
c, 11.11, 1.000000E+00;
p, Mo, 1.060000E-02
d, Mo, 6.401940E+01, 1.755380E+01, 6.500160E+00, 2.404820E+00, 1.342100E+00, 7.078230E-01, 3.603360E-01, 1.770770E-01, 8.366500E-02, 3.702600E-02;
c, 1.10, 1.670000E-04, 1.653000E-03, -1.329300E-02, 6.700700E-02, 2.091290E-01, 3.096950E-01, 3.139960E-01, 2.323510E-01, 1.119340E-01, 2.247000E-02;
c, 1.10, -0.00018, -0.001596, 0.01321, -0.074858, -0.235658, -0.325881, -0.083692, 0.34201, 0.486152, 0.226891
c, 1.10, 0.000373, 0.002229, -0.020737, 0.16632, 0.448983, 0.239912, -0.606679, -0.532691, 0.398569, 0.523508
c, 1.10, -0.000681, -0.002366, 0.028717, -0.259822, -0.785355, 0.666689, 0.972252, -1.104441, -0.31718, 0.836241
c, 10.10, 1.000000E+00;
d, Mo, 1.640000E-02;
f, Mo, 2.752371, 0.721366, 0.231569
g, Mo, 0.931871, 0.307939


!Tc cc-pVTZ-PP-F12
s, Tc, 7.011080E+03, 1.046100E+03, 2.304930E+02, 3.332180E+01, 2.081050E+01, 1.299750E+01, 4.830510E+00, 3.015520E+00, 1.370620E+00, 7.358360E-01, 3.788160E-01, 1.335490E-01, 6.015600E-02, 2.692300E-02;
c, 1.14, 9.000000E-06, 6.700000E-05, 2.740000E-04, 8.237000E-03, -6.063300E-02, 1.778160E-01, -4.220620E-01, -2.693360E-01, 5.218430E-01, 6.380050E-01, 2.160910E-01, 1.121200E-02, -3.020000E-04, 9.810000E-04;
c, 1.14, -3.000000E-06, -2.200000E-05, -9.300000E-05, -2.416000E-03, 1.832000E-02, -5.600100E-02, 1.511880E-01, 7.559700E-02, -2.027390E-01, -3.248550E-01, -1.823170E-01, 3.372970E-01, 6.378330E-01, 2.404290E-01;
c, 1.14, 0.000005, -0.000104, 0.000021, -0.011696, 0.060198, -0.145324, 0.398366, 0.051179, -0.362036, -1.443707, 1.159531, 1.515272, -1.022152, -0.495304
c, 1.14, -0.000047, 0.000126, -0.000816, 0.008014, 0.000882, -0.088273, 0.340126, 0.35248, -1.490568, -0.551706, 2.30933, -0.262974, -2.500383, 2.110922
c, 1.14, -0.000142, 0.000535, -0.002341, 0.041994, -0.096626, -0.007486, 0.26309, 0.984656, -3.946679, 2.371583, 2.400971, -5.714248, 5.920182, -2.530156
c, 14.14, 1.000000E+00;
s, Tc, 1.200000E-02;
p, Tc, 1.650311E+02, 1.079570E+01, 6.748410E+00, 3.482490E+00, 1.918530E+00, 1.001880E+00, 5.221550E-01, 2.608820E-01, 1.212740E-01, 5.540200E-02, 2.484800E-02;
c, 1.11, 9.400000E-05, 5.096400E-02, -1.500490E-01, -1.153530E-01, 2.970100E-01, 4.901870E-01, 3.265400E-01, 8.738400E-02, 6.065000E-03, 1.126000E-03, -1.220000E-04;
c, 1.11, -3.100000E-05, -1.550100E-02, 4.752400E-02, 3.264500E-02, -1.022890E-01, -1.840740E-01, -1.346980E-01, 1.036920E-01, 4.224280E-01, 4.828080E-01, 1.597840E-01;
c, 1.11, -0.000047, -0.025534, 0.078153, 0.057353, -0.177834, -0.32685, -0.187293, 0.37121, 0.625582, 0.208172, 0.006692
c, 1.11, -0.00004, -0.047488, 0.146635, 0.114555, -0.414009, -0.819345, 0.562964, 1.207255, -0.580519, -0.599361, -0.011058
c, 1.11, -0.000417, -0.057531, 0.186446, 0.400523, -1.596579, -0.202204, 2.736768, -1.860865, -0.582264, 1.032391, 0.00516
c, 11.11, 1.000000E+00;
p, Tc, 1.110000E-02;
d, Tc, 7.118130E+01, 1.953190E+01, 7.237430E+00, 2.611340E+00, 1.477340E+00, 7.880050E-01, 4.049350E-01, 2.003640E-01, 9.491100E-02,
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c, 1.10, -0.000187, -0.001693, 0.01395, -0.081829, -0.254474, -0.332943, -0.046221, 0.380006, 0.479648, 0.181576
c, 1.10, 0.000419, 0.002502, -0.023426, 0.20147, 0.52779, 0.137133, -0.74646, -0.390451, 0.516101, 0.385911
c, 1.10, -0.000381, -0.004538, 0.039997, -0.382303, -0.802336, 1.129787, 0.5467, -1.232345, 0.057121, 0.691253
c, 10.10, 1.000000E+00;
d, Tc, 1.850000E-02;
f, Tc, 0.257409, 0.828260, 3.385645
g, Tc, 0.345091, 1.091310

!Ru cc-pVTZ-PP-F12
s, Ru, 7.269890E+03, 1.087840E+03, 2.417870E+02, 3.545250E+01, 2.214150E+01, 1.382920E+01, 5.132130E+00, 3.170590E+00, 1.494870E+00, 8.005300E-01, 4.116380E-01, 1.424170E-01, 6.356300E-02, 2.829600E-02;
c, 1.14, 1.100000E-05, 7.800000E-05, 3.110000E-04, 8.734000E-03, -6.360400E-02, 1.857150E-01, -4.544900E-01, -2.563420E-01, 5.330450E-01, 6.399720E-01, 2.152730E-01, 1.126100E-02, -9.500000E-05, 1.107000E-03;
c, 1.14, -4.000000E-06, -2.500000E-05, -1.060000E-04, -2.497000E-03, 1.884200E-02, -5.758100E-02, 1.604580E-01, 6.912600E-02, -2.039790E-01, -3.204980E-01, -1.746560E-01, 3.326960E-01, 6.303210E-01, 2.464070E-01;
c, 1.14, 0.000030, -0.000205, 0.000163, -0.013509, 0.066751, -0.158561, 0.443513, 0.041152, -0.424062, -1.457142, 1.267890, 1.404596, -0.991828, -0.468081;
c, 1.14, -0.000134, 0.000391, -0.001606, 0.013643, -0.004164, -0.118323, 0.467525, 0.587880, -2.506434, -0.063273, 3.186107, -2.322619, -0.223854, 1.102847;
c, 1.14, -0.000247, 0.000679, -0.002297, 0.015245, 0.002102, -0.175255, 0.766531, 1.022593, -7.373964, 9.759134, -4.530420, -1.218047, 3.353400, -1.988427;
c, 14.14, 1.000000E+00;
s, Ru, 1.260000E-02;
p, Ru, 1.743070E+02, 1.150400E+01, 7.191760E+00, 3.574980E+00, 2.130780E+00, 1.089220E+00, 5.586370E-01, 2.704770E-01, 1.238960E-01, 5.582300E-02, 2.484200E-02;
c, 1.11, 1.030000E-04, 5.399400E-02, -1.610120E-01, -1.290380E-01, 3.147630E-01, 5.041410E-01, 3.252710E-01, 7.870200E-02, 3.763000E-03, 1.286000E-03, -2.150000E-04;
c, 1.11, -3.300000E-05, -1.571300E-02, 4.877200E-02, 3.519300E-02, -1.032230E-01, -1.811150E-01, -1.243880E-01, 1.120280E-01, 4.225110E-01, 4.772310E-01, 1.568200E-01;
c, 1.11, -0.000053, -0.029118, 0.090305, 0.069779, -0.204401, -0.375031, -0.139826, 0.463091, 0.583993, 0.150303, 0.004400;
c, 1.11, 0.000078, 0.051522, -0.161719, -0.150686, 0.500473, 0.838854, -0.800385, -1.035984, 0.744676, 0.472095, 0.003293;
c, 1.11, -0.000697, -0.053729, 0.182147, 0.626239, -2.108536, 0.413958, 2.364130, -2.129660, -0.075285, 0.850535, -0.016531;
c, 11.11, 1.000000E+00;
p, Ru, 1.110000E-02;
d, Ru, 7.537510E+01, 1.989010E+01, 7.879240E+00, 2.908340E+00, 1.638830E+00, 8.757300E-01, 4.504830E-01, 2.227700E-01, 1.053420E-01, 4.645500E-02;
c, 1.10, 1.800000E-04, 2.084000E-03, -1.867100E-02, 7.805400E-02, 2.263280E-01, 3.171000E-01, 3.050360E-01, 2.151500E-01, 9.975800E-02, 1.945100E-02;
c, 1.10, -0.000209, -0.002098, 0.019674, -0.090337, -0.284344, -0.336068, 0.002696, 0.407569, 0.451278, 0.156633;
c, 1.10, -0.000385, -0.003144, 0.032278, -0.195645, -0.575527, -0.061165, 0.786013, 0.306110, -0.548186, -0.354655;
c, 1.10, 0.00002, -0.007896, 0.063033, -0.468545, -0.789859, 1.350050, 0.281306, -1.188161, 0.179355, 0.616322;
c, 10.10, 1.000000E+00;
d, Ru, 2.050000E-02;
f, Ru, 4.27439, 0.998122, 0.307026
g, Ru, 1.297075, 0.402781

!Rh cc-pVTZ-PP-F12
s, Rh, 7.374220E+03, 1.114720E+03, 2.499380E+02, 3.753150E+01, 2.343850E+01, 1.463790E+01, 5.554210E+00, 3.422420E+00, 1.649280E+00, 8.832260E-01, 4.519700E-01, 1.530060E-01, 6.784900E-02, 2.993200E-02;
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c, 1.14, -4.000000E-06, -2.900000E-05, -1.190000E-04, -2.576000E-03, 1.941100E-02, -5.967800E-02, 1.589680E-01, 7.382600E-02, -1.968910E-01, -3.141660E-01, -1.768790E-01, 3.157110E-01, 6.247220E-01, 2.631610E-01;
c, 1.14, 0.000013, -0.000165, 0.000048, -0.013614, 0.068871, -0.166222, 0.446328, 0.051045, -0.406246, -1.436688, 1.20361, 1.349364, -0.826992,
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c, 1.14, -0.000054, 0.00007, -0.000886, 0.001349, 0.032514, -0.160912, 0.497639, 0.550158, -2.258254, -0.366069, 3.102678, -1.853498, -0.699551,
1.287148
c, 1.14, -0.00003, -0.000062, -0.001067, 0.006414, 0.025807, -0.207935, 0.768811, 1.160825, -7.336861, 9.048512, -3.640943, -1.80058, 3.610439,
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c, 14.14, 1.000000E+00;
s, Rh, 1.320000E-02;
p, Rh, 1.868620E+02, 1.230590E+01, 7.693580E+00, 3.779560E+00, 2.323260E+00, 1.184730E+00, 6.092370E-01, 2.968270E-01, 1.372710E-01,
6.212600E-02, 2.760600E-02;
c, 1.11, 1.090000E-04, 5.603100E-02, -1.675940E-01, -1.363730E-01, 3.251810E-01, 5.055390E-01, 3.232040E-01, 7.882100E-02, 4.065000E-03,
1.250000E-03, -1.920000E-04;
c, 1.11, -3.500000E-05, -1.674200E-02, 5.208500E-02, 3.857200E-02, -1.095340E-01, -1.882860E-01, -1.245600E-01, 1.171100E-01, 4.230670E-01,
4.736850E-01, 1.571330E-01;
c, 1.11, -0.000061, -0.031773, 0.098902, 0.080227, -0.22892, -0.402596, -0.107197, 0.47935, 0.557658, 0.15099, 0.005623
c, 1.11, 0.000096, 0.054421, -0.171427, -0.184503, 0.588396, 0.803855, -0.868061, -0.957533, 0.731992, 0.472377, 0.009297
c, 1.11, 0.000631, 0.064896, -0.219264, -0.695633, 2.377614, -0.775756, -2.122654, 2.115058, 0.017071, -0.809407, 0.000385
c, 11.11, 1.000000E+00;
p, Rh, 1.230000E-02;
d, Rh, 8.062040E+01, 2.212590E+01, 7.958340E+00, 3.195690E+00, 1.811370E+00, 9.713830E-01, 5.017970E-01, 2.490680E-01, 1.179700E-01,
5.195000E-02;
c, 1.10, 2.370000E-04, 2.237000E-03, -1.765000E-02, 7.883700E-02, 2.317500E-01, 3.192230E-01, 3.020620E-01, 2.104350E-01, 9.661000E-02,
1.870100E-02;
c, 1.10, -0.000286, -0.002328, 0.019144, -0.096112, -0.304235, -0.329289, 0.032473, 0.411307, 0.436475, 0.151987
c, 1.10, -0.000463, -0.00358, 0.031146, -0.195428, -0.59664, -0.0172, 0.795381, 0.269506, -0.556335, -0.347993
c, 1.10, 0.000062, -0.009504, 0.072551, -0.551917, -0.746975, 1.482553, 0.108248, -1.143338, 0.235721, 0.566417
c, 10.10, 1.000000E+00;
d, Rh, 2.290000E-02;
f, Rh, 5.152783, 1.139893, 0.347575
g, Rh, 1.512200, 0.452432


!Pd cc-pVTZ-PP-F12
s, Pd, 7.844890E+03, 1.169530E+03, 2.596440E+02, 3.922110E+01, 2.449340E+01, 1.529690E+01, 6.038960E+00, 3.762280E+00, 1.807100E+00,
9.743050E-01, 4.972030E-01, 1.620200E-01, 7.146000E-02, 3.131000E-02;
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s, Pd, 1.370000E-02;
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d, Pd, 7.834060E+01, 2.102350E+01, 7.518730E+00, 3.689330E+00, 2.019340E+00, 1.071760E+00, 5.516620E-01, 2.739330E-01, 1.301110E-01,
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d, Pd, 2.540000E-02;

f, Pd, 6.087489, 1.312443, 0.395519

g, Pd, 1.826266, 0.514321

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p, Y, 7.300000E-03;

d, Y, 4.540240E+01, 1.293340E+01, 4.800650E+00, 1.859340E+00, 1.116970E+00, 6.437090E-01, 3.523490E-01, 1.853680E-01, 9.312200E-02, 4.454000E-02, 2.006800E-02;

c, 1.11, 1.200000E-04, 1.099000E-03, -6.800000E-03, 3.035700E-02, 9.929900E-02, 1.802560E-01, 2.459700E-01, 2.811180E-01, 2.667400E-01, 1.692660E-01, 4.184000E-02;

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d, Y, 9.000000E-03;

f, Y, 2.071670, 0.546058, 0.188442, 0.067870

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d, Zr, 1.120000E-02;
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c, 1.13, -0.000232, 0.007073, 0.060781, -0.203187, -0.307328, 3.148563, -3.32716, -1.267267, 4.687273, -3.690306, 0.663273, 0.638174, 0.016664
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d, Nb, 1.120840E+02, 3.377140E+01, 1.247510E+01, 6.329390E+00, 2.021440E+00, 1.123280E+00, 5.991810E-01, 3.098940E-01, 1.547090E-01, 7.409100E-02, 3.323300E-02;
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f, Nb, 3.930761, 1.045703, 0.374306, 0.137688
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c, 1.16, 2.000000E-06, 1.400000E-05, 7.800000E-05, 2.490000E-04, 7.115000E-03, -5.648800E-02, 1.781580E-01, -3.068990E-01, -3.822290E-01, 3.634910E-01, 6.697260E-01, 3.223120E-01, 2.893000E-02, -3.173000E-03, 2.527000E-03, -1.220000E-04;
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p, Rh, 1.268950E+02, 2.215630E+01, 1.384160E+01, 8.649850E+00, 5.235650E+00, 2.096010E+00, 1.185610E+00, 6.548460E-01, 3.507950E-01, 1.768320E-01, 8.938100E-02, 4.492900E-02, 2.211800E-02;
c, 1.13, 1.770000E-04, -3.891000E-03, 5.123400E-02, -9.674300E-02, -1.392860E-01, 2.960810E-01, 4.480270E-01, 3.157510E-01, 1.047680E-01, 1.241000E-02, 1.422000E-03, 6.900000E-05, 2.500000E-05;
c, 1.13, 5.500000E-05, -1.152000E-03, 1.565100E-02, -3.162400E-02, -3.941700E-02, 1.048950E-01, 1.629630E-01, 1.292980E-01, -5.041100E-02, -2.914830E-01, -4.350730E-01, -3.172440E-01, -6.931300E-02;
c, 1.13, -0.000082, 0.001589, -0.02753, 0.0559, 0.082151, -0.220905, -0.354507, -0.151313, 0.338028, 0.543933, 0.286688, 0.045806, 0.001491
c, 1.13, -0.000091, 0.000648, -0.037832, 0.076266, 0.177268, -0.558416, -0.742908, 0.641266, 1.081125, -0.267437, -0.707464, -0.13308, -0.00729
c, 1.13, -0.000451, 0.007626, -0.084483, 0.164737, 0.305441, -1.837779, 0.3446, 2.569145, -1.596351, -1.016986, 0.949378, 0.245998, 0.011839
c, 1.13, 0.008018, -0.210025, 0.911209, -1.800506, 1.122017, 3.308756, -6.335249, 3.703764, 0.934345, -2.462335, 0.865306, 0.385266, 0.01148
c, 13.13, 1.000000E+00;
p, Rh, 1.090000E-02;
d, Rh, 1.695310E+02, 5.124170E+01, 1.804040E+01, 8.588040E+00, 2.949670E+00, 1.654420E+00, 8.904260E-01, 4.633730E-01, 2.323630E-01, 1.115080E-01, 4.985600E-02;
c, 1.11, 5.100000E-05, 4.110000E-04, 3.042000E-03, -1.667200E-02, 1.032810E-01, 2.481940E-01, 3.174060E-01, 2.885080E-01, 1.951360E-01, 8.691600E-02, 1.619200E-02;
c, 1.11, -0.000056, -0.000465, -0.003267, 0.01834, -0.127603, -0.327514, -0.293351, 0.083967, 0.42171, 0.4121, 0.134655
c, 1.11, -0.000131, -0.000533, -0.005876, 0.03153, -0.264722, -0.598886, 0.138622, 0.792287, 0.160809, -0.563459, -0.310327
c, 1.11, -0.000531, 0.00087, -0.016303, 0.071616, -0.687768, -0.523358, 1.588918, -0.201022, -1.057663, 0.329141, 0.519623
c, 1.11, -0.000421, 0.00239, 0.016235, -0.1097, 1.860692, -2.02637, -0.471204, 2.175115, -1.394534, -0.272487, 0.725087
c, 11.11, 1.000000E+00;
d, Rh, 2.230000E-02;
f, Rh, 8.352523, 2.273758, 0.739675, 0.262379
g, Rh, 2.627277, 0.888460, 0.339599
h, Rh, 1.089692, 0.410639


!Pd cc-pVQZ-PP-F12
s, Pd, 2.320580E+04, 3.771390E+03, 8.449990E+02, 2.259440E+02, 3.889630E+01, 2.417440E+01, 1.503650E+01, 6.373390E+00, 3.980440E+00, 1.913700E+00, 1.046850E+00, 5.411240E-01, 2.196040E-01, 1.112430E-01, 5.349300E-02, 2.578000E-02;
c, 1.16, 4.000000E-06, 2.600000E-05, 1.310000E-04, 4.110000E-04, 9.050000E-03, -7.043900E-02, 2.205020E-01, -3.870080E-01, -3.797990E-01, 4.295680E-01, 6.843810E-01, 2.882870E-01, 2.219700E-02, -1.596000E-03, 2.742000E-03, 1.660000E-04;
c, 1.16, -1.000000E-06, -8.000000E-06, -4.000000E-05, -1.360000E-04, -2.486000E-03, 2.014700E-02, -6.625600E-02, 1.325870E-01, 1.092390E-01, -1.627670E-01, -2.960000E-01, -2.160960E-01, 9.637400E-02, 4.558370E-01, 4.989750E-01, 1.441480E-01;
c, 1.16, -0.000002, -0.000019, -0.000095, -0.000292, -0.00606, 0.046624, -0.151309, 0.303232, 0.294202, -0.478541, -1.241567, 0.625976, 1.376096, -0.011598, -0.631481, -0.406473
c, 1.16, 0.000003, -0.000044, -0.000089, -0.000452, -0.006006, 0.052631, -0.184736, 0.336129, 0.685051, -1.621679, -1.272565, 3.019184, -0.117162, -1.946664, 0.188389, 1.034805
c, 1.16, 0.000025, -0.000018, 0.000345, 0.000466, 0.017891, -0.119739, 0.373422, -0.883291, -0.959765, 5.666293, -4.859345, -0.896286, 4.327901, -2.540017, -1.308918, 1.542643
c, 1.16, -0.000066, 0.000199, -0.000546, 0.0007, -0.030445, 0.138079, -0.292995, 0.928081, -0.919134, -0.78115, 2.188673, -1.936903, 0.9585, -0.059449, -0.510065, 0.309662
c, 16.16, 1.000000E+00;
s, Pd, 1.240000E-02;
p, Pd, 1.352730E+02, 2.307610E+01, 1.441340E+01, 9.004190E+00, 5.415840E+00, 2.350790E+00, 1.334400E+00, 7.335470E-01, 3.901660E-01, 1.885570E-01, 9.148200E-02, 4.439400E-02, 2.132400E-02;
c, 1.13, 1.860000E-04, -4.271000E-03, 5.723300E-02, -1.141790E-01, -1.393110E-01, 2.759960E-01, 4.534040E-01, 3.309520E-01, 1.132910E-01, 1.334100E-02, 8.830000E-04, 1.700000E-04, -1.300000E-05;
c, 1.13, 5.200000E-05, -1.117000E-03, 1.588800E-02, -3.391300E-02, -3.593300E-02, 8.982200E-02, 1.469780E-01, 1.251760E-01, -2.860400E-02, -2.727070E-01, -4.437890E-01, -3.369100E-01, -7.390200E-02;
c, 1.13, -0.000085, 0.001516, -0.031933, 0.068679, 0.095324, -0.237279, -0.404522, -0.135393, 0.428846, 0.529211, 0.19731, 0.02514, 0.000294
c, 1.13, -0.00011, 0.001037, -0.040946, 0.086692, 0.179855, -0.543274, -0.705223, 0.709096, 0.905479, -0.396913, -0.585017, -0.075177, -0.006485
c, 1.13, 0.000735, -0.01721, 0.137337, -0.290068, -0.252167, 1.97513, -0.63829, -2.306453, 1.669972, 0.755195, -0.934905, -0.148164, -0.015399
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c, 1.13, 0.007859, -0.221399, 1.017795, -2.156805, 1.564404, 3.095622, -6.48451, 4.282873, 0.179781, -2.035778, 0.918717, 0.275879, 0.01074
c, 13.13, 1.000000E+00;
p, Pd, 1.020000E-02;
d, Pd, 1.670870E+02, 5.000320E+01, 1.682140E+01, 8.372500E+00, 3.253000E+00, 1.809990E+00, 9.770620E-01, 5.108750E-01, 2.575330E-01, 1.240940E-01, 5.554800E-02;
c, 1.11, 6.700000E-05, 5.480000E-04, 4.804000E-03, -2.600800E-02, 1.117880E-01, 2.537740E-01, 3.178150E-01, 2.844650E-01, 1.902230E-01, 8.401400E-02, 1.547600E-02;
c, 1.11, -0.000053, -0.000751, -0.005144, 0.029848, -0.147466, -0.363895, -0.282977, 0.132251, 0.430448, 0.37771, 0.119195
c, 1.11, -0.000072, -0.000976, -0.007887, 0.046133, -0.27007, -0.604615, 0.204659, 0.764466, 0.129926, -0.570036, -0.325679
c, 1.11, -0.00028, -0.000407, -0.019531, 0.102467, -0.759606, -0.455961, 1.587736, -0.236882, -1.040661, 0.323916, 0.526165
c, 1.11, 0.001435, -0.006808, -0.010492, 0.14205, -2.04733, 2.403381, 0.082544, -1.989526, 1.393289, 0.208583, -0.679418
c, 11.11, 1.000000E+00;
d, Pd, 2.490000E-02;
f, Pd, 8.870777, 2.410920, 0.783805, 0.282428
g, Pd, 2.603678, 0.813746, 0.320399
h, Pd, 2.976523, 0.682088
```

D.1.4 Additional aug-cc-pVDZ-PP-F12 exponents

```
!Additional Y aug-cc-pVDZ-PP-F12 exponents
f, Y, 0.116542
!Additional Zr aug-cc-pVDZ-PP-F12 exponents
f, Zr, 0.177437
!Additional Nb aug-cc-pVDZ-PP-F12 exponents
f, Nb, 0.238530
!Additional Mo aug-cc-pVDZ-PP-F12 exponents
f, Mo, 0.306918
!Additional Tc aug-cc-pVDZ-PP-F12 exponents
f, Tc, 0.333888
!Additional Ru aug-cc-pVDZ-PP-F12 exponents
f, Ru, 0.398128
!Additional Rh aug-cc-pVDZ-PP-F12 exponents
f, Rh, 0.467566
!Additional Pd aug-cc-pVDZ-PP-F12 exponents
f, Pd, 0.529142
```

D.1.5 Additional aug-cc-pVTZ-PP-F12 exponents

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!Additional Y aug-cc-pVTZ-PP-F12 exponents
f, Y, 0.085714
g, Y, 0.143944
!Additional Zr aug-cc-pVTZ-PP-F12 exponents
f, Zr, 0.128964
g, Zr, 0.194614
!Additional Nb aug-cc-pVTZ-PP-F12 exponents
f, Nb, 0.181479
g, Nb, 0.262449
!Additional Mo aug-cc-pVTZ-PP-F12 exponents
f, Mo, 0.231569
g, Mo, 0.307939
!Additional Tc aug-cc-pVTZ-PP-F12 exponents
f, Tc, 0.257409
g, Tc, 0.345091
!Additional Ru aug-cc-pVTZ-PP-F12 exponents
```

f, Ru, 0.307026
g, Ru, 0.402781
!Additional Rh aug-cc-pVTZ-PP-F12 exponents
f, Rh, 0.347575
g, Rh, 0.452432
!Additional Pd aug-cc-pVTZ-PP-F12 exponents
f, Pd, 0.395519
g, Pd, 0.514321

D.1.6 Additional aug-cc-pVQZ-PP-F12 exponents

!Additional Y aug-cc-pVQZ-PP-F12 exponents
f, Y, 0.068135
g, Y, 0.094128
h, Y, 0.082926
!Additional Zr aug-cc-pVQZ-PP-F12 exponents
f, Zr, 0.103305
g, Zr, 0.138282
h, Zr, 0.098263
!Additional Nb aug-cc-pVQZ-PP-F12 exponents
f, Nb, 0.137688
g, Nb, 0.176550
h, Nb, 0.102275
!Additional Mo aug-cc-pVQZ-PP-F12 exponents
f, Mo, 0.176664
g, Mo, 0.232569
h, Mo, 0.110303
!Additional Tc aug-cc-pVQZ-PP-F12 exponents
f, Tc, 0.186294
g, Tc, 0.253220
h, Tc, 0.178432
!Additional Ru aug-cc-pVQZ-PP-F12 exponents
f, Ru, 0.225543
g, Ru, 0.275435
h, Ru, 0.297142
!Additional Rh aug-cc-pVQZ-PP-F12 exponents
f, Rh, 0.262046
g, Rh, 0.288706
h, Rh, 0.412903
!Additional Pd aug-cc-pVQZ-PP-F12 exponents
f, Pd, 0.282428
g, Pd, 0.320399
h, Pd, 0.682088

D.1.7 cc-pCVDZ-PP-F12

!Y cc-pCVDZ-PP-F12
s, Y, 1.215550E+02, 1.335080E+01, 8.343040E+00, 5.212620E+00, 2.848220E+00, 7.360920E-01, 3.395250E-01, 8.500000E-02, 4.571900E-02, 2.177500E-02;
c, 1.10, 3.990000E-04, -3.737400E-02, 2.104080E-01, -1.742590E-01, -4.490590E-01, 7.515460E-01, 5.039130E-01, 3.819000E-02, -1.681900E-02, 5.199000E-03;
c, 1.10, -1.380000E-04, 1.265500E-02, -7.257700E-02, 6.894600E-02, 1.410760E-01, -3.097690E-01, -3.640910E-01, 3.089760E-01, 6.183900E-01, 2.694800E-01;
c, 1.10, 0.000202, -0.005459, -0.024633, -0.033332, 0.389816, -1.018775, -0.030205, 2.753454, -1.825975, -0.494858

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c, 1.10, -0.001217, 0.02234, -0.109196, -0.008341, 0.671286, -2.760323, 2.77312, 0.590809, -3.3291, 2.327642
c, 10.10, 1.000000E+00;
s, Y, 1.040000E-02;
s, Y, 1.147915
p, Y, 1.570570E+01, 9.814340E+00, 3.951520E+00, 1.028730E+00, 5.203410E-01, 2.628060E-01, 1.191270E-01, 5.326300E-02, 2.338400E-02;
c, 1.9, -1.008000E-03, 1.845100E-02, -1.533130E-01, 3.882870E-01, 4.715490E-01, 2.442250E-01, 3.745500E-02, 9.170000E-04, 5.430000E-04;
c, 1.9, -1.460000E-04, -4.538000E-03, 4.661300E-02, -1.376680E-01, -1.888270E-01, -1.161280E-01, 3.231850E-01, 6.065240E-01, 2.419670E-01;
c, 1.9, -0.000266, -0.005748, 0.059726, -0.172697, -0.248414, -0.166389, 0.559808, 0.590163, 0.047867
c, 1.9, 0.002523, -0.016889, 0.124317, -0.381136, -0.870203, 1.1357, 0.859968, -1.082673, -0.135029
c, 9.9, 1.000000E+00;
p, Y, 1.030000E-02;
p, Y, 1.223225
d, Y, 1.585350E+01, 5.081830E+00, 1.450950E+00, 6.892770E-01, 3.133420E-01, 1.383830E-01, 5.955500E-02, 2.450300E-02;
c, 1.8, 9.920000E-04, -5.234000E-03, 8.678900E-02, 2.297090E-01, 3.256070E-01, 3.432860E-01, 2.503880E-01, 7.727600E-02;
c, 1.8, -0.001139, 0.006041, -0.124843, -0.333758, -0.379911, 0.17134, 0.61609, 0.204771
c, 1.8, 0.001367, -0.007516, 0.173784, 0.550371, -0.069211, -0.985771, 0.36704, 0.587747
c, 8.8, 1.000000E+00;
d, Y, 1.010000E-02;
d, Y, 1.221606
f, Y, 1.679589, 0.502276, 0.116542

!Zr cc-pCVDZ-PP-F12
s, Zr, 1.368260E+02, 1.451280E+01, 9.069810E+00, 5.666400E+00, 3.113190E+00, 8.234820E-01, 3.811930E-01, 9.779200E-02, 5.083900E-02,
2.369300E-02;
c, 1.10, 4.090000E-04, -3.851700E-02, 2.158150E-01, -1.733400E-01, -4.700670E-01, 7.634610E-01, 5.037400E-01, 3.785900E-02, -1.539000E-02,
4.804000E-03;
c, 1.10, -1.420000E-04, 1.314500E-02, -7.534100E-02, 6.997800E-02, 1.504360E-01, -3.253820E-01, -3.567120E-01, 3.070140E-01, 6.239180E-01,
2.680050E-01;
c, 1.10, 0.000278, -0.009060, -0.017385, -0.056478, 0.463722, -1.229328, 0.170601, 2.604994, -1.824965, -0.390928;
c, 1.10, -0.002769, 0.085123, -0.329796, 0.268501, 0.586346, -3.077496, 3.340782, -0.558668, -1.996079, 1.833570;
c, 10.10, 1.000000E+00;
s, Zr, 1.100000E-02;
s, Zr, 1.495055
p, Zr, 1.741190E+01, 1.087990E+01, 4.328040E+00, 1.138640E+00, 5.758550E-01, 2.886700E-01, 1.280140E-01, 5.529000E-02, 2.361300E-02;
c, 1.9, -1.183000E-03, 1.917400E-02, -1.600700E-01, 4.057620E-01, 4.736200E-01, 2.319610E-01, 3.266200E-02, 6.340000E-04, 3.910000E-04;
c, 1.9, -1.340000E-04, -4.609000E-03, 4.818900E-02, -1.454840E-01, -1.898740E-01, -7.781400E-02, 3.319510E-01, 5.837920E-01, 2.468610E-01;
c, 1.9, -0.000271, -0.006390, 0.067595, -0.199853, -0.284930, -0.097245, 0.650866, 0.499489, 0.021642;
c, 1.9, 0.003226, -0.018832, 0.135472, -0.454012, -0.800296, 1.278091, 0.602365, -1.057289, -0.080795;
c, 9.9, 1.000000E+00;
p, Zr, 1.010000E-02;
p, Zr, 1.395264
d, Zr, 1.807320E+01, 5.219590E+00, 1.699850E+00, 8.363230E-01, 3.933540E-01, 1.788240E-01, 7.827500E-02, 3.224800E-02;
c, 1.8, 1.141000E-03, -8.281000E-03, 9.337700E-02, 2.509730E-01, 3.439070E-01, 3.298380E-01, 2.121770E-01, 5.859000E-02;
c, 1.8, -0.001129, 0.008331, -0.111513, -0.299284, -0.334845, 0.111229, 0.571392, 0.339706;
c, 1.8, 0.001089, -0.009250, 0.182316, 0.473318, 0.056017, -0.854440, -0.050623, 0.811626;
c, 8.8, 1.000000E+00;
d, Zr, 1.330000E-02;
d, Zr, 1.421198
f, Zr, 2.196139, 0.641733, 0.177437

!Nb cc-pCVDZ-PP-F12
s, Nb, 1.530710E+02, 1.563630E+01, 9.772180E+00, 6.105440E+00, 3.390900E+00, 9.116760E-01, 4.221390E-01, 1.090790E-01, 5.562400E-02,
2.552400E-02;
c, 1.10, 4.270000E-04, -3.983400E-02, 2.232090E-01, -1.760000E-01, -4.860610E-01, 7.744000E-01, 5.027280E-01, 3.740300E-02, -1.464500E-02,
4.588000E-03;
c, 1.10, -1.480000E-04, 1.359700E-02, -7.819000E-02, 7.183800E-02, 1.563340E-01, -3.360430E-01, -3.472660E-01, 3.058060E-01, 6.211110E-01,
2.714220E-01;
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c, 1.10, 0.00044, -0.016989, 0.006401, -0.098276, 0.523419, -1.34261, 0.288912, 2.462278, -1.731197, -0.384551
c, 1.10, -0.004938, 0.17052, -0.62012, 0.638649, 0.411246, -3.148421, 3.523551, -0.978869, -1.471598, 1.613443
c, 10.10, 1.000000E+00;
s, Nb, 1.170000E-02;
s, Nb, 1.622437
p, Nb, 1.887130E+01, 1.179290E+01, 4.715290E+00, 1.255300E+00, 6.350230E-01, 3.175950E-01, 1.410540E-01, 6.049400E-02, 2.563000E-02;
c, 1.9, -1.383000E-03, 2.071000E-02, -1.677060E-01, 4.181250E-01, 4.741640E-01, 2.237340E-01, 3.068900E-02, 6.280000E-04, 3.150000E-04;
c, 1.9, -1.020000E-04, -5.079000E-03, 5.132100E-02, -1.541440E-01, -1.927810E-01, -6.314700E-02, 3.412080E-01, 5.757850E-01, 2.428800E-01;
c, 1.9, -0.00021, -0.007439, 0.075853, -0.226861, -0.30774, -0.039583, 0.674512, 0.453857, 0.018026
c, 1.9, 0.002791, -0.019272, 0.146631, -0.531006, -0.701985, 1.313725, 0.480003, -1.033874, -0.070944
c, 9.9, 1.000000E+00;
p, Nb, 1.090000E-02;
p, Nb, 1.592142
d, Nb, 2.089850E+01, 5.601340E+00, 1.938050E+00, 9.775120E-01, 4.697960E-01, 2.179050E-01, 9.691700E-02, 4.035600E-02;
c, 1.8, 1.239000E-03, -9.137000E-03, 9.741800E-02, 2.640250E-01, 3.520390E-01, 3.189190E-01, 1.905900E-01, 4.872700E-02;
c, 1.8, -0.001275, 0.009442, -0.123791, -0.324681, -0.320145, 0.156172, 0.563642, 0.315979
c, 1.8, 0.001464, -0.011899, 0.234277, 0.528187, -0.098693, -0.875487, 0.123318, 0.71165
c, 8.8, 1.000000E+00;
d, Nb, 1.680000E-02;
d, Nb, 1.627422
f, Nb, 2.929639, 0.815711, 0.23853

!Mo cc-pCVDZ-PP-F12
s, Mo, 1.700690E+02, 1.673380E+01, 1.045870E+01, 6.534340E+00, 3.679350E+00, 1.001920E+00, 4.631400E-01, 1.187270E-01, 5.951400E-02, 2.703900E-02;
c, 1.10, 4.530000E-04, -4.138000E-02, 2.326990E-01, -1.825190E-01, -4.983180E-01, 7.853790E-01, 5.013700E-01, 3.582900E-02, -1.403700E-02, 4.276000E-03;
c, 1.10, -1.560000E-04, 1.399200E-02, -8.096300E-02, 7.445400E-02, 1.588830E-01, -3.414150E-01, -3.366740E-01, 3.095560E-01, 6.149970E-01, 2.713550E-01;
c, 1.10, 0.000499, -0.019907, 0.013219, -0.113935, 0.549784, -1.383369, 0.349221, 2.319466, -1.591676, -0.421122;
c, 1.10, -0.005393, 0.196021, -0.722018, 0.783385, 0.34952, -3.189942, 3.583307, -1.133227, -1.232403, 1.493237;
c, 10.10, 1.000000E+00;
s, Mo, 1.230000E-02;
s, Mo, 1.781891
p, Mo, 2.030800E+01, 1.269070E+01, 5.119500E+00, 1.377830E+00, 6.968240E-01, 3.473670E-01, 1.528190E-01, 6.504900E-02, 2.733900E-02;
c, 1.9, -1.514000E-03, 2.216800E-02, -1.743690E-01, 4.279430E-01, 4.753060E-01, 2.174030E-01, 2.852400E-02, 4.610000E-04, 3.060000E-04;
c, 1.9, -8.300000E-05, -5.447000E-03, 5.320300E-02, -1.581500E-01, -1.918290E-01, -5.244900E-02, 3.447620E-01, 5.699340E-01, 2.420080E-01;
c, 1.9, -0.000169, -0.008387, 0.082481, -0.247272, -0.324684, 0.015956, 0.683036, 0.417834, 0.017267;
c, 1.9, 0.001652, -0.018677, 0.15689, -0.599832, -0.622281, 1.359233, 0.351888, -0.999922, -0.054939;
c, 9.9, 1.000000E+00;
p, Mo, 1.150000E-02;
p, Mo, 1.802494
d, Mo, 2.260320E+01, 6.339140E+00, 2.177630E+00, 1.107000E+00, 5.353720E-01, 2.489800E-01, 1.104090E-01, 4.537700E-02;
c, 1.8, 1.306000E-03, -1.243800E-02, 1.035120E-01, 2.776610E-01, 3.588570E-01, 3.092260E-01, 1.740360E-01, 4.269800E-02;
c, 1.8, -0.001231, 0.012107, -0.115324, -0.316715, -0.297884, 0.16358, 0.54045, 0.357338;
c, 1.8, 0.001592, -0.018131, 0.258039, 0.520842, -0.12153, -0.812424, 0.041985, 0.736926;
c, 8.8, 1.000000E+00;
d, Mo, 1.860000E-02;
d, Mo, 1.812005
f, Mo, 3.939733, 1.048621, 0.306918

!Tc cc-pCVDZ-PP-F12
s, Tc, 1.885090E+02, 1.780800E+01, 1.113100E+01, 6.954830E+00, 3.976400E+00, 1.093810E+00, 5.040080E-01, 1.272060E-01, 6.304700E-02, 2.840800E-02;
c, 1.10, 4.850000E-04, -4.306600E-02, 2.441460E-01, -1.935770E-01, -5.059760E-01, 7.962750E-01, 4.985920E-01, 3.414600E-02, -1.299100E-02, 4.184000E-03;
c, 1.10, -1.640000E-04, 1.434600E-02, -8.374100E-02, 7.842800E-02, 1.569650E-01, -3.397950E-01, -3.239530E-01, 3.005360E-01, 6.094500E-01,
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2.799160E-01;
c, 10.10, 1.000000E+00;
c, 1.10, 0.000658, -0.02949, 0.044493, -0.167566, 0.603497, -1.43773, 0.411672, 2.215836, -1.496613, -0.435643;
c, 1.10, -0.002441, 0.095036, -0.387603, 0.403361, 0.371126, -2.296074, 2.252037, 0.782609, -3.365703, 2.368472;
s, Tc, 1.280000E-02;
s, Tc, 1.795356
p, Tc, 2.164440E+01, 1.352680E+01, 5.542660E+00, 1.506110E+00, 7.616800E-01, 3.783660E-01, 1.635880E-01, 6.894100E-02, 2.867400E-02;
c, 1.9, -1.559000E-03, 2.370900E-02, -1.803710E-01, 4.355170E-01, 4.764540E-01, 2.128830E-01, 2.664300E-02, 1.880000E-04, 3.260000E-04;
c, 1.9, -9.600000E-05, -5.722000E-03, 5.394400E-02, -1.582580E-01, -1.873640E-01, -4.484600E-02, 3.427490E-01, 5.657040E-01, 2.454980E-01;
c, 1.9, -0.000278, -0.00925, 0.089333, -0.269572, -0.340806, 0.077042, 0.689067, 0.379664, 0.014777;
c, 1.9, 0.00051, -0.018416, 0.167242, -0.665936, -0.546456, 1.408708, 0.206838, -0.951805, -0.040152;
c, 9.9, 1.000000E+00;
p, Tc, 1.190000E-02;
p, Tc, 2.010951
d, Tc, 2.538280E+01, 6.985380E+00, 2.412170E+00, 1.241770E+00, 6.052420E-01, 2.828290E-01, 1.255600E-01, 5.148500E-02;
c, 1.8, 1.339000E-03, -1.328100E-02, 1.080380E-01, 2.860310E-01, 3.608340E-01, 3.011930E-01, 1.650010E-01, 4.042500E-02;
c, 1.8, -0.001296, 0.013245, -0.120612, -0.340102, -0.28903, 0.209852, 0.56057, 0.30187;
c, 1.8, 0.001969, -0.022368, 0.305719, 0.577539, -0.295248, -0.823245, 0.270203, 0.592692;
c, 8.8, 1.000000E+00;
d, Tc, 2.110000E-02;
d, Tc, 2.044317
f, Tc, 5.503083, 1.394245, 0.333888
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s, Ru, 2.082500E+02, 1.884710E+01, 1.178180E+01, 7.361950E+00, 4.277710E+00, 1.191070E+00, 5.485680E-01, 1.386940E-01, 6.765100E-02, 3.014100E-02;
c, 1.10, 5.230000E-04, -4.491300E-02, 2.576260E-01, -2.091300E-01, -5.106620E-01, 8.032470E-01, 4.984140E-01, 3.376600E-02, -1.209400E-02, 4.197000E-03;
c, 1.10, -1.750000E-04, 1.480300E-02, -8.752700E-02, 8.428200E-02, 1.549110E-01, -3.381410E-01, -3.160050E-01, 2.835260E-01, 6.092730E-01, 2.932010E-01;
c, 1.10, 0.000394, -0.020885, 0.011286, -0.134516, 0.613718, -1.500395, 0.473209, 2.127158, -1.421879, -0.432682;
c, 1.10, -0.003971, 0.160332, -0.633022, 0.687576, 0.427069, -3.214260, 3.568551, -1.175975, -1.125964, 1.432979;
c, 10.10, 1.000000
s, Ru, 1.340000E-02;
s, Ru, 2.038830
p, Ru, 2.277530E+01, 1.423400E+01, 5.987550E+00, 1.639240E+00, 8.278800E-01, 4.090100E-01, 1.718770E-01, 7.127100E-02, 2.922600E-02;
c, 1.9, -1.544000E-03, 2.577100E-02, -1.865980E-01, 4.427740E-01, 4.781510E-01, 2.083690E-01, 2.463500E-02, -2.190000E-04, 3.700000E-04;
c, 1.9, -1.480000E-04, -9.174000E-03, 8.137400E-02, -2.361250E-01, -2.943330E-01, 1.509800E-02, 6.560890E-01, 4.389440E-01, 1.816800E-02;
c, 1.9, -0.000358, -0.010825, 0.099246, -0.301294, -0.369041, 0.168038, 0.705934, 0.313602, 0.009083;
c, 1.9, 0.000345, -0.020720, 0.180233, -0.738149, -0.461626, 1.484084, -0.007921, -0.884623, -0.010899;
c, 9.9, 1.000000
p, Ru, 1.200000E-02;
p, Ru, 2.452927
d, Ru, 2.588380E+01, 7.592550E+00, 2.712930E+00, 1.397080E+00, 6.825650E-01, 3.193780E-01, 1.417810E-01, 5.801700E-02;
c, 1.8, 1.523000E-03, -1.816200E-02, 1.096910E-01, 2.915970E-01, 3.620440E-01, 2.975140E-01, 1.610370E-01, 3.897000E-02;
c, 1.8, -0.001546, 0.019269, -0.130688, -0.369171, -0.271534, 0.252098, 0.548800, 0.274524;
c, 1.8, 0.002631, -0.033274, 0.299483, 0.608895, -0.370795, -0.797920, 0.329762, 0.571476;
c, 8.8, 1.000000
d, Ru, 2.370000E-02;
c, 1.1, 1.000000E+00;
d, Ru, 4.764264
f, Ru, 7.098813, 1.814152, 0.398128
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s, Rh, 2.289320E+02, 1.990870E+01, 1.244680E+01, 7.778210E+00, 4.580060E+00, 1.290680E+00, 5.934140E-01, 1.491580E-01, 7.195300E-02, 3.175200E-02;
c, 1.10, 5.680000E-04, -4.680300E-02, 2.723670E-01, -2.301680E-01, -5.095540E-01, 8.098500E-01, 4.978760E-01, 3.315400E-02, -1.151300E-02,
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4.206000E-03;
c, 1.10, -1.860000E-04, 1.518000E-02, -9.113000E-02, 9.119900E-02, 1.503790E-01, -3.344630E-01, -3.074430E-01, 2.695540E-01, 6.048640E-01, 3.070670E-01;
c, 1.10, 0.000311, -0.01958, 0.004751, -0.129825, 0.614754, -1.478033, 0.460452, 1.992395, -1.193214, -0.537879
c, 1.10, -0.002843, 0.112088, -0.468617, 0.455369, 0.571321, -3.149643, 3.353112, -0.744556, -1.575198, 1.585372
c, 10.10, 1.000000E+00;
s, Rh, 1.400000E-02;
s, Rh, 2.221629
p, Rh, 2.421170E+01, 1.513310E+01, 6.447200E+00, 1.777760E+00, 8.990200E-01, 4.445220E-01, 1.886740E-01, 7.851400E-02, 3.219500E-02;
c, 1.9, -1.579000E-03, 2.719800E-02, -1.914630E-01, 4.476580E-01, 4.777240E-01, 2.058190E-01, 2.435200E-02, -5.800000E-05, 3.330000E-04;
c, 1.9, -1.320000E-04, -6.532000E-03, 5.644500E-02, -1.610630E-01, -1.842580E-01, -3.361000E-02, 3.445440E-01, 5.595730E-01, 2.467510E-01;
c, 1.9, -0.000122, -0.012728, 0.108665, -0.333076, -0.37623, 0.217222, 0.688442, 0.299196, 0.011732
c, 1.9, 0.001003, -0.024122, 0.192722, -0.799952, -0.375139, 1.482737, -0.078886, -0.852145, -0.022004
c, 9.9, 1.000000E+00;
p, Rh, 1.320000E-02;
p, Rh, 2.612291
d, Rh, 2.949980E+01, 7.404370E+00, 3.059590E+00, 1.582050E+00, 7.748340E-01, 3.630560E-01, 1.610470E-01, 6.562000E-02;
c, 1.8, 1.677000E-03, -1.843900E-02, 1.050760E-01, 2.937700E-01, 3.641780E-01, 2.972650E-01, 1.599580E-01, 3.867900E-02;
c, 1.8, -0.001787, 0.020316, -0.132675, -0.383604, -0.261824, 0.264271, 0.539346, 0.271947
c, 1.8, 0.003085, -0.035711, 0.286338, 0.630244, -0.387408, -0.79348, 0.341782, 0.572018
c, 8.8, 1.000000E+00;
d, Rh, 2.670000E-02;
d, Rh, 5.475315
f, Rh, 7.293379, 1.839933, 0.467566



!Pd cc-pCVDZ-PP-F12
s, Pd, 2.472020E+02, 2.079370E+01, 1.300190E+01, 8.125620E+00, 4.888420E+00, 1.392060E+00, 6.383820E-01, 1.588280E-01, 7.579300E-02, 3.318400E-02;
c, 1.10, 6.240000E-04, -5.019800E-02, 2.962420E-01, -2.640150E-01, -5.037150E-01, 8.177430E-01, 4.964090E-01, 3.231800E-02, -1.102300E-02, 4.217000E-03;
c, 1.10, -2.000000E-04, 1.586700E-02, -9.687000E-02, 1.017160E-01, 1.434910E-01, -3.291740E-01, -2.996310E-01, 2.591500E-01, 5.993290E-01, 3.186520E-01;
c, 1.10, 0.000144, -0.016787, -0.003892, -0.137673, 0.64008, -1.483671, 0.461522, 1.892092, -1.025108, -0.598172
c, 1.10, -0.002055, 0.075915, -0.336622, 0.247934, 0.698326, -3.019637, 3.069089, -0.281503, -2.057002, 1.759608
c, 10.10, 1.000000E+00;
s, Pd, 1.450000E-02;
s, Pd, 2.399017
p, Pd, 2.488240E+01, 1.555170E+01, 6.923430E+00, 1.922860E+00, 9.711910E-01, 4.769190E-01, 1.938660E-01, 7.879200E-02, 3.165300E-02;
c, 1.9, -1.722000E-03, 3.153400E-02, -2.010620E-01, 4.525720E-01, 4.799470E-01, 2.040450E-01, 2.251700E-02, -6.140000E-04, 4.090000E-04;
c, 1.9, -2.120000E-04, -6.801000E-03, 5.398800E-02, -1.486710E-01, -1.667440E-01, -3.472600E-02, 3.263210E-01, 5.599760E-01, 2.643670E-01;
c, 1.9, -0.000663, -0.01554, 0.126776, -0.393528, -0.411615, 0.384806, 0.665642, 0.177641, 0.007242
c, 1.9, 0.001856, -0.031032, 0.214604, -0.918703, -0.171037, 1.485386, -0.370775, -0.734498, 0.001632
c, 9.9, 1.000000E+00;
p, Pd, 1.270000E-02;
p, Pd, 2.926155
d, Pd, 2.902040E+01, 6.411490E+00, 3.997360E+00, 1.887420E+00, 9.132080E-01, 4.256750E-01, 1.877270E-01, 7.579000E-02;
c, 1.8, 2.172000E-03, -4.795800E-02, 1.033430E-01, 2.932100E-01, 3.716870E-01, 3.064560E-01, 1.666290E-01, 4.106300E-02;
c, 1.8, -0.002442, 0.057813, -0.137266, -0.422404, -0.284325, 0.283976, 0.529446, 0.256741
c, 1.8, 0.003816, -0.09517, 0.252292, 0.675294, -0.330274, -0.809732, 0.306929, 0.625382
c, 8.8, 1.000000E+00;
d, Pd, 3.060000E-02;
d, Pd, 6.817022
f, Pd, 9.680211, 2.555103, 0.529142
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D.1.8 cc-pCVTZ-PP-F12

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!Y cc-pCVTZ-PP-F12
s, Y, 5.177130E+03, 8.037880E+02, 1.768550E+02, 2.470940E+01, 1.543110E+01, 9.637060E+00, 3.655690E+00, 2.188790E+00, 9.669010E-01, 5.203350E-01, 2.687380E-01, 9.343100E-02, 4.427800E-02, 2.058600E-02;
c, 1.14, 6.000000E-06, 4.200000E-05, 1.850000E-04, 6.856000E-03, -5.141000E-02, 1.537220E-01, -3.427500E-01, -2.814160E-01, 4.317850E-01, 6.443500E-01, 2.560410E-01, 1.421600E-02, -8.570000E-04, 1.322000E-03;
c, 1.14, -2.000000E-06, -1.300000E-05, -6.300000E-05, -2.034000E-03, 1.568900E-02, -4.870300E-02, 1.209540E-01, 8.579500E-02, -1.647410E-01, -3.133730E-01, -2.505130E-01, 3.309260E-01, 6.689400E-01, 2.304090E-01;
c, 1.14, 0.000004, -0.000061, 0.00002, -0.008106, 0.043476, -0.108126, 0.278177, 0.053377, -0.129956, -1.291926, 0.57062, 2.055829, -1.162428, -0.599109
c, 1.14, -0.000048, 0.000127, -0.000585, 0.00035, 0.027479, -0.120737, 0.382173, 0.178348, -0.653718, -2.353402, 3.909156, -1.154712, -1.869095, 1.827747
c, 1.14, -0.000353, 0.001431, -0.00455, 0.099051, -0.289929, 0.263855, -0.357753, 1.627814, -3.97209, 2.047772, 2.704843, -6.44642, 7.049668, -3.063988
c, 14.14, 1.000000E+00;
s, Y, 9.600000E-03;
s, Y, 0.820793
p, Y, 1.074110E+02, 7.825370E+00, 4.889640E+00, 2.634670E+00, 1.290640E+00, 6.865630E-01, 3.642540E-01, 1.880790E-01, 9.064700E-02, 4.339300E-02, 2.034000E-02;
c, 1.11, 9.100000E-05, 4.127300E-02, -1.207510E-01, -9.130900E-02, 2.467110E-01, 4.542820E-01, 3.496890E-01, 1.146010E-01, 1.095500E-02, 1.613000E-03, -6.000000E-06;
c, 1.11, -3.000000E-05, -1.282000E-02, 3.891800E-02, 2.621700E-02, -8.505300E-02, -1.644870E-01, -1.767940E-01, 3.906100E-02, 4.379790E-01, 5.157770E-01, 1.527620E-01;
c, 1.11, -0.000039, -0.01627, 0.049061, 0.035306, -0.110046, -0.204525, -0.254978, 0.094509, 0.670929, 0.380375, 0.019995
c, 1.11, -0.000003, -0.034106, 0.101788, 0.067831, -0.206864, -0.719908, -0.102026, 1.529972, -0.092019, -0.864816, -0.043533
c, 1.11, -0.000086, -0.051308, 0.15981, 0.111308, -0.481858, -1.618528, 2.962499, -0.537254, -1.913963, 1.340141, 0.125845
c, 11.11, 1.000000E+00;
p, Y, 9.500000E-03;
p, Y, 1.496574
d, Y, 4.447070E+01, 1.222600E+01, 5.014590E+00, 1.665760E+00, 8.894000E-01, 4.492320E-01, 2.178540E-01, 1.023240E-01, 4.684000E-02, 2.059400E-02;
c, 1.10, 1.300000E-04, 1.245000E-03, -6.418000E-03, 5.152400E-02, 1.608100E-01, 2.592560E-01, 3.131190E-01, 2.970510E-01, 1.865630E-01, 4.596000E-02;
c, 1.10, -0.000186, -0.001583, 0.008224, -0.077074, -0.227683, -0.375791, -0.180837, 0.393034, 0.50354, 0.113022
c, 1.10, 0.000154, 0.002278, -0.011393, 0.096759, 0.37161, 0.417213, -0.669102, -0.615468, 0.668319, 0.350459
c, 1.10, -0.001514, 0.00309, -0.000104, -0.089066, -0.898614, 0.471007, 1.281507, -1.558363, 0.240058, 0.583139
c, 10.10, 1.000000E+00;
d, Y, 9.100000E-03;
d, Y, 0.549062
f, Y, 3.864438, 1.248867, 0.403595, 0.085714
g, Y, 1.535958, 0.555131, 0.143944

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s, Zr, 5.675240E+03, 8.631340E+02, 1.903400E+02, 2.690900E+01, 1.680390E+01, 1.049570E+01, 3.931680E+00, 2.406530E+00, 1.056280E+00, 5.710270E-01, 2.958580E-01, 1.043250E-01, 4.856300E-02, 2.235600E-02;
c, 1.14, 6.000000E-06, 4.600000E-05, 1.980000E-04, 7.057000E-03, -5.304900E-02, 1.577920E-01, -3.577070E-01, -2.830480E-01, 4.624190E-01, 6.391000E-01, 2.418360E-01, 1.361400E-02, -7.280000E-04, 1.189000E-03;
c, 1.14, -2.000000E-06, -1.500000E-05, -6.800000E-05, -2.135000E-03, 1.646500E-02, -5.081000E-02, 1.293950E-01, 8.582500E-02, -1.802650E-01, -3.258040E-01, -2.273070E-01, 3.456950E-01, 6.582420E-01, 2.259630E-01;
c, 1.14, 0.000005, -0.000074, 0.000022, -0.009156, 0.049112, -0.121954, 0.325018, 0.056044, -0.208793, -1.459935, 0.921776, 1.858515, -1.229171, -0.477992
c, 1.14, -0.000094, 0.000311, -0.001158, 0.011477, -0.004571, -0.091653, 0.357571, 0.34239, -1.252777, -1.737999, 4.016129, -2.053872, -0.872332, 1.436767
c, 1.14, -0.000356, 0.001441, -0.0047, 0.09978, -0.288496, 0.244086, -0.302131, 1.834897, -5.714581, 5.540954, -0.312634, -4.480546, 5.7936, -2.775522
c, 14.14, 1.000000E+00;
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s, Zr, 1.030000E-02;
s, Zr, 1.472405
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c, 1.11, 8.900000E-05, 4.318900E-02, -1.256900E-01, -9.845300E-02, 2.616530E-01, 4.684370E-01, 3.431180E-01, 1.015390E-01, 7.775000E-03, 1.468000E-03, -1.310000E-04;
c, 1.11, -2.900000E-05, -1.329200E-02, 4.026100E-02, 2.784200E-02, -9.002800E-02, -1.740550E-01, -1.576400E-01, 8.132800E-02, 4.341340E-01, 4.929950E-01, 1.520090E-01;
c, 1.11, -0.000039, -0.018783, 0.056514, 0.041589, -0.130112, -0.245527, -0.256485, 0.232923, 0.688611, 0.272127, 0.007375
c, 1.11, 0.000024, -0.03836, 0.11498, 0.067734, -0.238656, -0.779337, 0.137066, 1.482464, -0.390287, -0.735729, -0.017207
c, 1.11, -0.000069, -0.056109, 0.172314, 0.176225, -0.817504, -1.156575, 2.91158, -1.056247, -1.421402, 1.301555, 0.036931
c, 11.11, 1.000000E+00;
p, Zr, 9.300000E-03;
p, Zr, 1.771091
d, Zr, 4.864310E+01, 1.358350E+01, 5.394530E+00, 1.863000E+00, 1.007920E+00, 5.198200E-01, 2.594550E-01, 1.255900E-01, 5.893200E-02, 2.622900E-02;
c, 1.10, 1.600000E-04, 1.513000E-03, -9.133000E-03, 6.386900E-02, 1.893790E-01, 2.877480E-01, 3.152610E-01, 2.608760E-01, 1.415580E-01, 3.083200E-02;
c, 1.10, -0.000204, -0.00165, 0.010191, -0.083711, -0.237777, -0.350698, -0.110014, 0.369867, 0.487825, 0.173269
c, 1.10, 0.000301, 0.001936, -0.012565, 0.129514, 0.362574, 0.306264, -0.527782, -0.617773, 0.443537, 0.544729
c, 1.10, -0.000887, -0.000822, 0.014114, -0.199882, -0.766917, 0.442286, 1.156101, -1.114311, -0.330849, 0.826964
c, 10.10, 1.000000E+00;
d, Zr, 1.170000E-02;
d, Zr, 0.624970
f, Zr, 4.46913, 1.506952, 0.508131, 0.128964
g, Zr, 1.77835, 0.642643, 0.194614

!Nb cc-pCVTZ-PP-F12
s, Nb, 5.729360E+03, 8.987570E+02, 2.031540E+02, 2.908210E+01, 1.815960E+01, 1.134200E+01, 4.224540E+00, 2.638170E+00, 1.150990E+00, 6.250000E-01, 3.244810E-01, 1.141370E-01, 5.242300E-02, 2.390400E-02;
c, 1.14, 8.000000E-06, 5.200000E-05, 2.160000E-04, 7.396000E-03, -5.525100E-02, 1.632580E-01, -3.721490E-01, -2.827570E-01, 4.840580E-01, 6.333390E-01, 2.343950E-01, 1.324600E-02, -7.750000E-04, 1.138000E-03;
c, 1.14, -3.000000E-06, -1.700000E-05, -7.500000E-05, -2.252000E-03, 1.724200E-02, -5.286300E-02, 1.363550E-01, 8.454100E-02, -1.912600E-01, -3.296300E-01, -2.097360E-01, 3.537950E-01, 6.495660E-01, 2.230370E-01;
c, 1.14, 0.000009, -0.000102, 0.000065, -0.010654, 0.055053, -0.133014, 0.357541, 0.049344, -0.256141, -1.514658, 1.086488, 1.724257, -1.220764, -0.436103
c, 1.14, -0.000132, 0.000446, -0.001591, 0.018991, -0.02491, -0.078005, 0.359054, 0.452024, -1.706153, -1.275341, 4.025672, -2.539368, -0.285362, 1.185084
c, 1.14, -0.000337, 0.00133, -0.004462, 0.09184, -0.259338, 0.190008, -0.174843, 1.917658, -7.141763, 8.429109, -2.846465, -2.760189, 4.635096, -2.455319
c, 14.14, 1.000000E+00;
s, Nb, 1.090000E-02;
s, Nb, 1.561265
p, Nb, 1.384600E+02, 9.312380E+00, 5.820150E+00, 3.058960E+00, 1.590270E+00, 8.361380E-01, 4.360320E-01, 2.167160E-01, 1.018830E-01, 4.738700E-02, 2.174800E-02;
c, 1.11, 8.700000E-05, 4.608500E-02, -1.347720E-01, -1.053350E-01, 2.747760E-01, 4.792360E-01, 3.375730E-01, 9.415800E-02, 6.233000E-03, 1.469000E-03, -1.870000E-04;
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c, 1.11, -0.000039, -0.02137, 0.06477, 0.046926, -0.146161, -0.279494, -0.236595, 0.30512, 0.667685, 0.231227, 0.006332
c, 1.11, 0.000017, -0.042335, 0.128828, 0.072854, -0.273566, -0.826158, 0.326571, 1.393085, -0.513294, -0.668632, -0.013841
c, 1.11, -0.00002, -0.064431, 0.200749, 0.189574, -0.954516, -0.965464, 2.930836, -1.36921, -1.150249, 1.265704, 0.0033
c, 11.11, 1.000000E+00;
p, Nb, 1.000000E-02;
p, Nb, 2.018513
d, Nb, 5.552430E+01, 1.584300E+01, 5.792060E+00, 2.177680E+00, 1.220900E+00, 6.445770E-01, 3.278110E-01, 1.609180E-01, 7.613100E-02, 3.391100E-02;
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c, 1.10, 1.800000E-04, 1.565000E-03, -1.003600E-02, 5.851800E-02, 1.897930E-01, 2.945090E-01, 3.174790E-01, 2.524380E-01, 1.316200E-01, 2.799600E-02;
c, 1.10, -0.000217, -0.00169, 0.011005, -0.076727, -0.233244, -0.342938, -0.121789, 0.334395, 0.502004, 0.202853
c, 1.10, 0.000342, 0.00235, -0.015785, 0.140641, 0.40976, 0.313146, -0.583717, -0.613474, 0.451645, 0.51626
c, 1.10, -0.001068, -0.001157, 0.017771, -0.245347, -0.760142, 0.514699, 1.134331, -1.160223, -0.308984, 0.829126
c, 10.10, 1.000000E+00;
d, Nb, 1.510000E-02;
d, Nb, 0.665235
f, Nb, 5.331535, 1.822509, 0.622999, 0.181479
g, Nb, 2.112265, 0.763623, 0.262449

!Mo cc-pCVTZ-PP-F12
s, Mo, 6.711230E+03, 9.882620E+02, 2.162910E+02, 3.116170E+01, 1.946540E+01, 1.216030E+01, 4.517100E+00, 2.820320E+00, 1.260280E+00, 6.800130E-01, 3.514060E-01, 1.247460E-01, 5.668700E-02, 2.556900E-02;
c, 1.14, 8.000000E-06, 5.900000E-05, 2.440000E-04, 7.751000E-03, -5.775000E-02, 1.702780E-01, -3.983930E-01, -2.761780E-01, 5.039470E-01, 6.368170E-01, 2.246810E-01, 1.201300E-02, -7.040000E-04, 9.450000E-04;
c, 1.14, -3.000000E-06, -1.900000E-05, -8.400000E-05, -2.328000E-03, 1.783400E-02, -5.469700E-02, 1.452280E-01, 8.058100E-02, -1.986470E-01, -3.318030E-01, -1.945790E-01, 3.483100E-01, 6.441110E-01, 2.303200E-01;
c, 1.14, 0.000006, -0.000098, 0.000043, -0.011208, 0.057492, -0.138485, 0.377366, 0.051198, -0.322108, -1.443255, 1.088486, 1.625088, -1.103985, -0.483734
c, 1.14, -0.000097, 0.000345, -0.001595, 0.023009, -0.036037, -0.073364, 0.38666, 0.507221, -2.008688, -0.866568, 3.825101, -2.558134, -0.188364, 1.107442
c, 1.14, -0.000157, 0.000676, -0.003177, 0.073731, -0.201464, 0.107905, 0.045632, 1.787159, -7.557456, 9.441689, -3.895245, -1.944682, 3.996145, -2.222969
c, 14.14, 1.000000E+00;
s, Mo, 1.150000E-02;
s, Mo, 1.936718
p, Mo, 1.529580E+02, 1.004540E+01, 6.278690E+00, 3.252900E+00, 1.756190E+00, 9.164400E-01, 4.752100E-01, 2.340410E-01, 1.099870E-01, 5.090000E-02, 2.319800E-02;
c, 1.11, 8.900000E-05, 4.865800E-02, -1.429160E-01, -1.119240E-01, 2.872550E-01, 4.882670E-01, 3.325040E-01, 8.794500E-02, 5.137000E-03, 1.469000E-03, -2.090000E-04;
c, 1.11, -3.000000E-05, -1.511800E-02, 4.623700E-02, 3.216100E-02, -1.003680E-01, -1.878280E-01, -1.412290E-01, 1.129270E-01, 4.365490E-01, 4.735680E-01, 1.457880E-01;
c, 1.11, -0.000039, -0.023432, 0.071368, 0.051749, -0.159389, -0.305038, -0.20949, 0.347197, 0.642104, 0.214223, 0.006692
c, 1.11, -0.000003, -0.04546, 0.139671, 0.088855, -0.33194, -0.841033, 0.477726, 1.2959, -0.58288, -0.615162, -0.011913
c, 1.11, -0.000246, -0.059979, 0.193334, 0.285126, -1.242715, -0.620363, 2.865162, -1.685448, -0.801957, 1.142574, -0.001398
c, 11.11, 1.000000E+00;
p, Mo, 1.060000E-02
p, Mo, 2.288839
d, Mo, 6.401940E+01, 1.755380E+01, 6.500160E+00, 2.404820E+00, 1.342100E+00, 7.078230E-01, 3.603360E-01, 1.770770E-01, 8.366500E-02, 3.702600E-02;
c, 1.10, 1.670000E-04, 1.653000E-03, -1.329300E-02, 6.700700E-02, 2.091290E-01, 3.096950E-01, 3.139960E-01, 2.323510E-01, 1.119340E-01, 2.247000E-02;
c, 1.10, -0.00018, -0.001596, 0.01321, -0.074858, -0.235658, -0.325881, -0.083692, 0.34201, 0.486152, 0.226891
c, 1.10, 0.000373, 0.002229, -0.020737, 0.16632, 0.448983, 0.239912, -0.606679, -0.532691, 0.398569, 0.523508
c, 1.10, -0.000681, -0.002366, 0.028717, -0.259822, -0.785355, 0.666689, 0.972252, -1.104441, -0.31718, 0.836241
c, 10.10, 1.000000E+00;
d, Mo, 1.640000E-02;
d, Mo, 0.746470
f, Mo, 6.139581, 2.1111213, 0.725918, 0.231569
g, Mo, 2.192143, 0.721596, 0.307939

!Tc cc-pCVTZ-PP-F12
s, Tc, 7.011080E+03, 1.046100E+03, 2.304930E+02, 3.332180E+01, 2.081050E+01, 1.299750E+01, 4.830510E+00, 3.015520E+00, 1.370620E+00, 7.358360E-01, 3.788160E-01, 1.335490E-01, 6.015600E-02, 2.692300E-02;
c, 1.14, 9.000000E-06, 6.700000E-05, 2.740000E-04, 8.237000E-03, -6.063300E-02, 1.778160E-01, -4.220620E-01, -2.693360E-01, 5.218430E-01, 6.380050E-01, 2.160910E-01, 1.121200E-02, -3.020000E-04, 9.810000E-04;
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-3.248550E-01, -1.823170E-01, 3.372970E-01, 6.378330E-01, 2.404290E-01;
c, 1.14, 0.000005, -0.000104, 0.000021, -0.011696, 0.060198, -0.145324, 0.398366, 0.051179, -0.362036, -1.443707, 1.159531, 1.515272, -1.022152,
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c, 1.14, -0.000047, 0.000126, -0.000816, 0.008014, 0.000882, -0.088273, 0.340126, 0.35248, -1.490568, -0.551706, 2.30933, -0.262974, -2.500383,
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c, 1.14, -0.000142, 0.000535, -0.002341, 0.041994, -0.096626, -0.007486, 0.26309, 0.984656, -3.946679, 2.371583, 2.400971, -5.714248, 5.920182,
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c, 14.14, 1.000000E+00;
s, Tc, 1.200000E-02;
s, Tc, 2.097997
p, Tc, 1.650311E+02, 1.079570E+01, 6.748410E+00, 3.482490E+00, 1.918530E+00, 1.001880E+00, 5.221550E-01, 2.608820E-01, 1.212740E-01,
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1.126000E-03, -1.220000E-04;
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4.828080E-01, 1.597840E-01;
c, 1.11, -0.000047, -0.025534, 0.078153, 0.057353, -0.177834, -0.32685, -0.187293, 0.37121, 0.625582, 0.208172, 0.006692
c, 1.11, -0.00004, -0.047488, 0.146635, 0.114555, -0.414009, -0.819345, 0.562964, 1.207255, -0.580519, -0.599361, -0.011058
c, 1.11, -0.000417, -0.057531, 0.186446, 0.400523, -1.596579, -0.202204, 2.736768, -1.860865, -0.582264, 1.032391, 0.00516
c, 11.11, 1.000000E+00;
p, Tc, 1.110000E-02;
p, Tc, 2.636962
d, Tc, 7.118130E+01, 1.953190E+01, 7.237430E+00, 2.611340E+00, 1.477340E+00, 7.880050E-01, 4.049350E-01, 2.003640E-01, 9.491100E-02,
4.194500E-02;
c, 1.10, 1.750000E-04, 1.722000E-03, -1.383200E-02, 7.406600E-02, 2.185740E-01, 3.134600E-01, 3.079090E-01, 2.213540E-01, 1.051100E-01,
2.129200E-02;
c, 1.10, -1.940000E-04, -1.743000E-03, 1.440300E-02, -8.445900E-02, -2.669030E-01, -3.360340E-01, -3.150500E-02, 3.870680E-01, 4.744620E-01,
1.670810E-01;
c, 1.10, -0.000187, -0.001693, 0.01395, -0.081829, -0.254474, -0.332943, -0.046221, 0.380006, 0.479648, 0.181576
c, 1.10, 0.000419, 0.002502, -0.023426, 0.20147, 0.52779, 0.137133, -0.74646, -0.390451, 0.516101, 0.385911
c, 1.10, -0.000381, -0.004538, 0.039997, -0.382303, -0.802336, 1.129787, 0.5467, -1.232345, 0.057121, 0.691253
c, 10.10, 1.000000E+00;
d, Tc, 1.850000E-02;
d, Tc, 1.015160
f, Tc, 6.885940, 2.375181, 0.819276, 0.257409
g, Tc, 2.686101, 0.957092, 0.345091


!Ru cc-pCVTZ-PP-F12
s, Ru, 7.269890E+03, 1.087840E+03, 2.417870E+02, 3.545250E+01, 2.214150E+01, 1.382920E+01, 5.132130E+00, 3.170590E+00, 1.494870E+00,
8.005300E-01, 4.116380E-01, 1.424170E-01, 6.356300E-02, 2.829600E-02;
c, 1.14, 1.100000E-05, 7.800000E-05, 3.110000E-04, 8.734000E-03, -6.360400E-02, 1.857150E-01, -4.544900E-01, -2.563420E-01, 5.330450E-01,
6.399720E-01, 2.152730E-01, 1.126100E-02, -9.500000E-05, 1.107000E-03;
c, 1.14, -4.000000E-06, -2.500000E-05, -1.060000E-04, -2.497000E-03, 1.884200E-02, -5.758100E-02, 1.604580E-01, 6.912600E-02, -2.039790E-01,
-3.204980E-01, -1.746560E-01, 3.326960E-01, 6.303210E-01, 2.464070E-01;
c, 1.14, 0.000030, -0.000205, 0.000163, -0.013509, 0.066751, -0.158561, 0.443513, 0.041152, -0.424062, -1.457142, 1.267890, 1.404596, -0.991828,
-0.468081;
c, 1.14, -0.000134, 0.000391, -0.001606, 0.013643, -0.004164, -0.118323, 0.467525, 0.587880, -2.506434, -0.063273, 3.186107, -2.322619, -0.223854,
1.102847;
c, 1.14, -0.000247, 0.000679, -0.002297, 0.015245, 0.002102, -0.175255, 0.766531, 1.022593, -7.373964, 9.759134, -4.530420, -1.218047, 3.353400,
-1.988427;
c, 14.14, 1.000000E+00;
s, Ru, 1.260000E-02;
s, Ru, 2.018244
p, Ru, 1.743070E+02, 1.150400E+01, 7.191760E+00, 3.574980E+00, 2.130780E+00, 1.089220E+00, 5.586370E-01, 2.704770E-01, 1.238960E-01,
5.582300E-02, 2.484200E-02;
c, 1.11, 1.030000E-04, 5.399400E-02, -1.610120E-01, -1.290380E-01, 3.147630E-01, 5.041410E-01, 3.252710E-01, 7.870200E-02, 3.763000E-03,
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1.286000E-03, -2.150000E-04;
c, 1.11, -3.300000E-05, -1.571300E-02, 4.877200E-02, 3.519300E-02, -1.032230E-01, -1.811150E-01, -1.243880E-01, 1.120280E-01, 4.225110E-01, 4.772310E-01, 1.568200E-01;
c, 1.11, -0.000053, -0.029118, 0.090305, 0.069779, -0.204401, -0.375031, -0.139826, 0.463091, 0.583993, 0.150303, 0.004400;
c, 1.11, 0.000078, 0.051522, -0.161719, -0.150686, 0.500473, 0.838854, -0.800385, -1.035984, 0.744676, 0.472095, 0.003293;
c, 1.11, -0.000697, -0.053729, 0.182147, 0.626239, -2.108536, 0.413958, 2.364130, -2.129660, -0.075285, 0.850535, -0.016531;
c, 11.11, 1.000000E+00;
p, Ru, 1.110000E-02;
p, Ru, 2.738648
d, Ru, 7.537510E+01, 1.989010E+01, 7.879240E+00, 2.908340E+00, 1.638830E+00, 8.757300E-01, 4.504830E-01, 2.227700E-01, 1.053420E-01, 4.645500E-02;
c, 1.10, 1.800000E-04, 2.084000E-03, -1.867100E-02, 7.805400E-02, 2.263280E-01, 3.171000E-01, 3.050360E-01, 2.151500E-01, 9.975800E-02, 1.945100E-02;
c, 1.10, -0.000209, -0.002098, 0.019674, -0.090337, -0.284344, -0.336068, 0.002696, 0.407569, 0.451278, 0.156633;
c, 1.10, -0.000385, -0.003144, 0.032278, -0.195645, -0.575527, -0.061165, 0.786013, 0.306110, -0.548186, -0.354655;
c, 1.10, 0.00002, -0.007896, 0.063033, -0.468545, -0.789859, 1.350050, 0.281306, -1.188161, 0.179355, 0.616322;
c, 10.10, 1.000000E+00;
d, Ru, 2.050000E-02;
d, Ru, 0.801291
f, Ru, 7.811925, 2.640137, 0.892267, 0.307026
g, Ru, 2.959059, 1.038695, 0.402781


!Rh cc-pCVTZ-PP-F12
s, Rh, 7.374220E+03, 1.114720E+03, 2.499380E+02, 3.753150E+01, 2.343850E+01, 1.463790E+01, 5.554210E+00, 3.422420E+00, 1.649280E+00, 8.832260E-01, 4.519700E-01, 1.530060E-01, 6.784900E-02, 2.993200E-02;
c, 1.14, 1.300000E-05, 9.200000E-05, 3.570000E-04, 9.174000E-03, -6.669200E-02, 1.956740E-01, -4.574820E-01, -2.746970E-01, 5.224540E-01, 6.524920E-01, 2.257080E-01, 1.179500E-02, -1.350000E-04, 1.253000E-03;
c, 1.14, -4.000000E-06, -2.900000E-05, -1.190000E-04, -2.576000E-03, 1.941100E-02, -5.967800E-02, 1.589680E-01, 7.382600E-02, -1.968910E-01, -3.141660E-01, -1.768790E-01, 3.157110E-01, 6.247220E-01, 2.631610E-01;
c, 1.14, 0.000013, -0.000165, 0.000048, -0.013614, 0.068871, -0.166222, 0.446328, 0.051045, -0.406246, -1.436688, 1.20361, 1.349364, -0.826992, -0.559952
c, 1.14, -0.000054, 0.00007, -0.000886, 0.001349, 0.032514, -0.160912, 0.497639, 0.550158, -2.258254, -0.366069, 3.102678, -1.853498, -0.699551, 1.287148
c, 1.14, -0.00003, -0.000062, -0.001067, 0.006414, 0.025807, -0.207935, 0.768811, 1.160825, -7.336861, 9.048512, -3.640943, -1.80058, 3.610439, -1.992244
c, 14.14, 1.000000E+00;
s, Rh, 1.320000E-02;
s, Rh, 2.276219
p, Rh, 1.868620E+02, 1.230590E+01, 7.693580E+00, 3.779560E+00, 2.323260E+00, 1.184730E+00, 6.092370E-01, 2.968270E-01, 1.372710E-01, 6.212600E-02, 2.760600E-02;
c, 1.11, 1.090000E-04, 5.603100E-02, -1.675940E-01, -1.363730E-01, 3.251810E-01, 5.055390E-01, 3.232040E-01, 7.882100E-02, 4.065000E-03, 1.250000E-03, -1.920000E-04;
c, 1.11, -3.500000E-05, -1.674200E-02, 5.208500E-02, 3.857200E-02, -1.095340E-01, -1.882860E-01, -1.245600E-01, 1.171100E-01, 4.230670E-01, 4.736850E-01, 1.571330E-01;
c, 1.11, -0.000061, -0.031773, 0.098902, 0.080227, -0.22892, -0.402596, -0.107197, 0.47935, 0.557658, 0.15099, 0.005623
c, 1.11, 0.000096, 0.054421, -0.171427, -0.184503, 0.588396, 0.803855, -0.868061, -0.957533, 0.731992, 0.472377, 0.009297
c, 1.11, 0.000631, 0.064896, -0.219264, -0.695633, 2.377614, -0.775756, -2.122654, 2.115058, 0.017071, -0.809407, 0.000385
c, 11.11, 1.000000E+00;
p, Rh, 1.230000E-02;
p, Rh, 3.108147
d, Rh, 8.062040E+01, 2.212590E+01, 7.958340E+00, 3.195690E+00, 1.811370E+00, 9.713830E-01, 5.017970E-01, 2.490680E-01, 1.179700E-01, 5.195000E-02;
c, 1.10, 2.370000E-04, 2.237000E-03, -1.765000E-02, 7.883700E-02, 2.317500E-01, 3.192230E-01, 3.020620E-01, 2.104350E-01, 9.661000E-02, 1.870100E-02;
c, 1.10, -0.000286, -0.002328, 0.019144, -0.096112, -0.304235, -0.329289, 0.032473, 0.411307, 0.436475, 0.151987
c, 1.10, -0.000463, -0.00358, 0.031146, -0.195428, -0.59664, -0.0172, 0.795381, 0.269506, -0.556335, -0.347993
c, 1.10, 0.000062, -0.009504, 0.072551, -0.551917, -0.746975, 1.482553, 0.108248, -1.143338, 0.235721, 0.566417
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c, 10.10, 1.000000E+00;
d, Rh, 2.290000E-02;
d, Rh, 1.611287
f, Rh, 8.201125, 2.873635, 1.006908, 0.347575
g, Rh, 3.250837, 1.181396, 0.452432

!Pd cc-pCVTZ-PP-F12
s, Pd, 7.844890E+03, 1.169530E+03, 2.596440E+02, 3.922110E+01, 2.449340E+01, 1.529690E+01, 6.038960E+00, 3.762280E+00, 1.807100E+00, 9.743050E-01, 4.972030E-01, 1.620200E-01, 7.146000E-02, 3.131000E-02;
c, 1.14, 1.500000E-05, 1.070000E-04, 4.120000E-04, 9.864000E-03, -7.192200E-02, 2.128330E-01, -4.542200E-01, -2.996210E-01, 5.046120E-01, 6.622770E-01, 2.406810E-01, 1.264600E-02, -4.720000E-04, 1.443000E-03;
c, 1.14, -5.000000E-06, -3.300000E-05, -1.350000E-04, -2.716000E-03, 2.051700E-02, -6.368900E-02, 1.551180E-01, 8.005200E-02, -1.865700E-01, -3.054990E-01, -1.813090E-01, 3.039740E-01, 6.177640E-01, 2.753720E-01;
c, 1.14, 0.000009, -0.000167, -0.000009, -0.014271, 0.073918, -0.181874, 0.445982, 0.080095, -0.381302, -1.489062, 1.211833, 1.292298, -0.712088, -0.600801
c, 1.14, -0.000024, -0.000071, -0.000512, -0.007528, 0.060962, -0.197482, 0.493138, 0.515928, -1.971451, -0.623633, 2.926233, -1.341736, -1.187054, 1.484352
c, 1.14, 0.00001, -0.000294, -0.000518, -0.010899, 0.087758, -0.308101, 0.906555, 1.047697, -7.026921, 8.100446, -2.632698, -2.353999, 3.822262, -1.981281
c, 14.14, 1.000000E+00;
s, Pd, 1.370000E-02;
s, Pd, 2.441065
p, Pd, 9.882430E+01, 2.798590E+01, 1.748730E+01, 6.786380E+00, 1.987880E+00, 1.065730E+00, 5.838290E-01, 3.146360E-01, 1.357370E-01, 6.027700E-02, 2.654000E-02;
c, 1.11, 3.180000E-04, -4.671000E-03, 2.924100E-02, -1.992820E-01, 4.101390E-01, 4.471440E-01, 2.362210E-01, 6.246900E-02, 6.075000E-03, -8.500000E-05, 1.170000E-04;
c, 1.11, -5.100000E-05, 6.780000E-04, -6.679000E-03, 5.441500E-02, -1.382020E-01, -1.410000E-01, -1.010710E-01, 1.265930E-01, 4.211200E-01, 4.722370E-01, 1.605360E-01;
c, 1.11, -0.000036, 0.000795, -0.008594, 0.071358, -0.208689, -0.186865, 0.008849, 0.326449, 0.254801, 0.034013, 0.003575
c, 1.11, -0.000167, 0.002109, -0.014453, 0.10909, -0.312333, -0.290237, 0.008135, 0.49994, 0.396388, 0.054641, 0.005461
c, 1.11, -0.001037, 0.005765, 0.013628, -0.214909, 0.918509, 0.28106, -1.111261, -0.503318, 0.792, 0.34486, 0.000831
c, 11.11, 1.000000E+00;
p, Pd, 1.170000E-02;
p, Pd, 3.869500
d, Pd, 7.834060E+01, 2.102350E+01, 7.518730E+00, 3.689330E+00, 2.019340E+00, 1.071760E+00, 5.516620E-01, 2.739330E-01, 1.301110E-01, 5.747300E-02;
c, 1.10, 3.190000E-04, 3.169000E-03, -3.012800E-02, 8.205800E-02, 2.405330E-01, 3.254140E-01, 3.009480E-01, 2.050090E-01, 9.217700E-02, 1.744700E-02;
c, 1.10, -0.000447, -0.003355, 0.034472, -0.10516, -0.345712, -0.336399, 0.084781, 0.430443, 0.398668, 0.130624
c, 1.10, 0.000684, 0.004519, -0.051303, 0.184901, 0.62034, -0.036875, -0.788227, -0.222676, 0.566068, 0.35885
c, 1.10, -0.000112, -0.012719, 0.127751, -0.587489, -0.759007, 1.507672, 0.048755, -1.109818, 0.241301, 0.561067
c, 10.10, 1.000000E+00;
d, Pd, 2.540000E-02;
d, Pd, 1.692941
f, Pd, 8.97555, 3.218677, 1.154233, 0.395519
g, Pd, 3.65258, 1.350609, 0.514321
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D.1.9 cc-pCVQZ-PP-F12

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s, Y, 1.407980E+04, 2.247380E+03, 5.202370E+02, 1.508110E+02, 2.450300E+01, 1.524180E+01, 9.500840E+00, 3.823720E+00, 2.275860E+00, 1.064410E+00, 5.855490E-01, 3.053020E-01, 1.209720E-01, 6.638800E-02, 3.283800E-02, 1.637800E-02;
c, 1.16, 2.000000E-06, 1.200000E-05, 5.500000E-05, 1.820000E-04, 6.395000E-03, -5.076400E-02, 1.584540E-01, -3.025540E-01, -3.335140E-01, 3.230000E-01, 6.589720E-01, 3.425110E-01, 3.133000E-02, -5.626000E-03, 3.864000E-03, -2.600000E-04;
c, 1.16, -1.000000E-06, -4.000000E-06, -1.700000E-05, -6.300000E-05, -1.867000E-03, 1.541100E-02, -5.016300E-02, 1.063820E-01, 1.060530E-01,
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-1.261720E-01, -2.894070E-01, -2.983620E-01, 7.039600E-02, 5.421300E-01, 5.063430E-01, 9.288800E-02;

c, 1.16, -0.000004, 0.000004, -0.000072, -0.000011, -0.005615, 0.035128, -0.100289, 0.223785, 0.140952, -0.147398, -0.979832, -0.118486, 1.9001, 0.089553, -1.044868, -0.294789

c, 1.16, 0.000001, -0.000017, -0.000046, -0.000124, -0.00793, 0.052224, -0.152821, 0.371494, 0.195788, -0.345938, -2.472601, 2.886019, 1.649538, -3.886193, 1.019794, 0.862716

c, 1.16, -0.000082, 0.00037, -0.001066, 0.002743, -0.038719, 0.094977, -0.022813, -0.057325, -0.95671, 2.039069, 1.660753, -6.047836, 7.177663, -3.453021, -2.126277, 2.085221

c, 1.16, 0.00013, -0.000617, 0.001884, -0.00531, 0.09237, -0.259052, 0.160875, -0.08006, 2.704957, -10.824125, 14.538444, -7.964969, -0.895969, 6.342229, -6.560053, 2.746406

c, 16.16, 1.000000E+00;

s, Y, 8.200000E-03;

s, Y, 0.334433

p, Y, 7.791080E+01, 1.370370E+01, 8.556000E+00, 5.343350E+00, 3.130960E+00, 1.248130E+00, 7.057070E-01, 3.920400E-01, 2.128650E-01, 1.070420E-01, 5.434600E-02, 2.774800E-02, 1.427100E-02;

c, 1.13, 1.380000E-04, -2.543000E-03, 3.992200E-02, -8.363900E-02, -1.096760E-01, 2.329360E-01, 4.155860E-01, 3.493680E-01, 1.423730E-01, 2.060400E-02, 1.654000E-03, 4.450000E-04, -2.200000E-05;

c, 1.13, -4.400000E-05, 7.800000E-04, -1.256100E-02, 2.771500E-02, 3.210100E-02, -8.221400E-02, -1.470040E-01, -1.728880E-01, -1.594800E-02, 3.279480E-01, 5.086540E-01, 2.731240E-01, 3.207600E-02;

c, 1.13, -0.000052, 0.000911, -0.015739, 0.034599, 0.042308, -0.10483, -0.1852, -0.240442, -0.008504, 0.550901, 0.503494, 0.085111, 0.001915

c, 1.13, -0.000128, 0.002255, -0.031889, 0.067899, 0.088969, -0.205979, -0.638958, -0.292346, 1.356586, 0.44744, -0.935969, -0.218212, -0.005402

c, 1.13, 0.000689, -0.016095, 0.093171, -0.179679, -0.068969, 0.365451, 1.665973, -2.35145, -0.736659, 2.643649, -1.046138, -0.451953, -0.02065

c, 1.13, 0.000392, -0.006395, 0.096925, -0.235888, -0.281622, 2.738705, -1.962988, -2.917154, 5.232206, -3.109514, 0.021193, 0.891877, -0.053266

c, 13.13, 1.000000E+00;

p, Y, 7.300000E-03;

p, Y, 1.905815

d, Y, 4.540240E+01, 1.293340E+01, 4.800650E+00, 1.859340E+00, 1.116970E+00, 6.437090E-01, 3.523490E-01, 1.853680E-01, 9.312200E-02, 4.454000E-02, 2.006800E-02;

c, 1.11, 1.200000E-04, 1.099000E-03, -6.800000E-03, 3.035700E-02, 9.929900E-02, 1.802560E-01, 2.459700E-01, 2.811180E-01, 2.667400E-01, 1.692660E-01, 4.184000E-02;

c, 1.11, -0.00017, -0.001414, 0.008824, -0.046159, -0.139952, -0.265008, -0.318787, -0.063422, 0.41681, 0.461532, 0.102728

c, 1.11, 0.000055, 0.002366, -0.01316, 0.059309, 0.204398, 0.432063, 0.121034, -0.770765, -0.413641, 0.666468, 0.322519

c, 1.11, 0.000469, -0.005624, 0.027088, -0.124208, -0.339231, -0.774685, 1.308361, 0.48246, -1.450734, 0.380112, 0.519764

c, 1.11, 0.001538, -0.000592, -0.015605, 0.093166, 1.207771, -0.77774, -1.851702, 2.822574, -1.288549, -0.512274, 0.816837

c, 11.11, 1.000000E+00;

d, Y, 9.000000E-03;

d, Y, 0.375860

f, Y, 4.746443, 1.452883, 0.663967, 0.289968, 0.068135

g, Y, 4.839992, 1.357184, 0.51329, 0.094128

h, Y, 1.475077, 0.504869, 0.082926

!Zr cc-pCVQZ-PP-F12

s, Zr, 1.543750E+04, 2.465970E+03, 5.786510E+02, 1.627350E+02, 2.653350E+01, 1.657040E+01, 1.033030E+01, 4.148100E+00, 2.516130E+00, 1.165970E+00, 6.451250E-01, 3.370100E-01, 1.365970E-01, 7.262900E-02, 3.589300E-02, 1.788200E-02;

c, 1.16, 2.000000E-06, 1.300000E-05, 5.900000E-05, 1.980000E-04, 6.644000E-03, -5.257300E-02, 1.634440E-01, -3.059450E-01, -3.490550E-01, 3.455410E-01, 6.639130E-01, 3.281410E-01, 2.938800E-02, -4.159000E-03, 3.274000E-03, -1.900000E-04;

c, 1.16, -1.000000E-06, -4.000000E-06, -1.900000E-05, -7.000000E-05, -1.984000E-03, 1.625700E-02, -5.264200E-02, 1.103950E-01, 1.116980E-01, -1.375420E-01, -3.040570E-01, -2.837350E-01, 9.622600E-02, 5.363000E-01, 4.913850E-01, 9.321800E-02;

c, 1.16, -0.000002, -0.000003, -0.000061, -0.000060, -0.005968, 0.038772, -0.112779, 0.252894, 0.167295, -0.206785, -1.153591, 0.128764, 1.939337, -0.15175, -0.959421, -0.235768;

c, 1.16, 0.000001, -0.000024, -0.00003, -0.000246, -0.006141, 0.049129, -0.159954, 0.393458, 0.307586, -0.722923, -2.438268, 3.61988, 0.442505, -3.310386, 1.406314, 0.560689;

c, 1.16, -0.000047, 0.000244, -0.000718, 0.002375, -0.041611, 0.106663, -0.027277, -0.020563, -1.388605, 3.981918, -1.426308, -4.200952, 7.537391, -5.406119, -0.155010, 1.394831;

c, 1.16, 0.000049, -0.000261, 0.000642, -0.002355, 0.030693, -0.048508, -0.136417, 0.590259, 1.748234, -10.910583, 16.972985, -11.8959, 4.155011, 1.638535, -4.489657, 2.369898;

c, 16.16, 1.000000E+00;

s, Zr, 8.900000E-03;

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p, Zr, 8.660650E+01, 1.515550E+01, 9.465800E+00, 5.912520E+00, 3.453370E+00, 1.376110E+00, 7.768660E-01, 4.273720E-01, 2.277060E-01,
1.153640E-01, 5.940000E-02, 3.089900E-02, 1.585700E-02;
c, 1.13, 1.400000E-04, -2.786000E-03, 4.145100E-02, -8.441300E-02, -1.174270E-01, 2.476830E-01, 4.294190E-01, 3.444380E-01, 1.265660E-01,
1.571000E-02, 2.097000E-03, 6.500000E-05, 5.600000E-05;
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d, Zr, 1.120000E-02;
d, Zr, 0.460941
f, Zr, 5.023028, 1.624793, 0.758271, 0.354308, 0.103305
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c, 1.16, 2.000000E-06, 1.300000E-05, 6.900000E-05, 2.180000E-04, 6.677000E-03, -5.243400E-02, 1.685240E-01, -3.071400E-01, -3.656480E-01,
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d, Nb, 1.490000E-02;
d, Nb, 0.670711
f, Nb, 5.668261, 1.893312, 0.927448, 0.436962, 0.137688
g, Nb, 5.30447, 1.730939, 0.674426, 0.17655
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c, 1.16, 2.000000E-06, 1.400000E-05, 7.800000E-05, 2.490000E-04, 7.115000E-03, -5.648800E-02, 1.781580E-01, -3.068990E-01, -3.822290E-01, 3.634910E-01, 6.697260E-01, 3.223120E-01, 2.893000E-02, -3.173000E-03, 2.527000E-03, -1.220000E-04;
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s, Mo, 1.020000E-02;
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s, Tc, 1.040000E-02;
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d, Tc, 1.810000E-02;
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f, Tc, 7.920366, 2.98455, 1.382084, 0.810552, 0.186294
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s, Ru, 1.929980E+04, 3.177370E+03, 7.658330E+02, 2.114960E+02, 3.507570E+01, 2.190300E+01, 1.368020E+01, 5.315090E+00, 3.313490E+00,
1.581430E+00, 8.643690E-01, 4.506120E-01, 1.789360E-01, 9.125700E-02, 4.510000E-02, 2.235500E-02;
c, 1.16, 3.000000E-06, 2.000000E-05, 9.500000E-05, 3.080000E-04, 8.309000E-03, -6.321200E-02, 1.901360E-01, -4.067830E-01, -3.157160E-01,
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4.593270E-01, 6.609700E-01, 2.670720E-01, 1.995300E-02, -2.101000E-03, 2.611000E-03, -4.300000E-05;
c, 1.16, -1.000000E-06, -7.000000E-06, -3.000000E-05, -1.060000E-04, -2.358000E-03, 1.871300E-02, -5.903500E-02, 1.438090E-01, 9.174700E-02, -1.785050E-01, -3.084170E-01, -2.157970E-01, 1.485450E-01, 4.989270E-01, 4.586780E-01, 1.027500E-01;
c, 1.16, -0.000007, 0.000004, -0.000116, -0.000137, -0.006672, 0.045621, -0.136084, 0.34617, 0.191728, -0.465924, -1.263483, 0.705064, 1.625538, -0.367565, -0.717746, -0.249478
c, 1.16, 0.000002, -0.000044, -0.000043, -0.000487, -0.005021, 0.050754, -0.181433, 0.483931, 0.535569, -1.924015, -1.112499, 3.642511, -1.130544, -1.799893, 1.05392, 0.509249
c, 1.16, -0.000054, 0.000265, -0.000392, 0.001454, 0.006108, -0.08077, 0.300036, -0.993863, -0.709339, 6.39106, -7.101584, 1.147663, 4.419243, -4.670374, 0.757376, 0.89792
c, 1.16, 0.000074, -0.000268, 0.001459, -0.003294, 0.160107, -0.679387, 1.288863, -4.52661, 4.941019, 3.679574, -12.257928, 12.326669, -8.653246, 4.230428, 0.879749, -1.404141
c, 16.16, 1.000000E+00;
s, Ru, 1.110000E-02;
s, Ru, 1.666598
p, Ru, 1.172370E+02, 2.073330E+01, 1.295070E+01, 8.089950E+00, 4.849080E+00, 1.977880E+00, 1.145550E+00, 6.482270E-01, 3.551440E-01, 1.744130E-01, 8.695200E-02, 4.317900E-02, 2.101700E-02;
c, 1.13, 1.710000E-04, -3.791000E-03, 4.946000E-02, -9.350200E-02, -1.382150E-01, 2.683490E-01, 4.277090E-01, 3.304950E-01, 1.309020E-01, 1.898900E-02, 7.960000E-04, 4.620000E-04, -6.700000E-05;
c, 1.13, -5.100000E-05, 1.078000E-03, -1.464900E-02, 2.963100E-02, 3.821100E-02, -9.289600E-02, -1.473950E-01, -1.359030E-01, 1.649300E-02, 2.619010E-01, 4.379230E-01, 3.491360E-01, 8.487900E-02;
c, 1.13, -0.000072, 0.001404, -0.024957, 0.050865, 0.076959, -0.186532, -0.304596, -0.224847, 0.251902, 0.571956, 0.342401, 0.056813, 0.001522
c, 1.13, -0.000121, 0.001659, -0.039456, 0.080003, 0.15682, -0.446223, -0.744749, 0.28665, 1.242988, -0.030894, -0.801359, -0.157798, -0.009387
c, 1.13, -0.000599, 0.012318, -0.098907, 0.189696, 0.258259, -1.503598, -0.36638, 2.801201, -1.000524, -1.520764, 0.974951, 0.303192, 0.013395
c, 1.13, 0.004849, -0.122877, 0.567509, -1.129983, 0.426772, 3.915238, -6.194879, 2.284333, 2.240002, -2.73236, 0.679243, 0.494474, 0.002291
c, 13.13, 1.000000E+00;
p, Ru, 1.020000E-02;
p, Ru, 3.217001
d, Ru, 1.263940E+02, 3.844930E+01, 1.402140E+01, 8.716830E+00, 2.681440E+00, 1.490430E+00, 8.005330E-01, 4.157270E-01, 2.077370E-01, 9.943200E-02, 4.451500E-02;
c, 1.11, 6.200000E-05, 4.470000E-04, 4.672000E-03, -1.973400E-02, 1.027520E-01, 2.437180E-01, 3.148070E-01, 2.913270E-01, 1.999600E-01, 8.973400E-02, 1.674600E-02;
c, 1.11, -0.00007, -0.000473, -0.004865, 0.020899, -0.119541, -0.31073, -0.302934, 0.0556, 0.42162, 0.426774, 0.137995
c, 1.11, -0.000145, -0.000661, -0.00831, 0.035324, -0.264587, -0.576693, 0.084756, 0.795433, 0.197404, -0.560715, -0.315262
c, 1.11, -0.000577, 0.001079, -0.024263, 0.074188, -0.603544, -0.572295, 1.464386, -0.035598, -1.096516, 0.278589, 0.555937
c, 1.11, 0.000728, -0.002052, 0.046333, -0.141732, 1.711553, -1.635468, -0.870822, 2.322789, -1.313577, -0.377159, 0.755685
c, 11.11, 1.000000E+00;
d, Ru, 1.990000E-02;
d, Ru, 1.093117
f, Ru, 8.235875, 3.116919, 1.585707, 0.864386, 0.225543
g, Ru, 6.565205, 2.346395, 0.972967, 0.275435
h, Ru, 2.749421, 1.081144, 0.297142

!Rh cc-pCVQZ-PP-F12
s, Rh, 2.183270E+04, 3.389970E+03, 7.810700E+02, 2.160190E+02, 3.714780E+01, 2.310830E+01, 1.443170E+01, 5.830180E+00, 3.641440E+00, 1.744360E+00, 9.544830E-01, 4.957220E-01, 1.972170E-01, 1.007830E-01, 4.931200E-02, 2.414300E-02;
c, 1.16, 3.000000E-06, 2.400000E-05, 1.140000E-04, 3.550000E-04, 8.508000E-03, -6.609500E-02, 2.021170E-01, -3.922910E-01, -3.497620E-01, 4.436390E-01, 6.724460E-01, 2.789020E-01, 2.134100E-02, -2.165000E-03, 2.810000E-03, 3.300000E-05;
c, 1.16, -1.000000E-06, -8.000000E-06, -3.600000E-05, -1.200000E-04, -2.387000E-03, 1.930000E-02, -6.188300E-02, 1.369210E-01, 1.016360E-01, -1.709760E-01, -3.020800E-01, -2.162190E-01, 1.234140E-01, 4.756350E-01, 4.790980E-01, 1.237040E-01;
c, 1.16, -0.000003, -0.000013, -0.0001, -0.000204, -0.006774, 0.047486, -0.143971, 0.328825, 0.229293, -0.463153, -1.23503, 0.649308, 1.500916, -0.178837, -0.682017, -0.341253
c, 1.16, 0, -0.000043, -0.000052, -0.000577, -0.002895, 0.043401, -0.171986, 0.382769, 0.665772, -1.831799, -1.187609, 3.349616, -0.584864, -1.968612, 0.705795, 0.742106
c, 1.16, -0.000009, 0.000107, -0.000053, 0.001248, -0.001717, -0.048149, 0.251735, -0.718407, -1.13927, 6.246588, -6.04677, 0.026229, 4.67631, -3.95789, -0.131564, 1.202824
c, 1.16, 0.00013, -0.00056, 0.002831, -0.007035, 0.230108, -0.918325, 1.664428, -5.164165, 5.483238, 3.551125, -11.78233, 11.239477, -6.748922, 1.996572, 2.119354, -1.659292
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c, 16.16, 1.000000E+00;
s, Rh, 1.180000E-02;
s, Rh, 2.555162
p, Rh, 1.268950E+02, 2.215630E+01, 1.384160E+01, 8.649850E+00, 5.235650E+00, 2.096010E+00, 1.185610E+00, 6.548460E-01, 3.507950E-01, 1.768320E-01, 8.938100E-02, 4.492900E-02, 2.211800E-02;
c, 1.13, 1.770000E-04, -3.891000E-03, 5.123400E-02, -9.674300E-02, -1.392860E-01, 2.960810E-01, 4.480270E-01, 3.157510E-01, 1.047680E-01, 1.241000E-02, 1.422000E-03, 6.900000E-05, 2.500000E-05;
c, 1.13, 5.500000E-05, -1.152000E-03, 1.565100E-02, -3.162400E-02, -3.941700E-02, 1.048950E-01, 1.629630E-01, 1.292980E-01, -5.041100E-02, -2.914830E-01, -4.350730E-01, -3.172440E-01, -6.931300E-02;
c, 1.13, -0.000082, 0.001589, -0.02753, 0.0559, 0.082151, -0.220905, -0.354507, -0.151313, 0.338028, 0.543933, 0.286688, 0.045806, 0.001491
c, 1.13, -0.000091, 0.000648, -0.037832, 0.076266, 0.177268, -0.558416, -0.742908, 0.641266, 1.081125, -0.267437, -0.707464, -0.13308, -0.00729
c, 1.13, -0.000451, 0.007626, -0.084483, 0.164737, 0.305441, -1.837779, 0.3446, 2.569145, -1.596351, -1.016986, 0.949378, 0.245998, 0.011839
c, 1.13, 0.008018, -0.210025, 0.911209, -1.800506, 1.122017, 3.308756, -6.335249, 3.703764, 0.934345, -2.462335, 0.865306, 0.385266, 0.01148
c, 13.13, 1.000000E+00;
p, Rh, 1.090000E-02;
p, Rh, 3.529233
d, Rh, 1.695310E+02, 5.124170E+01, 1.804040E+01, 8.588040E+00, 2.949670E+00, 1.654420E+00, 8.904260E-01, 4.633730E-01, 2.323630E-01, 1.115080E-01, 4.985600E-02;
c, 1.11, 5.100000E-05, 4.110000E-04, 3.042000E-03, -1.667200E-02, 1.032810E-01, 2.481940E-01, 3.174060E-01, 2.885080E-01, 1.951360E-01, 8.691600E-02, 1.619200E-02;
c, 1.11, -0.000056, -0.000465, -0.003267, 0.01834, -0.127603, -0.327514, -0.293351, 0.083967, 0.42171, 0.4121, 0.134655
c, 1.11, -0.000131, -0.000533, -0.005876, 0.03153, -0.264722, -0.598886, 0.138622, 0.792287, 0.160809, -0.563459, -0.310327
c, 1.11, -0.000531, 0.00087, -0.016303, 0.071616, -0.687768, -0.523358, 1.588918, -0.201022, -1.057663, 0.329141, 0.519623
c, 1.11, -0.000421, 0.00239, 0.016235, -0.1097, 1.860692, -2.02637, -0.471204, 2.175115, -1.394534, -0.272487, 0.725087
c, 11.11, 1.000000E+00;
d, Rh, 2.230000E-02;
d, Rh, 1.271526
f, Rh, 9.477031, 4.021437, 1.950666, 0.989599, 0.262046
g, Rh, 6.445669, 2.505635, 1.072636, 0.288706
h, Rh, 3.144093, 1.326211, 0.412903


!Pd cc-pCVQZ-PP-F12
s, Pd, 2.320580E+04, 3.771390E+03, 8.449990E+02, 2.259440E+02, 3.889630E+01, 2.417440E+01, 1.503650E+01, 6.373390E+00, 3.980440E+00, 1.913700E+00, 1.046850E+00, 5.411240E-01, 2.196040E-01, 1.112430E-01, 5.349300E-02, 2.578000E-02;
c, 1.16, 4.000000E-06, 2.600000E-05, 1.310000E-04, 4.110000E-04, 9.050000E-03, -7.043900E-02, 2.205020E-01, -3.870080E-01, -3.797990E-01, 4.295680E-01, 6.843810E-01, 2.882870E-01, 2.219700E-02, -1.596000E-03, 2.742000E-03, 1.660000E-04;
c, 1.16, -1.000000E-06, -8.000000E-06, -4.000000E-05, -1.360000E-04, -2.486000E-03, 2.014700E-02, -6.625600E-02, 1.325870E-01, 1.092390E-01, -1.627670E-01, -2.960000E-01, -2.160960E-01, 9.637400E-02, 4.558370E-01, 4.989750E-01, 1.441480E-01;
c, 1.16, -0.000002, -0.000019, -0.000095, -0.000292, -0.00606, 0.046624, -0.151309, 0.303232, 0.294202, -0.478541, -1.241567, 0.625976, 1.376096, -0.011598, -0.631481, -0.406473
c, 1.16, 0.000003, -0.000044, -0.000089, -0.000452, -0.006006, 0.052631, -0.184736, 0.336129, 0.685051, -1.621679, -1.272565, 3.019184, -0.117162, -1.946664, 0.188389, 1.034805
c, 1.16, 0.000025, -0.000018, 0.000345, 0.000466, 0.017891, -0.119739, 0.373422, -0.883291, -0.959765, 5.666293, -4.859345, -0.896286, 4.327901, -2.540017, -1.308918, 1.542643
c, 1.16, -0.000066, 0.000199, -0.000546, 0.0007, -0.030445, 0.138079, -0.292995, 0.928081, -0.919134, -0.78115, 2.188673, -1.936903, 0.9585, -0.059449, -0.510065, 0.309662
c, 16.16, 1.000000E+00;
s, Pd, 1.240000E-02;
s, Pd, 2.844179
p, Pd, 1.352730E+02, 2.307610E+01, 1.441340E+01, 9.004190E+00, 5.415840E+00, 2.350790E+00, 1.334400E+00, 7.335470E-01, 3.901660E-01, 1.885570E-01, 9.148200E-02, 4.439400E-02, 2.132400E-02;
c, 1.13, 1.860000E-04, -4.271000E-03, 5.723300E-02, -1.141790E-01, -1.393110E-01, 2.759960E-01, 4.534040E-01, 3.309520E-01, 1.132910E-01, 1.334100E-02, 8.830000E-04, 1.700000E-04, -1.300000E-05;
c, 1.13, 5.200000E-05, -1.117000E-03, 1.588800E-02, -3.391300E-02, -3.593300E-02, 8.982200E-02, 1.469780E-01, 1.251760E-01, -2.860400E-02, -2.727070E-01, -4.437890E-01, -3.369100E-01, -7.390200E-02;
c, 1.13, -0.000085, 0.001516, -0.031933, 0.068679, 0.095324, -0.237279, -0.404522, -0.135393, 0.428846, 0.529211, 0.19731, 0.02514, 0.000294
c, 1.13, -0.00011, 0.001037, -0.040946, 0.086692, 0.179855, -0.543274, -0.705223, 0.709096, 0.905479, -0.396913, -0.585017, -0.075177, -0.006485
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c, 1.13, 0.000735, -0.01721, 0.137337, -0.290068, -0.252167, 1.97513, -0.63829, -2.306453, 1.669972, 0.755195, -0.934905, -0.148164, -0.015399
c, 1.13, 0.007859, -0.221399, 1.017795, -2.156805, 1.564404, 3.095622, -6.48451, 4.282873, 0.179781, -2.035778, 0.918717, 0.275879, 0.01074
c, 13.13, 1.000000E+00;
p, Pd, 1.020000E-02;
p, Pd, 3.904439
d, Pd, 1.670870E+02, 5.000320E+01, 1.682140E+01, 8.372500E+00, 3.253000E+00, 1.809990E+00, 9.770620E-01, 5.108750E-01, 2.575330E-01, 1.240940E-01, 5.554800E-02;
c, 1.11, 6.700000E-05, 5.480000E-04, 4.804000E-03, -2.600800E-02, 1.117880E-01, 2.537740E-01, 3.178150E-01, 2.844650E-01, 1.902230E-01, 8.401400E-02, 1.547600E-02;
c, 1.11, -0.000053, -0.000751, -0.005144, 0.029848, -0.147466, -0.363895, -0.282977, 0.132251, 0.430448, 0.37771, 0.119195
c, 1.11, -0.000072, -0.000976, -0.007887, 0.046133, -0.27007, -0.604615, 0.204659, 0.764466, 0.129926, -0.570036, -0.325679
c, 1.11, -0.00028, -0.000407, -0.019531, 0.102467, -0.759606, -0.455961, 1.587736, -0.236882, -1.040661, 0.323916, 0.526165
c, 1.11, 0.001435, -0.006808, -0.010492, 0.14205, -2.04733, 2.403381, 0.082544, -1.989526, 1.393289, 0.208583, -0.679418
c, 11.11, 1.000000E+00;
d, Pd, 2.490000E-02;
d, Pd, 1.463771
f, Pd, 10.280737, 4.511053, 2.238946, 1.138724, 0.282428
g, Pd, 6.630045, 2.708561, 1.202204, 0.320399
h, Pd, 3.71871, 1.668387, 0.682088

D.2 MP2Fit auxiliary basis sets

All auxiliary basis sets are provided in molpro format.

D.2.1 cc-pVDZ-PP-F12/MP2Fit

!Y cc-pVDZ-PP-F12/MP2Fit
s, Y, 6.83985, 3.44019, 2.61273, 1.63236, 0.70154, 0.43642, 0.206108, 0.119708, 0.077489, 0.03451, 0.011629, 0.004896
p, Y, 7.60948, 3.4852, 2.34085, 1.47518, 0.794341, 0.313665, 0.209142, 0.131998, 0.079323, 0.042229, 0.022476, 0.011875
d, Y, 3.65136, 2.74231, 1.75084, 0.723771, 0.535096, 0.30054, 0.163304, 0.105309, 0.059276, 0.029361
f, Y, 3.13108, 2.35831, 1.04405, 0.639261, 0.32472, 0.212456, 0.11566, 0.063909, 0.03836
g, Y, 2.27877, 1.20118, 0.701066, 0.32597, 0.159934, 0.081077, 0.040281
h, Y, 1.37285, 0.778991, 0.374211, 0.222014
i, Y, 0.288236

!Zr cc-pVDZ-PP-F12/MP2Fit
s, Zr, 8.39191, 4.06572, 3.05021, 1.91413, 0.842316, 0.521094, 0.247442, 0.143995, 0.092753, 0.041042, 0.01391, 0.005873
p, Zr, 9.13204, 4.17942, 2.80411, 1.76758, 0.955218, 0.552982, 0.273895, 0.170429, 0.098658, 0.062182, 0.025064, 0.014918
d, Zr, 4.39337, 3.28943, 2.12703, 0.866592, 0.638526, 0.359844, 0.195814, 0.126713, 0.071357, 0.035231
f, Zr, 3.61926, 2.75018, 1.23001, 0.760559, 0.382866, 0.253638, 0.137389, 0.076437, 0.045961
g, Zr, 2.75499, 1.53145, 0.793183, 0.383198, 0.190849, 0.097067, 0.048292
h, Zr, 1.64742, 0.932325, 0.449075, 0.266958
i, Zr, 0.346243

!Nb cc-pVDZ-PP-F12/MP2Fit
s, Nb, 10.1995, 4.80399, 3.56016, 2.23059, 1.00932, 0.626009, 0.304536, 0.179155, 0.114817, 0.048423, 0.015948, 0.00696
p, Nb, 11.002, 5.02437, 3.35867, 2.11135, 1.1458, 0.690163, 0.329382, 0.201202, 0.118096, 0.074532, 0.029536, 0.017564
d, Nb, 5.30767, 3.92323, 2.53234, 1.04431, 0.765347, 0.469439, 0.223161, 0.15086, 0.086458, 0.042582
f, Nb, 4.12691, 3.12837, 1.47831, 0.910568, 0.459472, 0.265749, 0.158296, 0.09739, 0.060669
g, Nb, 3.29104, 1.89734, 0.923059, 0.625028, 0.268143, 0.137056, 0.070733
h, Nb, 1.9769, 1.22634, 0.618721, 0.388848
i, Nb, 0.490498

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!Mo cc-pVDZ-PP-F12/MP2Fit
s, Mo, 12.8913, 5.51941, 3.86846, 2.38755, 1.22971, 0.720165, 0.339377, 0.205343, 0.130099, 0.052901, 0.01881, 0.00718
p, Mo, 13.5095, 6.09553, 3.97828, 2.46215, 1.37009, 0.839606, 0.393491, 0.241401, 0.141721, 0.089593, 0.035433, 0.021077
d, Mo, 6.44879, 4.58863, 2.91647, 1.25461, 0.83285, 0.542794, 0.298801, 0.187842, 0.100211, 0.045307
f, Mo, 4.58284, 3.52187, 1.68656, 0.957025, 0.534488, 0.3077, 0.189166, 0.116841, 0.072793
g, Mo, 3.78834, 2.25698, 1.17486, 0.702353, 0.319829, 0.162513, 0.084793
h, Mo, 2.37228, 1.47161, 0.742409, 0.466729
i, Mo, 0.588646

!Tc cc-pVDZ-PP-F12/MP2Fit
s, Tc, 15.9694, 6.39987, 4.28214, 2.61291, 1.43051, 0.870806, 0.40283, 0.244927, 0.162267, 0.063635, 0.022422, 0.008596
p, Tc, 16.4895, 7.35927, 4.70464, 2.8797, 1.63405, 1.02733, 0.471651, 0.288888, 0.169947, 0.106776, 0.042085, 0.025133
d, Tc, 7.68536, 5.30596, 3.34427, 1.66865, 1.0161, 0.657858, 0.362735, 0.216059, 0.127395, 0.05518
f, Tc, 5.1492, 3.90314, 1.94165, 1.09698, 0.632562, 0.368484, 0.226731, 0.140205, 0.087349
g, Tc, 4.28518, 2.56717, 1.23409, 0.828535, 0.345914, 0.18816, 0.100805
h, Tc, 2.84674, 1.80522, 0.93375, 0.531955
i, Tc, 0.704779

!Ru cc-pVDZ-PP-F12/MP2Fit
s, Ru, 19.6574, 7.47623, 4.78563, 2.91402, 1.68827, 1.07323, 0.475566, 0.290278, 0.198776, 0.082228, 0.02626, 0.010221
p, Ru, 19.8859, 8.87069, 5.64068, 3.4443, 1.99472, 1.27773, 0.559721, 0.344122, 0.205079, 0.127842, 0.049983, 0.029985
d, Ru, 9.11819, 6.12582, 3.85077, 2.05337, 1.23365, 0.790088, 0.436987, 0.263214, 0.147463, 0.066222
f, Ru, 5.687, 4.23453, 2.22438, 1.1815, 0.732047, 0.440642, 0.271531, 0.168053, 0.104803
g, Ru, 4.79455, 3.06433, 1.50125, 0.979695, 0.417994, 0.201809, 0.114401
h, Ru, 3.41609, 2.13796, 1.13405, 0.628519
i, Ru, 0.844258

!Rh cc-pVDZ-PP-F12/MP2Fit
s, Rh, 23.4883, 8.89805, 5.69007, 3.44915, 1.97689, 1.26366, 0.515627, 0.298691, 0.229886, 0.102319, 0.033043, 0.012474
p, Rh, 23.8567, 10.6451, 6.78317, 4.13054, 2.36666, 1.52081, 0.680637, 0.418088, 0.246009, 0.152715, 0.060258, 0.036082
d, Rh, 10.9123, 7.32346, 4.62088, 2.48766, 1.44866, 0.921885, 0.493066, 0.293172, 0.155174, 0.078043
f, Rh, 6.49798, 4.86472, 2.82728, 1.47896, 0.896324, 0.529816, 0.326897, 0.201995, 0.125695
g, Rh, 5.7539, 3.61614, 1.83677, 1.01154, 0.480359, 0.251221, 0.14262
h, Rh, 4.0445, 2.58521, 1.30306, 0.736989
i, Rh, 0.97997

!Pd cc-pVDZ-PP-F12/MP2Fit
s, Pd, 27.8516, 10.4416, 6.69321, 4.08913, 2.39537, 1.52866, 0.65476, 0.379365, 0.281852, 0.121789, 0.04247, 0.015322
p, Pd, 28.628, 12.7741, 8.13136, 4.94138, 2.78008, 1.8005, 0.828746, 0.509847, 0.293493, 0.18187, 0.072556, 0.04336
d, Pd, 13.0407, 8.73972, 5.53092, 3.03608, 1.79617, 1.10233, 0.587101, 0.379198, 0.218407, 0.094692
f, Pd, 7.61394, 5.75823, 3.4777, 1.81501, 1.08154, 0.64025, 0.378115, 0.207677, 0.140332
g, Pd, 7.07873, 4.19745, 2.17931, 1.2527, 0.522321, 0.262111, 0.151544
h, Pd, 4.67026, 3.21933, 1.50563, 0.822257
i, Pd, 1.11266
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D.2.2 cc-pVTZ-PP-F12/MP2Fit

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!Y cc-pVTZ-PP-F12/MP2Fit
s, Y, 3.80993, 2.87052, 1.75261, 0.93465, 0.495314, 0.284764, 0.151604, 0.083331, 0.048137, 0.028126, 0.016457, 0.009662, 0.005672, 0.003236
p, Y, 6.18749, 3.64957, 2.30945, 1.47088, 0.8006, 0.430032, 0.251137, 0.159724, 0.102603, 0.061724, 0.035649, 0.020533, 0.012004, 0.007036
d, Y, 5.37405, 3.51327, 1.83985, 1.08215, 0.528476, 0.310396, 0.160163, 0.091432, 0.048435, 0.022409, 0.01129, 0.00656
f, Y, 7.39697, 3.66659, 1.74312, 1.01807, 0.642974, 0.318825, 0.163516, 0.113487, 0.049943, 0.025418, 0.013205
g, Y, 3.03315, 1.76413, 0.892763, 0.507812, 0.306331, 0.182231, 0.098272, 0.056126, 0.032061
h, Y, 1.28732, 0.874136, 0.430214, 0.180992, 0.082763, 0.042766
i, Y, 1.03932, 0.568057, 0.294846, 0.154575
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!k, Y, 0.213485

!Zr cc-pVTZ-PP-F12/MP2Fit
s, Zr, 4.65041, 3.36919, 2.28659, 1.58481, 1.25961, 0.452956, 0.288848, 0.149751, 0.075, 0.039217, 0.020734, 0.011153, 0.006087, 0.003345
p, Zr, 6.49605, 4.0223, 2.79462, 1.9963, 1.49017, 0.87131, 0.47411, 0.383213, 0.23357, 0.109644, 0.066897, 0.039752, 0.020048, 0.007431
d, Zr, 4.5727, 2.8987, 2.38715, 1.15746, 0.595276, 0.380975, 0.226161, 0.138567, 0.080032, 0.04695, 0.023615, 0.00686
f, Zr, 6.90186, 3.17604, 2.23979, 1.05109, 0.759313, 0.407765, 0.217019, 0.133917, 0.075226, 0.037612, 0.014364
g, Zr, 3.29188, 2.54231, 1.16203, 0.70182, 0.380104, 0.219296, 0.12784, 0.061088, 0.030112
h, Zr, 2.22786, 1.25151, 0.646507, 0.302235, 0.168992, 0.053807
i, Zr, 1.27516, 0.705959, 0.361239, 0.186668
!k, Zr, 0.285860

!Nb cc-pVTZ-PP-F12/MP2Fit
s, Nb, 6.4379, 4.60463, 3.08916, 2.13845, 1.7025, 0.621972, 0.396683, 0.202299, 0.100027, 0.052231, 0.027683, 0.014952, 0.008189, 0.004509
p, Nb, 8.76557, 5.4301, 3.77274, 2.69501, 2.01173, 1.17627, 0.639714, 0.517022, 0.315301, 0.14802, 0.090311, 0.053664, 0.027055, 0.010032
d, Nb, 6.58119, 3.77781, 3.01317, 1.53482, 0.802394, 0.513954, 0.305319, 0.187477, 0.108449, 0.063515, 0.03189, 0.009261
f, Nb, 9.46343, 4.31423, 2.98125, 1.38687, 1.03888, 0.587547, 0.305006, 0.181768, 0.098512, 0.048829, 0.018937
g, Nb, 4.39168, 3.52968, 1.5017, 0.900671, 0.553371, 0.312228, 0.186533, 0.077639, 0.039512
h, Nb, 3.10838, 1.65064, 0.880199, 0.430575, 0.217462, 0.072433
i, Nb, 1.65555, 0.782041, 0.50487, 0.233992
!k, Nb, 0.343709

!Mo cc-pVTZ-PP-F12/MP2Fit
s, Mo, 9.04505, 6.24201, 3.99927, 2.71972, 1.45786, 0.772987, 0.519903, 0.269434, 0.13327, 0.070412, 0.037356, 0.020181, 0.011054, 0.006087
p, Mo, 11.819, 7.33112, 5.09709, 3.64062, 2.71598, 1.58796, 0.864006, 0.698621, 0.427849, 0.200404, 0.121909, 0.072412, 0.036513, 0.013542
d, Mo, 9.05758, 4.54142, 3.55152, 2.02278, 1.12865, 0.696911, 0.417632, 0.254325, 0.126123, 0.072099, 0.039687, 0.012336
f, Mo, 13.0156, 5.64573, 3.75275, 2.11995, 1.17446, 0.735626, 0.418665, 0.240242, 0.132129, 0.065858, 0.025558
g, Mo, 5.59074, 4.30758, 1.94735, 1.18392, 0.734548, 0.369946, 0.209856, 0.098118, 0.051872
h, Mo, 3.91815, 1.90818, 1.08089, 0.562825, 0.283957, 0.096418
i, Mo, 1.98451, 1.13537, 0.588862, 0.285255
!k, Mo, 0.409849

!Tc cc-pVTZ-PP-F12/MP2Fit
s, Tc, 12.122, 7.76581, 4.63418, 3.19616, 1.89364, 1.04387, 0.700793, 0.363002, 0.179473, 0.094952, 0.050409, 0.027244, 0.014923, 0.008217
p, Tc, 15.9562, 9.91461, 6.89449, 4.91929, 3.6662, 2.14512, 1.16915, 0.947135, 0.584135, 0.270156, 0.164128, 0.097432, 0.049167, 0.018266
d, Tc, 12.0559, 5.76376, 4.54615, 2.76242, 1.51438, 0.940824, 0.566184, 0.343913, 0.170508, 0.097383, 0.053586, 0.016654
f, Tc, 18.3854, 6.72633, 4.12808, 2.7813, 1.5114, 0.95615, 0.558489, 0.32279, 0.178025, 0.088837, 0.0345
g, Tc, 6.73859, 4.9201, 2.75713, 1.44055, 0.969147, 0.494759, 0.281274, 0.132091, 0.069965
h, Tc, 4.69586, 2.18138, 1.07163, 0.639492, 0.36918, 0.129041
i, Tc, 2.26816, 1.33379, 0.680394, 0.372791
!k, Tc, 0.503632

!Ru cc-pVTZ-PP-F12/MP2Fit
s, Ru, 16.3936, 10.5375, 6.29258, 4.36307, 2.55818, 1.40114, 0.9408, 0.488921, 0.242033, 0.128115, 0.068014, 0.03677, 0.020144, 0.011093
p, Ru, 21.5413, 13.3844, 9.30824, 6.64405, 4.94914, 2.89614, 1.57835, 1.2795, 0.794738, 0.364521, 0.220168, 0.130511, 0.066004, 0.024652
d, Ru, 16.2623, 7.80405, 6.17378, 3.75487, 2.03566, 1.26337, 0.764465, 0.464939, 0.230824, 0.131404, 0.072327, 0.02248
f, Ru, 24.8209, 8.96028, 5.48642, 3.7576, 2.0442, 1.28975, 0.753964, 0.438699, 0.240377, 0.119896, 0.04657
g, Ru, 8.13882, 5.51124, 3.87366, 1.84295, 1.2624, 0.659861, 0.380707, 0.176253, 0.093676
h, Ru, 5.72392, 2.47456, 1.41304, 0.860282, 0.480271, 0.171882
i, Ru, 2.88752, 1.83301, 0.857348, 0.502662
!k, Ru, 0.656473

!Rh cc-pVTZ-PP-F12/MP2Fit
s, Rh, 22.1502, 14.253, 8.50095, 5.88923, 3.15091, 1.728, 1.19929, 0.647098, 0.326823, 0.172981, 0.091805, 0.049638, 0.027195, 0.014976
p, Rh, 29.0805, 18.0688, 12.5664, 8.96977, 6.6816, 3.90979, 2.13076, 1.72761, 1.07341, 0.492076, 0.297263, 0.176312, 0.089091, 0.033273
d, Rh, 21.9753, 10.5661, 8.3583, 5.0812, 2.7482, 1.66572, 1.01692, 0.626266, 0.312338, 0.177134, 0.097441, 0.030316
f, Rh, 33.5156, 12.1167, 7.41458, 5.34645, 2.9542, 1.65384, 1.01883, 0.594064, 0.324435, 0.161519, 0.062816

g, Rh, 10.8721, 7.34269, 5.29315, 2.58246, 1.62206, 0.835382, 0.51529, 0.237618, 0.126214
h, Rh, 6.74971, 3.14908, 1.98435, 1.19323, 0.618888, 0.231495
i, Rh, 4.02905, 2.33004, 1.14597, 0.679338
!k, Rh, 0.882327

!Pd cc-pVTZ-PP-F12/MP2Fit
s, Pd, 29.903, 19.242, 11.4758, 7.94867, 4.253, 2.33535, 1.62429, 0.875135, 0.440877, 0.23324, 0.123859, 0.066998, 0.03671, 0.020216
p, Pd, 39.2608, 24.3954, 16.9673, 12.1122, 9.02362, 5.2807, 2.87475, 2.33068, 1.45121, 0.669731, 0.404089, 0.239608, 0.12005, 0.044748
d, Pd, 29.73, 14.3635, 11.3923, 6.94221, 3.68455, 2.21465, 1.37796, 0.852064, 0.421535, 0.238444, 0.130957, 0.040737
f, Pd, 45.4257, 16.5635, 10.1573, 7.30692, 3.99989, 2.21923, 1.37542, 0.809086, 0.437857, 0.217171, 0.084585
g, Pd, 14.7257, 9.96463, 7.20681, 3.53784, 2.1841, 1.13563, 0.703225, 0.318539, 0.169113
h, Pd, 7.66353, 4.92129, 2.73885, 1.67286, 0.752423, 0.311367
i, Pd, 5.7433, 2.95813, 1.65262, 0.829321
!k, Pd, 1.170706

D.2.3 cc-pVQZ-PP-F12/MP2Fit

!Y cc-pVQZ-PP-F12/MP2Fit
s, Y, 7.58929, 4.55704, 3.04288, 1.93454, 1.05919, 0.638274, 0.383698, 0.215328, 0.111716, 0.055683, 0.028032, 0.014914, 0.008085, 0.004456, 0.002464, 0.001365
p, Y, 19.3907, 9.91641, 4.8221, 2.45978, 1.51639, 1.05399, 0.682825, 0.407688, 0.205111, 0.147996, 0.081583, 0.038587, 0.019828, 0.010613, 0.005787, 0.003176
d, Y, 16.2825, 8.4299, 4.07625, 2.06911, 1.36318, 0.950527, 0.580293, 0.274243, 0.194507, 0.131339, 0.082466, 0.035222, 0.016882, 0.008861
f, Y, 13.3203, 6.37415, 3.10515, 2.03555, 1.30264, 0.682304, 0.471867, 0.248333, 0.165002, 0.091614, 0.0455, 0.024203, 0.013151
g, Y, 4.48896, 2.89312, 1.89033, 0.998841, 0.733918, 0.317309, 0.220261, 0.125488, 0.056068, 0.028923, 0.015674
h, Y, 2.80325, 1.88575, 1.00619, 0.675922, 0.32244, 0.194694, 0.125087, 0.056893
i, Y, 2.65861, 1.48887, 0.848012, 0.45473, 0.266115, 0.119489
!k, Y, 1.50401, 0.87802, 0.410005, 0.169158
!l, Y, 0.263355

!Zr cc-pVQZ-PP-F12/MP2Fit
s, Zr, 9.31091, 5.5406, 3.61704, 2.22441, 1.25053, 0.802956, 0.492467, 0.272318, 0.143012, 0.072303, 0.036056, 0.01898, 0.010205, 0.005599, 0.003088, 0.001708
p, Zr, 23.2746, 11.4282, 5.54803, 3.2619, 2.14984, 1.42854, 0.877194, 0.517942, 0.25735, 0.18539, 0.101996, 0.048255, 0.024786, 0.013267, 0.007234, 0.00397
d, Zr, 20.3501, 10.5454, 5.3255, 2.78966, 1.74573, 1.1806, 0.731068, 0.35024, 0.245049, 0.161208, 0.100035, 0.044101, 0.021259, 0.011128
f, Zr, 15.9827, 7.09802, 3.52648, 2.5102, 1.54178, 0.883452, 0.605783, 0.314638, 0.207342, 0.114382, 0.056959, 0.030307, 0.016456
g, Zr, 5.96402, 4.02517, 2.27039, 1.34451, 0.898207, 0.418412, 0.269249, 0.152188, 0.074146, 0.037979, 0.020161
h, Zr, 3.96937, 2.06447, 1.46362, 0.839727, 0.448798, 0.251971, 0.148236, 0.072221
i, Zr, 3.31884, 1.75743, 1.10452, 0.599946, 0.29387, 0.171307
!k, Zr, 1.85294, 0.993734, 0.484165, 0.191934
!l, Zr, 0.30484

!Nb cc-pVQZ-PP-F12/MP2Fit
s, Nb, 11.1399, 6.48718, 4.16616, 2.59498, 1.60445, 1.07729, 0.6871, 0.377321, 0.191257, 0.093418, 0.078134, 0.032489, 0.015012, 0.007649, 0.004056, 0.002195
p, Nb, 29.0019, 14.173, 6.92912, 4.12338, 2.71772, 1.72849, 1.07629, 0.663816, 0.332156, 0.236427, 0.13482, 0.065657, 0.032263, 0.016863, 0.009117, 0.004984
d, Nb, 25.1524, 12.8597, 6.41316, 3.56454, 2.32914, 1.44919, 0.924054, 0.483175, 0.316743, 0.214395, 0.134993, 0.060602, 0.027553, 0.014089
f, Nb, 19.5411, 8.35358, 4.29671, 3.1803, 1.81357, 1.11325, 0.780684, 0.405971, 0.25812, 0.144058, 0.071231, 0.037884, 0.020571
g, Nb, 7.45876, 5.01519, 2.81193, 1.75274, 1.03045, 0.609079, 0.298547, 0.275902, 0.099045, 0.048732, 0.025496
h, Nb, 4.96127, 2.58059, 1.68993, 0.974902, 0.51082, 0.318946, 0.15086, 0.130136
i, Nb, 4.14855, 2.01618, 1.38065, 0.752155, 0.367431, 0.214122
!k, Nb, 2.31617, 1.01624, 0.564683, 0.232563
!l, Nb, 0.362387

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!Mo cc-pVQZ-PP-F12/MP2Fit
s, Mo, 13.1092, 7.42782, 4.75985, 3.20262, 2.26495, 1.4177, 0.858167, 0.477168, 0.24243, 0.117498, 0.090668, 0.040909, 0.028984, 0.008755, 0.005227, 0.002869
p, Mo, 36.3615, 17.8566, 8.66543, 5.04427, 3.3028, 2.1495, 1.35736, 0.836382, 0.413537, 0.293456, 0.159514, 0.075675, 0.03879, 0.020741, 0.011306, 0.006204
d, Mo, 31.1463, 15.7667, 7.838, 4.57193, 2.97331, 1.75134, 1.12968, 0.595915, 0.383777, 0.249599, 0.154503, 0.068958, 0.033287, 0.017403
f, Mo, 23.8034, 9.79189, 5.14521, 3.92319, 2.2512, 1.40787, 0.976376, 0.499783, 0.325233, 0.179254, 0.089056, 0.047356, 0.025713
g, Mo, 9.1199, 6.06364, 3.51336, 2.14577, 1.24821, 0.740404, 0.417037, 0.34244, 0.116764, 0.059525, 0.031534
h, Mo, 6.2089, 3.23056, 2.164, 1.20502, 0.698792, 0.399489, 0.221234, 0.179826
i, Mo, 5.18569, 2.4593, 1.72198, 0.938406, 0.45961, 0.267677
!k, Mo, 2.89522, 1.52304, 0.696563, 0.248601
!l, Mo, 0.416133

!Tc cc-pVQZ-PP-F12/MP2Fit
s, Tc, 16.3477, 9.26659, 5.94968, 4.00351, 2.83138, 1.75648, 1.06672, 0.597169, 0.303802, 0.147039, 0.11344, 0.051141, 0.03623, 0.010943, 0.006534, 0.003586
p, Tc, 45.4519, 22.3208, 10.8318, 6.30534, 4.12826, 2.66255, 1.6781, 1.04336, 0.520136, 0.368486, 0.200272, 0.094924, 0.048547, 0.025941, 0.014137, 0.007756
d, Tc, 38.926, 19.6533, 9.77131, 5.72953, 3.71719, 2.16947, 1.41073, 0.750353, 0.480481, 0.309118, 0.191883, 0.086261, 0.041677, 0.021774
f, Tc, 29.5342, 12.0114, 6.37924, 4.91531, 2.79152, 1.74838, 1.2134, 0.629866, 0.405989, 0.224706, 0.111405, 0.059212, 0.032144
g, Tc, 10.6615, 6.94015, 4.43653, 2.70729, 1.56166, 0.944538, 0.489656, 0.385835, 0.153756, 0.076346, 0.039833
h, Tc, 7.55949, 3.87733, 2.78045, 1.51163, 0.882069, 0.498395, 0.280709, 0.226664
i, Tc, 6.46609, 3.20508, 2.08063, 1.1379, 0.56796, 0.347233
!k, Tc, 3.61903, 1.85423, 0.99588, 0.493292
!l, Tc, 0.700899

!Ru cc-pVQZ-PP-F12/MP2Fit
s, Ru, 20.3386, 11.5345, 7.41326, 4.97168, 3.48984, 2.15586, 1.33209, 0.761443, 0.38567, 0.184877, 0.142764, 0.064106, 0.045363, 0.013681, 0.008171, 0.004483
p, Ru, 56.773, 27.8517, 13.4952, 7.83297, 5.09487, 3.25238, 2.05068, 1.3042, 0.664581, 0.468352, 0.252549, 0.119392, 0.060867, 0.032467, 0.017676, 0.009698
d, Ru, 48.4302, 24.3038, 11.9459, 6.99512, 4.55742, 2.67224, 1.78261, 0.958937, 0.603313, 0.37392, 0.234486, 0.109184, 0.052838, 0.027422
f, Ru, 36.6079, 14.7215, 7.93104, 6.19129, 3.50213, 2.19588, 1.51168, 0.796669, 0.514398, 0.282757, 0.139484, 0.074054, 0.040189
g, Ru, 13.0999, 8.47205, 5.41176, 3.18512, 2.00757, 1.24951, 0.591783, 0.441457, 0.206438, 0.098619, 0.050391
h, Ru, 8.03075, 4.9466, 3.222, 1.86936, 1.13916, 0.633592, 0.357159, 0.285615
i, Ru, 8.07684, 3.94352, 2.61557, 1.30683, 0.724691, 0.447458
!k, Ru, 4.47839, 2.16581, 1.21543, 0.525717
!l, Ru, 0.799357

!Rh cc-pVQZ-PP-F12/MP2Fit
s, Rh, 25.4083, 14.4235, 9.28551, 6.23508, 4.37481, 2.69649, 1.66457, 0.952537, 0.483658, 0.231544, 0.178646, 0.080159, 0.056718, 0.017102, 0.010214, 0.005604
p, Rh, 70.8967, 34.7466, 16.8215, 9.76821, 6.36139, 4.06016, 2.55873, 1.63236, 0.812666, 0.569914, 0.313146, 0.151336, 0.076981, 0.040734, 0.022134, 0.012133
d, Rh, 60.4505, 30.2861, 14.8359, 8.68237, 5.66973, 3.33942, 2.24353, 1.22392, 0.753036, 0.442579, 0.276708, 0.139264, 0.068779, 0.035045
f, Rh, 45.7285, 18.3805, 9.92892, 7.75962, 4.3743, 2.74096, 1.88662, 1.00906, 0.6519, 0.35122, 0.174459, 0.092585, 0.050237
g, Rh, 16.278, 10.5267, 6.77594, 3.9769, 2.50276, 1.50122, 0.750427, 0.531623, 0.265533, 0.125722, 0.063372
h, Rh, 10.0188, 6.18247, 4.00653, 2.34943, 1.38826, 0.791965, 0.450632, 0.357364
i, Rh, 10.0633, 4.82369, 3.21984, 1.60883, 0.963637, 0.552029
!k, Rh, 5.57805, 2.35128, 1.48902, 0.690853
!l, Rh, 1.01425

!Pd cc-pVQZ-PP-F12/MP2Fit
s, Pd, 31.7566, 18.026, 11.602, 7.78507, 5.4536, 3.0979, 1.86852, 1.12194, 0.618818, 0.29421, 0.223474, 0.100239, 0.070918, 0.021379, 0.012768, 0.007005
p, Pd, 88.566, 43.3715, 20.9694, 12.1615, 7.90162, 4.93962, 3.13024, 2.06758, 1.05047, 0.736164, 0.392336, 0.190134, 0.096499, 0.050969,
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0.027682, 0.01517
d, Pd, 75.446, 37.7471, 18.4405, 10.7868, 7.025, 4.21272, 2.83431, 1.58714, 0.946449, 0.554385, 0.345592, 0.174146, 0.086049, 0.043825
f, Pd, 57.1564, 22.9814, 12.4329, 9.72033, 5.36081, 3.28059, 2.31067, 1.25655, 0.812955, 0.438295, 0.219246, 0.116127, 0.062872
g, Pd, 20.251, 13.1188, 8.50806, 4.50643, 3.12908, 1.69351, 0.955673, 0.651501, 0.329809, 0.158613, 0.079774
h, Pd, 12.1617, 7.70357, 4.75028, 3.27362, 1.73916, 0.996632, 0.567764, 0.446106
i, Pd, 12.5413, 5.88535, 3.86896, 1.96644, 1.19321, 0.555027
!k, Pd, 5.34779, 3.86056, 2.10637, 1.05066
!l, Pd, 1.48764

D.2.4 cc-pCVDZ-PP-F12/MP2Fit

!Y cc-pCVDZ-PP-F12/MP2Fit
s, Y, 10.3335, 5.71792, 3.466, 2.4122, 1.16191, 0.637056, 0.432993, 0.213448, 0.113583, 0.062722, 0.034363, 0.019816, 0.004372
p, Y, 10.7552, 5.80981, 3.53779, 2.25521, 1.26683, 0.876878, 0.498829, 0.269269, 0.165177, 0.093309, 0.056147, 0.030998, 0.016809
d, Y, 6.3867, 3.49423, 1.99814, 1.33676, 0.644565, 0.463053, 0.216826, 0.123743, 0.078608, 0.042354, 0.022262
f, Y, 4.04282, 2.37521, 1.46694, 0.68723, 0.624441, 0.325327, 0.173626, 0.105035, 0.051822, 0.021098
g, Y, 3.48705, 2.71236, 1.12024, 0.719088, 0.315618, 0.159812, 0.077762, 0.046298
h, Y, 2.33523, 1.46055, 0.759743, 0.316816, 0.177125
i, Y, 0.539914, 0.288236

!Zr cc-pCVDZ-PP-F12/MP2Fit
s, Zr, 13.4335, 7.44522, 4.54092, 3.1695, 1.51927, 0.837419, 0.576505, 0.288572, 0.149016, 0.079754, 0.043651, 0.025402, 0.005668
p, Zr, 13.9817, 7.54378, 4.59517, 2.93071, 1.64897, 1.14233, 0.648021, 0.347047, 0.21239, 0.120495, 0.072808, 0.040281, 0.021852
d, Zr, 8.24239, 4.02334, 2.34968, 1.73065, 0.842575, 0.598611, 0.282371, 0.160866, 0.101861, 0.054818, 0.028876
f, Zr, 4.7278, 2.79821, 1.9077, 0.862472, 0.787837, 0.421032, 0.225146, 0.136208, 0.067346, 0.027428
g, Zr, 4.31657, 3.40955, 1.48007, 0.91636, 0.404567, 0.207046, 0.101024, 0.060187
h, Zr, 3.0358, 1.89872, 0.987669, 0.411861, 0.230263
i, Zr, 0.647058, 0.34842

!Nb cc-pCVDZ-PP-F12/MP2Fit
s, Nb, 17.4635, 9.68222, 5.90687, 4.12252, 1.97491, 1.08662, 0.749116, 0.377158, 0.194399, 0.103608, 0.056836, 0.033048, 0.007366
p, Nb, 18.1762, 9.8069, 5.97369, 3.80992, 2.14366, 1.48503, 0.842013, 0.450917, 0.276109, 0.156643, 0.094725, 0.052393, 0.028407
d, Nb, 10.6747, 5.13177, 3.03954, 2.2794, 1.09503, 0.770919, 0.363572, 0.208746, 0.132527, 0.07138, 0.037523
f, Nb, 5.692, 3.41185, 2.49207, 1.10233, 1.01526, 0.567339, 0.283283, 0.173521, 0.085442, 0.035073
g, Nb, 5.57232, 4.38782, 1.82417, 1.43008, 0.677404, 0.322067, 0.194335, 0.074216
h, Nb, 3.86093, 2.45938, 1.31248, 0.541637, 0.295597
i, Nb, 0.87107, 0.490498

!Mo cc-pCVDZ-PP-F12/MP2Fit
s, Mo, 22.7026, 12.5892, 7.68172, 5.363, 2.57459, 1.39777, 0.95548, 0.482881, 0.250467, 0.134691, 0.073878, 0.042963, 0.009576
p, Mo, 23.6406, 12.7717, 7.78246, 4.96852, 2.80887, 1.95577, 1.11222, 0.60407, 0.381054, 0.198038, 0.113453, 0.063732, 0.035781
d, Mo, 13.9055, 6.71046, 3.98511, 2.98235, 1.43422, 1.04363, 0.543445, 0.303127, 0.152414, 0.075872, 0.043394
f, Mo, 7.06796, 4.23923, 3.19439, 1.40923, 1.30472, 0.738004, 0.357005, 0.223754, 0.110997, 0.045595
g, Mo, 7.0485, 5.45999, 2.26858, 1.58372, 0.793619, 0.408377, 0.250029, 0.095517
h, Mo, 4.98706, 3.19875, 1.68904, 0.681512, 0.384647
i, Mo, 1.04524, 0.588646

!Tc cc-pCVDZ-PP-F12/MP2Fit
s, Tc, 29.5207, 16.3669, 9.99392, 6.97882, 3.35381, 1.77881, 1.21918, 0.629718, 0.331095, 0.173682, 0.094698, 0.055191, 0.012434
p, Tc, 30.7559, 16.6255, 10.1312, 6.46992, 3.65832, 2.54315, 1.42219, 0.77546, 0.492489, 0.257701, 0.148406, 0.082953, 0.046534
d, Tc, 18.1319, 8.74737, 5.1728, 3.86398, 1.87486, 1.37194, 0.71771, 0.394565, 0.187852, 0.092949, 0.055016
f, Tc, 9.18066, 5.50163, 4.15269, 1.82942, 1.6945, 0.961487, 0.464064, 0.29088, 0.144296, 0.059274
g, Tc, 9.31419, 7.22049, 2.60529, 1.97138, 0.933619, 0.476977, 0.258828, 0.101581
h, Tc, 6.45308, 4.16057, 2.18355, 0.862368, 0.481576
i, Tc, 1.29832, 0.704779

!Ru cc-pCVDZ-PP-F12/MP2Fit
s, Ru, 38.4125, 21.2947, 13.011, 9.09207, 4.396, 2.35135, 1.62175, 0.830967, 0.430524, 0.221168, 0.12049, 0.070795, 0.016116
p, Ru, 39.9883, 21.6131, 13.1705, 8.40572, 4.75745, 3.30476, 1.84667, 1.00564, 0.645943, 0.338954, 0.195439, 0.10799, 0.060302
d, Ru, 25.9141, 13.4356, 7.91649, 5.65088, 2.52373, 1.77464, 0.872235, 0.464716, 0.222772, 0.114423, 0.07032
f, Ru, 12.1958, 7.44082, 5.75085, 2.31666, 2.17549, 1.27625, 0.61794, 0.377429, 0.176289, 0.07399
g, Ru, 11.8242, 7.73076, 3.47026, 2.36633, 1.09366, 0.553173, 0.263659, 0.146982
h, Ru, 7.81651, 5.37026, 2.72925, 1.07532, 0.598796
i, Ru, 1.5571, 0.844258

!Rh cc-pCVDZ-PP-F12/MP2Fit
s, Rh, 49.9482, 27.7224, 17.049, 11.9579, 5.82984, 3.09422, 2.12617, 1.07777, 0.549764, 0.285001, 0.156589, 0.091816, 0.020789
p, Rh, 51.9801, 28.0915, 17.1201, 10.9356, 6.21145, 4.30584, 2.4002, 1.30731, 0.864245, 0.449786, 0.262018, 0.137816, 0.075503
d, Rh, 39.1314, 21.6098, 9.71414, 6.30401, 2.9814, 2.13041, 0.962064, 0.543373, 0.267992, 0.148773, 0.095088
f, Rh, 18.9432, 12.8587, 9.10776, 5.23935, 2.5867, 1.68501, 0.805832, 0.464697, 0.211682, 0.091813
g, Rh, 12.27, 7.8112, 5.64875, 2.78589, 1.25213, 0.596005, 0.277697, 0.148577
h, Rh, 8.25136, 6.70722, 2.85506, 1.17859, 0.685663
i, Rh, 1.8354, 0.97997

!Pd cc-pCVDZ-PP-F12/MP2Fit
s, Pd, 64.9522, 36.063, 22.1895, 15.571, 7.59069, 4.01677, 2.75436, 1.39771, 0.721299, 0.378976, 0.208231, 0.120674, 0.02683
p, Pd, 67.58, 36.5194, 22.2627, 14.2255, 8.08496, 5.60454, 3.11868, 1.70248, 1.13419, 0.589434, 0.342225, 0.177328, 0.096893
d, Pd, 51.1064, 28.2197, 12.2907, 7.75785, 3.81227, 2.75012, 1.23001, 0.716984, 0.359637, 0.195992, 0.124838
f, Pd, 24.7734, 14.9915, 10.7945, 6.83519, 3.3511, 1.91967, 0.955344, 0.506889, 0.235593, 0.112617
g, Pd, 14.6415, 9.68246, 7.41179, 3.50704, 1.46897, 0.75334, 0.348198, 0.187151
h, Pd, 10.7293, 8.73569, 3.8016, 1.59996, 0.843476
i, Pd, 2.20162, 1.11266

D.2.5 cc-pCVTZ-PP-F12/MP2Fit

!Y cc-pCVTZ-PP-F12/MP2Fit
s, Y, 7.07473, 4.74046, 3.08861, 1.74911, 0.930627, 0.53802, 0.308354, 0.157403, 0.085071, 0.048747, 0.028321, 0.016508, 0.009659, 0.005668, 0.003233
p, Y, 10.3065, 5.66657, 3.37766, 2.13954, 1.42878, 0.923529, 0.505681, 0.272397, 0.171898, 0.111154, 0.065798, 0.036869, 0.020874, 0.012102, 0.007057
d, Y, 8.25462, 5.18535, 3.71051, 1.6099, 1.12153, 0.619786, 0.380573, 0.188731, 0.120772, 0.067672, 0.027872, 0.012327, 0.006868
f, Y, 11.3876, 6.49143, 4.11213, 1.88006, 1.21234, 0.743659, 0.359089, 0.180195, 0.118109, 0.057526, 0.027461, 0.013669
g, Y, 7.75422, 4.39795, 2.01632, 1.18347, 0.749885, 0.413998, 0.211316, 0.108145, 0.057578, 0.032308
h, Y, 4.47141, 2.31689, 1.07843, 0.687927, 0.329962, 0.156265, 0.049945
i, Y, 2.23403, 1.0112, 0.596277, 0.278887, 0.150604, 0.085114
!k, Y, 0.409255, 0.213485

!Zr cc-pCVTZ-PP-F12/MP2Fit
s, Zr, 8.95001, 5.88668, 3.75236, 2.1049, 1.1509, 0.679262, 0.394866, 0.208096, 0.115279, 0.065316, 0.037424, 0.021564, 0.012589, 0.007377, 0.004208
p, Zr, 13.3974, 7.36574, 4.38979, 2.78037, 1.85864, 1.2036, 0.659096, 0.356437, 0.223608, 0.144494, 0.085532, 0.047928, 0.027135, 0.015732, 0.009173
d, Zr, 10.6239, 6.58419, 4.64811, 2.02834, 1.44723, 0.800834, 0.492958, 0.248348, 0.161558, 0.094331, 0.039435, 0.016524, 0.009068
f, Zr, 14.6465, 8.31603, 5.25056, 2.12409, 1.48574, 0.903895, 0.463677, 0.253573, 0.169736, 0.081466, 0.037161, 0.018059
g, Zr, 4.87086, 2.47884, 1.56542, 0.975762, 0.52951, 0.27178, 0.14326, 0.075616, 0.042085
h, Zr, 5.259, 2.46124, 1.4192, 0.798338, 0.433157, 0.22848, 0.065143
i, Zr, 2.4933, 1.2939, 0.805561, 0.369618, 0.195889, 0.110788
!k, Zr, 0.546362, 0.28586

!Nb cc-pCVTZ-PP-F12/MP2Fit

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s, Nb, 11.1089, 7.11563, 4.4045, 2.45173, 1.38687, 0.866647, 0.532422, 0.300007, 0.16586, 0.091622, 0.050441, 0.028562, 0.016526, 0.009642, 0.005486
p, Nb, 17.4166, 9.57441, 5.70562, 3.60974, 2.41094, 1.54413, 0.860001, 0.468415, 0.291752, 0.187431, 0.111192, 0.062348, 0.035293, 0.020457, 0.011926
d, Nb, 13.3618, 8.03951, 5.56179, 2.57845, 1.91223, 1.04894, 0.660885, 0.342924, 0.222263, 0.133002, 0.055379, 0.022021, 0.011924
f, Nb, 18.3891, 9.94698, 5.92654, 2.69345, 2.00323, 1.16265, 0.651288, 0.342596, 0.225263, 0.107035, 0.048477, 0.023503
g, Nb, 5.77293, 3.06743, 2.01919, 1.19703, 0.655698, 0.357121, 0.192077, 0.103464, 0.056494
h, Nb, 6.441, 3.24658, 1.85939, 1.1954, 0.611391, 0.332058, 0.084792
i, Nb, 3.11645, 1.68147, 1.07025, 0.484388, 0.254599, 0.144024
!k, Nb, 0.745156, 0.387416

!Mo cc-pCVTZ-PP-F12/MP2Fit
s, Mo, 13.9862, 8.88135, 5.54725, 3.24669, 1.91199, 1.16026, 0.710716, 0.399037, 0.21879, 0.114861, 0.064929, 0.037125, 0.021484, 0.012535, 0.007132
p, Mo, 22.64, 12.4467, 7.41564, 4.6896, 3.13017, 2.00136, 1.12398, 0.614332, 0.380856, 0.24366, 0.14455, 0.081058, 0.045881, 0.026594, 0.015504
d, Mo, 17.2439, 10.3395, 6.78152, 3.49745, 2.64654, 1.34192, 0.862158, 0.452789, 0.292643, 0.191835, 0.096646, 0.033776, 0.01691
f, Mo, 23.0164, 11.8728, 6.83813, 3.51153, 2.58566, 1.45863, 0.862862, 0.454125, 0.293024, 0.139146, 0.063024, 0.030554
g, Mo, 6.69937, 3.97546, 2.74282, 1.45879, 0.854754, 0.488047, 0.479159, 0.234352, 0.103649
h, Mo, 7.91823, 3.76059, 2.69894, 1.4027, 0.802575, 0.423989, 0.11023
i, Mo, 4.05139, 2.18591, 1.39903, 0.629704, 0.600602, 0.250087
!k, Mo, 0.846354, 0.423542

!Tc cc-pCVTZ-PP-F12/MP2Fit
s, Tc, 16.7017, 9.99752, 6.2439, 3.78782, 2.31646, 1.9286, 1.23492, 0.694937, 0.339091, 0.172386, 0.092361, 0.050678, 0.028692, 0.016548, 0.009353
p, Tc, 29.3625, 16.1093, 9.55588, 5.9015, 3.85767, 2.48491, 1.45932, 0.815282, 0.500948, 0.318759, 0.188224, 0.105364, 0.059685, 0.034575, 0.020155
d, Tc, 20.5741, 11.7313, 7.52042, 3.94065, 3.03438, 1.85848, 1.32426, 0.697147, 0.425055, 0.187312, 0.154872, 0.08946, 0.030585
f, Tc, 28.3669, 13.7228, 7.55211, 4.06128, 3.02058, 1.75553, 1.15612, 0.60977, 0.38118, 0.183664, 0.082409, 0.03976
g, Tc, 7.0339, 4.52167, 2.80715, 1.7791, 1.28708, 0.7118, 0.677294, 0.328531, 0.14002
h, Tc, 9.04101, 4.96305, 3.75878, 1.76503, 1.05807, 0.538645, 0.145418
i, Tc, 4.38343, 3.2821, 1.85513, 0.837999, 0.786074, 0.334698
!k, Tc, 1.09206, 0.56679

!Ru cc-pCVTZ-PP-F12/MP2Fit
s, Ru, 21.7098, 12.9847, 8.11871, 4.91582, 2.99772, 2.4959, 1.62483, 0.956275, 0.482553, 0.229616, 0.120565, 0.065883, 0.037253, 0.021495, 0.012158
p, Ru, 38.1717, 20.9429, 12.4227, 7.64787, 4.97093, 3.20428, 1.92125, 1.08816, 0.660437, 0.413493, 0.244476, 0.137158, 0.077777, 0.045022, 0.026224
d, Ru, 26.3348, 14.9015, 9.6041, 5.08961, 3.82259, 2.14338, 1.48538, 0.873367, 0.57774, 0.261172, 0.203767, 0.1107, 0.041741
f, Ru, 35.9355, 16.9074, 9.43606, 5.4658, 4.06361, 2.35825, 1.51712, 0.771895, 0.460538, 0.251989, 0.112969, 0.052828
g, Ru, 7.97967, 6.0763, 3.77204, 1.94489, 1.37606, 0.745084, 0.657574, 0.340869, 0.184312
h, Ru, 9.55274, 6.25434, 4.03634, 1.86151, 1.14501, 0.574366, 0.207667
i, Ru, 5.66082, 3.98551, 2.10979, 1.08292, 0.964173, 0.526416
!k, Ru, 1.43726, 0.785603

!Rh cc-pCVTZ-PP-F12/MP2Fit
s, Rh, 28.076, 16.7712, 10.4671, 6.24915, 3.62992, 2.94335, 1.81618, 1.08127, 0.615076, 0.316802, 0.165252, 0.088663, 0.04944, 0.028263, 0.015903
p, Rh, 49.6191, 27.2212, 16.141, 9.91051, 6.4077, 4.11606, 2.48889, 1.42416, 0.861935, 0.537496, 0.317881, 0.178554, 0.101261, 0.058576, 0.034103
d, Rh, 34.2282, 19.3618, 12.4691, 6.59094, 4.94367, 2.76834, 1.91922, 1.12265, 0.736745, 0.336681, 0.256338, 0.138779, 0.055449
f, Rh, 46.6871, 21.9376, 12.2359, 6.95011, 4.99904, 2.7999, 1.82334, 1.02914, 0.60676, 0.340398, 0.150321, 0.069301
g, Rh, 10.3387, 7.96521, 4.79798, 2.5578, 1.81056, 0.889697, 0.755212, 0.363687, 0.195672
h, Rh, 11.7584, 7.96048, 4.36237, 2.26666, 1.39366, 0.68634, 0.287603
i, Rh, 7.28727, 4.81118, 2.67769, 1.45687, 1.2832, 0.67978
!k, Rh, 1.83928, 1.00136

!Pd cc-pCVTZ-PP-F12/MP2Fit
s, Pd, 36.403, 21.7417, 13.5733, 8.1442, 4.88385, 3.85714, 2.59308, 1.76631, 1.13426, 0.431636, 0.211345, 0.112291, 0.063183, 0.036354, 0.020553
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p, Pd, 64.4382, 35.223, 20.7682, 12.642, 8.11393, 5.05498, 3.23394, 2.00524, 1.22882, 0.713942, 0.416743, 0.23246, 0.131625, 0.076118, 0.044324
d, Pd, 44.4618, 25.0666, 16.1058, 8.53374, 6.42453, 3.56588, 2.48724, 1.46987, 0.99527, 0.439206, 0.339406, 0.183546, 0.071667
f, Pd, 60.5906, 28.2568, 15.4463, 8.69919, 6.06927, 3.58393, 2.43537, 1.47514, 0.851693, 0.458041, 0.200748, 0.090826
g, Pd, 12.942, 9.47968, 4.93556, 2.77827, 1.98268, 1.1282, 0.780292, 0.300629, 0.176772
h, Pd, 14.4111, 9.73458, 4.88055, 2.73492, 1.72995, 0.876704, 0.494013
i, Pd, 9.19142, 5.84507, 3.52183, 1.96994, 1.68238, 0.792766
!k, Pd, 2.3033, 1.25843
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D.2.6 cc-pCVQZ-PP-F12/MP2Fit

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!Y cc-pCVQZ-PP-F12/MP2Fit
s, Y, 10.6606, 6.08965, 3.55642, 2.29129, 1.42926, 0.882812, 0.591472, 0.37621, 0.23834, 0.11927, 0.056338, 0.046525, 0.018469, 0.00836, 0.004227, 0.002233, 0.001205
p, Y, 27.7746, 15.8207, 7.6833, 3.75598, 2.24547, 1.47762, 0.939035, 0.588306, 0.37429, 0.192198, 0.133192, 0.074158, 0.036155, 0.017736, 0.00925, 0.004999, 0.002732
d, Y, 23.5549, 13.1866, 6.52083, 3.24718, 1.91677, 1.31455, 0.828344, 0.463337, 0.315902, 0.219847, 0.142137, 0.082175, 0.034965, 0.015409, 0.007788
f, Y, 15.8189, 7.84983, 3.86919, 2.41569, 2.24375, 1.09066, 0.645702, 0.466765, 0.247769, 0.148645, 0.080689, 0.039385, 0.020858, 0.01129
g, Y, 7.57078, 4.79928, 2.77305, 1.64811, 1.06043, 0.596374, 0.327272, 0.15793, 0.144358, 0.056386, 0.027352, 0.014113
h, Y, 4.16258, 3.30592, 1.86306, 1.01499, 0.580616, 0.352095, 0.182865, 0.090086, 0.075319
i, Y, 3.88517, 2.24578, 1.19968, 0.724131, 0.448557, 0.210322, 0.118067
!k, Y, 2.23083, 1.27053, 0.687927, 0.326342, 0.137739
!l, Y, 0.599994, 0.263355

!Zr cc-pCVQZ-PP-F12/MP2Fit
s, Zr, 14.4179, 8.23869, 4.80898, 3.0934, 1.92649, 1.18952, 0.79808, 0.508908, 0.323073, 0.16141, 0.076018, 0.06276, 0.024921, 0.011285, 0.005706, 0.003014, 0.001627
p, Zr, 37.4999, 21.3648, 10.383, 5.07993, 3.03239, 1.99126, 1.26418, 0.79291, 0.505138, 0.259542, 0.179791, 0.100027, 0.04877, 0.023936, 0.012486, 0.006748, 0.003688
d, Zr, 32.0399, 18.0005, 8.76307, 4.19643, 2.53568, 1.7858, 1.13839, 0.63089, 0.426829, 0.295468, 0.190746, 0.110332, 0.047012, 0.020776, 0.01051
f, Zr, 21.3776, 10.5684, 5.18862, 3.26382, 3.03544, 1.47006, 0.86527, 0.626956, 0.333687, 0.200559, 0.108811, 0.053154, 0.028155, 0.015241
g, Zr, 9.58803, 5.44446, 3.62952, 2.10436, 1.34988, 0.767524, 0.431802, 0.211482, 0.193625, 0.075981, 0.036901, 0.019049
h, Zr, 4.41356, 3.76302, 2.19951, 1.28609, 0.769458, 0.472898, 0.249267, 0.119804, 0.100759
i, Zr, 5.14538, 2.5479, 1.59231, 0.97121, 0.6035, 0.283508, 0.159318
!k, Zr, 3.0028, 1.71587, 0.929003, 0.440438, 0.186165
!l, Zr, 0.693636, 0.30484

!Nb cc-pCVQZ-PP-F12/MP2Fit
s, Nb, 19.3593, 11.0032, 6.33003, 3.98851, 2.4311, 1.50428, 1.03712, 0.693135, 0.406677, 0.214778, 0.102197, 0.08443, 0.033469, 0.0152, 0.007697, 0.00407, 0.002199
p, Nb, 50.7442, 28.9919, 14.1651, 6.92961, 4.1289, 2.72187, 1.72783, 1.07334, 0.661606, 0.331749, 0.236403, 0.13523, 0.066012, 0.032348, 0.016879, 0.009121, 0.004985
d, Nb, 41.9477, 22.9767, 10.7672, 5.53776, 3.86294, 2.33666, 1.40085, 0.875061, 0.474876, 0.317318, 0.215668, 0.135424, 0.060955, 0.027632, 0.014104
f, Nb, 33.4224, 18.7825, 8.04878, 4.35797, 3.21153, 1.84928, 1.13904, 0.80086, 0.415428, 0.260529, 0.144444, 0.071307, 0.037903, 0.020576
g, Nb, 11.6071, 7.1371, 5.6573, 2.89767, 1.81934, 1.11369, 0.677029, 0.303372, 0.276093, 0.100744, 0.04905, 0.025568
h, Nb, 8.53841, 6.55734, 2.65126, 1.56062, 0.971883, 0.565701, 0.333141, 0.153138, 0.131521
i, Nb, 6.57872, 3.52844, 2.47663, 1.39612, 0.801583, 0.378572, 0.215263
!k, Nb, 3.7359, 2.56193, 1.1411, 0.573548, 0.23426
!l, Nb, 0.757531, 0.362387

!Mo cc-pCVQZ-PP-F12/MP2Fit
s, Mo, 26.1227, 14.8423, 8.53481, 5.38063, 3.29378, 2.15014, 1.54193, 1.05184, 0.607351, 0.307941, 0.137998, 0.114195, 0.0454, 0.020574, 0.010405, 0.005498, 0.00297
p, Mo, 68.2595, 38.8906, 18.8848, 9.07357, 5.13261, 3.00921, 1.86814, 1.29424, 0.919605, 0.494678, 0.337417, 0.18741, 0.090244, 0.043904,
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0.022843, 0.012328, 0.006734
d, Mo, 55.8612, 30.2238, 13.8072, 6.95833, 4.75721, 2.81758, 1.86494, 1.30328, 0.729831, 0.459873, 0.295067, 0.185456, 0.085099, 0.038179, 0.019252
f, Mo, 45.0473, 25.2778, 10.7688, 5.76381, 3.97066, 2.24974, 1.44134, 1.0501, 0.577887, 0.35713, 0.198016, 0.09678, 0.051267, 0.027798
g, Mo, 15.378, 9.27003, 7.18001, 3.1448, 2.41249, 1.39243, 0.921397, 0.418985, 0.359638, 0.143807, 0.068053, 0.034886
h, Mo, 10.7743, 7.80496, 3.17004, 2.17822, 1.39545, 0.837355, 0.446374, 0.2079, 0.176747
i, Mo, 8.66368, 4.7607, 3.071, 1.76804, 1.14582, 0.512713, 0.291771
!k, Mo, 4.86375, 2.98172, 1.33812, 0.808646, 0.242448
!l, Mo, 1.03, 0.416133

!Tc cc-pCVQZ-PP-F12/MP2Fit
s, Tc, 35.2363, 20.0353, 11.4818, 7.25942, 4.50674, 2.65278, 1.92817, 1.31273, 0.790844, 0.414962, 0.268712, 0.219794, 0.074226, 0.030264, 0.014644, 0.007587, 0.004058
p, Tc, 91.7907, 52.1104, 25.065, 11.6834, 6.25417, 3.54431, 2.37543, 1.75477, 1.29799, 0.710914, 0.470971, 0.258793, 0.129924, 0.061948, 0.0315, 0.016817, 0.009131
d, Tc, 75.3537, 40.7439, 18.6067, 9.4133, 6.44809, 3.58478, 2.34243, 1.68624, 1.00714, 0.644647, 0.41432, 0.261529, 0.138835, 0.062453, 0.028413
f, Tc, 59.9619, 33.1457, 13.4601, 6.99553, 4.70297, 2.74685, 1.91719, 1.46501, 0.89182, 0.533279, 0.283138, 0.133864, 0.069875, 0.037664
g, Tc, 20.0691, 11.6671, 8.86446, 4.20952, 2.79522, 1.60085, 1.19153, 0.609649, 0.437605, 0.279275, 0.110615, 0.050789
h, Tc, 12.0745, 8.29192, 5.1982, 3.15262, 1.97413, 1.28515, 0.618341, 0.313847, 0.24215
i, Tc, 11.6377, 6.23924, 3.80042, 2.43922, 1.39259, 0.743453, 0.427498
!k, Tc, 6.56619, 3.27259, 1.53487, 0.991481, 0.354091
!l, Tc, 1.35889, 0.700899

!Ru cc-pCVQZ-PP-F12/MP2Fit
s, Ru, 47.4044, 26.8931, 15.3755, 9.70269, 6.00337, 3.52397, 2.6025, 1.85289, 1.1824, 0.619122, 0.385715, 0.309176, 0.118333, 0.04656, 0.021134, 0.010605, 0.005582
p, Ru, 123.788, 70.214, 33.6985, 15.6598, 8.41176, 4.83061, 3.23749, 2.37168, 1.74094, 0.951741, 0.620567, 0.345789, 0.178904, 0.085633, 0.043014, 0.022781, 0.012333
d, Ru, 101.614, 54.8796, 24.9732, 12.5359, 8.52367, 4.69302, 3.10698, 2.25407, 1.35389, 0.863079, 0.518734, 0.31341, 0.176749, 0.087065, 0.039879
f, Ru, 80.8199, 44.5975, 17.9868, 9.33143, 6.33376, 3.77238, 2.6054, 1.96438, 1.12382, 0.670215, 0.363053, 0.192995, 0.097163, 0.051494
g, Ru, 26.4115, 14.9357, 11.167, 5.51016, 3.90152, 2.43484, 1.82336, 0.943365, 0.591401, 0.3262, 0.166795, 0.072676
h, Ru, 16.2242, 11.1373, 6.96439, 3.95237, 2.45227, 1.52056, 0.923802, 0.468479, 0.336053
i, Ru, 15.6819, 8.39123, 4.87438, 3.31115, 1.7214, 1.04723, 0.501658
!k, Ru, 8.74499, 3.91795, 1.87908, 1.29973, 0.532307
!l, Ru, 1.62246, 0.799357

!Rh cc-pCVQZ-PP-F12/MP2Fit
s, Rh, 63.8861, 36.2032, 20.6627, 13.0058, 7.96159, 4.5002, 3.21237, 2.21707, 1.41858, 0.771243, 0.490435, 0.397182, 0.165646, 0.066587, 0.029346, 0.014524, 0.007591
p, Rh, 164.944, 92.584, 43.4816, 19.9157, 11.2791, 6.75074, 4.13039, 2.71164, 2.10721, 1.23782, 0.846873, 0.470745, 0.251611, 0.121236, 0.059901, 0.031257, 0.016788
d, Rh, 135.169, 71.9107, 31.307, 14.361, 9.41775, 5.70758, 4.1062, 2.69807, 1.55667, 1.05061, 0.664176, 0.406246, 0.243987, 0.128101, 0.059555
f, Rh, 107.82, 58.7908, 23.0014, 12.4581, 9.17858, 5.39627, 3.12666, 2.31711, 1.38683, 0.919237, 0.525835, 0.292914, 0.136616, 0.070537
g, Rh, 34.5823, 18.8744, 13.7788, 7.24105, 5.39196, 3.28376, 2.05979, 1.13794, 0.732423, 0.410526, 0.237555, 0.101834
h, Rh, 21.088, 13.8672, 8.26309, 5.13082, 3.39257, 2.03489, 1.33552, 0.667249, 0.448833
i, Rh, 19.1544, 8.16129, 4.76615, 3.91116, 2.0713, 1.33537, 0.555904
!k, Rh, 10.9292, 4.44705, 2.45999, 1.71681, 0.713029
!l, Rh, 1.87112, 1.01425

!Pd cc-pCVQZ-PP-F12/MP2Fit
s, Pd, 84.2188, 46.9103, 26.1057, 16.1684, 9.87115, 5.33531, 3.52541, 2.30812, 1.58444, 1.03799, 0.704501, 0.570088, 0.240709, 0.100677, 0.042154, 0.020242, 0.010418
p, Pd, 222.633, 124.923, 58.6169, 26.7687, 15.0638, 8.96902, 5.52611, 3.67332, 2.86242, 1.66541, 1.1259, 0.623128, 0.340827, 0.166326, 0.08156, 0.042348, 0.022706
d, Pd, 181.818, 96.3562, 41.5131, 18.8395, 12.4836, 7.53523, 5.07772, 3.08103, 1.94039, 1.45585, 0.990353, 0.58792, 0.324766, 0.173233, 0.086758
f, Pd, 145.469, 79.0779, 30.6529, 16.1906, 11.5698, 6.47215, 4.07768, 3.237, 1.99283, 1.28583, 0.690131, 0.3823, 0.189262, 0.09801
g, Pd, 44.2241, 22.7154, 15.9649, 8.81437, 6.29622, 3.58031, 2.07977, 1.34822, 0.947782, 0.513859, 0.297925, 0.153518
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h, Pd, 28.334, 18.5715, 10.9884, 6.80985, 4.36222, 2.71783, 1.80941, 0.926055, 0.488539
i, Pd, 24.2061, 8.08196, 5.25343, 3.27026, 2.12717, 1.34081, 0.568825
!k, Pd, 14.631, 5.33301, 3.0854, 2.14894, 1.03821
!l, Pd, 2.85162, 1.48764
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D.3 OPTRI auxiliary basis sets

All auxiliary basis sets are provided in molpro format.

D.3.1 cc-pVDZ-PP-F12/OPTRI

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!Y cc-pVDZ-PP-F12/OPTRI
s, Y, 1.937258, 1.35876, 0.96787, 0.320666, 0.171657, 0.061969
p, Y, 4.485708, 1.975529, 0.561177, 0.179397, 0.08284
d, Y, 7.170734, 5.110605, 0.695051, 0.247715, 0.138545, 0.090072
f, Y, 4.859776, 1.262875, 0.309276, 0.217405, 0.022933
g, Y, 1.141306, 0.460943, 0.218761
h, Y, 1.085668, 0.365478, 0.086535
i, Y, 1.108861, 0.3299

!Zr cc-pVDZ-PP-F12/OPTRI
s, Zr, 2.54717485, 1.80116812, 1.25274143, 0.45216177, 0.3091989, 0.07963953
p, Zr, 5.720291, 2.248907, 0.629904, 0.216924, 0.102742
d, Zr, 7.453895, 5.031228, 0.817727, 0.405891, 0.288338, 0.123247
f, Zr, 3.493059, 1.487367, 0.425762, 0.303928, 0.054244
g, Zr, 1.317507, 0.521784, 0.278878
h, Zr, 1.419493, 0.511669, 0.121149
i, Zr, 1.341203, 0.38893

!Nb cc-pVDZ-PP-F12/OPTRI
s, Nb, 7.079903, 3.734457, 2.082702, 0.475299, 0.251065, 0.173156
p, Nb, 10.672994, 3.062918, 0.845594, 0.554591, 0.192714
d, Nb, 8.512142, 5.948486, 1.102373, 0.744073, 0.512129, 0.198494
f, Nb, 3.945034, 1.821776, 1.259589, 0.444895, 0.091003
g, Nb, 1.970111, 0.826213, 0.341924
h, Nb, 2.14921, 0.91443, 0.375574
i, Nb, 1.52917, 0.539012

!Mo cc-pVDZ-PP-F12/OPTRI
s, Mo, 12.743595, 4.046291, 2.654823, 0.998955, 0.691135, 0.254272
p, Mo, 10.983514, 4.12697, 1.064365, 0.64066, 0.233552
d, Mo, 13.544949, 6.751487, 1.659514, 1.176277, 0.514094, 0.318306
f, Mo, 5.668874, 2.19117, 1.561055, 0.645266, 0.218055
g, Mo, 2.086213, 0.842877, 0.305305
h, Mo, 2.6603994, 1.0746012, 0.44319592
i, Mo, 1.57157599, 0.50673193

!Tc cc-pVDZ-PP-F12/OPTRI
s, Tc, 13.956505, 4.751161, 2.499106, 1.436959, 0.92797, 0.297472
p, Tc, 10.51739, 6.321185, 1.863398, 0.881551, 0.363993
d, Tc, 17.182462, 10.482496, 2.347956, 1.645918, 0.696355, 0.376553
f, Tc, 10.738615, 4.246724, 2.637365, 0.749599, 0.20883
g, Tc, 2.82701607, 0.90216509, 0.46149426
h, Tc, 3.87362849, 1.25031377, 0.54838131
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i, Tc, 1.76917986, 0.6085862

!Ru cc-pVDZ-PP-F12/OPTRI
s, Ru, 14.2809, 8.463082, 3.97227, 1.705765, 1.063541, 0.328411
p, Ru, 12.13281, 7.38627, 2.080019, 0.997431, 0.448954
d, Ru, 14.13336, 9.400036, 3.265249, 2.323582, 1.001969, 0.467913
f, Ru, 10.88878, 3.064512, 2.175279, 0.74902, 0.278831
g, Ru, 2.556627, 1.134543, 0.483509
h, Ru, 3.062866, 1.423764, 0.576176
i, Ru, 2.342546, 0.905039

!Rh cc-pVDZ-PP-F12/OPTRI
s, Rh, 13.535227, 9.100654, 3.92012, 1.80959, 1.074329, 0.274085
p, Rh, 20.461639, 10.784616, 2.508142, 1.205208, 0.524989
d, Rh, 17.333678, 11.503552, 4.479843, 3.179886, 1.321488, 0.62971
f, Rh, 15.770814, 4.09107, 2.904217, 0.892418, 0.331866
g, Rh, 2.81953, 1.271909, 0.542708
h, Rh, 3.353117, 1.536836, 0.625848
i, Rh, 2.593423, 0.994251

!Pd cc-pVDZ-PP-F12/OPTRI
s, Pd, 18.764883, 12.018436, 8.244044, 3.067599, 2.181566, 0.387722
p, Pd, 28.75009, 12.468455, 4.147888, 1.710007, 0.868465
d, Pd, 26.82735, 12.731383, 6.435822, 4.17121, 1.6835, 0.800967
f, Pd, 21.479713, 5.331117, 3.412272, 1.072529, 0.370532
g, Pd, 2.988848, 1.355604, 0.580855
h, Pd, 3.538045, 1.6324, 0.657116
i, Pd, 2.970892, 1.177903

D.3.2 cc-pVTZ-PP-F12/OPTRI

!Y cc-pVQZ-PP-F12/OPTRI
s, Y, 2.959885, 1.872431, 1.231524, 0.77519, 0.50612, 0.137492, 0.041407
p, Y, 7.783204, 1.978853, 1.401851, 0.995694, 0.685446, 0.155548, 0.067184
d, Y, 7.065481, 4.940635, 2.591024, 1.445864, 0.277664, 0.128752, 0.081917
f, Y, 6.122718, 2.927694, 1.976979, 0.607864, 0.187133, 0.056328, 0.018094
g, Y, 4.031126, 2.111933, 0.817024, 0.517925, 0.259223
h, Y, 3.398723, 1.15377, 0.413794, 0.082254
i, Y, 1.330799, 0.538098, 0.369066

!Zr cc-pVQZ-PP-F12/OPTRI
s, Zr, 3.856551, 2.597844, 1.616023, 1.143719, 0.558732, 0.174735, 0.069221
p, Zr, 9.435778, 2.260545, 1.578722, 1.099314, 0.702898, 0.29811, 0.061527
d, Zr, 8.325007, 5.28065, 3.132869, 1.887897, 0.413142, 0.158747, 0.1121
f, Zr, 4.591145, 3.283874, 2.233807, 0.781538, 0.223688, 0.090814, 0.018856
g, Zr, 4.729377, 2.35744, 1.026436, 0.406115, 0.283188
h, Zr, 2.001769, 0.850481, 0.371962, 0.143188
i, Zr, 1.888453, 0.886055, 0.408201

!Nb cc-pVQZ-PP-F12/OPTRI
s, Nb, 5.241863, 3.06952, 2.033938, 1.45126, 0.708335, 0.225269, 0.085469
p, Nb, 9.616579, 3.099561, 2.090149, 1.429074, 0.66228, 0.383117, 0.090492
d, Nb, 9.997726, 5.606141, 3.897827, 2.454543, 0.476864, 0.236757, 0.147274
f, Nb, 5.507339, 3.213462, 1.814053, 1.236046, 0.450001, 0.13986, 0.02104
g, Nb, 4.424491, 2.748097, 1.49157, 0.934315, 0.367089

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h, Nb, 2.451214, 1.264292, 0.552679, 0.220683
i, Nb, 2.396004, 1.190384, 0.531264

!Mo cc-pVQZ-PP-F12/OPTRI
s, Mo, 7.333431, 3.990334, 2.788871, 1.97212, 0.771657, 0.271418, 0.090384
p, Mo, 8.677207, 3.732601, 2.611135, 1.839727, 0.746086, 0.463052, 0.140937
d, Mo, 13.220162, 7.038264, 4.92376, 3.172977, 0.626499, 0.319674, 0.194142
f, Mo, 10.506849, 5.740011, 3.918855, 1.358796, 0.44727, 0.137239, 0.028071
g, Mo, 6.753604, 4.109046, 1.699962, 0.859073, 0.430264
h, Mo, 2.85056, 1.593161, 0.833539, 0.433394
i, Mo, 2.843815, 1.257035, 0.52551

!Tc cc-pVQZ-PP-F12/OPTRI
s, Tc, 7.056705, 4.754542, 3.020944, 2.144649, 1.287925, 0.318407, 0.088568
p, Tc, 13.231492, 9.381289, 3.4875, 2.379031, 0.853893, 0.468038, 0.136055
d, Tc, 17.305799, 11.540206, 4.814913, 3.100253, 0.703601, 0.409634, 0.201142
f, Tc, 11.660004, 6.899974, 4.867972, 1.579827, 0.501341, 0.165321, 0.032975
g, Tc, 6.575152, 3.632828, 1.841816, 0.729628, 0.418033
h, Tc, 3.470411, 2.083784, 1.138181, 0.526592
i, Tc, 3.45926426, 1.42252587, 0.53014348

!Ru cc-pVQZ-PP-F12/OPTRI
s, Ru, 10.707917, 6.612513, 4.520977, 2.904731, 1.036788, 0.546364, 0.229722
p, Ru, 17.982136, 12.317593, 4.103314, 2.843169, 1.058748, 0.497497, 0.130024
d, Ru, 21.284844, 9.716583, 6.348006, 3.38772, 0.805652, 0.442526, 0.264053
f, Ru, 13.235595, 8.907106, 6.067352, 1.887116, 0.588464, 0.199354, 0.033723
g, Ru, 8.13269, 3.832934, 2.204718, 0.750582, 0.285215
h, Ru, 4.516396, 2.98271, 1.435425, 0.6252
i, Ru, 7.387513, 2.235846, 0.886802

!Rh cc-pVQZ-PP-F12/OPTRI
s, Rh, 15.065675, 8.190267, 4.737075, 3.113892, 1.341055, 0.744455, 0.299887
p, Rh, 21.590261, 8.143051, 4.867166, 3.083795, 1.346764, 0.671022, 0.191485
d, Rh, 26.220292, 10.292312, 7.122889, 4.078712, 1.256301, 0.606947, 0.358062
f, Rh, 14.780111, 10.468831, 7.284526, 2.17914, 0.651197, 0.236048, 0.044415
g, Rh, 7.89271, 3.388311, 2.422256, 0.856111, 0.312429
h, Rh, 11.702062, 4.364318, 1.943415, 0.81389
i, Rh, 4.957705, 2.188266, 0.909298

!Pd cc-pVQZ-PP-F12/OPTRI
s, Pd, 17.113077, 12.104436, 6.744928, 3.941963, 2.503509, 0.944325, 0.366217
p, Pd, 15.231966, 10.640498, 7.037084, 3.491912, 1.998252, 0.790692, 0.216494
d, Pd, 39.666265, 14.299163, 9.480478, 6.541024, 1.499045, 0.772719, 0.397673
f, Pd, 20.823258, 12.977677, 9.054984, 2.503735, 0.754262, 0.259664, 0.071261
g, Pd, 10.269396, 4.925128, 3.469023, 0.975591, 0.357412
h, Pd, 18.952429, 5.79617, 2.315279, 0.915704
i, Pd, 4.593882, 2.041191, 0.835644
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D.3.3 cc-pVQZ-PP-F12/OPTRI

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!Y cc-pVQZ-PP-F12/OPTRI
s, Y, 7.928862, 5.598057, 1.597813, 0.760138, 0.374145, 0.195533, 0.011492
p, Y, 16.713192, 11.537558, 3.547909, 2.163773, 0.417473, 0.170919, 0.064271
d, Y, 6.475539, 4.372979, 2.81184, 1.822916, 0.613894, 0.305706, 0.093304
f, Y, 7.622029, 4.248885, 2.924554, 1.244725, 0.794532, 0.280147, 0.099644, 0.026722
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g, Y, 2.619843, 1.724497, 1.015086, 0.495757, 0.349028, 0.029262
h, Y, 1.905005, 0.748568, 0.386941, 0.066543
i, Y, 1.174153, 0.439585, 0.174344

!Zr cc-pVQZ-PP-F12/OPTRI
s, Zr, 9.622721, 6.499615, 2.309255, 0.780484, 0.419613, 0.221183, 0.012487
p, Zr, 18.914657, 11.120494, 3.815799, 2.082335, 0.569846, 0.200628, 0.084143
d, Zr, 9.852932, 5.106246, 3.504505, 2.34681, 0.695989, 0.285641, 0.113243
f, Zr, 16.593767, 5.870074, 4.340158, 1.796808, 1.282433, 0.143676, 0.076746, 0.035332
g, Zr, 3.13286, 1.775025, 0.693161, 0.50036, 0.240794, 0.095482
h, Zr, 2.341165, 0.692144, 0.491839, 0.145741
i, Zr, 2.536737, 0.712785, 0.399608

!Nb cc-pVQZ-PP-F12/OPTRI
s, Nb, 10.313482, 6.276892, 2.455665, 1.079719, 0.503785, 0.258605, 0.013336
p, Nb, 22.547718, 12.23948, 3.736862, 2.451581, 0.680941, 0.223228, 0.09956
d, Nb, 8.357335, 5.74043, 3.626046, 2.584853, 0.796471, 0.395685, 0.121478
f, Nb, 14.998365, 6.274723, 2.891318, 2.100189, 1.498302, 0.274592, 0.091261, 0.031993
g, Nb, 3.724606, 2.028983, 0.860257, 0.627449, 0.323983, 0.112583
h, Nb, 2.573191, 1.029917, 0.56813, 0.16634
i, Nb, 2.963181, 1.084762, 0.489862

!Mo cc-pVQZ-PP-F12/OPTRI
s, Mo, 11.188005, 6.388294, 2.961819, 1.16714, 0.532883, 0.28242, 0.014336
p, Mo, 22.958959, 14.094402, 4.04076, 2.821176, 0.74203, 0.280304, 0.11259
d, Mo, 9.610935, 6.601495, 4.169953, 2.972581, 0.915942, 0.455038, 0.132678
f, Mo, 17.114419, 7.693561, 3.559433, 2.576982, 1.855622, 0.342068, 0.11484, 0.029916
g, Mo, 3.458031, 2.267306, 1.105515, 0.806996, 0.406015, 0.112785
h, Mo, 3.883528, 1.714501, 1.087983, 0.778283
i, Mo, 3.207069, 1.176165, 0.512022

!Tc cc-pVQZ-PP-F12/OPTRI
s, Tc, 11.673455, 6.423743, 4.263362, 1.370322, 0.626245, 0.330611, 0.014727
p, Tc, 18.955564, 10.139944, 5.34579, 3.453615, 0.708392, 0.303762, 0.132837
d, Tc, 11.62282, 7.695014, 5.25373, 3.118713, 0.988726, 0.515383, 0.154501
f, Tc, 11.466828, 7.709447, 3.69118, 2.82397, 2.074782, 0.717295, 0.12678, 0.032244
g, Tc, 4.010456, 2.827488, 1.360608, 0.971844, 0.45096, 0.133105
h, Tc, 2.258065, 1.610657, 1.178008, 0.870059
i, Tc, 3.386255, 1.42044, 0.580907

!Ru cc-pVQZ-PP-F12/OPTRI
s, Ru, 12.294689, 7.293004, 2.290712, 1.611365, 0.673016, 0.380702, 0.02017
p, Ru, 16.757396, 11.240871, 7.28466, 4.505956, 1.113207, 0.501846, 0.109948
d, Ru, 22.789254, 9.317365, 6.275712, 3.36844, 1.138181, 0.455644, 0.176317
f, Ru, 19.586958, 4.710707, 2.758631, 1.265969, 0.88254, 0.447507, 0.319161, 0.064015
g, Ru, 8.413112, 2.990163, 1.478319, 1.03934, 0.512967, 0.166786
h, Ru, 3.081461, 2.05698, 1.443373, 1.053803
i, Ru, 3.670648, 1.724256, 0.703965

!Rh cc-pVQZ-PP-F12/OPTRI
s, Rh, 16.951574, 9.960408, 4.828962, 1.786634, 0.865728, 0.449253, 0.017226
p, Rh, 20.407102, 14.450259, 9.686573, 6.845064, 1.303467, 0.439506, 0.141081
d, Rh, 31.343973, 10.065846, 6.94393, 3.587307, 1.191073, 0.508924, 0.229321
f, Rh, 20.917937, 5.800603, 3.5819, 1.556847, 1.037718, 0.514707, 0.366763, 0.074151
g, Rh, 7.456711, 4.149339, 1.874156, 1.281379, 0.477605, 0.143464
h, Rh, 4.089411, 2.743571, 1.705377, 0.572114
i, Rh, 3.484246, 1.59538, 0.691303
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!Pd cc-pVQZ-PP-F12/OPTRI
s, Pd, 19.252288, 12.119027, 3.86448, 2.013482, 0.777842, 0.424912, 0.035874
p, Pd, 26.781038, 17.619765, 11.214575, 6.738652, 1.522007, 0.495762, 0.154017
d, Pd, 23.92849, 12.792955, 8.728328, 5.30943, 1.557843, 0.63102, 0.221808
f, Pd, 23.267412, 6.150528, 4.264034, 1.677249, 1.186836, 0.560656, 0.400078, 0.088682
g, Pd, 7.469757, 4.067638, 1.858265, 1.30266, 0.573836, 0.227762
h, Pd, 4.175611, 1.905733, 1.36055, 0.951934
i, Pd, 4.930538, 2.185519, 0.928518
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