Density Fitting in Explicitly Correlated Electronic Structure Theory

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Abstract

Obtaining chemical accuracy in electronic structure calculations on systems of more than a few atoms can be computationally very expensive. This is often due to the poor convergence of the correlation energy with respect to the basis set size used for the calculation. Explicitly correlated methods are significantly better at describing electron correlation by incorporating the inter-electronic distance explicitly into the wavefunction. However, the early work that proved very encouraging in this area could not be extended to systems of more than a few electrons. The reason for this is the large number multi-electron integrals required, which are computationally expensive and difficult to evaluate.

Since the late 1980s and early 1990s these methods have been developed with renewed interest. This is due to the introduction of an approximation known as the resolution of identity which allows many electron integrals to be reduced to products of two-electron integrals.

The methods developed subsequently were able to produce good results, significantly better than not using an explicitly correlated wavefunction. However, they still require large basis sets and do not give answers as good as one would hope for the extra work incurred.

The aim of this work is to investigate the approximations in the explicitly correlated MP2-R12 method in order to try and increase the convergence of correlation energy with respect to basis size. New methods are introduced and new integrals derived and calculated. A detailed analysis of the errors is given in the results chapter and summarised in the conclusions, where recommendations are given for future work that should be undertaken.

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Author’s Declaration

”I declare that the work in this dissertation was carried out in accordance with the Regulations of the University of Bristol. The work is original except where indicated by special reference in the text and no part of the dissertation has been submitted for any other degree. Any views expressed in the dissertation are those of the author and in no way represent those of the University of Bristol. The dissertation has not been presented to any other University for examination either in the United Kingdom or overseas.

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Chapter 1

Introduction

By the late Nineteenth century some physicists believed that they were in a position where the fundamental laws of physics had been found. However, the discovery of quantum mechanics by Einstein in the early twentieth century, motivated by observations of phenomena such as the photoelectric effect, transformed the field of physics and had a profound effect upon the field of chemistry. Quantum mechanics, along with statistical mechanics, forms the theoretical basis of chemistry. In essence quantum mechanics tells us that the forces which hold together atoms and molecules cannot be fully described by classical mechanics.

In 1925 Erwin Schrödinger and Werner Heisenberg independently developed new quantum theories which subsequently proved to be mathematically equivalent. The easier to interpret physically is Schrödinger's wave-mechanics [1, 2] and thus the Schrödinger equation is the starting equation for this thesis. The time-independent form of the Schrödinger equation is given by

$$\hat{H}\Psi = E\Psi, \tag{1.1}$$

where Ψ is the wavefunction of the atomic or molecular system in question and the Hamiltonian $\hat{H}$ is the operator corresponding to the energy of the system, E. The Hamiltonian for a molecule is a two-term expression comprising of a kinetic and potential operator acting upon all particles in the system. When these operators are expanded for a system of N nuclei and n-electrons it generates a five term Hamiltonian with the form

$$\hat{H} = -\sum_{i=1}^{n} \frac{\nabla_i^2}{2} - \sum_{i=1}^{n}\sum_{A=1}^{N} \frac{Z_A}{R_{iA}} + \sum_{i=1}^{n}\sum_{j>i}^{n} \frac{1}{r_{ij}} - \sum_{A=1}^{N} \frac{\nabla_A^2}{2M_A} + \sum_{A=1}^{N}\sum_{B>A}^{N} \frac{Z_A Z_B}{R_{AB}} \tag{1.2}$$

where Z denotes a nuclear charge, M a nuclear mass and all quantities are expressed in terms of atomic units. One of the problems with the Hamiltonian is that it generates a continuous spectrum of energies. The reason for this is that a freely translating atom or molecule has kinetic energy which could take any value, hence a complete distribution of energies are accessible by the system.

The first step in simplifying the Hamiltonian is to use the Born-Oppenheimer (BO) approximation [3], a fundamental approximation in the field of quantum chemistry. The BO approximation makes use of the fact that nuclei are at least 1800 times more massive than electrons, and travel much more slowly. This allows the motion of nuclei and electrons to be uncoupled and hence one can treat nuclei as stationary particles that move in a potential generated by the electrons. The BO approximation gives only small errors in expectation values for many problems of interest. This gives rise to an electronic Hamiltonian

$$\hat{H}_{\text{elec}}\Psi_{\text{elec}} = E_{\text{elec}}(\underline{R})\Psi_{\text{elec}} \tag{1.3}$$

that depends only parametrically on the coordinates of the nuclei and generates electronic energies and wavefunctions. The function $E_{\text{elec}}(\underline{R})$ is known as a potential energy surface and can be evaluated at fixed $\underline{R}$ to give energies. Approximate solutions to equation 1.3 are termed *ab initio* providing no empirical fitting to experimental data has been employed. From here onwards the subscripts of equation 1.3 will be dropped and it is always assumed that it is the electronic form that is referred to.

The Variational Principle

Equation 1.3 is still too complicated to solve analytically. The reason for this is that the electron-electron interaction resulting from the electron-electron repulsion operator in the electronic Hamiltonian

$$\sum_{i=1}^{n}\sum_{j=i+1}^{n}\frac{1}{r_{ij}} \tag{1.4}$$

couples the coordinates of all of the electrons. One way to get around this problem does not involve further simplification to the Hamiltonian, rather an approximate construction of the wavefunction. The approximate wavefunction Ψ_{approx} gives rise to an approximate energy E_{approx} which is evaluated by using the Rayleigh-Ritz expression

$$E_{\text{approx}} = \frac{\langle\Psi_{\text{approx}}|\hat{H}|\Psi_{\text{approx}}\rangle}{\langle\Psi_{\text{approx}}|\Psi_{\text{approx}}\rangle}. \tag{1.5}$$

The variational principle states that the approximate energy E_{approx} is always above the exact energy E_{exact}, i.e.

$$E_{\text{approx}} \geq E_{\text{exact}} \tag{1.6}$$

provided Ψ_{approx} is an acceptable wavefunction. An acceptable wavefunction must obey the Pauli principle and must have a finite kinetic energy, i.e. be sufficiently smooth, and be able to be normalised. If all of these are obeyed then equation 1.6 holds true.

Molecular Orbitals

The BO electronic Hamiltonian operator takes the form

$$\hat{H} = -\sum_{i=1}^{n} \frac{\nabla_i^2}{2} - \sum_{i=1}^{n} \sum_{A=1}^{N} \frac{Z_A}{R_{iA}} + \sum_{i=1}^{n} \sum_{j>i}^{n} \frac{1}{r_{ij}}. \tag{1.7}$$

Despite this approximation the electronic Schrödinger equation is still too complicated to solve analytically for all but the very simplest systems, such as the hydrogen atom. In most cases it is necessary to use numerical methods, that is to say methods that assume the real wavefunction is too complicated to be found directly, but can be usefully approximated by a simpler function. In Hartree theory the n-electron wavefunction is represented as a product of one-electron wavefunctions known as molecular orbitals (MOs) such that

$$\Psi(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_n) = \prod_{i=1}^{n} \psi_i(\vec{r}_i). \tag{1.8}$$

The MOs are usually expanded in a basis set of atomic functions

$$\psi_i(\vec{r}_i) = \sum_{\alpha=1}^{n_{\text{bas}}} c_{i\alpha} \phi_\alpha(\vec{r}_i) \tag{1.9}$$

where n_{bas} is the number of basis functions in the basis set and $c_{i\alpha}$ are expansion coefficients. The summation of the atomic functions is commonly known as the Linear Combination of Atomic Orbitals (LCAO) method. There are two types of atomic functions in common use within quantum chemistry, Slater type orbitals (STOs) and Gaussian type orbitals (GTOs). STO basis sets generally give more accurate wavefunctions than GTO basis sets consisting of the same number of functions. This is because the STO functions have the correct form at short range. However, STO basis sets lead to many-centre two-electron integrals that cannot be evaluated analytically. GTOs on the other hand lead to much more tractable integrals and for this reason they will be used throughout. There are several fast analytical methods for solving integrals over GTOs and this more than compensates for the slightly larger number of functions needed when using a GTO basis set.

Electrons are indistinguishable, i.e. they cannot be differentiated from each other. Mathematically this means that the wavefunction must be constructed in such a manner that interchange of electrons does not change the probability distribution. This can be achieved by either using a symmetric or antisymmetric wavefunction. Experiment shows that electrons (like all fermions) have wavefunctions that are antisymmetric with respect to interchange of electrons (particles that require a symmetric wavefunction are known as bosons). If one were to proceed using a symmetric wavefunction for the electrons the ground state found would involve electrons very close together, whereas the ground state using an antisymmetric wavefunction has particles avoiding each other.

The Pauli principle that two electrons cannot occupy the same spin orbital results directly from the fact that the wavefunction must be antisymmetric with respect to electron interchange. For example, an acceptable two-electron wavefunction could have the form

$$\Psi(\vec{x}_1, \vec{x}_2) = \varphi_1(\vec{x}_1)\varphi_2(\vec{x}_2) - \varphi_1(\vec{x}_2)\varphi_2(\vec{x}_1). \tag{1.10}$$

If however the electrons occupied the same orbital, i.e. $\varphi_1 = \varphi_2$ then $\Psi(\vec{x}_1, \vec{x}_2) = 0$ which is not a valid state.

Hartree products alone do not make acceptable wavefunctions as they do not ensure the Pauli principle. By using a Slater Determinant (SD) [4] antisymmetry can be enforced in the wavefunction, and as a result the Pauli principle is satisfied, namely two electrons cannot occupy the same spin orbital. Each spatial orbital can take either α or β spin, thus forming two spin orbitals

$$\varphi(\vec{x}) = \psi_i(\vec{r})\alpha(\sigma) \quad \text{or} \quad \psi_i(\vec{r})\beta(\sigma), \tag{1.11}$$

where $\vec{x} = \{\vec{r}, \sigma\}$, $\sigma \pm \frac{1}{2}$ and

$$\begin{array}{ll} \alpha\left(\frac{1}{2}\right) = 1 & \beta\left(\frac{1}{2}\right) = 0 \\ \alpha\left(-\frac{1}{2}\right) = 0 & \beta\left(-\frac{1}{2}\right) = 1. \end{array} \tag{1.12}$$

A SD can be written concisely as

$$\Psi(\vec{x}_1, \vec{x}_2, \cdots, \vec{x}_n) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \varphi_1(\vec{x}_1) & \varphi_2(\vec{x}_1) & \cdots & \varphi_n(\vec{x}_1) \\ \varphi_1(\vec{x}_2) & \varphi_2(\vec{x}_2) & \cdots & \varphi_n(\vec{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_1(\vec{x}_n) & \varphi_2(\vec{x}_n) & \cdots & \varphi_n(\vec{x}_n) \end{vmatrix}. \tag{1.13}$$

1.1 Hartree Fock Theory

Hartree Fock (HF) [5] theory was originally formulated by Douglas Hartree who devised the self consistent field (SCF) method. The method was subsequently modified by Vladimir Fock to obey the Pauli principle [6]. Most *ab initio* quantum chemistry methods use HF theory as their starting point. Equation 1.5 is minimised using a SD as the approximate wavefunction Ψ_{approx}. The SD chosen is that which leads to the lowest expectation value of the Hamiltonian $\hat{H}$. This process leads to n coupled 1-particle integro-differential equations, known as the Fock equations

$$\hat{f}|\psi_i(\vec{r})\rangle = \varepsilon_i|\psi_i(\vec{r})\rangle \tag{1.14}$$

where $\hat{f}$ is the Fock operator

$$\hat{f} = -\frac{\nabla^2}{2} - \sum_{A=1}^{N} \frac{Z_A}{r_A} + [\hat{J} - \hat{K}] \tag{1.15}$$

and ε_i is the energy of orbital i. The Coulomb operator $\hat{J}$ and exchange operator $\hat{K}$ are defined as

$$\hat{J}\psi_j(\vec{r}_1) = \psi_j(\vec{r}_1) \sum_i \int d\vec{r}_2 \frac{|\psi_i(\vec{r}_2)|^2}{r_{12}}, \tag{1.16}$$

and

$$\hat{K}\psi_j(\vec{r}_1) = \sum_i \psi_i(\vec{r}_1) \int d\vec{r}_2 \frac{\psi_i^*(\vec{r}_2)\psi_j(\vec{r}_2)}{r_{12}}. \tag{1.17}$$

The Fock equations are solved using the self consistent field (SCF) method. The SCF method is an iterative procedure around the eigensystem equation

$$\mathbf{Fc} = \mathbf{Sc}\boldsymbol{\varepsilon} \tag{1.18}$$

where $\mathbf{F}$ is the Fock matrix, $\mathbf{S}$ is the overlap matrix and $\boldsymbol{\varepsilon}$ is a diagonal matrix containing the orbital eigenvalues on the diagonal. In restricted HF theory for a closed-shell system the Fock matrix is constructed as

$$F_{\alpha\beta} = H_{\alpha\beta} + \Gamma_{\gamma\delta}[2(\alpha\beta|\gamma\delta) - (\alpha\gamma|\beta\delta)]; \tag{1.19}$$

here and in what follows Einstein summation over repeated indices is assumed. The density matrix, $\mathbf{\Gamma}$, is given by

$$\Gamma_{\alpha\beta} = \sum_{i \in occ} c^*_{i\alpha} c_{i\beta}, \tag{1.20}$$

and

$$H_{\alpha\beta} = \langle \eta_\alpha | -\frac{1}{2}\nabla_1^2 - \sum_{A=1}^{N} \frac{Z_A}{R_{A1}} | \eta_\beta \rangle. \tag{1.21}$$

where η_α and η_β are AOs. In the first instance the Fock matrix could be defined to be the one-electron Hamiltonian matrix in order to start the iterative procedure. Other initial guesses can be constructed, for example guesses based on atomic densities. This allows the density matrix to be constructed and the iteration to begin.

Solving the HF equations yields a wavefunction with special properties. One of the most important in the present context is the Brillouin condition which states that the ground state HF wavefunction does not interact with singly excited determinants. The Brillouin condition itself is exact within the HF framework and results in

$$\langle i|\hat{f}|a\rangle = 0, \tag{1.22}$$

where the indices i and a represent occupied and virtual indices respectively, forms an alternative definition of HF theory. There are several approximations based upon the Brillouin condition known as the generalised Brillouin condition (GBC) and extended Brillouin condition (EBC) which are described in the theory chapter.

1.2 Size extensivity and size consistency

When describing methods in quantum chemistry two important concepts are that of *size consistency* and *size extensivity*.

1.2.1 Size consistency

The first definition of size consistency was made by Pople as a criterion for constructing a well formed quantum method. It can be demonstrated with two neon atoms. At large separation distances the neon atoms are not interacting with each other, they are said to be in the non-interacting limit. At this large distance the energy of the system should be exactly twice that of a system containing a single neon atom. This original formulation of size consistency simply ensured something known as additive separability. The definition of size consistency has more recently been expanded such that a method must correctly describe the system at all separation distances in order to be size consistent. This can cause confusion as RHF is size consistent under the original Pople definition, but not under the modified definition.

1.2.2 Size extensivity

Size extensivity states that the total energy must scale correctly, i.e. in a linear manner, with respect to the number of electrons in the system. Methods that are not size extensive will have energies that increase in error from the exact value as the number of electrons is increased.

1.3 Electron correlation

The motion of electrons in an atom or molecule is correlated. HF theory does not include any electron correlation, thus it assumes that electrons behave independently of each other. Of course this is not the case and electron correlation must be accounted for to perform accurate calculations of system properties. In terms of energy the HF total energy differs from the exact non-relativistic energy by an amount which is known as the correlation energy. The correlation energy can be subdivided into *static* correlation and *dynamic* correlation.

1.3.1 Static correlation

Static correlation, also known as non-dynamical correlation, can be demonstrated using the simple hydrogen molecule. When one electron is near nucleus A it is expected that the other electron will spend more time in the vicinity of nucleus B. This is a result of basic electrostatics, attraction of opposite charges and repulsion of like charges. Indeed this is exactly the case for the exact probability distribution of H_2. However, this is not what is obtained in HF theory. As shown in figure 1.1 the hydrogen molecule does not dissociate to twice the energy of two hydrogen atoms.

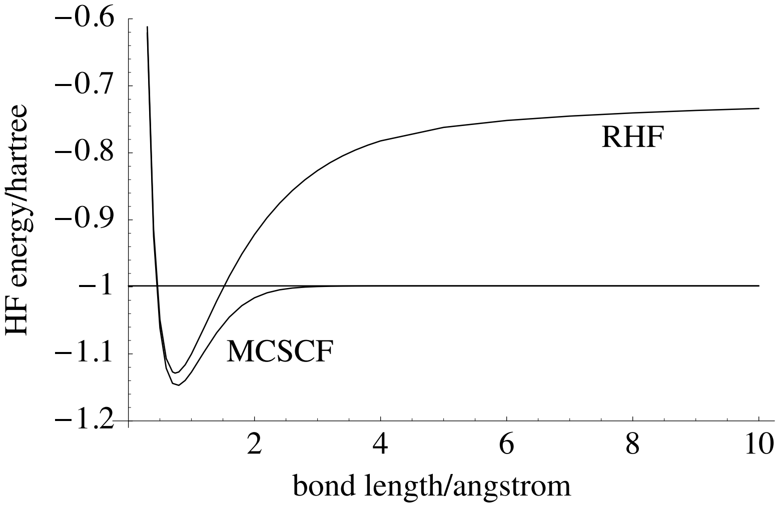

Figure 1.1: Plot of RHF and MCSCF energy for H_2 at varying bond lengths. Horizontal line is twice the RHF energy of a H atom.

Static correlation occurs due to near degeneracy and can be addressed by increasing the flexibility of the reference wavefunction. Multi-reference methods incorporate the effects of static correlation by including enough SDs in the wavefunction to describe the degenerate or near-degenerate states independently. In figure 1.1 the MCSCF [7] calculation uses both the ground state and excited state configurations in order to lower the energy of the system, thus describing correctly the dissociation process.

1.3.2 Dynamic correlation

Dynamic correlation arises because the motion of one electron depends on the instantaneous positions of all of the others. All systems of more than one-electron have dynamic correlation.

In HF theory electrons only see an average potential arising from the other electrons. As a result in the example of helium the probability distribution for electron 1 does not depend on the position of electron 2. This phenomenon results from the use of one-electron orbitals to describe an n-electron problem. In probability theory, the probability of two entirely independent events is given by

$$P(A \text{ and } B) = P(A)P(B). \tag{1.23}$$

This is the relation used in HF theory when describing electrons. However, it is not accurate as the instantaneous positions of electrons are not independent of each other.

This loss of information about the position of all of the other electrons results in expectation values for the energy being greater than the exact answer due to the variational principle.

Pictorially this can be demonstrated by a plot of the wavefunction for the simple two-electron problem of helium shown by figure 1.2. The HF wavefunction is obviously not correct at $r_{12} = 0$ as it does not have a cusp. However, since the probability density is calculated by integration with r_{12}^2 this does not cause significant error in the area around $r_{12} = 0$. It is instead the region between $r_{12} = 0$ and the exact most probable value of r_{12} where the HF method is introducing the bulk of its error.

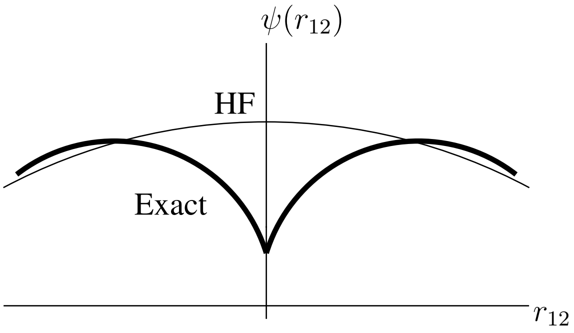

Figure 1.2: Sketch of HF and exact wavefunction for the helium atom

1.3.3 Configuration Interaction

Configuration interaction (CI) is the simplest (conceptually) way to try to correct for the inaccurate description of electrons in HF theory. The error comes from the attempt to describe an n-electron problem as a product of n one-electron problems. The CI method uses a sum of products of n one-electron functions instead. Put simply the trial wavefunction is constructed from a linear combination of SDs.

The trial wavefunction is typically constructed from the ground state SD and excited state SDs for the atom or molecule. For a general problem this leads to the following expression for the CI wavefunction

$$|\mathrm{CI}\rangle = (1 + \hat{T})|0\rangle \tag{1.24}$$

where $|0\rangle$ is the ground state SD and $\hat{T}$ is known as the cluster operator. The cluster operator has the form

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \cdots \tag{1.25}$$

where $\hat{T}_1$ is the singles cluster operator, $\hat{T}_2$ the doubles cluster operator etc. The CI wavefunction is then constructed as

$$|\mathrm{CI}\rangle = (1 + \hat{T}_1 + \hat{T}_2 + \cdots)|0\rangle = |0\rangle + \hat{T}_1|0\rangle + \hat{T}_2|0\rangle + \cdots \tag{1.26}$$

where the excited SDs are constructed by applying excitation operators to the ground state SD. The first two cluster operators in second quantisation [7] have the form

$$\hat{T}_1 = c_a^i \hat{a}^\dagger \hat{i} \tag{1.27}$$

$$\hat{T}_2 = \sum_{i<j} \sum_{a<b} c_{ab}^{ij} \hat{a}^\dagger \hat{b}^\dagger \hat{i} \hat{j} = \frac{1}{4} c_{ab}^{ij} \hat{a}^\dagger \hat{b}^\dagger \hat{i} \hat{j} \tag{1.28}$$

where coefficients c_a^i etc. are known as the amplitudes and $\hat{a}^\dagger$ and $\hat{i}$ are annihilation and excitation operators respectively.

The total number of SDs that could be constructed is given by the binomial coefficient of n electrons and m molecular orbitals:

$$N_{\mathrm{SD}} = \binom{m}{n} = \frac{m!}{n!(m-n)!}. \tag{1.29}$$

The number of possible SDs rises sharply with the size of the basis set. The CI method that uses all of the possible SDs in a given basis set is known as full CI (FCI). FCI is exceptionally computationally expensive and is limited to the smallest of problems. It is nevertheless an exceptionally accurate method which gives answers that are exact within the limits of the AO basis: for that reason it is used to benchmark calculations on very small systems.

Attempting to perform FCI calculations on systems of more than around ten electrons is simply not practical. However, the FCI expansion can be truncated such that excitation operators only up to a certain level are included. The wavefunctions for three such methods, CI singles (CIS), CI doubles (CID), and CI singles and doubles (CISD) are given by

$$|\mathrm{CIS}\rangle = (1 + \hat{T}_1)|0\rangle \tag{1.30}$$

$$|\mathrm{CID}\rangle = (1 + \hat{T}_2)|0\rangle \tag{1.31}$$

$$|\mathrm{CISD}\rangle = (1 + \hat{T}_1 + \hat{T}_2)|0\rangle. \tag{1.32}$$

Singly excited determinants do not mix with the HF ground state SD (Brillouin condition) so it may seem odd to bother with a CIS method [8]. Although singly excited determinants do not increase the accuracy of the ground state energy they do provide a simple method for extracting information about excited states from a HF solution.

The simplest CI method that improves the HF ground state energy is CID [8]. Historically the CID method was employed, but today the singles are almost always included since there is almost no extra computational cost and they can only improve the solution. This leads to the CISD method [8]. Singly excited determinants do not interact with the ground state SD, but they do interact with the doubly excited determinants, and consequently improve the ground state energy.

The method for optimising the energy is to minimise the CI energy expression with respect to the amplitudes. First it is useful to rewrite the energy expression as

$$E = \frac{\langle \mathrm{CI}|\hat{H}|\mathrm{CI}\rangle}{\langle \mathrm{CI}|\mathrm{CI}\rangle} = \frac{c_I^* c_J \langle I|\hat{H}|J\rangle}{c_I^* c_J \langle I|J\rangle} = \frac{c_I^* c_J H_{IJ}}{c_I^* c_J S_{IJ}} \tag{1.33}$$

where the identity $|\mathrm{CI}\rangle = c_I|I\rangle$ has been used. Rearranging the expression for the CI energy and differentiating with respect to one of the CI coefficients yields

$$\frac{\partial}{\partial c_K} c_I^* c_J H_{IJ} = \frac{\partial}{\partial c_K} E c_I^* c_J S_{IJ} \tag{1.34}$$

which upon completion of the differentiation gives

$$2c_J H_{KJ} = \left(\frac{\partial E}{\partial c_K}\right) c_I^* c_J S_{IJ} + 2E c_J S_{KJ}. \tag{1.35}$$

At the minimum energy the gradient $\partial E/\partial c_K$ will be zero and hence the expression becomes

$$c_J H_{KJ} = E c_J S_{KJ}, \tag{1.36}$$

which can be written in matrix notation as

$$\mathbf{Hc} = E\mathbf{Sc}. \tag{1.37}$$

This generalised eigenvalue problem can be solved exactly to obtain the CI eigenvalues and coefficients. The equation is of the same type that is solved at every iteration of a HF-SCF calculation.

1.3.4 Coupled Cluster Theory

Coupled cluster theory was initially developed in the late 1950s by Coester and Kümmel for studying nuclear physics [9] but was later reformulated by Čížek [10] for dealing with the electron correlation problem. Coupled cluster (CC) theory differs from CI theory by introducing the exponential of the cluster operator to create a wavefunction

$$|\mathrm{CC}\rangle = \exp(\hat{T})|0\rangle \tag{1.38}$$

where the cluster operator $\hat{T}$ is that defined in equation 1.25. The exponential form of the cluster operator can be expanded in a Taylor series to give

$$\exp(\hat{T}) = 1 + \hat{T} + \frac{1}{2}\hat{T}^2 + \cdots \tag{1.39}$$

which yields the expression for the CC wavefunction as

$$\begin{aligned}
|\mathrm{CC}\rangle =& (1 + \hat{T} + \frac{1}{2}\hat{T}^2 + \cdots)|0\rangle && (1.40)\\
=& |0\rangle + \hat{T}|0\rangle + \frac{1}{2}\hat{T}^2|0\rangle + \cdots && (1.41)\\
=& |0\rangle + (1 + \hat{T}_1 + \hat{T}_2 + \cdots)|0\rangle + \frac{1}{2}(1 + \hat{T}_1 + \hat{T}_2 + \cdots)^2|0\rangle + \cdots && (1.42)
\end{aligned}$$

The key difference between CC and CI is the addition of so-called *disconnected* terms in the wavefunction. For example the connected doubles $\hat{T}_2$ are supplemented by the disconnected term $\hat{T}_1^2$. This has the effect of increasing the number of terms in the wavefunction and this can be shown by collecting together terms in the expansion that contribute the same level of excitation:

$$\begin{array}{rcl}
|\mathrm{CC}\rangle & = & \Big[1 + \hat{T}_1 \;+\; (\hat{T}_2 + \tfrac{1}{2}\hat{T}_1^2) \;+\; (\hat{T}_3 + \hat{T}_1\hat{T}_2 + \tfrac{1}{6}\hat{T}_1^3) \;+\cdots\Big]|0\rangle \\
|\mathrm{CI}\rangle & = & \Big[1 + \hat{T}_1 \;+\; \hat{T}_2 \;+\; \hat{T}_3 \;+\cdots\Big]|0\rangle \quad .
\end{array} \tag{1.43}$$

When the theories are truncated at the second-order level (forming CCSD and CISD) then the comparison looks like

$$\begin{array}{rcl}
|\mathrm{CCSD}\rangle & = & \Big[1 + \hat{T}_1 \;+\; (\hat{T}_2 + \tfrac{1}{2}\hat{T}_1^2) \;+\; (\hat{T}_1\hat{T}_2 + \tfrac{1}{6}\hat{T}_1^3) \;+\cdots\Big]|0\rangle \\
|\mathrm{CISD}\rangle & = & \Big[1 + \hat{T}_1 \;+\; \hat{T}_2 \Big]|0\rangle \quad .
\end{array} \tag{1.44}$$

The CISD wavefunction cannot approximate the triple and higher contributions as it contains no terms of that level. The CCSD wavefunction contains no connected contributions above two-body, but does contain disconnected contributions.

The variational principle could in theory be applied to give the expression for the CC energy

$$E = \frac{\langle \mathrm{CC}|\hat{H}|\mathrm{CC}\rangle}{\langle \mathrm{CC}|\mathrm{CC}\rangle} = \frac{\langle 0|\exp(\hat{T})^{\dagger}\hat{H}\exp(\hat{T})|0\rangle}{\langle 0|\exp(\hat{T})^{\dagger}\exp(\hat{T})|0\rangle} \tag{1.45}$$

which could be minimised with respect to the cluster amplitudes. However if one proceeds with this method a set of non-linear equations result which contain contributions from every determinant in the FCI expansion. This obviously means that minimisation by use of the variational principle is impractical.

In CI theory it can be shown that minimising the energy with respect to the coefficients is exactly equivalent to projecting the Schrödinger equation to the left with the determinants and integrating. However, it is not exact to use the same method for a truncated CC method. Nevertheless, the error associated with a non-variational CCSD method is very much smaller than the error associated with CISD not being size extensive. Proceeding by the projection method yields the amplitude equations

$$\langle \mu|\exp(-\hat{T})\hat{H}\exp(\hat{T})|0\rangle = 0 \tag{1.46}$$

and energy equation

$$\langle 0|\exp(-\hat{T})\hat{H}\exp(\hat{T})|0\rangle = E \tag{1.47}$$

where the Schrödinger equation has been multiplied to the left by $\exp(-\hat{T})$ for convenience, and where $|\mu\rangle$ represents all excited SDs truncated to the given excitation level.

The energy equations can be simplified by observing

$$\langle 0|\exp(-\hat{T}) = \langle 0|(1 - \hat{T} + \frac{1}{2}\hat{T}^2 + \cdots) = \langle 0|. \tag{1.48}$$

This identity exists as the hermitian conjugate of an excitation operator is a de-excitation operator, and de-exciting from a HF ground state gives zero. Therefore the energy equation reduces to

$$\langle 0|\hat{H}\exp(\hat{T})|0\rangle = E \tag{1.49}$$

which on expansion of the exponential yields

$$\langle 0|\hat{H}(1 + \hat{T} + \frac{1}{2}\hat{T}^2 + \cdots)|0\rangle = E. \tag{1.50}$$

The energy equations simplify because nearly all of the matrix elements of the form $\langle 0|\hat{H}\hat{\tau}_\mu|0\rangle$ vanish, where $\hat{\tau}_\mu$ is an excitation operator. Elements containing only single excitations vanish through the Brillouin theorem. Triple and higher-order terms vanish as the Hamiltonian has at most two-particle operators. Thus the energy expression simplifies enormously retaining only double excitation terms

$$\langle 0|\hat{H}(1+\hat{T}_2+\frac{1}{2}\hat{T}_1^2)|0\rangle = E. \tag{1.51}$$

The amplitude equations can be expanded using the identity of Baker, Campbell and Hausdorff which fortunately in this case terminate exactly at fourth order

$$\begin{aligned}\langle\mu|\exp(-\hat{T})\hat{H}\exp(\hat{T})|0\rangle &= \langle\mu|\hat{H}|0\rangle + \langle\mu|[\hat{H},\hat{T}]|0\rangle + \frac{1}{2!}\langle\mu|[[\hat{H},\hat{T}],\hat{T}]|0\rangle \\ &+ \frac{1}{3!}\langle\mu|[[[\hat{H},\hat{T}],\hat{T}],\hat{T}]|0\rangle + \frac{1}{4!}\langle\mu|[[[[\hat{H},\hat{T}],\hat{T}],\hat{T}],\hat{T}]|0\rangle. \end{aligned} \tag{1.52}$$

As with the energy expression, the simplification arises from the two-body nature of the Hamiltonian. Furthermore, when CC theory is truncated equation 1.52 simplifies still further. For example, in CCD theory

$$\langle\mu|\exp(-\hat{T})\hat{H}\exp(\hat{T}_2)|0\rangle = \langle\mu|\hat{H}|0\rangle + \langle\mu|[\hat{H},\hat{T}_2]|0\rangle + \frac{1}{2!}\langle\mu|[[\hat{H},\hat{T}_2],\hat{T}_2]|0\rangle. \tag{1.53}$$

The CC equations are of comparable cost to the CI equations to solve but the most important difference is that CC theory is size extensive for a given level of truncation, whereas CI theory is not. This considerably increases the accuracy of a calculation for a given level of truncation of the cluster operator. Obviously without truncation both methods are equivalent to FCI.

1.3.5 Perturbation Theory

The Schrödinger equation in its original form cannot be solved for all but the simplest problems. However, in many cases it is possible to split the Hamiltonian into a large part whose Schrödinger equation can be solved and a small, difficult correction

$$\hat{H} = \hat{H}_0 + \hat{H}_1. \tag{1.54}$$

The zeroth order Hamiltonian $\hat{H}_0$ is simple enough that the Schrödinger equation can be solved exactly to give a ground state solution to the zeroth order problem

$$\hat{H}_0|0\rangle = E_0|0\rangle. \tag{1.55}$$

The small correction $\hat{H}_1$ is known as the *perturbation*.

The exact energy and wavefunction are approximated by introducing a parameter λ which moderates the perturbation so that $\hat{H} = \hat{H}_0 + \lambda\hat{H}_1$. The parameter λ can take values $0 \leq \lambda \leq 1$, where $\lambda = 0$ represents the zeroth-order approximation and $\lambda = 1$ represents the true situation. However, the equations could be solved for all allowed values of λ and one expects to find a smooth variation in energy as λ is changed. Since $\hat{H}$ depends upon λ it eigenvectors and eigenvalues must also, thus

$$(\hat{H}_0+\lambda\hat{H}_1)(|0\rangle+\lambda|1\rangle+\lambda^2|2\rangle+\cdots) = (E_0+\lambda E_1+\lambda^2 E_2+\cdots)(|0\rangle+\lambda|1\rangle+\lambda^2|2\rangle+\cdots). \tag{1.56}$$

Expanding this expression, terms of varying powers of λ are obtained on both the left and right hand side of the expression. If the equality indeed holds for all allowed values of λ then equalities must hold for each given power of λ independently. Using this one can obtain n-th order expressions

$$\hat{H}_0|0\rangle = E_0|0\rangle \qquad n = 0 \tag{1.57}$$

$$\hat{H}_0|1\rangle + \hat{H}_1|0\rangle = E_0|1\rangle + E_1|0\rangle \qquad n = 1 \tag{1.58}$$

$$\hat{H}_0|2\rangle + \hat{H}_1|1\rangle = E_0|2\rangle + E_1|1\rangle + E_2|0\rangle \qquad n = 2 \tag{1.59}$$

$$\vdots$$

The level of perturbation theory is determined how many equation are solved, for example if the series is truncated at $n = 1$ then it is first-order perturbation theory.

Starting with the first-order expression, projecting to the left with the zeroth-order ground state and rearranging gives

$$\langle 0|\hat{H}_0 - E_0|1\rangle + \langle 0|\hat{H}_1 - E_1|0\rangle = 0. \tag{1.60}$$

On inspection the first term in this expression is zero as it is identical to the zeroth-order equation when one considers the hermiticity of the Hamiltonian operator. This leaves the following expression for the first-order energy

$$E_1 = \langle 0|\hat{H}_1|0\rangle. \tag{1.61}$$

This expression is of the utmost importance as it allows the computation of the first-order energy of a system without needing to compute the first-order correction to the wavefunction. Exactly this type of expression is used throughout quantum mechanics when perturbatively evaluating, for example, relativistic corrections, BO corrections and responses to weak external fields.

The first-order correction to the wavefunction can of course be obtained by rearranging the first-order equation to yield

$$|1\rangle = -(\hat{H}_0 - E_0)^{-1}(\hat{H}_1 - E_1)|0\rangle. \tag{1.62}$$

Although not necessary for evaluating the first-order energy it is needed for higher perturbation levels.

The second-order equation can also be projected with the zeroth-order ground state and rearranged to give

$$\langle 0|\hat{H}_0 - E_0|2\rangle + \langle 0|\hat{H}_1 - E_1|1\rangle = E_2\langle 0|0\rangle. \tag{1.63}$$

Removing the first term for the same reason as used in the derivation of the first-order energy and observing that $\langle 0|0\rangle = 1$ simplifies the expression to

$$E_2 = \langle 0|\hat{H}_1 - E_1|1\rangle. \tag{1.64}$$

It is not necessary to assume that the zeroth-order and first-order wavefunction are orthogonal, but if they are not, then the expression becomes

$$E_2 = \langle 0|\hat{H}_1 - E_1|1 + \delta 0\rangle. \tag{1.65}$$

where δ is an arbitrary constant. However, on expansion this yields

$$E_2 = \langle 0|\hat{H}_1 - E_1|1\rangle + \delta\langle 0|\hat{H}_1 - E_1|0\rangle \tag{1.66}$$

where the second term is clearly zero. Therefore it has no effect to assume that the zeroth-order and first-order wavefunction are orthogonal ($\langle 0|1\rangle = 0$), and doing so gives the expression for the second-order energy as

$$E_2 = \langle 0|\hat{H}_1|1\rangle. \tag{1.67}$$

By inspection there is a pattern emerging: the $(n+1)$th-order energy can be expressed generally as

$$E_{n+1} = \langle 0|\hat{H}_1|n\rangle. \tag{1.68}$$

1.3.6 Møller-Plesset Theory

Møller-Plesset (MP) theory [7, 11] is PT when the zeroth-order problem is defined to be HF theory. It is also referred to as many-body perturbation theory in some texts. The zeroth-order energy is not however defined to be the HF energy. The HF energy is the sum of the zeroth-order and first-order energies, thus the correct expression for the HF energy is

$$E_{\text{HF}} = \langle 0|\hat{H}|0\rangle = \langle 0|\hat{H}_0 + \hat{H}_1|0\rangle = E_0 + E_1. \tag{1.69}$$

The first-order Hamiltonian is simply the HF n-electron Hamiltonian defined as a sum of Fock operators, one for each electron

$$\hat{H}_0 = \sum_{i=1}^{n} \hat{f}(i). \tag{1.70}$$

Inserting the Hamiltonian $\hat{H}_0$ into the Schrödinger equation yields the Fock equations which when solved yield the zeroth-order energy calculated as the sum of HF eigenvalues

$$E_0 = \sum_{i=1}^{n} \varepsilon_i. \tag{1.71}$$

Rearranging equation 1.69 defines the first-order Hamiltonian as

$$\hat{H}_1 = \hat{H} - \hat{H}_0. \tag{1.72}$$

Using the definition of $\hat{H}$ defined earlier in equation 1.7 and the definition of the one-electron Fock operator (assuming spin orbitals)

$$\hat{f} = -\frac{\nabla^2}{2} - \sum_{A=1}^{N} \frac{Z_A}{r_A} + [\hat{J} - \hat{K}], \tag{1.73}$$

the expression for the first-order Hamiltonian can be obtained

$$\hat{H}_1 = \sum_{i<j}^{n} \frac{1}{r_{ij}} - \sum_{i=1}^{n} [\hat{J}(i) - \hat{K}(i)]. \tag{1.74}$$

Closer inspection of this expression shows that it is the difference between the exact two-electron interaction and the effective model interaction of HF theory.

Having established in equation 1.69 that first-order MP theory is automatically incorporated into HF theory then what of higher-order MP perturbations? The next perturbation is second-order MP theory, which is denoted as MP2. The expression for the MP2 energy was derived earlier and is given by

$$E_2 = \langle 0|\hat{H}_1|1\rangle. \tag{1.75}$$

The expression contains the first-order wavefunction, which is given in equation 1.62 and contains the resolvent operator $(\hat{H}_0 - E_0)^{-1}$. Treating the equation without further simplification would prove difficult, but if one expands everything in a basis set then things become much more simple. This is because the operators become matrices, and operations involving matrices, such as inversion, are easy to evaluate.

The first-order wavefunction can be expanded, in a manner similar to full CI, as

$$|1\rangle = t_\mu|\mu\rangle, \tag{1.76}$$

where the first-order wavefunction is chosen to be orthogonal to the zeroth-order wavefunction. Expansion of the first-order wavefunction may initially seem to be an odd thing to do, but as will be seen many of the terms disappear. Substitution of the above expression into equation 1.62 gives

$$t_\mu(\hat{H}_0 - E_0)|\mu\rangle = -(\hat{H}_1 - E_1)|0\rangle. \tag{1.77}$$

By projecting the equation to the left with all of the determinants one obtains

$$t_\mu\langle\nu|\hat{H}_0 - E_0|\mu\rangle = -\langle\nu|\hat{H}_1 - E_1|0\rangle. \tag{1.78}$$

As with all of the methods discussed thus far, many of the matrix elements turn out to be zero. For the matrix elements of the form $\langle 0|\hat{H}_1 - E_1|\nu\rangle$ only the doubly excited determinants yield non-zero matrix elements. Singly excited determinants do not interact with $|0\rangle$ (the Brillouin condition) and determinants that are more than doubly excited do not interact due to the Hamiltonian being a two-body operator. Thus only doubly excited determinants are required in the first-order expansion. This vastly simplifies things such that

$$\langle 0|\hat{H}_1 - E_1|\nu\rangle = \langle 0|\hat{H}_1 - E_1|0_{ij}^{ab}\rangle = \langle 0|\hat{H}_1|0_{ij}^{ab}\rangle \tag{1.79}$$

since $\langle 0|E_1|0_{ij}^{ab}\rangle = 0$. This can be further simplified by evaluating the matrix element to give

$$\langle 0|\hat{H}_1 - E_1|\nu\rangle = \langle ij|ab\rangle - \langle ij|ba\rangle. \tag{1.80}$$

The other type of matrix element in equation 1.78 simplifies such that

$$\langle\nu|\hat{H}_0 - E_0|\mu\rangle = \delta_{\mu\nu}\langle\nu|\hat{H}_0 - E_0|\nu\rangle. \tag{1.81}$$

Using the fact that only doubly excited determinants contribute in the first order equations yields a much simpler expression to solve

$$t_{ab}^{ij}\langle 0_{ij}^{ab}|\hat{H}_0 - E_0|0_{ij}^{ab}\rangle = -\langle ij|ab\rangle + \langle ij|ba\rangle. \tag{1.82}$$

The matrix elements between two doubly excited determinants are given by

$$\begin{aligned}\langle 0_{ij}^{ab}|\hat{H}_0 - E_0|0_{ij}^{ab}\rangle &= \langle 0_{ij}^{ab}|\hat{H}_0|0_{ij}^{ab}\rangle - E_0 \\ &= \varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j\end{aligned} \tag{1.83}$$

which allows one to rewrite equation 1.82 as

$$t_{ab}^{ij} = -\frac{\langle ij|ab\rangle - \langle ij|ba\rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j}. \tag{1.84}$$

The above amplitudes combined with equation 1.76 completely define the first-order wavefunction. Inserting the first-order wavefunction into the second-order energy expression now yields

$$E_2 = \langle 0|\hat{H}_1|1\rangle = t_{ab}^{ij}\langle 0|\hat{H}_1|0_{ij}^{ab}\rangle. \tag{1.85}$$

The matrix element $\langle 0|\hat{H}_1|0_{ij}^{ab}\rangle = \langle ij|ab\rangle - \langle ij|ba\rangle$, and using this and the expression for the amplitudes yields the final expression for the second-order energy correction

$$E_2 = -\sum_{i<j}\sum_{a<b}\frac{|\langle ij|ab\rangle - \langle ij|ba\rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j}. \tag{1.86}$$

The MP2 energy can be calculated from

$$E_{\text{MP2}} = E_{\text{HF}} + E_2 = E_0 + E_1 + E_2. \tag{1.87}$$

Higher levels of MP theory are possible. MP4 theory is the most widely used beyond second-order MP theory. The higher the level of MP theory the greater the accuracy of the calculation for any given basis set. It is of course implied that the higher the level of MP theory invoked the greater the cost of calculation.

For a given level of MP theory the energy convergence is poor with respect to basis set. In figure 1.3 plots of the MP2 wavefunction with respect to basis set are shown. As

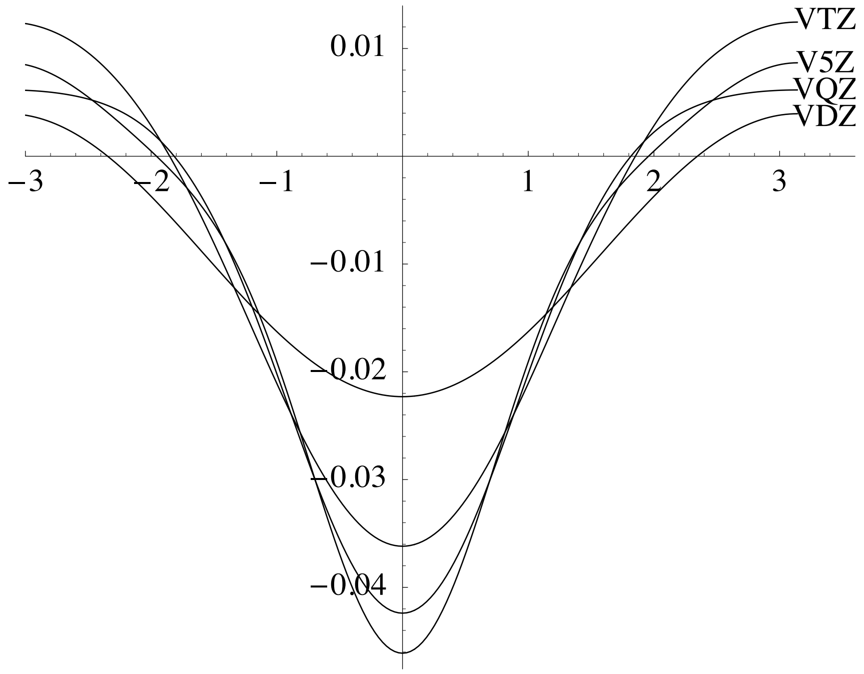

Figure 1.3: Plot of the MP2 wavefunction with respect to basis set for the helium atom. The data for the plot was obtained by evaluating the wavefunction at fixed distance of 1 Bohr from the nucleus. The horizontal axis is the angle between the two electrons in radians. Plot shows the correlation hole slowly converging as the basis set increases

one increases the basis set the wavefunction converges towards the exact cusp-like picture. However the extra expense of using the next basis set in cardinal number yields only a small increase in the accuracy.

Thus from what has been discussed above one realises that much work is needed to get the basis set limit for a MP calculation. The basis set limit is still some way off the exact energy for low order MP theory. For increased accuracy higher level MP theory or CC theory are required, which come at a greater computational cost but are capable of delivering chemical accuracy.

1.3.7 CCSD(T) theory

CC theory has been discussed previously and included details of the CCSD truncation. Sadly CCSD does not give energies that are chemically accurate. The next level of truncation, CCSDT is simply too expensive to consider for all but the smallest systems. However, a method where the triples are included perturbatively is more tractable and is denoted as CCSD(T) [12]. The cost of a CCSD(T) calculation is approximately one-order of magnitude higher than a CCSD theory, computed in a single non-iterative step. It is one-order of magnitude lower in cost than the CCSDT method which obviously allows a greater number of problems to be treated.

The perturbative triples correction has the form

$$E_{(T)} = \sum_{\mu \in \mathrm{SD}} t_\mu \langle \mu | [\hat{H}_1, \hat{T}_3^{(2)}] | 0 \rangle \tag{1.88}$$

where the operator $\hat{T}_3^{(2)}$ has the same form as $\hat{T}_3$ with modified amplitudes

$$\hat{T}_3^{(2)} = \sum_{i<j<k} \sum_{a<b<c} t_{abc}^{ijk\ (2)} \hat{a}^\dagger \hat{b}^\dagger \hat{c}^\dagger \hat{i} \hat{j} \hat{k}. \tag{1.89}$$

The modified amplitudes have the form

$$t_{abc}^{ijk\ (2)} = -\hat{P}_{ijl}^{abc} \frac{L_{ijk}^{abc} - M_{ijk}^{abc}}{\varepsilon_a + \varepsilon_b + \varepsilon_c - \varepsilon_i - \varepsilon_j - \varepsilon_k} \tag{1.90}$$

where

$$L_{ijk}^{abc} = \sum_d t_{ad}^{ij} \langle ck | bd \rangle \qquad \text{and} \qquad M_{ijk}^{abc} = \sum_l t_{ab}^{il} \langle ck | lj \rangle. \tag{1.91}$$

and the operator $\hat{P}_{ijl}^{abc}$ symmetrises over particle permutations. Clearly there are notable similarities between the form of $t_{abc}^{ijk\ (2)}$ and the amplitudes of MP2 theory.

MP2, CCSD and CCSD(T) energies can be combined together as detailed in [7] to produce very accurate results. The method involves making use of the accuracy of the CCSD(T) method and the relative cheapness of a MP2 calculation. The formula has the form

$$\begin{aligned} E_{\text{accurate}} &= E_{\text{MP2}}(\text{large}) \\ &+ E_{\text{CCSD}}(\text{medium}) - E_{\text{MP2}}(\text{medium}) \\ &+ E_{\text{CCSD(T)}}(\text{small}) - E_{\text{CCSD}}(\text{small}) \end{aligned} \tag{1.92}$$

where the subscript denotes the method and the size in parenthesis denotes the size of the basis set employed.

1.3.8 Correlation-consistent basis sets

There are two important criteria for forming basis sets which allow approach towards the limit in a systematic manner. Firstly the energy should converge smoothly towards the full basis set limit as more and more functions are added. Secondly, the smallest basis set should be able to recover the largest portion of the energy. Development of basis sets is very challenging due to the difficulty associated with optimising the parameters, namely the exponents and contraction coefficients. The difficulty arises from the non-linear nature of the equations that need to be solved for optimisation.

There have been many GTO basis sets developed over the years but in recent years the most widely used are the correlation-consistent basis sets of Dunning [13–18]. Developed in the late 1980s and early 1990s the correlation-consistent basis sets are denoted as cc-pVXZ where X is called the cardinal number. The possible values of X are D, T, Q, 5 and 6 which are referred to as valence double-, triple-, quadruple-, quintuple-, and sextuple- zeta respectively. There are two other basis sets based upon the standard correlation-consistent basis sets. These basis sets are known as the augmented correlation-consistent basis set [14], denoted by aug-cc-pVXZ, and the polarised core-valence correlation-consistent basis set [17], denoted by cc-pCVXZ. The augmented correlation-consistent basis sets are primarily used to describe situations involving diffuse electronic structure such as excited states and anions. The polarised core-valence correlation-consistent basis sets are used for calculations involving correlation of the core electrons with both themselves and the valence electrons. Table 1.1 shows the number of functions for the three types of basis sets for each cardinal number for second-row atoms.

Cardinality	cc-pVXZ	aug-cc-pVXZ	cc-pCVXZ
D	3s,2p,1d	4s,3p,2d	4s,3p,1d
T	4s,3p,2d,1f	5s,4p,3d,2f	6s,5p,3d,1f
Q	5s,4p,3d,2f,1g	6s,5p,4d,3f,2g	8s,7p,5d,3f,1g
5	6s,5p,4d,3f,2g,1h	7s,6p,5d,4f,3g,2h	10s,9p,7d,5f,3g,1h
6	7s,6p,5d,4f,3g,2h,1i	8s,7p,6d,5f,4g,3h,2i	12s,11p,9d,7f,5g,3h,1i

Table 1.1: Number of functions for second row atoms for the cc-pVXZ, aug-cc-pVXZ and cc-pCVXZ basis sets.

The smooth convergence of the correlation-consistent basis sets led people to consider the basis set dependence of computed molecular properties in terms of these basis sets. Being able to make use of the smoothness would allow more accurate results from cheaper calculations. It has been observed that the convergence of the correlation energy with respect to the correlation-consistent basis sets is approximately proportional to X^{-3}. Using this relationship and performing two calculations with cardinal numbers X and Y allows a two point extrapolation using the following formula [19, 20]

$$E_{\mathrm{V[X,Y]Z}} = \frac{E_{\mathrm{VYZ}} \times \mathrm{Y}^3 - E_{\mathrm{VXZ}} \times \mathrm{X}^3}{\mathrm{Y}^3 - \mathrm{X}^3}. \tag{1.93}$$

The notation V[X,Y]Z denotes an extrapolated calculation using calculations performed with basis sets of cardinal numbers X and Y. The notation V∞Z is also sometimes used as the formula is an approximation to the basis set limit. As with most extrapolation techniques, the closer to the asymptote the data the more accurate the extrapolated value, thus a V[5,6]Z calculation will give a significantly more accurate value than a V[D,T]Z calculation. It is important to note that the extrapolation formula is valid only for the correlation contribution towards the energy, not the HF contribution. Any method hoping to take account of the extrapolation technique must therefore be able to separate these two contributions in order to apply the formula.

1.3.9 Basis set superposition error

Basis set superposition error (BSSE) is a problem that results from the incompleteness of a one-electron basis set. BSSE can be demonstrated with a simple system of two helium atoms weakly bound together. To calculate the binding energy generally one subtracts twice the energy of the helium atom from the energy of the bound system. However, the energy of the atomic helium is typically calculated in a smaller basis set than the bound system since functions for just one centre are included. This is the source of the BSSE, since each helium atom in the bound system has more functions to help lower the energy.

BSSE can be attributed to the use of fintite basis sets. The most common method to correct for this is known as the counterpoise (CP) correction [21, 22]. The CP correction is evaluated by performing the calculations on the monomers in the dimer basis set, thus including functions not on the atomic centres of the monomer being treated. BSSE disappears for a complete basis set, but it does not necessarily converge smoothly as the basis set is increased. The reason for this is that as more functions are added they may be able to lower the energy, irrespective of their centre, and hence increase the BSSE. This makes BSSE hard to predict for a given basis set.

1.4 Explicitly Correlated Methods

The aim of all of the *ab initio* methods described thus far, assuming a reasonably converged HF wavefunction, is to treat the electron correlation of a system. Up until now all have constructed their wavefunctions from a basis set of one-electron AO functions, used to create MOs. The trouble with these methods is that they often require large basis sets to obtain accurate results or, to put it another way, the wavefunction converges slowly with respect to the size of the basis set. The reason for this is that the basis set does not contain any functions of the correct shape, i.e. that correctly describe the electronic cusp. The basis functions required to describe correlation must take into account the fundamental property of correlation: it is at the very least two-body. The way to solve this is to include basis functions that depend upon the position of more than one electron. The argument for use of multi-electron basis functions is almost the same as whether STOs or GTOs should be used as one-electron basis functions. In that case STOs are better at describing the nuclear cusp, and here multi-electron basis functions are better at describing electron correlation. However, both these types of basis functions lead to integrals that are much harder to evaluate than standard one-electron GTO functions. Before proceeding it is worth noting that inclusion of a correlation factor into the wavefunction is equivalent to having multi-electron basis functions.

The pioneering work on multi-electron basis expansions was done by Hylleraas as early as 1929 [23]. His work centred around including the inter-electronic distance r_{12} into the wavefunction for the helium atom, the simplest charge neutral case of electron correlation. In the initial work on helium [23] and subsequent work on its isoelectronic series [24] an accurate wavefunction was constructed for the ^{1}S ground state. The ansatz used was of the form

$$\Psi(ks, kt, ku) = e^{-s/2} \sum_{n,l,m=0} c_{n,2l,m} s^n t^{2l} u^m \tag{1.94}$$

where

$$s = r_1 + r_2, \qquad t = -r_1 + r_2 \qquad \text{and} \qquad u = r_{12}. \tag{1.95}$$

In the above ansatz it is the coordinate u which contributes the crucial difference from traditional *ab initio* methods. The scaling factor k and expansion coefficients c_i for several selected sets of non-negative integers $\{n, l, m\}$ are determined on the basis of the variational principle. The energy obtained by Hylleraas was only fractionally higher than the exact value and was a vast improvement upon any other calculated value of the time. In 1979 Jolly [25] proved that the scaling factor k obtained by Hylleraas was not optimal and improved the energy. Further work by Koga [26] confirmed this and improved upon the set of integers for the six-term expansion to decrease the energy even more. His work also continued onto optimal Hylleraas expansions of up to twenty terms [27]. The wavefunction has been modified for the more general cases of half-integral powers [28] and negative integers [29] for the variables m, n and l. These modifications both increase the flexibility of the wavefunction.

The Hylleraas results were astoundingly good and it was not long before others started using this idea. In 1933 James and Coolidge extended the idea of using a correlation factor to the hydrogen molecule [30]: however, subsequent progress was slow. Even by the late fifties the most advanced calculations using a correlation factor were restricted to ground and excited state atoms [31–33] and later the potential energy curve of the hydrogen molecule [34], building on the earlier work of James and Coolidge.

The reason for the lack of progress to larger systems was the presence of integrals depending upon the positions of more than two electrons. These occur numerously throughout explicitly correlated theories and are also very difficult to evaluate. This severely hampered the progress of explicitly correlated theories until the eighties when several breakthroughs occurred for the approximate evaluation of many-electron integrals. Some of the resulting theories are documented in this section.

1.4.1 Transcorrelated Method

The transcorrelated method was really the only significant explicitly correlated method to be developed prior to the breakthroughs of the 1980s. Suggested by Boys and Handy in 1969 [35] it involves transforming the Hamiltonian with an exponential correlation factor to yield the transcorrelated Hamiltonian

$$\hat{H}_C = \exp(-\hat{C})\hat{H}\exp(\hat{C}) \tag{1.96}$$

where

$$\hat{C} = \sum_{i<j} f(\vec{r}_i, \vec{r}_j). \tag{1.97}$$

This transformation is similar to the one in CC theory, except a correlation operator is used instead of a cluster operator. In fact, as a result of this, much of the theory in the transcorrelated method bears great similarity to CC theory.

The correlation function $f(\vec{r}_i, \vec{r}_j)$ is given as

$$f(\vec{r}_i, \vec{r}_j) = \sum_k D_k G_k(r_{ij}) + \sum_k d_k(g_k(\vec{r}_i) + g_k(\vec{r}_j)) \tag{1.98}$$

where g_k and G_k are one-electron and two-electron functions. The first order form of $G_k(r_{ij})$ presented by Boys and Handy was

$$G_k(r_{ij}) = \frac{1}{2}\frac{ar_{ij}}{a + r_{ij}}. \tag{1.99}$$

It is important to remember $G_k(r_{ij})$ constitutes $\hat{C}$ which is used as an exponent, thus the correlation factor used is related to an exponential Slater-like function, not a linear one as equation 1.99 might imply. The form of the correlation factor can be chosen such that there are no singularities in the transcorrelated Hamiltonian [36]. The wavefunction used by Boys and Handy in their transcorrelated method was a CI expansion of SDs. The method introduced three-electron integrals, but no integrals of more than three electrons. This is a distinct feature of the transcorrelated method when compared with other explicitly correlated methods described later which do introduce integrals of more than three electrons. Recently Ten-no has used the transcorrelated Hamiltonian with a frozen Gaussian geminal as the correlation factor [37, 38].

1.4.2 R12 Theory

R12 theory, as the name implies, is an explicitly correlated method where the correlation factor is very simply r_{12}. Whilst r_{12} may be the simplest possible form, it does not follow that it will lead to the simplest possible theory. Indeed, the transcorrelated method came about over a decade earlier because of the advantages of using a exponential form of r_{12}. R12 theory itself was pioneered by Kutzelnigg [39]. The basic theory involves adding an explicitly correlated term based on the linear correlation factor r_{12} to the wavefunction as Hylleraas did many years before. The crucial difference in R12 theory is the method for evaluating three- and four-electron integrals, known as the resolution of identity (RI) approximation. This approximation is so important that it will be described at some length a little later on.

The R12 method was quickly applied to MP2 theory by Kutzelnigg and Klopper [40] with great success yielding a so-called MP2-R12 theory. This theory has been developed extensively over the past decade with various ansätze resulting. Details of these ansätze and associated approximations will be given in the next chapter.

R12 theory has also been applied to the more accurate CC theory by Noga *et al.* [41, 42] resulting in a CC-R12 theory. Perturbative approximations of the form CCSD(R12) and CCSD-R12(T) [43] have also been developed.

The resolution of identity approximation

The RI approximation comes from the need to evaluate three- and four-electron integrals which occur numerously in explicitly correlated methods. The RI approximation can be expressed simply by the projection operator

$$\hat{P}_n \psi(n) = \int d\vec{r} p'(\vec{r}) p'(n) \psi(\vec{r}) \approx \psi(n) \tag{1.100}$$

where $\{p'(n)\}$ is an orthonormal orbital basis set for electron n. The MO basis set can be used and provides the simplest ansatz but generally an auxiliary RI basis set is employed. Using an example three-electron integral one can write

$$\langle ijk | r_{12} r_{23}^{-1} | lmn \rangle \approx \langle ijk | r_{12} \hat{P}_2 r_{23}^{-1} | lmn \rangle \tag{1.101}$$

which on expansion of $\hat{P}_2$ yields

$$\langle ijk | r_{12} r_{23}^{-1} | lmn \rangle \approx \langle ijkp' | r_{12} \hat{\pi}_{24} r_{23}^{-1} | lmnp' \rangle, \tag{1.102}$$

where $\hat{\pi}_{24}$ is the permutation operator that transposes electrons two and four. Applying the permutation operator gives the following expression

$$\langle ijk|r_{12}r_{23}^{-1}|lmn\rangle \approx \langle ijkp'|r_{12}r_{34}^{-1}|lp'nm\rangle. \tag{1.103}$$

which when written as

$$\langle ijk|r_{12}r_{23}^{-1}|lmn\rangle \approx \langle ij|r_{12}|lp'\rangle\langle kp'|r_{12}^{-1}|nm\rangle \tag{1.104}$$

can be seen to be a sum of products of two-electron integrals which can be readily evaluated. Analysis of the error associated with the RI approximation will feature as part of the results of this thesis.

Until 2002 only two methods were widely used for the evaluation of three-electron integrals: exact computation [38, 44–46] and RI in the AO basis set [39, 47]. The former method is practical for molecules only when both the atomic orbitals and the correlation factor are expanded in Gaussians (see for example [48, 49]). The latter uses the identity operator in the AO basis set to approximately resolve the three-electron integrals into sums of products of two-electron integrals.

Over the past few years there have been several developments. First amongst these chronologically as well as in terms of importance is the use of the RI approximation in an auxiliary basis set [50]. This allows one to study the effect of the accuracy of the integrals independently, and also allows one to converge the accuracy of the many-electron integrals whilst retaining a reasonably modest basis set for the molecular orbitals.

The idea has been extended to formulations that need only the RI approximation in the orthogonal complement of the AO basis [51]. Density fitting (DF) can also be used as an alternative to the RI approximation for the three-electron integrals although this does not appear to offer significant advantages; however combined RI/DF approaches offer enhanced efficiency [52] and accuracy [53]. Finally one can use numerical quadrature for the many-electron integrals as shown by Boys and Handy [35] and recently by Tenno [54].

1.4.3 Gaussian Geminals

Gaussian Geminals (GG) methods were developed by Szalewicz *et al.* for PT [49, 55]. The correlation factor used is expanded in Gaussian functions instead of linear r_{12}. The

Gaussian correlation factor is inserted into the wavefunction which is the difference from the transcorrelated method where the Hamiltonian is transformed with a Gaussian correlation factor. The first order wavefunction has the form

$$u_{ij} = a_k \exp\{-\alpha_k(r_i - A_k) - \beta_k(r_j - B_k) - \gamma_k r_{ij}^2\}, \tag{1.105}$$

where the parameters a_k, α_k, A_k, β_k, B_k, and γ_{ij} are optimised for each GG pair function. The GG function entirely replaces the traditional functions for the doubles so that the doubles are entirely constructed from explicitly correlated terms, whereas in R12 theory they supplement the doubly excited terms. For instance, in the case of CC theory the cluster operator has the form

$$\hat{T} = 1 + \hat{T}_1 + \hat{G}_2 + \hat{T}_3 + \cdots \tag{1.106}$$

where $\hat{G}_2$ represents double excitations into the new explicitly correlated basis functions.

1.5 Aims of this work

This chapter should by now have given the background information required to put this work into context. Given the poor convergence of orbital based methods it is clear that explicitly correlated methods warrant some work. Whilst explicitly correlated methods do give a marked improvement upon the convergence of energies with respect to basis set, the improvement is not as great as one might hope for, certainly when one considers the success of the work of Hylleraas. The aim of this thesis is to investigate the errors associated with R12 theory and investigate an alternative to the RI approximation, with the hope of increasing the convergence with respect to basis set. As will be seen later, complexities associated with implementing such a method led to an implementation of a theory for a frozen Gaussian geminal as opposed to linear r_{12}. This twist of fate actually resulted in a program where the correlation factor could be set arbitrarily by altering the fitting criteria of the frozen Gaussian geminal and actually led to the most interesting conclusions.

Chapter two describes in detail how the various R12 methods were derived. It also gives details of all of the ansätze which exist as a result of approximations that can be made when evaluating the matrix elements.

Chapter three describes the development of new classes of integrals and is the core of the theoretical work presented in the thesis. Details of the integral derivations are given along with their final recurrence relations. The computer implementations in chapter four are shown mainly in pseudo code to make them more accessible to the general reader.

Chapter five contains results of calculations performed with the new programs and analysis of the errors associated with them. The final conclusions and comment are then given in chapter six.

Chapter 2

Theory

The theories derived in this Chapter are based on the R12 methods of Kutzelnigg and Klopper [39,40] with the derivations closely following those of Klopper and Samson [50]. Firstly the notation that will be used throughout is defined, the convention for labels used being

$i, j, k, \ldots$	occupied in the reference Slater determinant
$a, b, c, \ldots$	unoccupied, but contained in the given basis
$p, q, r, \ldots$	arbitrary, but contained in the given basis
$\alpha, \beta, \gamma, \ldots$	unoccupied, belonging to a complete set
$\kappa, \lambda, \mu, \ldots$	arbitrary, forming a complete basis.

This can be viewed illustratively as shown in figure 2.1.

<table>
<tr><td colspan="2">Given basis</td><td>Complete basis</td></tr>
<tr><td>occupied</td><td colspan="2">unoccupied</td></tr>
<tr><td>$i, j, k, \ldots$</td><td>$a, b, c, \ldots$</td><td></td></tr>
<tr><td colspan="2">$p, q, r, \ldots$</td><td></td></tr>
<tr><td></td><td colspan="2">$\alpha, \beta, \gamma, \ldots$</td></tr>
<tr><td colspan="3">$\kappa, \lambda, \mu, \ldots$</td></tr>
</table>

Figure 2.1: Graphical representation of notation for orbital indices

The MP2-R12 theories contain several matrix elements which must be evaluated. Various approximations can be applied to make their evaluation more attainable and these lead to various ansätze. Details of the approximations and ansätze will be given later but first an account of the basic equations and their origin will be given. The derivations presented will be for an MP2-F12 method where F12 indicates an arbitrary correlation factor that is a function of r_{12}.

The start point is to minimise the Hylleraas pair functional [24, 56]

$$\epsilon_{ij}^{(2)} = \langle u_{ij}|\hat{f}_1 + \hat{f}_2 - \varepsilon_i - \varepsilon_j|u_{ij}\rangle + 2\langle u_{ij}|r_{12}^{-1}|ij\rangle, \tag{2.1}$$

where in the F12 ansatz the standard MP2 basis of doubly excited determinants is augmented by explicitly correlated terms construced from a products of occupied orbitals

$$|u_{ij}\rangle = t_{ab}^{ij}|ab\rangle + t_{kl}^{ij}\hat{Q}_{12}f_{12}|kl\rangle. \tag{2.2}$$

The function f_{12} is an arbitrary function of r_{12} whose form will be discussed in the next chapter.

On expanding the Hylleraas functional one obtains

$$\epsilon_{ij}^{(2)} = \epsilon_{ij}^{(\text{MP2})} + \epsilon_{ij}^{(\text{F12})} + 2t_{ab}^{ij}t_{kl}^{ij}\langle kl|f_{12}\hat{Q}_{12}(\hat{f}_1 + \hat{f}_2 - \varepsilon_i - \varepsilon_j)|ab\rangle \tag{2.3}$$

where $\epsilon_{ij}^{(\text{MP2})}$ is the conventional MP2 pair energy expression, $\epsilon_{ij}^{(\text{F12})}$ is the F12 pair contribution and the third term in the expression is a coupling between the two terms. The second and third term contain a projection operator, $\hat{Q}_{12}$ which can take several forms depending on the exact method; details of which projection operator used will always be given. The F12 contribution, $\epsilon_{ij}^{(\text{F12})}$, is defined as

$$\epsilon_{ij}^{(\text{F12})} = t_{kl}^{ij}B_{kl,mn}^{ij}t_{mn}^{ij} + 2t_{kl}^{ij}V_{kl}^{ij}, \tag{2.4}$$

where the matrix elements $B_{kl,mn}^{ij}$ and V_{kl}^{ij} are defined as

$$B_{kl,mn}^{ij} = \langle mn|f_{12}\hat{Q}_{12}(\hat{f}_1 + \hat{f}_2 - \varepsilon_i - \varepsilon_j)\hat{Q}_{12}f_{12}|kl\rangle, \tag{2.5}$$

and

$$V_{kl}^{ij} = \langle kl|f_{12}\hat{Q}_{12}r_{12}^{-1}|ij\rangle. \tag{2.6}$$

The matrix element $C_{kl,ab}^{ij}$ is also defined

$$C_{kl,ab}^{ij} = \langle kl|f_{12}\hat{Q}_{12}(\hat{f}_1 + \hat{f}_2 - \varepsilon_i - \varepsilon_j)|ab\rangle \tag{2.7}$$

for the coupling term of equation 2.3 and a matrix element $X_{kl,mn}$ is defined for use later in the derivations

$$X_{kl,mn} = \langle mn|f_{12}\hat{Q}_{12}f_{12}|kl\rangle. \tag{2.8}$$

All of the derivations that will be presented differ only in their method of evaluation for the key matrices $B^{ij}_{kl,mn}$, V^{ij}_{kl}, $C^{ij}_{kl,ab}$ and $X_{kl,mn}$. In some cases the difference in evaluation comes only from the choice of the projection operator $\hat{Q}_{12}$, but in others it comes from the various approximations that are used within the different ansätze. An account of the approximations used within these theories is now given along with a summary of the resulting ansätze.

The Resolution of Identity approximation

The Resolution of Identity (RI) approximation is the only approximation which will be used universally in these methods. The RI approximation arises from the need to evaluate three-electron integrals which occur in great numbers in these theories. Not only are these integrals numerous, they are immensely difficult to evaluate individually in terms of CPU time. The solution proposed by Kutzelnigg and Klopper [39, 40] in their original method is as follows,

$$\langle ijk|r_{12}r_{13}^{-1}|lmn\rangle \approx \langle ij|r_{12}|pm\rangle\langle kp|r_{12}^{-1}|nl\rangle, \tag{2.9}$$

where the MO basis has been used for the RI. A more general choice for the RI [50] is given by

$$\langle ijk|r_{12}r_{13}^{-1}|lmn\rangle \approx \langle ij|r_{12}|p'm\rangle\langle kp'|r_{12}^{-1}|nl\rangle, \tag{2.10}$$

where an auxiliary RI basis has been used. Further details of the RI approximation are given in the introduction.

The Generalised and Extended Brillouin conditions

The generalised Brillouin condition (GBC) and extended Brillouin condition (EBC) are important approximations that when used can make evaluation of certain integrals much simpler. The GBC states that

$$\hat{f}|i\rangle = \varepsilon_i|i\rangle \tag{2.11}$$

which is exactly equivalent to $\langle i|\hat{f}|\alpha\rangle = 0$. The extended Brillouin condition takes the approximation one step further, and as such is a less accurate approximation. The EBC states that

$$\hat{f}|a\rangle = \varepsilon_a|a\rangle \tag{2.12}$$

which is exactly equivalent to $\langle a|\hat{f}|\sigma\rangle = 0$.

Projection Operators

The projection operator $\hat{Q}_{12}$ has not been discussed in any detail up until now. The purpose of $\hat{Q}_{12}$ is to ensure orthogonality of the explicitly correlated space to the occupied orbitals. There are two projection operators in common use in this field. The first is the projection operator that ensures orthogonality to all the MOs

$$\hat{Q}_{12} = (1 - \hat{P}_1)(1 - \hat{P}_2) \tag{2.13}$$

where

$$\hat{P}_1 = \sum_p |p(1)\rangle\langle p(1)|. \tag{2.14}$$

When this projection operator is used the ansatz name will contain a **1** to denote its use [50]. The second choice of projection operator ensures orthogonality to the occupied space only

$$\hat{Q}_{12} = (1 - \hat{O}_1)(1 - \hat{O}_2) \tag{2.15}$$

where

$$\hat{O}_1 = \sum_i |i(1)\rangle\langle i(1)|. \tag{2.16}$$

and methods using this projection operator will contain a **2** in their ansatz name. The choice of ansatz **1** or **2** is not an approximation, it is in fact a different wavefunction expansion so any differences in expectation values are due to the differences in size of these expansions.

A computationally more convenient projection operator (which leads to the same theory as equation 2.15) ensures orthogonality to the virtual space:

$$\hat{Q}_{12} = (1 - \hat{O}_1)(1 - \hat{O}_2)(1 - \hat{V}_1\hat{V}_2) \tag{2.17}$$

where

$$\hat{V}_1 = \sum_i |a(1)\rangle\langle a(1)|. \tag{2.18}$$

The (diag) energy

The (diag) energy can be calculated for all methods and is non-invariant. This means that there are no excitations to all occupied pairs and the pair function is defined by replacing equation 2.2 by

$$|u_{ij}\rangle = t^{ij}_{ab}|ab\rangle + \hat{Q}_{12} f_{12}|ij\rangle. \tag{2.19}$$

The energy can be calculated easily enough for any of the methods. All that must be done is to take certain parts of the matrices V, B, X and C and recompute the energy. Mainly this involves using the diagonal elements only, hence the name (diag).

2.1 The MP2-F12/2*A and 2*A' methods

These methods are the natural starting point when embarking on implementing such theories due to the large number of approximations. This makes derivation of the method and writing a computer code implementation a little more tractable for a first attempt. In order to implement any method the evaluation of the four matrix elements V^{ij}_{kl}, $B^{ij}_{kl,mn}$, $X_{kl,mn}$ and $C^{ij}_{kl,ab}$ must be considered. Each of these matrices will be dealt with in turn stating all of the approximations used. Subsequent methods will only detail the differences from this method. The nomenclature of these methods is based on that of Klopper and Samson [50].

2.1.1 Matrix V

The matrix V^{ij}_{kl} is the simplest and this provides the starting point for the derivation. The first step is to insert the definition of the occupied projection operator into equation 2.6. For convenience the alternate form of $\hat{Q}_{12}$ given in equation 2.17 is used. To obtain the expressions for the occupied projection operator that does not ensure orthogonality to the virtual space simply delete the last term from all of the expressions for V. Expanding out the projection operator gives the five term expression

$$V^{ij}_{kl} = \langle kl|f_{12}r^{-1}_{12}|ij\rangle - \langle kl|f_{12}\hat{O}_1 r^{-1}_{12}|ij\rangle - \langle kl|f_{12}\hat{O}_2 r^{-1}_{12}|ij\rangle + \langle kl|f_{12}\hat{O}_1\hat{O}_2 r^{-1}_{12}|ij\rangle - \langle kl|f_{12}\hat{V}_1\hat{V}_2 r^{-1}_{12}|ij\rangle. \quad (2.20)$$

The next step is to insert the definition of the projectors to form

$$V^{ij}_{kl} = \langle kl|f_{12}r^{-1}_{12}|ij\rangle - \langle klm|f_{12}r^{-1}_{23}|mji\rangle - \langle klm|f_{12}r^{-1}_{13}|imj\rangle + \langle klmn|f_{12}r^{-1}_{34}|mnij\rangle - \langle klab|f_{12}r^{-1}_{34}|abij\rangle. \quad (2.21)$$

which contains two-, three- and four-electron integrals. Two-electron integrals can be evaluated easily and by observation it can be seen that the four-electron integrals can decouple to products of two-electron integrals

$$\begin{aligned} V_{kl}^{ij} &= \langle kl|f_{12}r_{12}^{-1}|ij\rangle - \langle klm|f_{12}r_{23}^{-1}|mji\rangle - \langle klm|f_{12}r_{13}^{-1}|imj\rangle \\ &\quad + \langle kl|f_{12}|mn\rangle\langle mn|r_{12}^{-1}|ij\rangle - \langle kl|f_{12}|ab\rangle\langle ab|r_{12}^{-1}|ij\rangle. \end{aligned} \tag{2.22}$$

To evaluate the three-electron integrals in the above expression the RI approximation is inserted as follows

$$\begin{aligned} V_{kl}^{ij} &= \langle kl|f_{12}r_{12}^{-1}|ij\rangle - \langle klm|f_{12}\hat{P}_2' r_{23}^{-1}|mji\rangle - \langle klm|f_{12}\hat{P}_1' r_{13}^{-1}|imj\rangle \\ &\quad + \langle kl|f_{12}|mn\rangle\langle mn|r_{12}^{-1}|ij\rangle - \langle kl|f_{12}|ab\rangle\langle ab|r_{12}^{-1}|ij\rangle. \end{aligned} \tag{2.23}$$

Expanding the RI projectors gives

$$\begin{aligned} V_{kl}^{ij} &= \langle kl|f_{12}r_{12}^{-1}|ij\rangle - \langle kl|f_{12}|mp'\rangle\langle mp'|r_{12}^{-1}|ij\rangle - \langle kl|f_{12}|p'm\rangle\langle mp'|r_{12}^{-1}|ji\rangle \\ &\quad + \langle kl|f_{12}|mn\rangle\langle mn|r_{12}^{-1}|ij\rangle - \langle kl|f_{12}|ab\rangle\langle ab|r_{12}^{-1}|ij\rangle, \end{aligned} \tag{2.24}$$

which is the final expression for V_{kl}^{ij} as all the integrals are two-electron and can be evaluated by the methods discussed in the next chapter. It is worth noting that the only approximation employed in evaluating V_{kl}^{ij} was the RI approximation which is used in all the methods. As a consequence the expression for V_{kl}^{ij} is general for all methods that use the same projection operator, $\hat{Q}_{12}$. The projection operator used above ensures orthogonality to both the occupied and virtual space. To obtain the expression for the projection operator that ensures orthogonality to the occupied space only one simply needs to delete the last term of the expression for V_{kl}^{ij}.

2.1.2 Matrix B

The matrix element $B_{kl,mn}^{ij}$ is a little more complicated

$$B_{kl,mn}^{ij} = \langle mn|f_{12}\hat{Q}_{12}(\hat{f}_1 + \hat{f}_2 - \varepsilon_i - \varepsilon_j)\hat{Q}_{12}f_{12}|kl\rangle. \tag{2.25}$$

The first step to simplification is to make use of the identity

$$\begin{aligned} f_{12}\hat{Q}_{12}(\hat{f}_1 + \hat{f}_2 - \varepsilon_i - \varepsilon_j)\hat{Q}_{12}f_{12} &= \frac{1}{2}f_{12}\hat{Q}_{12}[\hat{f}_1 + \hat{f}_2, \hat{Q}_{12}f_{12}] \\ &\quad + \frac{1}{2}[f_{12}\hat{Q}_{12}, \hat{f}_1 + \hat{f}_2]\hat{Q}_{12}f_{12} \\ &\quad + \frac{1}{2}f_{12}\hat{Q}_{12}\hat{Q}_{12}f_{12}(\hat{f}_1 + \hat{f}_2 - \varepsilon_i - \varepsilon_j) \\ &\quad + \frac{1}{2}(\hat{f}_1 + \hat{f}_2 - \varepsilon_i - \varepsilon_j)f_{12}\hat{Q}_{12}\hat{Q}_{12}f_{12} \end{aligned} \tag{2.26}$$

which when substituted into the expression for $B^{ij}_{kl,mn}$ gives

$$\begin{aligned}B^{ij}_{kl,mn} &= \frac{1}{2}\langle mn|f_{12}\hat{Q}_{12}[\hat{f}_1+\hat{f}_2,\hat{Q}_{12}f_{12}]|kl\rangle \\ &+\frac{1}{2}\langle mn|[f_{12}\hat{Q}_{12},\hat{f}_1+\hat{f}_2]\hat{Q}_{12}f_{12}|kl\rangle \\ &+\frac{1}{2}\langle mn|f_{12}\hat{Q}_{12}f_{12}(\hat{f}_1+\hat{f}_2-\varepsilon_i-\varepsilon_j)|kl\rangle \\ &+\frac{1}{2}\langle mn|(\hat{f}_1+\hat{f}_2-\varepsilon_i-\varepsilon_j)f_{12}\hat{Q}_{12}f_{12}|kl\rangle \qquad (2.27)\end{aligned}$$

where the simplification $\hat{Q}_{12}=\hat{Q}_{12}\hat{Q}_{12}$ has been used since the operator $\hat{Q}_{12}$ is idempotent. The identity used maintains symmetry thus ensuring that the operator remains Hermitian. Assuming the GBC and making use of the Hermiticity of the Fock operator allows the last two terms to be simplified as

$$\begin{aligned}B^{ij}_{kl,mn} &= \frac{1}{2}\left\{B_{kl,mn}+B_{mn,kl}\right\} \\ &+\frac{1}{2}(\varepsilon_k+\varepsilon_l-\varepsilon_i-\varepsilon_j)\langle mn|f_{12}\hat{Q}_{12}f_{12}|kl\rangle \\ &+\frac{1}{2}(\varepsilon_m+\varepsilon_n-\varepsilon_i-\varepsilon_j)\langle mn|f_{12}\hat{Q}_{12}f_{12}|kl\rangle \qquad (2.28)\end{aligned}$$

where the matrix elements used to represent the first two terms are given by

$$B_{kl,mn}=\langle mn|f_{12}\hat{Q}_{12}[\hat{f}_1+\hat{f}_2,\hat{Q}_{12}f_{12}]|kl\rangle. \qquad (2.29)$$

Factorising this expression and rewriting in terms of a matrix element X yields

$$B^{ij}_{kl,mn}=\frac{1}{2}\left\{B_{kl,mn}+B_{mn,kl}\right\}+\frac{1}{2}(\varepsilon_k+\varepsilon_l+\varepsilon_m+\varepsilon_n-2\varepsilon_i-2\varepsilon_j)X_{kl,mn} \qquad (2.30)$$

where details on evaluating matrix element X will be given later.

The matrix element $B_{kl,mn}$ is also simplified by use of the EBC as under the EBC $[\hat{f}_1+\hat{f}_2,\hat{Q}_{12}]=0$ and thus

$$[\hat{f}_1+\hat{f}_2,\hat{Q}_{12}f_{12}]=\hat{Q}_{12}[\hat{f}_1+\hat{f}_2,f_{12}]=\hat{Q}_{12}[\hat{T}_1+\hat{T}_2,f_{12}]-\hat{Q}_{12}[\hat{K}_1+\hat{K}_2,f_{12}] \qquad (2.31)$$

since only the kinetic and exchange operators do not commute. Under ansatz A of the MP2-F12 method there is one further approximation which is that the contribution from the exchange commutators are assumed to be zero and hence

$$[\hat{f}_1+\hat{f}_2,f_{12}]=[\hat{T}_1+\hat{T}_2,f_{12}]. \qquad (2.32)$$

Substituting this into equation 2.29 yields

$$B_{kl,mn} = \langle mn|f_{12}\hat{Q}_{12}[\hat{T}_1 + \hat{T}_2, f_{12}]|kl\rangle \tag{2.33}$$

where the idempotency of $\hat{Q}_{12}$ has been observed. The next step is to expand the projection operator to yield the five term expression

$$\begin{aligned} B_{kl,mn} = {} & \langle mn|f_{12}[\hat{T}_1 + \hat{T}_2, f_{12}]|kl\rangle \\ & - \langle mn|f_{12}\hat{O}_1[\hat{T}_1 + \hat{T}_2, f_{12}]|kl\rangle - \langle mn|f_{12}\hat{O}_2[\hat{T}_1 + \hat{T}_2, f_{12}]|kl\rangle \\ & + \langle mn|f_{12}\hat{O}_1\hat{O}_2[\hat{T}_1 + \hat{T}_2, f_{12}]|kl\rangle - \langle mn|f_{12}\hat{V}_1\hat{V}_2[\hat{T}_1 + \hat{T}_2, f_{12}]|kl\rangle. \end{aligned} \tag{2.34}$$

Inserting the definition of the projector yields

$$\begin{aligned} B_{kl,mn} = {} & \langle mn|f_{12}[\hat{T}_1 + \hat{T}_2, f_{12}]|kl\rangle \\ & - \langle mno|f_{12}[\hat{T}_2 + \hat{T}_3, f_{23}]|olk\rangle - \langle mno|f_{12}[\hat{T}_1 + \hat{T}_3, f_{13}]|kol\rangle \\ & + \langle mnop|f_{12}[\hat{T}_3 + \hat{T}_4, f_{34}]|opkl\rangle - \langle mnab|f_{12}[\hat{T}_3 + \hat{T}_4, f_{34}]|abkl\rangle. \end{aligned} \tag{2.35}$$

where in this case the index p in the fourth term is used to represent an occupied orbital. The four-electron integrals are now decoupled and the RI approximation is inserted into the three-electron integrals

$$\begin{aligned} B_{kl,mn} = {} & \langle mn|f_{12}[\hat{T}_1 + \hat{T}_2, f_{12}]|kl\rangle \\ & - \langle mno|f_{12}\hat{P}_2'[\hat{T}_2 + \hat{T}_3, f_{23}]|olk\rangle - \langle mno|f_{12}\hat{P}_1'[\hat{T}_1 + \hat{T}_3, f_{13}]|kol\rangle \\ & + \langle mn|f_{12}|op\rangle\langle op|[\hat{T}_1 + \hat{T}_2, f_{12}]|kl\rangle - \langle mn|f_{12}|ab\rangle\langle ab|[\hat{T}_1 + \hat{T}_2, f_{12}]|kl\rangle. \end{aligned} \tag{2.36}$$

Expansion of the RI projector and decoupling the integrals give the final expression in terms of integrals that can be evaluated as detailed in the next chapter

$$\begin{aligned} B_{kl,mn} = {} & \langle mn|f_{12}[\hat{T}_1 + \hat{T}_2, f_{12}]|kl\rangle \\ & - \langle mn|f_{12}|op'\rangle\langle op'|[\hat{T}_1 + \hat{T}_2, f_{12}]|kl\rangle - \langle mn|f_{12}|op'\rangle\langle p'o|[\hat{T}_1 + \hat{T}_2, f_{12}]|lk\rangle \\ & + \langle mn|f_{12}|op\rangle\langle op|[\hat{T}_1 + \hat{T}_2, f_{12}]|kl\rangle - \langle mn|f_{12}|ab\rangle\langle ab|[\hat{T}_1 + \hat{T}_2, f_{12}]|kl\rangle. \end{aligned} \tag{2.37}$$

2.1.3 Matrix X

The form of $X_{kl,mn}$ is given in equation 2.8. Under ansatz A the approximation $X_{kl,mn} = 0$ is made, thus there is never a need to evaluate $X_{kl,mn}$. The difference, and this is indeed the only difference, between the A' and A ansätze is that the matrix element $X_{kl,mn}$ is evaluated under the A' ansatz. Starting with equation 2.8 and expanding the projection operator $\hat{Q}_{12}$ yields

$$X_{kl,mn} = \langle mn|f_{12}^2|kl\rangle - \langle mn|f_{12}\hat{O}_1 f_{12}|kl\rangle - \langle mn|f_{12}\hat{O}_2 f_{12}|kl\rangle + \langle mn|f_{12}\hat{O}_1\hat{O}_2 f_{12}|kl\rangle + \langle mn|f_{12}\hat{V}_1\hat{V}_2 f_{12}|kl\rangle. \quad (2.38)$$

Inserting the definition of the projection operator gives

$$X_{kl,mn} = \langle mn|f_{12}^2|kl\rangle - \langle mno|f_{12}f_{23}|olk\rangle - \langle mno|f_{12}f_{13}|kol\rangle + \langle mnop|f_{12}f_{34}|opkl\rangle + \langle mnab|f_{12}f_{34}|abkl\rangle \quad (2.39)$$

where the index p represents an occupied orbital. The four-electron integral can be decoupled and the RI is inserted into the three-electron integrals to give

$$X_{kl,mn} = \langle mn|f_{12}^2|kl\rangle - \langle mno|f_{12}\hat{P}'_2 f_{23}|olk\rangle - \langle mno|f_{12}\hat{P}'_1 f_{13}|kol\rangle + \langle mn|f_{12}|op\rangle\langle op|f_{12}|kl\rangle + \langle mn|f_{12}|ab\rangle\langle ab|f_{12}|kl\rangle. \quad (2.40)$$

Expanding the RI projection operators and decoupling the integrals yields the final expression

$$X_{mn,kl} = \langle mn|f_{12}^2|kl\rangle - \langle mn|f_{12}|op'\rangle\langle op'|f_{12}|kl\rangle - \langle mn|f_{12}|p'o\rangle\langle op'|f_{12}|lk\rangle + \langle mn|f_{12}|op\rangle\langle op|f_{12}|kl\rangle + \langle mn|f_{12}|ab\rangle\langle ab|f_{12}|kl\rangle. \quad (2.41)$$

Just as was the case for matrix element V_{kl}^{ij} the only approximation used in the evaluation of $X_{kl,mn}$ is the RI approximation which makes the derivation of $X_{kl,mn}$ valid for all ansatz **2** methods.

2.1.4 Matrix C

The matrix element $C_{kl,ab}^{ij}$ given by equation 2.7 reduces under the EBC to

$$C_{kl,ab}^{ij} = (\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j)\langle kl|f_{12}\hat{Q}_{12}|ab\rangle. \quad (2.42)$$

Expansion of the operator $\hat{Q}_{12}$ yields the expression

$$C_{kl,ab}^{ij} = (\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j)\Big\{\langle kl|f_{12}|ab\rangle - \langle kl|f_{12}\hat{O}_1|ab\rangle - \langle kl|f_{12}\hat{O}_2|ab\rangle + \langle kl|f_{12}\hat{O}_1\hat{O}_2|ab\rangle - \langle kl|f_{12}\hat{V}_1\hat{V}_2|ab\rangle\Big\}, \quad (2.43)$$

which upon insertion of the definition of the occupied and virtual projectors gives

$$C^{ij}_{kl,ab} = (\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j)\left\{\langle kl|f_{12}|ab\rangle - \langle klm|f_{12}|mba\rangle \right.$$
$$\left. -\langle klm|f_{12}|amb\rangle + \langle klmn|f_{12}|mnab\rangle - \langle klcd|f_{12}|cdab\rangle\right\}. \quad (2.44)$$

Factorising the integrals in the above expression gives

$$C^{ij}_{kl,ab} = (\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j)\left\{\langle kl|f_{12}|ab\rangle - \langle kl|f_{12}|mb\rangle\langle m|a\rangle \right.$$
$$\left. -\langle kl|f_{12}|am\rangle\langle m|b\rangle + \langle kl|f_{12}|mn\rangle\langle mn|ab\rangle - \langle kl|f_{12}|cd\rangle\langle cd|ab\rangle\right\} \quad (2.45)$$

where the overlap integrals can be simplified such that

$$\begin{aligned} C^{ij}_{kl,ab} &= (\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j)\left\{\langle kl|f_{12}|ab\rangle - \langle kl|f_{12}|cd\rangle\delta_{ac}\delta_{bd}\right\} \\ &= (\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j)\left\{\langle kl|f_{12}|ab\rangle - \langle kl|f_{12}|ab\rangle\right\} = 0. \end{aligned} \quad (2.46)$$

Thus, under the **2*** ansatz the matrix $C^{ij}_{kl,ab}$ does not require evaluation since it is zero.

2.2 The MP2-F12/2A and /2A' methods

These methods do not assume the EBC which has consequences on the way in which the matrix elements in the method are evaluated. In the previous section the projection operator chosen ensured orthogonality to both the occupied and virtual space. This was convenient as $C^{ij}_{kl,ab} = 0$. However, when the EBC cannot be assumed this form of $\hat{Q}_{12}$ does not allow the same sort of simplifications needed for the evaluation of matrix B as before. Because of this the projection operator that ensures orthogonality to the occupied space only

$$\hat{Q}_{12} = (1 - \hat{O}_1)(1 - \hat{O}_2) \quad (2.47)$$

will be used.

The new choice of projection operator and lack of EBC will affect all of the matrix elements. In the case of V and X it is only the form of $\hat{Q}_{12}$ that has an effect. Their new form can be obtained simply by deleting the last term of their **2***A' expressions to give

$$V^{ij}_{kl} = \langle kl|f_{12}r_{12}^{-1}|ij\rangle - \langle kl|f_{12}|mp'\rangle\langle mp'|r_{12}^{-1}|ij\rangle$$
$$- \langle kl|f_{12}|p'm\rangle\langle mp'|r_{12}^{-1}|ji\rangle + \langle kl|f_{12}|mn\rangle\langle mn|r_{12}^{-1}|ij\rangle, \quad (2.48)$$

and

$$X_{mn,kl} = \langle mn|f_{12}^2|kl\rangle - \langle mn|f_{12}|op'\rangle\langle op'|f_{12}|kl\rangle \\ - \langle mn|f_{12}|p'o\rangle\langle op'|f_{12}|lk\rangle + \langle mn|f_{12}|op\rangle\langle op|f_{12}|kl\rangle. \quad (2.49)$$

Matrix element B assumed the EBC in equation 2.31. However, using the different form of $\hat{Q}_{12}$ means that equation 2.31 still applies as only the GBC is now required for it to stand. Thus, as in the case of V and X the new expression for B is simply the previous one without the last term

$$B_{kl,mn} = \langle mn|f_{12}[\hat{T}_1 + \hat{T}_2, f_{12}]|kl\rangle - \langle mn|f_{12}|op'\rangle\langle op'|[\hat{T}_1 + \hat{T}_2, f_{12}]|kl\rangle \\ - \langle mn|f_{12}|op'\rangle\langle p'o|[\hat{T}_1 + \hat{T}_2, f_{12}]|lk\rangle + \langle mn|f_{12}|op\rangle\langle op|[\hat{T}_1 + \hat{T}_2, f_{12}]|kl\rangle. \quad (2.50)$$

2.2.1 Matrix C

This leaves matrix C; removing the restriction of the EBC means that matrix C is no longer zero. The expression for $C^{ij}_{kl,ab}$ is given by

$$C^{ij}_{kl,ab} = \langle kl|f_{12}\hat{Q}_{12}(\hat{f}_1 + \hat{f}_2 - \varepsilon_i - \varepsilon_j)|ab\rangle. \quad (2.51)$$

Using the different projection operator allows one to write

$$C^{ij}_{kl,ab} = \langle kl|[f_{12}, (\hat{f}_1 + \hat{f}_2 - \varepsilon_i - \varepsilon_j)]|ab\rangle + \langle kl|(\hat{f}_1 + \hat{f}_2 - \varepsilon_i - \varepsilon_j)f_{12}\hat{Q}_{12}|ab\rangle \quad (2.52)$$

using the GBC only. Making use of the hermiticity of the Fock operator and using the GBC to simplify the second term gives

$$C^{ij}_{kl,ab} = \langle kl|[f_{12}, (\hat{f}_1 + \hat{f}_2 - \varepsilon_i - \varepsilon_j)]|ab\rangle + (\varepsilon_k + \varepsilon_l - \varepsilon_i - \varepsilon_j)\langle kl|f_{12}\hat{Q}_{12}|ab\rangle. \quad (2.53)$$

The integral in the second term is identical to the one given in equation 2.42 except the form of $\hat{Q}_{12}$ has changed. Using the same method to evaluate this term with the different form of $\hat{Q}_{12}$ leads to

$$C^{ij}_{kl,ab} = \langle kl|[f_{12}, (\hat{f}_1 + \hat{f}_2 - \varepsilon_i - \varepsilon_j)]|ab\rangle + (\varepsilon_k + \varepsilon_l - \varepsilon_i - \varepsilon_j)\langle kl|f_{12}|ab\rangle. \quad (2.54)$$

The eigenvalues in the first term commute with f_{12}, as do all parts of the Fock operators except for the kinetic and exchange operators, thus

$$C^{ij}_{kl,ab} = \langle kl|[f_{12}, (\hat{T}_1 + \hat{T}_2 - \hat{K}_1 - \hat{K}_2)]|ab\rangle + (\varepsilon_k + \varepsilon_l - \varepsilon_i - \varepsilon_j)\langle kl|f_{12}|ab\rangle. \quad (2.55)$$

Expanding out the expression for $C^{ij}_{kl,ab}$ gives

$$C^{ij}_{kl,ab} = \langle kl|[f_{12}, \hat{T}_1 + \hat{T}_2]|ab\rangle - \langle kl|[f_{12}, \hat{K}_1 + \hat{K}_2]|ab\rangle + (\varepsilon_k + \varepsilon_l - \varepsilon_i - \varepsilon_j)\langle kl|f_{12}|ab\rangle. \tag{2.56}$$

The matrix $C^{ij}_{kl,ab}$ requires three integral classes, of which two classes occur elsewhere in the method leaving only the exchange integrals. The exchange term can be decomposed by expanding the commutator and separating out $\hat{K}_1$ and $\hat{K}_2$ yielding

$$\langle kl|[f_{12}, \hat{K}_1 + \hat{K}_2]|ab\rangle = \langle kl|f_{12}\hat{K}_1|ab\rangle + \langle kl|f_{12}\hat{K}_2|ab\rangle - \langle kl|\hat{K}_1 f_{12}|ab\rangle - \langle kl|\hat{K}_2 f_{12}|ab\rangle. \tag{2.57}$$

The next step is to make the RI approximation by inserting the projection operator $\hat{P}'$ in order to isolate the exchange operator

$$\begin{aligned}\langle kl|[f_{12}, \hat{K}_1 + \hat{K}_2]|ab\rangle \approx{}& \langle kl|f_{12}\hat{P}'_1\hat{K}_1|ab\rangle + \langle kl|f_{12}\hat{P}'_2\hat{K}_2|ab\rangle \\ &- \langle kl|\hat{K}_1\hat{P}'_1 f_{12}|ab\rangle - \langle kl|\hat{K}_2\hat{P}'_2 f_{12}|ab\rangle,\end{aligned} \tag{2.58}$$

and using the hermiticity of the operator expand to give

$$\begin{aligned}\langle kl|[f_{12}, \hat{K}_1 + \hat{K}_2]|ab\rangle ={}& \langle klp'|f_{12}\hat{K}_3|p'ba\rangle + \langle klp'|f_{12}\hat{K}_3|ap'b\rangle \\ &- \langle p'lk|\hat{K}_3 f_{12}|abp'\rangle - \langle kp'l|\hat{K}_3 f_{12}|abp'\rangle.\end{aligned} \tag{2.59}$$

The three-electron integrals then decompose to products

$$\begin{aligned}\langle kl|[f_{12}, \hat{K}_1 + \hat{K}_2]|ab\rangle ={}& \langle kl|f_{12}|p'b\rangle\langle p'|\hat{K}_1|a\rangle + \langle kl|f_{12}|ap'\rangle\langle p'|\hat{K}_1|b\rangle \\ &- \langle p'l|f_{12}|ab\rangle\langle k|\hat{K}_1|p'\rangle - \langle kp'|f_{12}|ab\rangle\langle l|\hat{K}_1|p'\rangle.\end{aligned} \tag{2.60}$$

The above expression contains F type integrals which occur elsewhere in the method, but also some one-electron exchange integrals which when expanded out, for example

$$\langle p'|\hat{K}_1|a\rangle = \langle p'i|r_{12}^{-1}|ia\rangle, \tag{2.61}$$

give special cases of two-electron J type integrals. These integrals can be evaluated by calculating the more general case $\langle p'i|r_{12}^{-1}|ja\rangle$ and then summing over the correct components where $j = i$.

In this chapter two distinct methods, the MP2-F12/**2***A' and MP2-F12/**2**A' methods, have been described as these were the ones derived and implemented during this PhD. There are many more flavours of MP2-R12 in existence which using similar methods could produce their F12 counterparts.

Chapter 3

Integrals

All the integrals for the programs described in the previous chapter will be constructed using Gaussian type orbital (GTO) basis sets [57]. Unnormalised Cartesian Gaussian functions have the form

$$|\mathbf{a}) \equiv g(\vec{r}, \alpha, \mathbf{a}, \vec{A}) = (x - A_x)^{a_x} (y - A_y)^{a_y} (z - A_z)^{a_z} \exp\left\{-\alpha|\vec{r} - \vec{A}|^2\right\} \tag{3.1}$$

where $\vec{r}$ represents the coordinates of the electron and where $\vec{A}$ is the centre of the Gaussian function. The orbital exponent is given by α, and $\mathbf{a}$ is the vector of angular momentum exponents

$$\mathbf{a} = (a_x, a_y, a_z) \tag{3.2}$$

where a_x, a_y and a_z are nonnegative integers. These are then transformed to spherical Gaussians, contracted and normalised using standard routines in MOLPRO [58].

The integrals that arise from the derivations of the MP2-F12 methods are either four-index two-electron integrals or six-index three-electron integrals. There are several methods of integral evaluation in existence for evaluating Coulomb integrals of which the most important are: Obara and Saika (OS) [59]; McMurchie and Davidson (MD) [60]; Pople and Hehre (PH) [61]; and Dupuis, Rys and King (DRK) [62, 63]. All of these methods work directly for integrals in four-index form.

Obara & Saika Integral Evaluation

The OS [59] integral method produces expressions in the form of recursive formulae with respect to the angular momentum of functions in the integral. This means any integral can be represented as a linear combination of lower angular momentum integrals, with the exception of the zero angular momentum case which must always be explicitly calculated. This method of integral evaluation will be used in this work for three reasons. Firstly, the expressions are relatively simple both to derive and to implement for all the integral classes required. Secondly, the expressions are entirely general for all values of angular momentum which is ideal as the code will continue to function when the angular momentum in the basis set is increased. Finally, the OS method is fast in terms of CPU time, and compares well if not better than many of the other methods available; see section V of [59].

McMurchie & Davidson Integral Evaluation

The MD [60] integral method is based around using one-centre Hermite Gaussian functions to represent Gaussian overlap distributions. Hermite Gaussian functions, like their Cartesian counterparts, are separable and can be represented as

$$h(\vec{r},\alpha,\mathbf{a},\vec{A}) = \left(\frac{\partial}{\partial A_x}\right)^{a_x}\left(\frac{\partial}{\partial A_y}\right)^{a_y}\left(\frac{\partial}{\partial A_z}\right)^{a_z}\exp[-\alpha|\vec{r}-\vec{A}|^2], \tag{3.3}$$

where the definition of $\vec{r}$, $\vec{A}$, α and $\mathbf{a}$ are analogous with the definitions for Cartesian Gaussian functions. This results in the integration over two-centre functions being reduced to a set of integrals over one-centre functions. The resulting one-centre functions by their nature are well suited to integration. A set of recurrence relations can then be derived using these one-centre Hermite functions.

Pople & Hehre Integral Evaluation

The PH [61] integral evaluation method is based on using a local coordinate system and is exceptionally fast compared to many of the other methods. However there are several problems related to the method including rounding errors and most notably the inability to apply the method to integrals containing angular momentum greater than p functions. This certainly makes this method of integral evaluation a non-starter for the MP2-F12 methods as they require basis sets with angular momentum functions greater than p functions.

Dupuis, Rys and King Integral Evaluation

The DRK [62, 63] method of integral evaluation is the very different from the OS and MD methods which both require evaluation of the Boys function [57] when evaluating Coulomb integrals. The DRK method employs a Gaussian quadrature scheme which creates an entirely different method for evaluation of integrals. For basis functions of angular momentum greater than zero there are polynomial-like terms in the x, y and z direction. Their integrands can be exactly represented as a sum of polynomials. The number of polynomials required is double the maximum cardinality of the original polynomial. A weight function is needed, and in the case of a Gaussian integral one chooses the exponential part to perform this task. This gives rise to a very efficient quadrature scheme which is exact for Gaussian integrals. Integrals over other functions and operators can be approximated by increasing the number of integration points and careful choice of the weight function.

Integrals and Indices

In order to speed up the evaluation of integrals the DF approximation is used which results in the need for three-index integrals. Details of the DF approximation will be given in the next section. The three-index integrals are built from two-index integrals using the Gaussian product theorem (GPT). More details of the GPT will follow shortly.

Firstly it is necessary to introduce some new notation for writing integrals. Mulliken notation, or charge density notation as it is otherwise known, can be used instead of the normal Dirac notation. As the nomenclature implies the new notation represents integrals in terms of charge density denoted by a change in shape of the 'bra-ket' and a reordering of the indices. For example a four-index two-electron Coulomb integral can be represented in both Dirac and Mulliken notation as,

$$\langle pq|r_{12}^{-1}|rs\rangle \equiv (pr|r_{12}^{-1}|qs) \equiv (pr|qs). \tag{3.4}$$

The indices on the right of equation 3.4 now correspond to densities $|pr)$ for electron one and $|qs)$ for electron two. Now that the indices in each of these densities correspond to the same electron it is possible to contract the indices by either the GPT or DF approximation.

The Gaussian Product Theorem

The GPT [57] is the most common method of reducing indices as it allows the product of two Gaussian functions

$$g_1 g_2 = g(\vec{r}, \alpha, \mathbf{a}, \vec{A}) g(\vec{r}, \beta, \mathbf{b}, \vec{B}) \tag{3.5}$$

to be represented *exactly* as a small expansion in single Gaussian functions. The simplest case of two Gaussian functions with zero angular momentum is expressed as

$$g(\vec{r}, \alpha, \mathbf{0}, \vec{A}) g(\vec{r}, \beta, \mathbf{0}, \vec{B}) = \exp\left\{-\alpha|\vec{r} - \vec{A}|^2\right\} \exp\left\{-\beta|\vec{r} - \vec{B}|^2\right\} \tag{3.6}$$

which can be algebraically rearranged to give

$$\begin{aligned} g(\vec{r}, \alpha, \mathbf{0}, \vec{A}) g(\vec{r}, \beta, \mathbf{0}, \vec{B}) &= \exp\left\{-\xi|\overline{\mathrm{AB}}|^2\right\} \exp\left\{-\zeta|\vec{r} - \vec{P}|^2\right\} \\ &= \exp\left\{-\xi|\overline{\mathrm{AB}}|^2\right\} g(\vec{r}, \zeta, \mathbf{0}, \vec{P}) \end{aligned} \tag{3.7}$$

where

$$\zeta = \alpha + \beta, \qquad \xi = \frac{\alpha\beta}{\zeta}, \qquad \vec{P} = \frac{\alpha\vec{A} + \beta\vec{B}}{\zeta}, \qquad \text{and} \qquad \overline{\mathrm{AB}} = \vec{A} - \vec{B}. \tag{3.8}$$

For the more general case of arbitrary angular momentum shown in equation 3.5 the expansion is more complicated and is given by

$$\begin{aligned} g_1 g_2 = &(x - A_x)^{a_x} (y - A_y)^{a_y} (z - A_z)^{a_z} \exp\left\{-\alpha|\vec{r} - \vec{A}|^2\right\} \\ &\times (x - B_x)^{b_x} (y - B_y)^{b_y} (z - B_z)^{b_z} \exp\left\{-\beta|\vec{r} - \vec{B}|^2\right\}. \end{aligned} \tag{3.9}$$

The first obvious step when attempting to combine the Gaussian functions is to substitute in equation 3.7 to take care of the exponential terms

$$\begin{aligned} g_1 g_2 = &\exp\left\{-\xi|\overline{\mathrm{AB}}|^2\right\} \exp\left\{-\zeta|\vec{r} - \vec{P}|^2\right\} \\ &\times (x - A_x)^{a_x} (y - A_y)^{a_y} (z - A_z)^{a_z} (x - B_x)^{b_x} (y - B_y)^{b_y} (z - B_z)^{b_z}. \end{aligned} \tag{3.10}$$

Terms such as $(x - A_x)^{a_x}$ must be expressed using a binomial expansion

$$(x - A_x)^{a_x} = [(x - P_x) + \mathrm{PA}_x]^{a_x} = \sum_{i=0}^{a_x} \binom{a_x}{i} (x - P_x)^i \mathrm{PA}_x^{a_x - i} \tag{3.11}$$

and this allows everything to be shifted to the new centre $\vec{P}$. Products of such terms of the same Cartesian coordinate can be thus be represented as follows

$$\begin{aligned}(x-A_x)^{a_x}(x-B_x)^{b_x} &= \sum_{i=0}^{a_x}\binom{a_x}{i}(x-P_x)^i \mathrm{PA}_x^{a_x-i}\sum_{j=0}^{b_x}\binom{b_x}{j}(x-P_x)^j \mathrm{PB}_x^{b_x-j} \\ &= \sum_{k=0}^{a_x+b_x}(x-P_x)^k f_k(a_x,b_x,\mathrm{PA}_x,\mathrm{PB}_x) \qquad (3.12)\end{aligned}$$

where

$$\begin{aligned}f_k(a_x,b_x,\mathrm{PA}_x,\mathrm{PB}_x) = & \sum_{i=0,a_x}^{i+j=k}\sum_{j=0,b_x}\binom{a_x}{i}\binom{b_x}{j}\mathrm{PA}_x^{a_x-i}\mathrm{PB}_x^{b_x-j} \\ &= \sum_{i=0}^{k}\binom{a_x}{i}\binom{b_x}{k-i}\mathrm{PA}_x^{a_x-i}\mathrm{PB}_x^{b_x-k+i}. \qquad (3.13)\end{aligned}$$

Substituting expressions of the kind above for each of the Cartesian coordinates yields the final expression for the new single-centred Gaussian expansion

$$\begin{aligned}g_1g_2 = &\exp\left\{-\xi|\overline{\mathrm{AB}}|^2\right\}\exp\left\{-\zeta|\vec{r}-\vec{P}|^2\right\}\times \\ &\left[\sum_{i=0}^{a_x+b_x}(x-P_x)^i f_i(a_x,b_x,\mathrm{PA}_x,\mathrm{PB}_x)\right]\times \\ &\left[\sum_{j=0}^{a_y+b_y}(y-P_y)^j f_j(a_y,b_y,\mathrm{PA}_y,\mathrm{PB}_y)\right]\times \\ &\left[\sum_{k=0}^{a_z+b_z}(z-P_z)^k f_k(a_z,b_z,\mathrm{PA}_z,\mathrm{PB}_z)\right]. \qquad (3.14)\end{aligned}$$

When applied to integrals the GPT can be used to reduce a four-index integral to a sum of three-index integrals

$$(\mathbf{ab}|r_{12}^{-1}|\mathbf{cd}) = \sum_p T_p^{ab}(\mathbf{p}|r_{12}^{-1}|\mathbf{cd}), \qquad (3.15)$$

with transformation coefficients

$$T_p^{ab} = f_{p_x}(a_x,b_x,\mathrm{PA}_x,\mathrm{PB}_x)f_{p_y}(a_y,b_y,\mathrm{PA}_y,\mathrm{PB}_y)f_{p_z}(a_z,b_z,\mathrm{PA}_z,\mathrm{PB}_z)\exp\left\{-\xi|\overline{\mathrm{AB}}|^2\right\}. \qquad (3.16)$$

The GPT can be used once again to reduce the integral to a two-index integral, thus giving

$$(\mathbf{ab}|r_{12}^{-1}|\mathbf{cd}) = \sum_{pq} T_p^{ab}T_q^{cd}(\mathbf{p}|r_{12}^{-1}|\mathbf{q}), \qquad (3.17)$$

with additional set of transformation coefficients T_q^{cd}.

The form of F12

In order to evaluate the integrals a form of f_{12} must be decided. The important factors when deciding the form of f_{12} are that the resulting integrals have analytical solutions and that the shape of f_{12} reflects a sensible choice of correlation factor. The argument of the shape of the correlation factor is similar to the choice of atomic orbital basis functions: STOs would be best, but GTOs are easier. Therefore we choose a Gaussian expansion for f_{12} for ease of implementation. This also conveniently solves the problem of the shape of the function when it is noted that a linear combination of Gaussians can be used to least squares fit to almost any function of choice. This linear combination of Gaussians is written explicitly as

$$f_{12} = c_i \exp\left\{-\gamma_i r_{12}^2\right\}, \tag{3.18}$$

and is defined by a Gaussian geminal basis set of exponents γ_i and coefficients c_i. Frozen geminals have been discussed in the work of Persson and Taylor [64, 65] and also by Ten-no [37, 38].

The least squares fitting method briefly goes as follows. From a list of exponents γ the vector $\mathbf{a}$ and matrix $\mathbf{A}$ are constructed as

$$a_i = \int_0^\infty dr f(r) w(r) e^{-\gamma_i r^2} \qquad \text{and} \qquad A_{ij} = \int_0^\infty dr\; w(r) e^{-(\gamma_i+\gamma_j) r^2} \tag{3.19}$$

where $f(r)$ is the function being fitted and $w(r)$ is a known as the weight function, for example $\exp\{-\omega r^2\}$, and is used for damping. The coefficients for each Gaussian function $\mathbf{c}$ are then determined by solving the matrix equation

$$\mathbf{A}\mathbf{c} = \mathbf{a}. \tag{3.20}$$

3.1 Density Fitting

The DF method is an approximation in which an orbital product density is expanded in an auxiliary basis. The advantage of using the DF approximation over the GPT is that computationally the DF approximation is significantly faster and allows calculation of problems that would otherwise prove inaccessible.

As mentioned in the previous section the DF approximation is a method for reducing the quantity of indices in the integrals, thereby increasing the speed of evaluation. As the DF approximation is a non-exact method there will be an error compared to exact methods such as the GPT.

The DF approximation has been in use in many contexts over a long period of time, often not explicitly referred to by the DF title. Perhaps the first use of a DF like approximation was made by Boys and Shavitt in their calculation of the potential energy surface of H_3 using STOs [66]. During their calculation they avoid the evaluation of the intractable three-centre Coulomb integrals by performing a least squares fit of two-centre products in a small auxiliary basis set. DF also made an early appearance in density functional theory (DFT) [67] also using STO basis sets with least squares fitting.

A key paper in the history of the DF approximation is that of Whitten [68]. As briefly mentioned in the previous section the DF approximation can be used to represent an orbital product density in an auxiliary basis

$$|pq) \approx |\widetilde{pq}) = D^A_{pq}|A). \tag{3.21}$$

Thus an integral $(pq|rs)$ can be approximated using DF as

$$(pq|rs) \approx (\widetilde{pq}|\widetilde{rs}) = D^A_{pq}D^B_{rs}(A|B), \tag{3.22}$$

resulting in the need for calculation of the integrals $(A|B)$ and coefficients D^A_{pq}. Whitten came to two important conclusions in his work. Firstly he concluded that the coefficients that best describe $|pq)$, namely D^A_{pq}, are entirely independent of the ket density $|rs)$. This is very important since if it were not the case then the DF approximation would increase the work required to evaluate the said integral. The second conclusion made was that the coefficients D^A_{pq} should be obtained not by using least squares fitting but rather by minimising

$$\Delta_{pq} = (pq - \widetilde{pq}|pq - \widetilde{pq}). \tag{3.23}$$

The quantity Δ_{pq} is the Coulomb energy of the fitting residual $|pq - \widetilde{pq})$ and is a measure of the error in the fitting. This second conclusion was also made independently by Dunlap *et al.* [69] when addressing fitting whole densities in DFT.

Since the integrals $(A|B)$ can be readily evaluated all that is left is to obtain the coefficients. The method as mentioned above is to minimise Δ_{pq} which is achieved by setting

$$\frac{\partial \Delta_{pq}}{\partial D^A_{pq}} = 0. \tag{3.24}$$

The expression for Δ_{pq} is given in equation 3.23 and can be expanded as

$$\Delta_{pq} = (pq|pq) - D^A_{pq}(A|pq) - D^B_{pq}(pq|B) + D^A_{pq}D^B_{pq}(A|B). \tag{3.25}$$

Differentiating with respect to D^A_{pq} and setting to zero yields the following linear equation

$$\frac{\partial \Delta_{pq}}{\partial D^A_{pq}} = -2(A|pq) + 2D^B_{pq}(A|B) = 0. \tag{3.26}$$

Here it is convenient to introduce a compact notation for writing Coulomb integrals, illustrated by the examples $J^A_B = (A|B)$ and $J^A_{pq} = (A|pq)$. Using this notation we can rewrite equation 3.26 as

$$-J^A_{pq} + D^B_{pq}J^A_B = 0, \tag{3.27}$$

which is simply rearranged to give the expression for the coefficients

$$D^B_{pq} = J^A_{pq}(\mathbf{J}^{-1})^A_B. \tag{3.28}$$

Having determined the coefficients the integral $(pq|rs)$ can be written using the DF approximation as

$$(pq|rs) \approx (\widetilde{pq}|\widetilde{rs}) = J^A_{pq}(\mathbf{J}^{-1})^A_B J^B_{rs}. \tag{3.29}$$

One must now consider the error in an integral evaluated using the DF approximation. The expression for the error between the exact and fitted integral is given by

$$(pq|rs) - (\widetilde{pq}|\widetilde{rs}) = (pq - \widetilde{pq}|rs - \widetilde{rs}) + (\widetilde{pq}|rs - \widetilde{rs}) + (pq - \widetilde{pq}|\widetilde{rs}). \tag{3.30}$$

The last two terms in the above equation are zero as shown by equation 3.26 which leaves

$$(pq|rs) - (\widetilde{pq}|\widetilde{rs}) = (pq - \widetilde{pq}|rs - \widetilde{rs}), \tag{3.31}$$

as the expression for the error in performing the fitting. The above expression shows that the error associated with fitting the integral is quadratic in the error of fitting the densities. Expressions of this kind are known as *robust* fitting expressions. This analysis was first conducted by Dunlap [69], whose more recent accounts of robust fitting in various contexts including DFT can be found in the literature [70, 71].

The concise notation introduced above to represent Coulomb integrals is now expanded for greater generality. Brackets are placed around the J to signify the type of notation being used, i.e. Dirac or Mulliken. For example the integral $(pq|rs)$ can be written as either $(J)^{pq}_{rs}$ or as $\langle J\rangle^{pr}_{qs}$ (note the order of the indices). Different classes of integrals are represented by replacing J with the abbreviated form of the operator, for instance F in the case of f_{12}.

There are several other classes of two-electron integral that must be fitted in the MP2-F12 methods, and it is important to make sure they are fitted robustly [52, 72]. If one considers a general two-electron integral with operator $\hat{O}$ then performing the same process as for the Coulomb integrals we would expect the integral to be approximated as

$$(pq|\hat{O}|rs) \approx (\widetilde{pq}|\hat{O}|\widetilde{rs}) = D^{A}_{pq} D^{B}_{rs} (A|\hat{O}|B). \tag{3.32}$$

The coefficients can then be obtained by minimising

$$\Delta_{pq} = (pq - \widetilde{pq}|\hat{O}|pq - \widetilde{pq}), \tag{3.33}$$

which on setting to zero gives

$$\frac{\partial \Delta_{pq}}{\partial D^{A}_{pq}} = -2(A|\hat{O}|pq) + 2D^{B}_{pq}(A|\hat{O}|B) = 0, \tag{3.34}$$

and yields

$$D^{B}_{pq} = (O)^{A}_{pq} (\mathbf{O}^{-1})^{A}_{B}. \tag{3.35}$$

This would seem to give a general method for fitting all types of integral. However, this can only work if Δ_{pq} is positive or, equivalently, if $\hat{O}$ is positive definite. This condition arises from the need to invert $(O)^{A}_{B}$ when calculating the coefficients. There are ways of working around this requirement for certain types of integral, for example integrals of the form $(pq|r_{12}|rs)$ [73]. However the fitting is not always as accurate as required and a more general fitting scheme is desirable. As seen previously, fitting using the r_{12}^{-1} criterion is very successful owing to the positive definite nature of the Coulomb operator.

A fitting scheme using the Coulomb fitting criterion gives a method of fitting that works for most integral types. However, when the Coulomb fitting criterion is used for different integral types the equations become non-robust. A non-robust fitting scheme introduces unacceptable errors in the fitting and so a robust scheme [70, 71] using the Coulomb fitting criterion must be used. This fitting scheme has the form

$$(pq|\hat{O}|rs) \approx (\widetilde{pq}|\hat{O}|rs) + (pq|\hat{O}|\widetilde{rs}) - (\widetilde{pq}|\hat{O}|\widetilde{rs}) \tag{3.36}$$

and once again reduces the error in the integral to be quadratic in the error in the fitting. To illustrate this explicitly with an example the integral $(F)^{pq}_{rs}$ is given robustly by

$$(F)^{pq}_{rs} \approx (J)^{pq}_{A}(\mathbf{J}^{-1})^{A}_{B}(F)^{B}_{rs} + (F)^{pq}_{A}(\mathbf{J}^{-1})^{A}_{B}(J)^{B}_{rs} - (J)^{pq}_{A}(\mathbf{J}^{-1})^{A}_{B}(F)^{B}_{C}(J)^{D}_{rs}(\mathbf{J}^{-1})^{C}_{D}. \tag{3.37}$$

The above formula generalises for many of the operators that appear in the R12 and F12 theories reducing them to three-index objects which are then subsequently reduced to two-index objects using the GPT.

However, the commutator integrals over the remaining operators have to be treated slightly differently. Take for example the operator $[\hat{t}_1, f_{12}]$, the commutator of kinetic energy and f_{12}, which contains the differential operator $\hat{t}_1 = -\frac{1}{2}\nabla_1^2$. A complication arises when converting from Dirac to Mulliken notation

$$\langle pr|[\hat{t}_1, f_{12}]|qs\rangle \equiv (pq|[\hat{t}_1, f_{12}]|rs) \tag{3.38}$$

because the Mulliken notation does not show explicitly that the operator $\hat{t}_1$ is only acting upon the p-index, not on the whole density $|pq)$. A simple solution would be to fit the integral non-robustly, i.e.

$$(pq|[\hat{t}_1, f_{12}]|rs) \approx (pq|[\hat{t}_1, f_{12}]|\widetilde{rs}) \approx (FT)^{pq}_A(\mathbf{J}^{-1})^A_B(J)^B_{rs}, \tag{3.39}$$

where

$$(FT)^{pq}_A = (pq|[\hat{t}_1, f_{12}]|A), \tag{3.40}$$

as the problems only arise in fitting the density $|pq)$. However not performing the fitting robustly leads to large errors in the integrals as shown by Manby [52]. The solution is to observe

$$\langle pr|[\hat{t}_1, f_{12}]|qs\rangle = ([pq]|f_{12}|rs), \tag{3.41}$$

where

$$|[pq]) = |\{\hat{t}_1 p\}q - p\hat{t}_1 q). \tag{3.42}$$

The object $|[pq])$ is itself a density, and can also be fitted as before to give a robust fitting expression similar to that of a multiplicative operator

$$\begin{aligned}([pq]|f_{12}|rs) \approx (Y)^{pq}_A(\mathbf{J}^{-1})^A_B(F)^B_{rs} + (FT)^{pq}_A(\mathbf{J}^{-1})^A_B(J)^B_{rs} \\ - (Y)^{pq}_A(\mathbf{J}^{-1})^A_B(F)^B_C(\mathbf{J}^{-1})^C_D(J)^D_{rs},\end{aligned} \tag{3.43}$$

where the letter Y denotes the Coulomb integral over $[pq]$

$$(Y)^{pq}_A = (\{\hat{t}_1 p\}q - p\hat{t}_1 q|A). \tag{3.44}$$

3.2 Recurrence Relations

From the derivations of the MP2-F12 methods it is clear that many classes of integrals must be evaluated. In the case of four-index integrals these will all be decomposed by use of the DF approximation and GPT to two-index integrals, and in the case of six-index integrals they will be reduced to three-index integrals. The nomenclature of table 3.1 will be used from now onwards to refer to the integrals.

Name	Definition
S	$\langle \mathbf{a} \vert \mathbf{b} \rangle$
J	$(\mathbf{a} \vert \mathbf{b})$
G	$(\mathbf{a} \vert e^{-\gamma r_{12}^2} \vert \mathbf{b})$
F	$(\mathbf{a} \vert f_{12} \vert \mathbf{b})$
GJ	$(\mathbf{a} \vert e^{-\gamma r_{12}^2} r_{12}^{-1} \vert \mathbf{b})$
FJ	$(\mathbf{a} \vert f_{12} r_{12}^{-1} \vert \mathbf{b})$
FF	$(\mathbf{a} \vert f_{12}^2 \vert \mathbf{b})$
FT	$(\mathbf{ab} \vert [\hat{t}_1, f_{12}] \vert \mathbf{c})$
FTF	$(\mathbf{a} \vert \frac{1}{2}[f_{12}, [\hat{t}_1 + \hat{t}_2, f_{12}]] \vert \mathbf{b})$
F-F	$(\mathbf{a} \vert f_{12} \vert \mathbf{b} \vert f_{23} \vert \mathbf{c})$
J-F	$(\mathbf{a} \vert r_{12}^{-1} \vert \mathbf{b} \vert f_{23} \vert \mathbf{c})$
X	$(\mathbf{ab} \vert [\hat{t}_1, r_{12}] \vert \mathbf{c})$
Y	$(\mathbf{ab} \vert [\hat{t}_1, r_{12}^{-1}] \vert \mathbf{c})$

Table 3.1: Nomenclature of integrals. Bold characters denote Cartesian Gaussian primitives.

A key concept in constructing integrals is the concept of ’integral shells’. Recurrence relations inherently build upon previous results, and in the case of the integral recurrence relations the recursion is over angular momentum components of the Cartesian Gaussian functions. Thus for integrals over d functions integrals over both s and p functions are required. In the case of two-index integrals lower angular momentum is required for both Cartesian Gaussian functions. An example of the complete shell that is required for a normal implementation of a recurrence relation for a two-index integral with d angular momentum in both functions is shown in figure 3.1. Sections with the same shading share the same quantity of angular momentum.

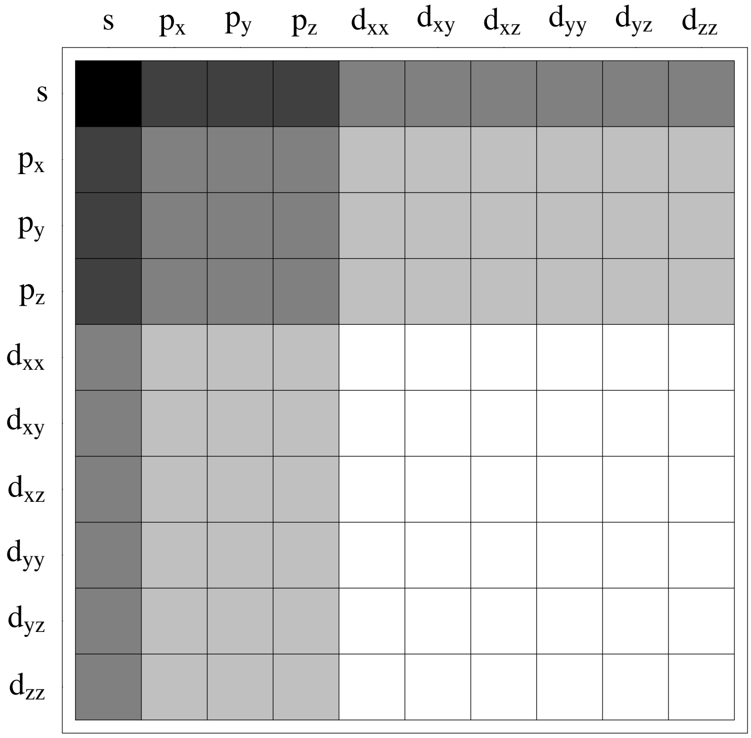

Figure 3.1: A ’shell’ of integrals up to angular momentum d for both functions $|\mathbf{a})$ and $|\mathbf{b})$.

As discussed previously the Obara and Saika method of integral evaluation will form the basis of all of the integral recurrence relations. The key relation when deriving these integrals is the derivative expression

$$\frac{\partial}{\partial A_i} g(\vec{r}, \alpha, \mathbf{a}, \vec{A}) = 2\alpha g(\vec{r}, \alpha, \mathbf{a} + \mathbf{1}_i, \vec{A}) - a_i g(\vec{r}, \alpha, \mathbf{a} - \mathbf{1}_i, \vec{A}) \tag{3.45}$$

where i can take the value of x, y or z and where $\mathbf{1}_i = (\delta_{ix}, \delta_{iy}, \delta_{iz})$ is defined in terms of the Kronecker delta.

Integral class S — overlap integrals

Recurrence relations for the integral class S, two-index one-electron overlap integrals, have already been derived [59], but warrant some attention here since these form the basis of many of the derivations presented in this work. The two-index one-electron overlap integrals are defined explicitly as

$$\langle \mathbf{a} | \mathbf{b} \rangle = \int d\vec{r}\, g(\vec{r}, \alpha, \mathbf{a}, \vec{A}) g(\vec{r}, \beta, \mathbf{b}, \vec{B}). \tag{3.46}$$

According to equation 3.45 the integral $\langle \mathbf{a} + \mathbf{1}_i | \mathbf{b} \rangle$ can be decomposed as

$$\langle \mathbf{a} + \mathbf{1}_i | \mathbf{b} \rangle = \frac{1}{2\alpha} \frac{\partial}{\partial A_i} \langle \mathbf{a} | \mathbf{b} \rangle + \frac{a_i}{2\alpha} \langle \mathbf{a} - \mathbf{1}_i | \mathbf{b} \rangle. \tag{3.47}$$

The integral $\langle \mathbf{a} | \mathbf{b} \rangle$ can be factored using the GPT as

$$\begin{aligned} \langle \mathbf{a} | \mathbf{b} \rangle = \int d\vec{r}\, \exp\left\{-\zeta |\vec{r} - \vec{P}|^2\right\} \exp\left\{-\xi |\overline{\mathrm{AB}}|^2\right\} \left[\sum_{i=0}^{a_x + b_x} (x - P_x)^i f_i(a_x, b_x, \mathrm{PA}_x, \mathrm{PB}_x) \right] \\ \times \left[\sum_{j=0}^{a_y + b_y} (y - P_y)^j f_j(a_y, b_y, \mathrm{PA}_y, \mathrm{PB}_y) \right] \left[\sum_{k=0}^{a_z + b_z} (z - P_z)^k f_k(a_z, b_z, \mathrm{PA}_z, \mathrm{PB}_z) \right] \end{aligned} \tag{3.48}$$

where the objects such as $f_i(a_x, b_x, \mathrm{PA}_x, \mathrm{PB}_x)$ are defined in equation 3.13. Rearranging the above expression and factorising the integral over $\vec{r}$ into its Cartesian components yields

$$
\begin{aligned}
\langle \mathbf{a}|\mathbf{b}\rangle = {} & \exp\left\{-\xi|\overline{\mathrm{AB}}|^2\right\} \\
& \times \left[\sum_{i=0}^{a_x+b_x} f_i(a_x, b_x, \mathrm{PA}_x, \mathrm{PB}_x) \int dx\ (x-P_x)^i \exp\left\{-\zeta(x-P_x)^2\right\}\right] \\
& \times \left[\sum_{j=0}^{a_y+b_y} f_j(a_y, b_y, \mathrm{PA}_y, \mathrm{PB}_y) \int dy\ (y-P_y)^j \exp\left\{-\zeta(y-P_y)^2\right\}\right] \\
& \times \left[\sum_{k=0}^{a_z+b_z} f_k(a_z, b_z, \mathrm{PA}_z, \mathrm{PB}_z) \int dz\ (z-P_z)^k \exp\left\{-\zeta(z-P_z)^2\right\}\right]. \qquad (3.49)
\end{aligned}
$$

Integrals of the form

$$\int_{-\infty}^{\infty} dx\ (x-P_x)^i \exp\left\{-\zeta(x-P_x)^2\right\} = \int_{-\infty}^{\infty} du\ u^i \exp\left\{-\zeta u^2\right\} \qquad (3.50)$$

must be evaluated (where the substitution $u = x - P_x$ has been used). These integrals have a known result which is given by

$$\int_{-\infty}^{\infty} du\ u^i \exp\left\{-\zeta u^2\right\} = \frac{(i-1)!!}{2\zeta^{i/2}}\left(\frac{\pi}{\zeta}\right)^{1/2} \qquad (3.51)$$

if i is even and zero otherwise. Using the above relationship the integration in equation 3.49 can be completed to give

$$
\begin{aligned}
\langle \mathbf{a}|\mathbf{b}\rangle = {} & \exp\left\{-\xi|\overline{\mathrm{AB}}|^2\right\} \\
& \times \left[\sum_{i=0}^{a_x+b_x} f_i(a_x, b_x, \mathrm{PA}_x, \mathrm{PB}_x) \frac{(i-1)!!}{2\zeta^{i/2}}\left(\frac{\pi}{\zeta}\right)^{1/2}\right] \\
& \times \left[\sum_{j=0}^{a_y+b_y} f_j(a_y, b_y, \mathrm{PA}_y, \mathrm{PB}_y) \frac{(j-1)!!}{2\zeta^{j/2}}\left(\frac{\pi}{\zeta}\right)^{1/2}\right] \\
& \times \left[\sum_{k=0}^{a_z+b_z} f_k(a_z, b_z, \mathrm{PA}_z, \mathrm{PB}_z) \frac{(k-1)!!}{2\zeta^{k/2}}\left(\frac{\pi}{\zeta}\right)^{1/2}\right]. \qquad (3.52)
\end{aligned}
$$

Now all that is needed is to evaluate

$$\frac{1}{2\alpha}\frac{\partial}{\partial A_i}\langle \mathbf{a}|\mathbf{b}\rangle. \qquad (3.53)$$

To proceed the product rule is used on the expression for $\langle \mathbf{a}|\mathbf{b}\rangle$ in equation 3.52. The product being between the exponential part

$$\frac{1}{2\alpha}\frac{\partial}{\partial A_i}\exp\left\{-\xi|\overline{\mathrm{AB}}|^2\right\} = \frac{\xi \mathrm{BA}_i}{\alpha}\exp\left\{-\xi|\overline{\mathrm{AB}}|^2\right\} \qquad (3.54)$$

and the non-exponential parts. The non-exponential parts have only one term that contains A_i with the rest of the expression being constant. Concentrating on this part only

$$\frac{\partial}{\partial A_i} f_k(a_i, b_i, \mathrm{PA}_i, \mathrm{PB}_i) = \frac{\partial}{\partial A_i} \sum_{j=0}^{k} \binom{a_i}{j} \binom{b_i}{k-j} \mathrm{PA}_i^{a_i-j} \mathrm{PB}_i^{b_i-k+j} \tag{3.55}$$

and using the product rule yields

$$\frac{\partial}{\partial A_i} f_k(a_i, b_i, \mathrm{PA}_i, \mathrm{PB}_i) = \sum_{j=0}^{k} \binom{a_i}{j} \binom{b_i}{k-j} \times$$
$$\left(-\frac{\beta}{\alpha+\beta}(a_i - j)\mathrm{PA}_i^{a_i-j-1} \mathrm{PB}_i^{b_i-k+j} - \mathrm{PA}_i^{a_i-j} \frac{\alpha}{\alpha+\beta}(b_i - k + j)\mathrm{PB}_i^{b_i-k+j-1} \right). \tag{3.56}$$

Using the equalities

$$\binom{a_i}{j}(a_i - j) = a_i \binom{a_i - 1}{j} \quad \text{and} \quad \binom{b_i}{k-j}(b_i - k + j) = b_i \binom{b_i - 1}{k-j} \tag{3.57}$$

the differential can be written as

$$\begin{aligned} \frac{\partial}{\partial A_i} f_k(a_i, b_i, \mathrm{PA}_i, \mathrm{PB}_i) = &- \frac{\beta}{\alpha+\beta} a_i \sum_{j=0}^{k} \binom{a_i - 1}{j} \binom{b_i}{k-j} \mathrm{PA}_i^{a_i-j-1} \mathrm{PB}_i^{b_i-k+j} \\ &- \frac{\alpha}{\alpha+\beta} b_i \sum_{j=0}^{k} \binom{a_i}{j} \binom{b_i - 1}{k-j} \mathrm{PA}_i^{a_i-j} \mathrm{PB}_i^{b_i-k+j-1}. \end{aligned} \tag{3.58}$$

By inspection this can be seen to be

$$\frac{\partial}{\partial A_i} f_k(a_i, b_i, \mathrm{PA}_i, \mathrm{PB}_i) = - \frac{\beta}{\alpha+\beta} a_i f_k(a_i - 1, b_i, \mathrm{PA}_i, \mathrm{PB}_i) \tag{3.59}$$
$$- \frac{\alpha}{\alpha+\beta} b_i f_k(a_i, b_i - 1, \mathrm{PA}_i, \mathrm{PB}_i). \tag{3.60}$$

Using the above expression and the expression for the differential of the exponential part given in equation 3.54 one can write down the differential given in equation 3.53

$$\frac{1}{2\alpha} \frac{\partial}{\partial A_i} \langle \mathbf{a} | \mathbf{b} \rangle = \frac{\xi \mathrm{BA}_i}{\alpha} \langle \mathbf{a} | \mathbf{b} \rangle - \frac{\beta}{2\alpha(\alpha+\beta)} a_i \langle \mathbf{a} - \mathbf{1}_i | \mathbf{b} \rangle - \frac{1}{2(\alpha+\beta)} b_i \langle \mathbf{a} | \mathbf{b} - \mathbf{1}_i \rangle, \tag{3.61}$$

which upon insertion to equation 3.47 and simplifying yields the recurrence relation for increasing angular momentum for $|\mathbf{a})$ as

$$\langle \mathbf{a} + \mathbf{1}_i | \mathbf{b} \rangle = (P_i - A_i) \langle \mathbf{a} | \mathbf{b} \rangle + \frac{a_i}{2\zeta} \langle \mathbf{a} - \mathbf{1}_i | \mathbf{b} \rangle + \frac{b_i}{2\zeta} \langle \mathbf{a} | \mathbf{b} - \mathbf{1}_i \rangle. \tag{3.62}$$

The starting case for the recurrence relation is given by

$$\langle \mathbf{0}_A | \mathbf{0}_B \rangle = \left(\frac{\pi}{\zeta} \right)^{3/2} \exp\{ -\xi |\overline{\mathrm{AB}}|^2 \}. \tag{3.63}$$

In the next two sections the recurrence relations for all two- and three-electron integrals needed will be presented. For existing recurrence relations, that is to say ones that have previously been documented in the literature the final relation and starting case only will be presented. Integral classes novel in this work will be presented in detail with a full explanation of their derivation, many of which have been published in a recent paper regarding this work [72].

3.2.1 Two-electron recurrence relations

The recurrence relations and derivations where appropriate are based on the work of Obara and Saika [59] with the two-index one-electron recurrence relation presented in the previous section acting as the start point for many of the derivations.

Integral class J — Coulomb integrals

The Coulomb integrals are defined as

$$(\mathbf{a}|\mathbf{b}) = \int d\vec{r_1} \int d\vec{r_2}\; g(\vec{r_1}, \alpha, \mathbf{a}, \vec{A}) \frac{1}{r_{12}} g(\vec{r_2}, \beta, \mathbf{b}, \vec{B}). \tag{3.64}$$

The recursion formula for the two-index two-electron integrals is given explicitly in the literature [52], and can also be deduced from the four-index two-electron Coulomb integrals presented in [59]. The recursion relation for incrementing angular momentum in $|\mathbf{a})$ is thus given by

$$(\mathbf{a}+\mathbf{1}_i|\mathbf{b})^{(m)} = \mathrm{PA}_i(\mathbf{a}|\mathbf{b})^{(m+1)} + \frac{a_i}{2\alpha}\left\{(\mathbf{a}-\mathbf{1}_i|\mathbf{b})^{(m)} - \frac{\beta}{\zeta}(\mathbf{a}-\mathbf{1}_i|\mathbf{b})^{(m+1)}\right\} + \frac{b_i}{2\xi}(\mathbf{a}|\mathbf{b}-\mathbf{1}_i)^{(m+1)}, \tag{3.65}$$

where

$$\xi = \frac{\alpha\beta}{\zeta}. \tag{3.66}$$

The starting case for the recurrence relation is given by

$$(\mathrm{s}|\mathrm{s})^{(m)} = \frac{2\pi}{\alpha\beta\zeta^{1/2}} F_m(T), \tag{3.67}$$

where

$$T = \xi|\overline{\mathrm{AB}}|^2, \tag{3.68}$$

and

$$F_m(T) = \int_0^1 dt\, t^{2m} \exp\left\{-Tt^2\right\}. \tag{3.69}$$

The integral denoted by the function $F_m(T)$ is known as the Boys function [57] and is evaluated though standard methods as described in the book by Helgaker *et al.* [7].

Integral class G — Gaussian integrals

The integral type G does not appear in any of the derivations for the MP2-F12 methods explicitly, however it does form the base for several of the other integral classes required. Integrals of class G are integrals over a single Gaussian function and are identical to F integrals when the function f_{12} comprises only a single Gaussian function. The exponent of this single Gaussian function will always be referred to as γ and thus G type integrals are defined as

$$(\mathbf{a}|e^{-\gamma r_{12}^2}|\mathbf{b}) = \int d\vec{r_1} \int d\vec{r_2}\; g(\vec{r_1}, \alpha, \mathbf{a}, \vec{A}) e^{-\gamma r_{12}^2}\, g(\vec{r_2}, \beta, \mathbf{b}, \vec{B}). \tag{3.70}$$

When considering the evaluation of G type integrals it is important to realise that the Gaussian geminal function itself can be written as a Cartesian Gaussian function with zero angular momentum

$$e^{-\gamma r_{12}^2} = g(\vec{r_1}, \gamma, \mathbf{0}, \vec{r_2}) \equiv g_{12}^{\gamma}. \tag{3.71}$$

The strategy for evaluating the integral is similar to that for the electron repulsion integrals by Obara and Saika [59]. On inspection of the definition of G type integrals it is clear that the expression can be integrated in two distinct steps over coordinates $\vec{r_1}$ and $\vec{r_2}$. The order of integration is entirely arbitrary and here the choice is made to integrate with respect to $\vec{r_1}$ first:

$$(\mathbf{a} + \mathbf{1}_i|g_{12}^{\gamma}|\mathbf{b}) = \int d\vec{r_2}\; g(\vec{r_2}, \beta, \mathbf{b}, \vec{B}) \langle \mathbf{a} + \mathbf{1}_i|g_{12}^{\gamma}\rangle. \tag{3.72}$$

The integral over the coordinate space of $|\mathbf{a})$ is a known result [59] and is given by the recurrence relation in equation 3.62. As g_{12}^{γ} has zero angular momentum the last term of the recurrence relation vanishes and this results in a two term recurrence relation

$$\langle \mathbf{a} + \mathbf{1}_i|g_{12}^{\gamma}\rangle = (P_{Ai} - A_i)\langle \mathbf{a}|g_{12}^{\gamma}\rangle + \frac{a_i}{2\zeta_a}\langle \mathbf{a} - \mathbf{1}_i|g_{12}^{\gamma}\rangle, \tag{3.73}$$

where

$$\zeta_a = \alpha + \gamma \qquad \text{and} \qquad \vec{P}_A = \frac{\alpha\vec{A} + \gamma\vec{r_2}}{\zeta_a}. \tag{3.74}$$

Insertion of the expression for $\vec{P}_A$ into equation (3.73) gives

$$\langle \mathbf{a}+\mathbf{1}_i|g_{12}^{\gamma}\rangle = \left(\frac{\gamma(r_{2i}-A_i)}{\zeta_a}\right)\langle \mathbf{a}|g_{12}^{\gamma}\rangle + \frac{a_i}{2\zeta_a}\langle \mathbf{a}-\mathbf{1}_i|g_{12}^{\gamma}\rangle. \tag{3.75}$$

Now integrating over $\vec{r}_2$ with $|\mathbf{b})$ gives

$$(\mathbf{a}+\mathbf{1}_i|g_{12}^{\gamma}|\mathbf{b}) = \int d\vec{r}_2\ \mathbf{b}\left[\left(\frac{\gamma(r_{2i}-A_i)}{\zeta_a}\right)\langle \mathbf{a}|g_{12}^{\gamma}\rangle + \frac{a_i}{2\zeta_a}\langle \mathbf{a}-\mathbf{1}_i|g_{12}^{\gamma}\rangle\right]. \tag{3.76}$$

By shifting the centre of the first term of the recurrence relation to $\vec{B}$ it is possible to arrive at

$$(\mathbf{a}+\mathbf{1}_i|g_{12}^{\gamma}|\mathbf{b}) = \int d\vec{r}_2\ \mathbf{b}\left[\left(\frac{\gamma(r_{2i}-B_i+\mathrm{BA}_i)}{\zeta_a}\right)\langle \mathbf{a}|g_{12}^{\gamma}\rangle + \frac{a_i}{2\zeta_a}\langle \mathbf{a}-\mathbf{1}_i|g_{12}^{\gamma}\rangle\right], \tag{3.77}$$

which can be expanded to

$$(\mathbf{a}+\mathbf{1}_i|g_{12}^{\gamma}|\mathbf{b}) = \int d\vec{r}_2\ \mathbf{b}\left[\frac{\gamma\mathrm{BA}_i}{\zeta_a}\langle \mathbf{a}|g_{12}^{\gamma}\rangle + \frac{\gamma(r_{2i}-B_i)}{\zeta_a}\langle \mathbf{a}|g_{12}^{\gamma}\rangle + \frac{a_i}{2\zeta_a}\langle \mathbf{a}-\mathbf{1}_i|g_{12}^{\gamma}\rangle\right], \tag{3.78}$$

which on completion of the integration yields

$$(\mathbf{a}+\mathbf{1}_i|g_{12}^{\gamma}|\mathbf{b}) = \frac{\gamma\mathrm{BA}_i}{\zeta_a}(\mathbf{a}|g_{12}^{\gamma}|\mathbf{b}) + \frac{\gamma}{\zeta_a}(\mathbf{a}|g_{12}^{\gamma}|\mathbf{b}+\mathbf{1}_i) + \frac{a_i}{2\zeta_a}(\mathbf{a}-\mathbf{1}_i|g_{12}^{\gamma}|\mathbf{b}). \tag{3.79}$$

The choice to integrate over the coordinate space of $|\mathbf{a})$ first and $|\mathbf{b})$ second was completely arbitrary. The integration can also be done by integrating over the coordinate space of $|\mathbf{b})$ first and $|\mathbf{a})$ second leading to

$$(\mathbf{a}|g_{12}^{\gamma}|\mathbf{b}+\mathbf{1}_i) = \frac{\gamma\mathrm{AB}_i}{\zeta_b}(\mathbf{a}|g_{12}^{\gamma}|\mathbf{b}) + \frac{\gamma}{\zeta_b}(\mathbf{a}+\mathbf{1}_i|g_{12}^{\gamma}|\mathbf{b}) + \frac{b_i}{2\zeta_b}(\mathbf{a}|g_{12}^{\gamma}|\mathbf{b}-\mathbf{1}_i). \tag{3.80}$$

Both of these recurrence relations, equations 3.79 and 3.80, contain a positive increment in angular momentum on the RHS of the expression. It is necessary to have expressions for incrementing angular momentum on the LHS without incrementing angular momentum on the RHS in order to be able to build integrals from the zero angular momentum case. By treating equations 3.79 and 3.80 as a pair of simultaneous equations and using the fact that $\mathrm{AB}_i = -\mathrm{BA}_i$ one can yield two separate expressions for incrementing $|\mathbf{a})$ and $|\mathbf{b})$.

$$(\mathbf{a}+\mathbf{1}_i|g_{12}^{\gamma}|\mathbf{b}) = -\frac{\beta\gamma\mathrm{AB}_i}{\eta}(\mathbf{a}|g_{12}^{\gamma}|\mathbf{b}) + \frac{\gamma b_i}{2\eta}(\mathbf{a}|g_{12}^{\gamma}|\mathbf{b}-\mathbf{1}_i) + \frac{(\beta+\gamma)a_i}{2\eta}(\mathbf{a}-\mathbf{1}_i|g_{12}^{\gamma}|\mathbf{b}), \tag{3.81}$$

$$(\mathbf{a}|g_{12}^{\gamma}|\mathbf{b}+\mathbf{1}_i) = \frac{\alpha\gamma\mathrm{AB}_i}{\eta}(\mathbf{a}|g_{12}^{\gamma}|\mathbf{b}) + \frac{\gamma a_i}{2\eta}(\mathbf{a}-\mathbf{1}_i|g_{12}^{\gamma}|\mathbf{b}) + \frac{(\alpha+\gamma)b_i}{2\eta}(\mathbf{a}|g_{12}^{\gamma}|\mathbf{b}-\mathbf{1}_i), \tag{3.82}$$

where

$$\eta = \alpha\beta + \beta\gamma + \gamma\alpha. \tag{3.83}$$

In order to use these recursion relations a starting integral must be evaluated. In this case the zero angular momentum integral is calculated explicitly and the expression is given by

$$(\mathrm{s}|g_{12}^{\gamma}|\mathrm{s}) = \exp\left\{\frac{-|\overline{\mathrm{AB}}|^2\alpha\beta\gamma}{\eta}\right\}\left(\frac{\pi}{\sqrt{\eta}}\right)^3. \tag{3.84}$$

With the recurrence relations for incrementing angular momentum in $|\mathbf{a})$ and $|\mathbf{b})$ and the above zero angular momentum case G type integrals can now be evaluated.

It is possible to treat the two recursion relationships in equations 3.81 and 3.82 as simultaneous equations. One can then eliminate γ from the coefficients and create a 'transfer equation' for angular momentum

$$\alpha(\mathbf{a}+\mathbf{1}_i|g_{12}^{\gamma}|\mathbf{b}) + \beta(\mathbf{a}|g_{12}^{\gamma}|\mathbf{b}+\mathbf{1}_i) = \frac{a_i}{2}(\mathbf{a}-\mathbf{1}_i|g_{12}^{\gamma}|\mathbf{b}) + \frac{b_i}{2}(\mathbf{a}|g_{12}^{\gamma}|\mathbf{b}-\mathbf{1}_i). \tag{3.85}$$

Further discussion of applications of this equation will feature later in the description of other classes of integrals.

The recurrence relations are at a stage where they can be implemented in the form of a computer code. Details of the implementation will be given in the next chapter along with general descriptions of how the code was tested. However specific mathematical properties of the integral will be given here and these can be utilised when testing the computer code. The first property is that when applying the limit $\gamma \rightarrow \infty$ into the expression for the Gaussian function one obtains

$$\lim_{\gamma\to\infty}\left(\frac{\gamma}{\pi}\right)^{3/2} e^{-\gamma r_{12}^2} = \delta(r_{12}). \tag{3.86}$$

Inserting this limit into the definition of G type integrals yields the following expression

$$\lim_{\gamma\to\infty}\left(\frac{\gamma}{\pi}\right)^{3/2}(\mathbf{a}|e^{-\gamma r_{12}^2}|\mathbf{b}) = \langle\mathbf{a}|\mathbf{b}\rangle, \tag{3.87}$$

which is the expression for overlap integrals. Therefore in order to test the G type integrals the size of γ must be increased and, if correct, will converge to the corresponding overlap integrals. Another property is that the expression for the G integrals when integrated should yield the expression for the J integrals presented earlier. This is due to the well known Gaussian transform which will be discussed in more detail when describing the FJ integrals later. Finally in the limit $\gamma \to 0$ the integral factorises

$$\lim_{\gamma\to 0}(\mathbf{a}|e^{-\gamma r_{12}^2}|\mathbf{b}) = \left[\int d\vec{r}\,\mathbf{a}(\vec{r})\right]\left[\int d\vec{r}\,\mathbf{b}(\vec{r})\right] \tag{3.88}$$

providing an additional test.

Integral class F — Gaussian geminal integrals

The integrals of type F are the most obvious result of an F12 theory: they involve integration over the correlation factor f_{12}, defined previously as a linear combination of Gaussian functions. The integrals are defined explicitly as

$$(\mathbf{a}|f_{12}|\mathbf{b}) = \int d\vec{r_1} \int d\vec{r_2}\; g(\vec{r_1}, \alpha, \mathbf{a}, \vec{A}) f_{12}\; g(\vec{r_2}, \beta, \mathbf{b}, \vec{B}). \tag{3.89}$$

Having derived the expressions for the G type integrals it is clear to see one might easily obtain F type integrals by a simple summation over G integrals and their coefficients

$$(\mathbf{a}|f_{12}|\mathbf{b}) = c_\gamma(\mathbf{a}|g_{12}^{\gamma}|\mathbf{b}). \tag{3.90}$$

The above expression yields exact F type integrals and this provides an exceptionally easy method to implement the integrals. However, this method is not the most efficient way to evaluate the integrals, and more efficient methods can be achieved by use of the transfer equation 3.85 discussed earlier. The key to the transfer equation is that its coefficients do not contain γ which allows the summation over γ to happen earlier in the evaluation. The earlier this summation occurs the faster the integral evaluation will be due to the saving in repeated operations.

On further examination of the transfer equation one will notice that it contains increments in both $|\mathbf{a})$ and $|\mathbf{b})$. This means it cannot be used alone to evaluate integrals as there are too many unknowns when attempting to start the recurrence relation. Instead, one of the original recurrence relations must be used to build angular momentum in one function, and then angular momentum is transferred to the other. The downside to this is that generally integrals of twice the angular momentum must be computed for one of the functions. This does *not* necessarily mean more integrals in total need be evaluated. For example a (s|f) shell of integrals contains 10 individual integrals and has total angular momentum of 3. By comparison a (d|p) shell also has angular momentum of 3 but contains 18 individual integrals. The higher the angular momentum one goes to the greater the savings. This is of course on top of the savings already incurred for not generating separate shells for each value of γ.

Using the naive implementation for constructing a shell of integrals for each value of γ it is approximately true to say the amount of time required to build a shell of F integrals scales linearly with the number of Gaussian functions comprising the geminal. For a Gaussian geminal comprising of nine Gaussian functions one would therefore expect the integrals to take around nine times the time for the G integrals. With the transfer equation most of the time is spent in processes that do not scale with increasing number of Gaussian functions.

Integral class FJ

The integral type FJ is defined explicitly as

$$(\mathbf{a}|f_{12}r_{12}^{-1}|\mathbf{b}) = \int d\vec{r_1} \int d\vec{r_2}\; g(\vec{r_1},\alpha,\mathbf{a},\vec{A}) f_{12} \frac{1}{r_{12}}\; g(\vec{r_2},\beta,\mathbf{b},\vec{B}), \tag{3.91}$$

and from the name it is no surprise to see the operators from the F and J type integrals both present. The first thing to notice is that, just as the F integrals could be calculated as a sum of G integrals, the FJ integrals can be represented as a sum of GJ integrals

$$(\mathbf{a}|f_{12}r_{12}^{-1}|\mathbf{b}) = c_\gamma(\mathbf{a}|g_{12}^{\gamma}r_{12}^{-1}|\mathbf{b}). \tag{3.92}$$

The integrals have now been reduced to the product of a single Gaussian and r_{12}^{-1}. It is now noted that the operator r_{12}^{-1} has a Gaussian transform [57]

$$r_{12}^{-1} = \frac{2}{\sqrt{\pi}} \int_0^\infty du\; e^{-u^2 r_{12}^2}, \tag{3.93}$$

so the GJ integrals share a very close relationship to G integrals. Using this important relation one can represent the GJ integral as

$$(\mathbf{a}|g_{12}^{\gamma}r_{12}^{-1}|\mathbf{b}) = \frac{2}{\sqrt{\pi}} \int_0^\infty du\; (\mathbf{a}|g_{12}^{\gamma}e^{-u^2 r_{12}^2}|\mathbf{b}) = \frac{2}{\sqrt{\pi}} \int_0^\infty du\; (\mathbf{a}|g_{12}^{\gamma+u^2}|\mathbf{b}), \tag{3.94}$$

where

$$g_{12}^{\gamma+u^2} = g_{12}^{\gamma} g_{12}^{u^2} = e^{-(\gamma+u^2)r_{12}^2}. \tag{3.95}$$

On inspection of the above equation one can observe the similarity to the G type integrals. In fact the only differences are the integration over u and the substitution $\gamma \rightarrow (\gamma + u^2)$.

By performing the substitution $\gamma \rightarrow (\gamma + u^2)$ in equation 3.81 the following recurrence relation is obtained

$$\begin{aligned}(\mathbf{a}+\mathbf{1}_i|g_{12}^{\gamma+u^2}|\mathbf{b}) = &-\frac{\beta(\gamma+u^2)\mathrm{AB}_i}{\eta'}(\mathbf{a}|g_{12}^{\gamma+u^2}|\mathbf{b}) \\ &+\frac{(\gamma+u^2)b_i}{2\eta'}(\mathbf{a}|g_{12}^{\gamma+u^2}|\mathbf{b}-\mathbf{1}_i)+\frac{(\beta+\gamma+u^2)a_i}{2\eta'}(\mathbf{a}-\mathbf{1}_i|g_{12}^{\gamma+u^2}|\mathbf{b}), \end{aligned} \tag{3.96}$$

with

$$\eta' = \eta + (\alpha+\beta)u^2. \tag{3.97}$$

To proceed further it is necessary to introduce an auxiliary integral in order to complete the integration in a similar manner to Obara and Saika [59]:

$$(\mathbf{a}|g_{12}^{\gamma}r_{12}^{-1}|\mathbf{b})^{(m)} = \frac{2}{\sqrt{\pi}}\int_0^\infty du\left(\frac{u^2}{u^2+\frac{\eta}{\zeta}}\right)^m(\mathbf{a}|g_{12}^{\gamma+u^2}|\mathbf{b}). \tag{3.98}$$

It is therefore necessary to rearrange the recurrence relations into a form where each term has the form of the integrand in equation 3.98. In order to do this it is essential to make use of the formula

$$\frac{1}{\kappa+u^2} = \frac{1}{\kappa}\left\{1-\frac{u^2}{\kappa+u^2}\right\}, \tag{3.99}$$

which gives

$$\begin{aligned}(\mathbf{a}+\mathbf{1}_i|g_{12}^{\gamma+u^2}|\mathbf{b}) = &-\frac{\beta\mathrm{AB}_i}{\eta}\left[\gamma+\xi\left(\frac{u^2}{u^2+\rho}\right)\right](\mathbf{a}|g_{12}^{\gamma+u^2}|\mathbf{b}) \\ &+\frac{b_i}{2\eta}\left[\gamma+\xi\left(\frac{u^2}{u^2+\rho}\right)\right](\mathbf{a}|g_{12}^{\gamma+u^2}|\mathbf{b}-\mathbf{1}_i) \\ &+\frac{a_i}{2\eta}\left[\gamma+\beta-\frac{\beta^2}{\zeta}\left(\frac{u^2}{u^2+\rho}\right)\right](\mathbf{a}-\mathbf{1}_i|g_{12}^{\gamma+u^2}|\mathbf{b}) \end{aligned} \tag{3.100}$$

where

$$\rho = \frac{\eta}{\zeta}, \qquad \xi = \frac{\alpha\beta}{\zeta}, \qquad \text{and} \qquad \zeta = \alpha+\beta. \tag{3.101}$$

The integration can now be performed using equation 3.98 in order to give the final recurrence relationship for incrementing angular momentum in $|\mathbf{a})$ for the GJ type integrals

$$\begin{aligned}(\mathbf{a}+\mathbf{1}_i|g_{12}^{\gamma}r_{12}^{-1}|\mathbf{b})^{(m)} = &\frac{\beta\mathrm{BA}_i}{\eta}\left[\gamma(\mathbf{a}|g_{12}^{\gamma}r_{12}^{-1}|\mathbf{b})^{(m)}+\xi(\mathbf{a}|g_{12}^{\gamma}r_{12}^{-1}|\mathbf{b})^{(m+1)}\right] \\ &+\frac{b_i}{2\eta}\left[\gamma(\mathbf{a}|g_{12}^{\gamma}r_{12}^{-1}|\mathbf{b}-\mathbf{1}_i)^{(m)}+\xi(\mathbf{a}|g_{12}^{\gamma}r_{12}^{-1}|\mathbf{b}-\mathbf{1}_i)^{(m+1)}\right] \\ &+\frac{a_i}{2\eta}\left[(\gamma+\beta)(\mathbf{a}-\mathbf{1}_i|g_{12}^{\gamma}r_{12}^{-1}|\mathbf{b})^{(m)}-\frac{\beta^2}{\zeta}(\mathbf{a}-\mathbf{1}_i|g_{12}^{\gamma}r_{12}^{-1}|\mathbf{b})^{(m+1)}\right]. \end{aligned} \tag{3.102}$$

Using a similar process as described above one can obtain a recurrence relationship for incrementing angular momentum in $|\mathbf{b})$

$$\begin{aligned}(\mathbf{a}|g_{12}^{\gamma}r_{12}^{-1}|\mathbf{b}+\mathbf{1}_i)^{(m)} = {} & \frac{\alpha \mathrm{AB}_i}{\eta}\left[\gamma(\mathbf{a}|g_{12}^{\gamma}r_{12}^{-1}|\mathbf{b})^{(m)}+\xi(\mathbf{a}|g_{12}^{\gamma}r_{12}^{-1}|\mathbf{b})^{(m+1)}\right] \\ & +\frac{a_i}{2\eta}\left[\gamma(\mathbf{a}-\mathbf{1}_i|g_{12}^{\gamma}r_{12}^{-1}|\mathbf{b})^{(m)}+\xi(\mathbf{a}-\mathbf{1}_i|g_{12}^{\gamma}r_{12}^{-1}|\mathbf{b})^{(m+1)}\right] \\ & +\frac{b_i}{2\eta}\left[(\gamma+\alpha)(\mathbf{a}|g_{12}^{\gamma}r_{12}^{-1}|\mathbf{b}-\mathbf{1}_i)^{(m)}-\frac{\alpha^2}{\zeta}(\mathbf{a}|g_{12}^{\gamma}r_{12}^{-1}|\mathbf{b}-\mathbf{1}_i)^{(m+1)}\right].\end{aligned} \tag{3.103}$$

The starting $(\mathrm{s}|g_{12}^{\gamma}r_{12}^{-1}|\mathrm{s})$ case for the recurrence relation is now all that is left to be calculated

$$\begin{aligned}&(\mathrm{s}|g_{12}^{\gamma}r_{12}^{-1}|\mathrm{s})^{(m)} = \\ &\quad \frac{2}{\sqrt{\pi}}\int_0^{\infty} du \left(\frac{u^2}{u^2+\frac{\eta}{\zeta}}\right)^m \int d\vec{r}_1 \int d\vec{r}_2\, e^{-\alpha|\vec{r}_1-\vec{A}|^2} e^{-(u^2+\gamma)|\vec{r}_1-\vec{r}_2|^2} e^{-\beta|\vec{r}_2-\vec{B}|^2}.\end{aligned} \tag{3.104}$$

The part of the expression for $(\mathrm{s}|g_{12}^{\gamma}r_{12}^{-1}|\mathrm{s})$ to be integrated over $\vec{r}_1$ and $\vec{r}_2$ is identical to that of G integrals but once again with the substitution $\gamma \longrightarrow (\gamma+u^2)$ giving

$$(\mathrm{s}|g_{12}^{\gamma}r_{12}^{-1}|\mathrm{s})^{(m)} = \frac{2}{\sqrt{\pi}}\int_0^{\infty} du \left(\frac{u^2}{u^2+\frac{\eta}{\zeta}}\right)^m \left(\frac{\pi}{\sqrt{\zeta u^2+\eta}}\right)^3 \exp\left\{\frac{-|\overline{\mathrm{AB}}|^2\alpha\beta(\gamma+u^2)}{\zeta u^2+\eta}\right\}. \tag{3.105}$$

Just like the recurrence relations the expression for $(\mathrm{s}|g_{12}^{\gamma}r_{12}^{-1}|\mathrm{s})$ must be rearranged by making use of equation 3.99. This process is presented in the next several steps for clarity on how the rearrangement has taken place

$$\begin{aligned}(\mathrm{s}|g_{12}^{\gamma}r_{12}^{-1}|\mathrm{s})^{(m)} = 2\pi^{5/2}\int_0^{\infty} du & \left(\frac{u^2}{u^2+\frac{\eta}{\zeta}}\right)^m \left(\frac{1}{\zeta u^2+\eta}\right)^{3/2} \\ & \exp\left\{-|\overline{\mathrm{AB}}|^2\alpha\beta\left[\frac{\gamma}{\eta}+\frac{\xi}{\eta}\left(\frac{u^2}{u^2+\frac{\eta}{\zeta}}\right)\right]\right\}\end{aligned} \tag{3.106}$$

$$\begin{aligned}(\mathrm{s}|g_{12}^{\gamma}r_{12}^{-1}|\mathrm{s})^{(m)} = \frac{2\pi^{5/2}}{\zeta^{3/2}}e^{-|\overline{\mathrm{AB}}|^2\alpha\beta\gamma/\eta}\int_0^{\infty} du & \left(\frac{u^2}{u^2+\frac{\eta}{\zeta}}\right)^m \left(\frac{1}{u^2+\frac{\eta}{\zeta}}\right)^{3/2} \\ & \exp\left\{-T\left(\frac{u^2}{u^2+\frac{\eta}{\zeta}}\right)\right\}\end{aligned} \tag{3.107}$$

$$(\mathrm{s}|g_{12}^{\gamma}r_{12}^{-1}|\mathrm{s})^{(m)} = \frac{2\pi^{5/2}}{\eta^{3/2}}e^{-|\overline{\mathrm{AB}}|^2\alpha\beta\gamma/\eta}\int_0^{\infty} du\left(\frac{u^2}{u^2+\frac{\eta}{\zeta}}\right)^m\left(1-\frac{u^2}{u^2+\frac{\eta}{\zeta}}\right)^{3/2} \exp\left\{-T\left(\frac{u^2}{u^2+\frac{\eta}{\zeta}}\right)\right\} \tag{3.108}$$

where

$$T = \frac{|\overline{\mathrm{AB}}|^2\alpha\beta\xi}{\eta}. \tag{3.109}$$

The integral over u can now be performed by transforming variable from u to t. The following substitution is made

$$t^2 = \frac{u^2}{u^2+\frac{\eta}{\zeta}}, \tag{3.110}$$

which leads to the following expression for the starting case

$$(\mathrm{s}|g_{12}^{\gamma}r_{12}^{-1}|\mathrm{s})^{(m)} = \frac{2\pi^{5/2}}{\eta^{3/2}}e^{-|\overline{\mathrm{AB}}|^2\alpha\beta\gamma/\eta}\int_0^{\infty} du\frac{dt}{dt}\, t^{2m}(1-t^2)^{3/2}\exp\left\{-Tt^2\right\}. \tag{3.111}$$

The quantity du/dt is now calculated by rearranging equation 3.110 and differentiating, thus

$$\frac{du}{dt} = \left(\frac{\eta}{\zeta}\right)^{1/2}(1-t^2)^{-3/2} \tag{3.112}$$

and using this and changing the limits gives

$$(\mathrm{s}|g_{12}^{\gamma}r_{12}^{-1}|\mathrm{s})^{(m)} = \frac{2\pi^{5/2}}{\eta^{3/2}}e^{-|\overline{\mathrm{AB}}|^2\alpha\beta\gamma/\eta}\int_0^{1} dt\left(\frac{\eta}{\zeta}\right)^{1/2}(1-t^2)^{-3/2}t^{2m}(1-t^2)^{3/2}\exp\left\{-Tt^2\right\}. \tag{3.113}$$

Applying further simplification this reduces to

$$(\mathrm{s}|g_{12}^{\gamma}r_{12}^{-1}|\mathrm{s})^{(m)} = \frac{2\pi^{5/2}}{\eta\zeta^{1/2}}e^{-|\overline{\mathrm{AB}}|^2\alpha\beta\gamma/\eta}\int_0^{1} dt\, t^{2m}\exp\left\{-Tt^2\right\} \tag{3.114}$$

$$= \frac{2\pi^{5/2}}{\eta\zeta^{1/2}}e^{-|\overline{\mathrm{AB}}|^2\alpha\beta\gamma/\eta}F_m(T). \tag{3.115}$$

This now provides a way of evaluating the starting case for the recurrence relation for GJ integrals described above which can be summed over as in equation 3.92 to give FJ integrals. This derivation is made considerably less complicated due to the Gaussian transform for r_{12}^{-1}. The transfer equation 3.85 discussed earlier holds for all operators for which there is a Gaussian transform and so holds for the FJ integrals. This leads to the same computational savings made for the F integrals.

The GJ integral recurrence relations can be checked by setting γ to zero, yielding the recurrence relation for J integrals. This also provides a very easy way to test the computer implementation.

Integral class FF

The integral type FF is defined explicitly as

$$(\mathbf{a}|f_{12}^2|\mathbf{b}) = \int d\vec{r_1} \int d\vec{r_2}\; g(\vec{r_1}, \alpha, \mathbf{a}, \vec{A}) f_{12}^2\; g(\vec{r_2}, \beta, \mathbf{b}, \vec{B}). \tag{3.116}$$

When deriving the F integrals it was shown that they could be constructed from G integrals and the same is true for the FF integrals. The function f_{12}^2 can be expanded as

$$(\mathbf{a}|f_{12}^2|\mathbf{b}) = c_\mu c_\nu (\mathbf{a}|g_{12}^\mu g_{12}^\nu|\mathbf{b}), \tag{3.117}$$

which contains the operator $g_{12}^\mu g_{12}^\nu$. Since the g_{12}^μ and g_{12}^ν represent Gaussian functions their product will also be a Gaussian function

$$g_{12}^\mu g_{12}^\nu = e^{-\mu r_{12}^2} e^{-\nu r_{12}^2} = e^{-(\mu+\nu) r_{12}^2} = g_{12}^{\mu+\nu}. \tag{3.118}$$

Thus the FF integrals can be represented as

$$(\mathbf{a}|f_{12}^2|\mathbf{b}) = c_\mu c_\nu (\mathbf{a}|g_{12}^{\mu+\nu}|\mathbf{b}), \tag{3.119}$$

which is simply a summation over G type integrals. The number of terms in the expression above is quadratic in the size of the geminal expansion. It is important to note that the G type integrals are calculated with the modified exponents $\mu + \nu$. These integrals are not constructed in any way from normal F integrals, or the G integrals used to calculate them. Once again, since the operator is only a Gaussian transform the transfer equation 3.85 still applies, and here it brings even greater computational savings, because f_{12}^2 has more terms than f_{12} itself.

Integral class FT

The integral type FT is defined explicitly through the operator $[\hat{t}_1+\hat{t}_2, f_{12}]$. These integrals are computed directly in three-index form. Using the work of Manby [52] and the earlier work of Klopper and Röhse [74] one can write

$$(\mathbf{ab}|[\hat{t}_1, f_{12}]|\mathbf{c}) = \frac{1}{2}\frac{\alpha-\beta}{\alpha+\beta}(\mathbf{ab}|\{\nabla_1^2 f_{12}\}|\mathbf{c}) + \vec{\nabla}_P \cdot \vec{\nabla}_{\mathrm{AB}} (\mathbf{ab}|f_{12}|\mathbf{c}). \tag{3.120}$$

The integrals over $\nabla_1^2 f_{12}$ are computed using the relation

$$\nabla_1^2 f_{12} = 4 r_{12}^2 f_{12}^{(2)} - 6 f_{12}^{(1)} \tag{3.121}$$

where

$$f_{12}^{(n)} = c_\gamma \gamma^n g_{12}^\gamma. \tag{3.122}$$

The integrals over r_{12}^2 multiplied by a geminal expansion are discussed in the next section. The evaluation of integrals analogous to the second term on the right hand side of equation (3.120) is discussed elsewhere [52].

Integral class FTF

The integral type FTF is defined in symmetrised form explicitly as

$$(\mathbf{a}|\frac{1}{2}[f_{12},[\hat{t}_1+\hat{t}_2,f_{12}]]|\mathbf{b}) = \int d\vec{r_1} \int d\vec{r_2}\, g(\vec{r_1},\alpha,\mathbf{a},\vec{A})\frac{1}{2}[f_{12},[\hat{t}_1+\hat{t}_2,f_{12}]]\, g(\vec{r_2},\beta,\mathbf{b},\vec{B}). \tag{3.123}$$

By expanding the commutator in the above expression the following two term expression is obtained

$$\frac{1}{2}(\mathbf{a}|[f_{12},[\hat{t}_1+\hat{t}_2,f_{12}]]|\mathbf{b}) = \frac{1}{2}(\mathbf{a}|f_{12}[\hat{t}_1+\hat{t}_2,f_{12}]|\mathbf{b}) - \frac{1}{2}(\mathbf{a}|[\hat{t}_1+\hat{t}_2,f_{12}]f_{12}|\mathbf{b}). \tag{3.124}$$

Considering the integral contained in the first term of equation 3.124, the most obvious thing to do is to expand the expression into two terms for each kinetic energy operator

$$f_{12}[\hat{t}_1+\hat{t}_2,f_{12}] = f_{12}[\hat{t}_1,f_{12}] + f_{12}[\hat{t}_2,f_{12}]. \tag{3.125}$$

The evaluation of the integral over $\hat{t}_1$ shall be considered, its counterpart over $\hat{t}_2$ will be given later by symmetry and inspection. Inserting the definition of the kinetic energy operator gives

$$f_{12}[\hat{t}_1,f_{12}] = -\frac{1}{2}f_{12}[\nabla_1^2,f_{12}] = -\frac{1}{2}f_{12}\{\nabla_1^2 f_{12} - f_{12}\nabla_1^2\}. \tag{3.126}$$

The first term inside the bracket of equation 3.126 can be expressed as

$$\nabla_1^2 f_{12} = \vec{\nabla}_1\cdot\vec{\nabla}_1 f_{12}, \tag{3.127}$$

and expanded using the product rule as

$$\nabla_1^2 f_{12} = \vec{\nabla}_1\cdot\{(\vec{\nabla}_1 f_{12}) + f_{12}\vec{\nabla}_1\}. \tag{3.128}$$

Expanding the bracket and using the product rule on both of the terms yields

$$\nabla_1^2 f_{12} = (\nabla_1^2 f_{12}) + 2(\vec{\nabla}_1 f_{12})\cdot\vec{\nabla}_1 + f_{12}\nabla_1^2. \tag{3.129}$$

The above expression can now be substituted into equation 3.126 and terms cancelled to give

$$f_{12}[\hat{t}_1, f_{12}] = -\frac{1}{2} f_{12}\{(\nabla_1^2 f_{12}) + 2(\vec{\nabla}_1 f_{12}) \cdot \vec{\nabla}_1\}. \tag{3.130}$$

Another expression can be obtained when considering the second term of equation 3.124 and following a similar derivation to the one presented above

$$[\hat{t}_1, f_{12}] f_{12} = -\frac{1}{2}\{(\nabla_1^2 f_{12}) + 2(\vec{\nabla}_1 f_{12}) \cdot \vec{\nabla}_1\} f_{12}. \tag{3.131}$$

By combining equations 3.130 and 3.131 one can obtain the expression for the commutator

$$[f_{12}, [\hat{t}_1, f_{12}]] = -\frac{1}{2}\left\{f_{12}\{(\nabla_1^2 f_{12}) + 2(\vec{\nabla}_1 f_{12}) \cdot \vec{\nabla}_1\} - \{(\nabla_1^2 f_{12}) + 2(\vec{\nabla}_1 f_{12}) \cdot \vec{\nabla}_1\} f_{12}\right\} \tag{3.132}$$

which on expansion and cancellation of like terms yields

$$[f_{12}, [\hat{t}_1, f_{12}]] = -f_{12}(\vec{\nabla}_1 f_{12}) \cdot \vec{\nabla}_1 + (\vec{\nabla}_1 f_{12}) \cdot \vec{\nabla}_1 f_{12}. \tag{3.133}$$

Using the product rule for a final time gives

$$[f_{12}, [\hat{t}_1, f_{12}]] = -f_{12}(\vec{\nabla}_1 f_{12}) \cdot \vec{\nabla}_1 + (\vec{\nabla}_1 f_{12}) \cdot (\vec{\nabla}_1 f_{12}) + (\vec{\nabla}_1 f_{12}) \cdot f_{12}\vec{\nabla}_1. \tag{3.134}$$

which simplifies to the final expression

$$[f_{12}, [\hat{t}_1, f_{12}]] = |\vec{\nabla}_1 f_{12}|^2. \tag{3.135}$$

Now all that must be considered is the evaluation of $\vec{\nabla}_1 f_{12}$. This expression can be evaluated by expanding the form of f_{12} such that

$$\vec{\nabla}_1 f_{12} = \vec{\nabla}_1 c_\gamma e^{-\gamma r_{12}^2} = -2\vec{r}_{12}\gamma c_\gamma e^{-\gamma r_{12}^2}. \tag{3.136}$$

Inserting this into equation 3.135 gives following equation

$$[f_{12}, [\hat{t}_1, f_{12}]] = 4r_{12}^2 \mu\nu c_\mu c_\nu e^{-\mu r_{12}^2} e^{-\nu r_{12}^2} = r_{12}^2 f_{12}^{(t)}. \tag{3.137}$$

where

$$f_{12}^{(t)} = 4\mu\nu c_\mu c_\nu e^{-(\mu+\nu) r_{12}^2} \tag{3.138}$$

Finally r_{12}^2 is expanded into vector form

$$r_{12}^2 = |\vec{r}_1 - \vec{r}_2|^2, \tag{3.139}$$

and vectors $\vec{A}$ and $\vec{B}$ are added in equal positive and negative quantities to give

$$r_{12}^2 = |\vec{r}_1 - \vec{A} - (\vec{r}_2 - \vec{B}) + \overline{\mathrm{AB}}|^2. \tag{3.140}$$

This expression can be expanded to give

$$r_{12}^2 = |\vec{r}_1-\vec{A}|^2-2(\vec{r}_1-\vec{A})\cdot(\vec{r}_2-\vec{B})+2(\vec{r}_1-\vec{A})\cdot\overline{\mathrm{AB}}+|\vec{r}_2-\vec{B}|^2-2(\vec{r}_2-\vec{B})\cdot\overline{\mathrm{AB}}+|\overline{\mathrm{AB}}|^2. \tag{3.141}$$

The FTF integrals for $\hat{t}_1$ can now be expressed as

$$(\mathbf{a}|[f_{12},[\hat{t}_1,f_{12}]]|\mathbf{b}) = (\mathbf{a}|r_{12}^2 f_{12}^{(t)}|\mathbf{b}). \tag{3.142}$$

which on expansion of r_{12}^2 leads to the recurrence relation

$$\begin{aligned}(\mathbf{a}|[f_{12},[\hat{t}_1,f_{12}]]|\mathbf{b}) = \sum_{i=x,y,z} \Big\{ &(\mathbf{a}+\mathbf{2}_i|f_{12}^{(t)}|\mathbf{b}) - 2(\mathbf{a}+\mathbf{1}_i|f_{12}^{(t)}|\mathbf{b}+\mathbf{1}_i) \\ &+2\mathrm{AB}_i(\mathbf{a}+\mathbf{1}_i|f_{12}^{(t)}|\mathbf{b}) + (\mathbf{a}|f_{12}^{(t)}|\mathbf{b}+\mathbf{2}_i) - 2\mathrm{AB}_i(\mathbf{a}|f_{12}^{(t)}|\mathbf{b}+\mathbf{1}_i) + \mathrm{AB}_i^2(\mathbf{a}|f_{12}^{(t)}|\mathbf{b})\Big\}.\end{aligned} \tag{3.143}$$

The recurrence relation above contains increments in both $|\mathbf{a})$ and $|\mathbf{b})$, however by making use of the transfer equation

$$2\alpha(\mathbf{a}+\mathbf{1}_i|f_{12}^{(t)}|\mathbf{b}) + 2\beta(\mathbf{a}|f_{12}^{(t)}|\mathbf{b}+\mathbf{1}_i) = a_i(\mathbf{a}-\mathbf{1}_i|f_{12}^{(t)}|\mathbf{b}) + b_i(\mathbf{a}|f_{12}^{(t)}|\mathbf{b}-\mathbf{1}_i), \tag{3.144}$$

which is still valid for these integrals, the recurrence relation can be rearranged so there is never a need for greater angular momentum in both $|\mathbf{a})$ and $|\mathbf{b})$ than in the target integral. The kernel of the integrals, $f_{12}^{(t)}$ is simply a sum of G type integrals, which is evaluated in much the same manner as the FF class of integrals. The recurrence relation resulting from removing an increment in angular momentum from equation 3.143 is shown each time this process is used. Firstly the $(\mathbf{a}+\mathbf{2}_i|f_{12}^{(t)}|\mathbf{b})$ term is removed to yield

$$\begin{aligned}(\mathbf{a}|f_{12}[\nabla_1^2,f_{12}]|\mathbf{b}) = \sum_{i=x,y,z} \Big\{ &\frac{a_i+1}{2\alpha}(\mathbf{a}|f_{12}^{(t)}|\mathbf{b}) + \frac{b_i}{2\alpha}(\mathbf{a}+\mathbf{1}_i|f_{12}^{(t)}|\mathbf{b}-\mathbf{1}_i) \\ &-\frac{\beta}{\alpha}(\mathbf{a}+\mathbf{1}_i|f_{12}^{(t)}|\mathbf{b}+\mathbf{1}_i) - 2(\mathbf{a}+\mathbf{1}_i|f_{12}^{(t)}|\mathbf{b}+\mathbf{1}_i) + 2\mathrm{AB}_i(\mathbf{a}+\mathbf{1}_i|f_{12}^{(t)}|\mathbf{b}) \\ &+(\mathbf{a}|f_{12}^{(t)}|\mathbf{b}+\mathbf{2}_i) - 2\mathrm{AB}_i(\mathbf{a}|f_{12}^{(t)}|\mathbf{b}+\mathbf{1}_i) + \mathrm{AB}_i^2(\mathbf{a}|f_{12}^{(t)}|\mathbf{b})\Big\}.\end{aligned} \tag{3.145}$$

Then the transfer equation is used again to remove the $(\mathbf{a}+\mathbf{1}_i|f_{12}^{(t)}|\mathbf{b}+\mathbf{1}_i)$ term from the recurrence relation

$$\begin{aligned}(\mathbf{a}|f_{12}[\nabla_1^2, f_{12}]|\mathbf{b}) = \sum_{i=x,y,z} \Bigg\{ & \frac{b_i}{2\alpha}(\mathbf{a}+\mathbf{1}_i|f_{12}^{(t)}|\mathbf{b}-\mathbf{1}_i) \\ & - \left(\frac{\beta}{\alpha}+2\right)\frac{a_i}{2\alpha}(\mathbf{a}-\mathbf{1}_i|f_{12}^{(t)}|\mathbf{b}+\mathbf{1}_i) \\ & + \left(\frac{\beta^2}{\alpha^2}+\frac{2\beta}{\alpha}+1\right)(\mathbf{a}|f_{12}^{(t)}|\mathbf{b}+\mathbf{2}_i) + 2\mathrm{AB}_i(\mathbf{a}+\mathbf{1}_i|f_{12}^{(t)}|\mathbf{b}) \\ & -2\mathrm{AB}_i(\mathbf{a}|f_{12}^{(t)}|\mathbf{b}+\mathbf{1}_i) + \left(\mathrm{AB}_i^2 + \frac{a_i+1}{2\alpha} - \frac{\beta(b_i+1)}{2\alpha^2} - \frac{b_i+1}{\alpha}\right)(\mathbf{a}|f_{12}^{(t)}|\mathbf{b})\Bigg\}.\end{aligned} \tag{3.146}$$

Next the transfer equation is applied to the $(\mathbf{a}+\mathbf{1}_i|f_{12}^{(t)}|\mathbf{b})$ term which leads to

$$\begin{aligned}(\mathbf{a}|f_{12}[\nabla_1^2, f_{12}]|\mathbf{b}) = \sum_{i=x,y,z} \Bigg\{ & \frac{b_i}{2\alpha}(\mathbf{a}+\mathbf{1}_i|f_{12}^{(t)}|\mathbf{b}-\mathbf{1}_i) \\ & - \left(\frac{\beta}{\alpha}+2\right)\frac{a_i}{2\alpha}(\mathbf{a}-\mathbf{1}_i|f_{12}^{(t)}|\mathbf{b}+\mathbf{1}_i) + \left(\frac{\beta^2}{\alpha^2}+\frac{2\beta}{\alpha}+1\right)(\mathbf{a}|f_{12}^{(t)}|\mathbf{b}+\mathbf{2}_i) \\ & + \frac{\mathrm{AB}_i b_i}{\alpha}(\mathbf{a}|f_{12}^{(t)}|\mathbf{b}-\mathbf{1}_i) + \frac{\mathrm{AB}_i a_i}{\alpha}(\mathbf{a}-\mathbf{1}_i|f_{12}^{(t)}|\mathbf{b}) - 2\mathrm{AB}_i\left(1+\frac{\beta}{\alpha}\right)(\mathbf{a}|f_{12}^{(t)}|\mathbf{b}+\mathbf{1}_i) \\ & + \left(\mathrm{AB}_i^2 + \frac{a_i+1}{2\alpha} - \frac{\beta(b_i+1)}{2\alpha^2} - \frac{b_i+1}{\alpha}\right)(\mathbf{a}|f_{12}^{(t)}|\mathbf{b})\Bigg\}.\end{aligned} \tag{3.147}$$

The final term which contains positive increments in $|\mathbf{a})$ is the $(\mathbf{a}+\mathbf{1}_i|f_{12}^{(t)}|\mathbf{b}-\mathbf{1}_i)$ term, and applying the transfer equation once again yields the final recurrence relation

$$\begin{aligned}(\mathbf{a}|f_{12}[\nabla_1^2, f_{12}]|\mathbf{b}) = \sum_{i=x,y,z} \Bigg\{ & -\left(\frac{\beta}{\alpha}+2\right)\frac{a_i}{2\alpha}(\mathbf{a}-\mathbf{1}_i|f_{12}^{(t)}|\mathbf{b}+\mathbf{1}_i) \\ & + \frac{a_i b_i}{4\alpha^2}(\mathbf{a}-\mathbf{1}_i|f_{12}^{(t)}|\mathbf{b}-\mathbf{1}_i) + \left(\frac{\beta^2}{\alpha^2}+\frac{2\beta}{\alpha}+1\right)(\mathbf{a}|f_{12}^{(t)}|\mathbf{b}+\mathbf{2}_i) \\ & + \frac{\mathrm{AB}_i b_i}{\alpha}(\mathbf{a}|f_{12}^{(t)}|\mathbf{b}-\mathbf{1}_i) + \frac{\mathrm{AB}_i a_i}{\alpha}(\mathbf{a}-\mathbf{1}_i|f_{12}^{(t)}|\mathbf{b}) \\ & + \frac{b_i(b_i-1)}{4\alpha^2}(\mathbf{a}|f_{12}^{(t)}|\mathbf{b}-\mathbf{2}_i) - 2\mathrm{AB}_i\left(1+\frac{\beta}{\alpha}\right)(\mathbf{a}|f_{12}^{(t)}|\mathbf{b}+\mathbf{1}_i) \\ & + \left(\mathrm{AB}_i^2 + \frac{a_i+1}{2\alpha} - \frac{\beta(2b_i+1)}{2\alpha^2} - \frac{b_i+1}{\alpha}\right)(\mathbf{a}|f_{12}^{(t)}|\mathbf{b})\Bigg\},\end{aligned} \tag{3.148}$$

which only contains positive increments in $|\mathbf{b})$. The advantage of this over equation 3.143 is that the shell of $f_{12}^{(t)}$ integrals required to build the target FT integrals is significantly smaller, thus increasing their speed of evaluation.

This now concludes the derivation of all of the two-electron integrals. One observes that the G type integrals form the core of almost all of the new integrals presented. In fact, all but the FJ class of integral use combinations of G integrals in their construction.

3.2.2 Three-electron Recurrence Relations

As mentioned in the theory chapter, three-electron integrals occur in vast numbers in the R12 and F12 methods. However, use of the RI approximation eradicates the need for direct evaluation of these integrals. It is of course desirable to be able to evaluate the accuracy of the RI approximation, and for this exact three-electron integrals are required. They are also required for a DF implementation of three-electron integrals which was one of the original aims of this work. Since work in this area did not prove successful the primary reasons for deriving the recurrence relations were evaluating the accuracy of RI and testing the RI code. Therefore only two classes of three-electron integral were derived and implemented, $(\mathbf{a}|f_{12}|\mathbf{b}|f_{23}|\mathbf{c})$ and $(\mathbf{a}|r_{12}^{-1}|\mathbf{b}|f_{23}|\mathbf{c})$, and their derivations will be presented in this section.

Integral class F-F

Integral class F-F is defined explicitly as

$$(\mathbf{a}|f_{12}|\mathbf{b}|f_{23}|\mathbf{c}) = \int d\vec{r_1} \int d\vec{r_2} \int d\vec{r_3}\; g(\vec{r_1}, \alpha, \mathbf{a}, \vec{A}) f_{12}\; g(\vec{r_2}, \beta, \mathbf{b}, \vec{B}) f_{23}\; g(\vec{r_3}, \gamma, \mathbf{c}, \vec{C}). \tag{3.149}$$

Using a similar approach to the two-electron F type integrals the F-F integrals are expressed as a sum of G-G integrals

$$(\mathbf{a}|f_{12}|\mathbf{b}|f_{23}|\mathbf{c}) = c_\mu c_\nu (\mathbf{a}|g_{12}^\mu|\mathbf{b}|g_{23}^\nu|\mathbf{c}). \tag{3.150}$$

The G-G integrals can be written as

$$(\mathbf{a}|g_{12}^\mu|\mathbf{b}|g_{23}^\nu|\mathbf{c}) = \int d\vec{r_1} \int d\vec{r_3}\; g(\vec{r_1}, \alpha, \mathbf{a}, \vec{A}) \langle g_{12}^\mu|\mathbf{b}|g_{23}^\nu\rangle g(\vec{r_3}, \gamma, \mathbf{c}, \vec{C}), \tag{3.151}$$

where the integral $\langle g_{12}^\mu|\mathbf{b}|g_{23}^\nu\rangle$ is a three-centre one-electron overlap integral. Now the three-centre overlap integral recursion relation by Obara and Saika [59] is used, substituting the two Gaussian functions for two of the centres gives

$$\langle g_{12}^\mu|\mathbf{b}+\mathbf{1}_i|g_{23}^\nu\rangle = (G_i - B_i)\langle g_{12}^\mu|\mathbf{b}|g_{23}^\nu\rangle + \frac{b_i}{2(\mu+\beta+\nu)}\langle g_{12}^\mu|\mathbf{b}-\mathbf{1}_i|g_{23}^\nu\rangle, \tag{3.152}$$

where

$$G_i = \frac{\mu r_{1i} + \beta B_i + \nu r_{3i}}{\mu + \beta + \nu}. \tag{3.153}$$

By substituting in $\vec{G}$ and inserting $\vec{A}$ and $\vec{C}$ in equal positive and negative amounts yields

$$\begin{aligned}\langle g_{12}^{\mu}|\mathbf{b}+\mathbf{1}_i|g_{23}^{\nu}\rangle = {} & \frac{\mu(r_{1i} - A_i + \mathrm{AB}_i) + \nu(r_{3i} - C_i + \mathrm{CB}_i)}{\mu+\beta+\nu}\langle g_{12}^{\mu}|\mathbf{b}|g_{23}^{\nu}\rangle \\ & + \frac{b_i}{2(\mu+\beta+\nu)}\langle g_{12}^{\mu}|\mathbf{b}-\mathbf{1}_i|g_{23}^{\nu}\rangle, \end{aligned} \tag{3.154}$$

Integration over $\vec{r}_1$ and $\vec{r}_3$ with $|\mathbf{a})$ and $|\mathbf{c})$ and expanding out the terms gives

$$\begin{aligned}(\mathbf{a}|g_{12}^{\mu}|\mathbf{b}+\mathbf{1}_i|g_{23}^{\nu}|\mathbf{c}) = {} & \frac{\mu\mathrm{AB}_i + \nu\mathrm{CB}_i}{\mu+\beta+\nu}(\mathbf{a}|g_{12}^{\mu}|\mathbf{b}|g_{23}^{\nu}|\mathbf{c}) + \frac{\mu}{\mu+\beta+\nu}(\mathbf{a}+\mathbf{1}_i|g_{12}^{\mu}|\mathbf{b}|g_{23}^{\nu}|\mathbf{c}) \\ & + \frac{\nu}{\mu+\beta+\nu}(\mathbf{a}|g_{12}^{\mu}|\mathbf{b}|g_{23}^{\nu}|\mathbf{c}+\mathbf{1}_i) + \frac{b_i}{2(\mu+\beta+\nu)}(\mathbf{a}|g_{12}^{\mu}|\mathbf{b}-\mathbf{1}_i|g_{23}^{\nu}|\mathbf{c}). \end{aligned} \tag{3.155}$$

The method for deriving recurrence relations for incrementing angular momentum in $|\mathbf{a})$ and $|\mathbf{c})$ are similar to each other, but different from $|\mathbf{b})$. The derivation for incrementing $|\mathbf{a})$ will be presented along with the result if one goes through the same sort of procedure for $|\mathbf{c})$. Instead of the integral representation defined in equation 3.149 the integral can be represented as

$$(\mathbf{a}|g_{12}^{\mu}|\mathbf{b}|g_{23}^{\nu}|\mathbf{c}) = \int d\vec{r_2}\langle \mathbf{a}|g_{12}^{\mu}\rangle g(\vec{r_2}, \beta, \mathbf{b}, \vec{B})\langle g_{23}^{\nu}|\mathbf{c}\rangle. \tag{3.156}$$

Using the two-centre one-electron overlap recurrence relation described earlier and substituting g_{12}^{μ} in the ket gives

$$\langle \mathbf{a}+\mathbf{1}_i|g_{12}^{\mu}\rangle = (P_{Ai} - A_i)\langle \mathbf{a}|g_{12}^{\mu}\rangle + \frac{a_i}{2(\alpha+\mu)}\langle \mathbf{a}-\mathbf{1}_i|g_{12}^{\mu}\rangle. \tag{3.157}$$

Following exactly the same steps as when deriving the G type integrals one obtains

$$\langle \mathbf{a}+\mathbf{1}_i|g_{12}^{\mu}\rangle = \frac{\mu(r_{2i} - B_i - \mathrm{AB}_i)}{\alpha+\mu}\langle \mathbf{a}|g_{12}^{\mu}\rangle + \frac{a_i}{2(\alpha+\mu)}\langle \mathbf{a}-\mathbf{1}_i|g_{12}^{\mu}\rangle. \tag{3.158}$$

Multiplying this expression by $\mathbf{b}\langle g_{23}^{\nu}|\mathbf{c}\rangle$, integrating and expanding out gives

$$\begin{aligned}(\mathbf{a}+\mathbf{1}_i|g_{12}^{\mu}|\mathbf{b}|g_{23}^{\nu}|\mathbf{c}) = {} & -\frac{\mu\mathrm{AB}_i}{\alpha+\mu}(\mathbf{a}|g_{12}^{\mu}|\mathbf{b}|g_{23}^{\nu}|\mathbf{c}) + \frac{\mu}{\alpha+\mu}(\mathbf{a}|g_{12}^{\mu}|\mathbf{b}+\mathbf{1}_i|g_{23}^{\nu}|\mathbf{c}) \\ & + \frac{a_i}{2(\alpha+\mu)}(\mathbf{a}-\mathbf{1}_i|g_{12}^{\mu}|\mathbf{b}|g_{23}^{\nu}|\mathbf{c}). \end{aligned} \tag{3.159}$$

The corresponding expression for incrementing angular momentum in $|\mathbf{c})$ is given by

$$\begin{aligned}(\mathbf{a}|g_{12}^{\mu}|\mathbf{b}|g_{23}^{\nu}|\mathbf{c}+\mathbf{1}_i) = {} & \frac{\nu\mathrm{BC}_i}{\gamma+\nu}(\mathbf{a}|g_{12}^{\mu}|\mathbf{b}|g_{23}^{\nu}|\mathbf{c}) + \frac{\nu}{\gamma+\nu}(\mathbf{a}|g_{12}^{\mu}|\mathbf{b}+\mathbf{1}_i|g_{23}^{\nu}|\mathbf{c}) \\ & + \frac{c_i}{2(\gamma+\nu)}(\mathbf{a}|g_{12}^{\mu}|\mathbf{b}|g_{23}^{\nu}|\mathbf{c}-\mathbf{1}_i). \end{aligned} \tag{3.160}$$

As with all the integral classes presented previously, one must have a recurrence relation that contains only one increment in angular momentum. This can be obtained by treating equations 3.155, 3.159 and 3.160 as simultaneous equations. The process is lengthy, although not complex and yields the following recurrence relations for incrementing $|\mathbf{a})$, $|\mathbf{b})$ and $|\mathbf{c})$

$$\begin{aligned}(\mathbf{a}+\mathbf{1}_i|g_{12}^{\mu}|\mathbf{b}|g_{12}^{\nu}|\mathbf{c}) &= -\frac{\mu}{\omega}\left[(\gamma\nu+\beta(\gamma+\nu))\mathrm{AB}_i+\gamma\nu\mathbf{BC}_i\right](\mathbf{a}|g_{12}^{\mu}|\mathbf{b}|g_{12}^{\nu}|\mathbf{c})\\ &+\frac{\gamma(\beta+\mu)+\nu(\beta+\gamma+\mu)}{2\omega}a_i(\mathbf{a}-\mathbf{1}_i|g_{12}^{\mu}|\mathbf{b}|g_{12}^{\nu}|\mathbf{c})+\frac{\mu(\gamma+\nu)b_i}{2\omega}(\mathbf{a}|g_{12}^{\mu}|\mathbf{b}-\mathbf{1}_i|g_{12}^{\nu}|\mathbf{c})+\frac{\mu\nu c_i}{2\omega}(\mathbf{a}|g_{12}^{\mu}|\mathbf{b}|g_{12}^{\nu}|\mathbf{c}-\mathbf{1}_i),\end{aligned} \tag{3.161}$$

$$\begin{aligned}(\mathbf{a}|g_{12}^{\mu}|\mathbf{b}+\mathbf{1}_i|g_{12}^{\nu}|\mathbf{c}) &= \frac{\alpha\mu(\gamma+\nu)\mathrm{AB}_i+\gamma\nu(\alpha+\mu)\mathrm{BC}_i}{\omega}(\mathbf{a}|g_{12}^{\mu}|\mathbf{b}|g_{12}^{\nu}|\mathbf{c})\\ &+\frac{\mu(\gamma+\nu)a_i}{2\omega}(\mathbf{a}-\mathbf{1}_i|g_{12}^{\mu}|\mathbf{b}|g_{12}^{\nu}|\mathbf{c})+\frac{(\alpha+\mu)(\gamma+\nu)b_i}{2\omega}(\mathbf{a}|g_{12}^{\mu}|\mathbf{b}-\mathbf{1}_i|g_{12}^{\nu}|\mathbf{c})+\frac{\nu(\alpha+\mu)c_i}{2\omega}(\mathbf{a}|g_{12}^{\mu}|\mathbf{b}|g_{12}^{\nu}|\mathbf{c}-\mathbf{1}_i),\end{aligned} \tag{3.162}$$

$$\begin{aligned}(\mathbf{a}|g_{12}^{\mu}|\mathbf{b}|g_{12}^{\nu}|\mathbf{c}+\mathbf{1}_i) &= \frac{\nu}{\omega}\left[\alpha\mu\mathrm{AB}_i+(\alpha\mu+\beta(\alpha+\mu)\mathrm{BC}_i)\right](\mathbf{a}|g_{12}^{\mu}|\mathbf{b}|g_{12}^{\nu}|\mathbf{c})\\ &+\frac{\mu\nu a_i}{2\omega}(\mathbf{a}-\mathbf{1}_i|g_{12}^{\mu}|\mathbf{b}|g_{12}^{\nu}|\mathbf{c})+\frac{\nu(\alpha+\mu)b_i}{2\omega}(\mathbf{a}|g_{12}^{\mu}|\mathbf{b}-\mathbf{1}_i|g_{12}^{\nu}|\mathbf{c})+\frac{\alpha(\beta+\nu)+\mu(\beta+\alpha+\nu)}{2\omega}c_i(\mathbf{a}|g_{12}^{\mu}|\mathbf{b}|g_{12}^{\nu}|\mathbf{c}-\mathbf{1}_i),\end{aligned} \tag{3.163}$$

where

$$\omega=\alpha\beta\gamma+\alpha\gamma\mu+\beta\gamma\mu+\alpha\beta\nu+\alpha\gamma\nu+\alpha\mu\nu+\beta\mu\nu+\gamma\mu\nu. \tag{3.164}$$

The starting term for the recurrence relation is given by

$$(\mathrm{s}|g_{12}^{\mu}|s|g_{12}^{\nu}|\mathrm{s})=\exp\left\{\frac{-|\overline{\mathrm{AB}}|^2(\alpha\beta\gamma\mu+\alpha\beta\mu\nu)-|\overline{\mathrm{BC}}|^2(\alpha\beta\gamma\nu+\beta\gamma\mu\nu)-|\overline{\mathrm{AC}}|^2\alpha\gamma\mu\nu}{\omega}\right\}\left(\frac{\pi^{9/2}}{\omega^{3/2}}\right). \tag{3.165}$$

The F-F integrals are related to F type integrals in structure and one would expect them to share many similarities. This is indeed the case and the most useful similarity is the existence of a so-called 'transfer equation' for these three-electron integrals. The transfer equation can be derived by treating the three recurrence relation for incrementing angular momentum as simultaneous equations. However, there is another slightly easier method to derive the equation. Starting with the equation

$$\left(\frac{\partial}{\partial A_i}+\frac{\partial}{\partial B_i}+\frac{\partial}{\partial C_i}\right)(\mathbf{a}|\mathbf{b}|\mathbf{c})=0 \tag{3.166}$$

and then expanding out and using equation 3.45 yields the three-electron transfer equation

$$\begin{aligned}&\alpha(\mathbf{a}+\mathbf{1}_i|g_{12}^{\mu}|\mathbf{b}|g_{12}^{\nu}|\mathbf{c})+\beta(\mathbf{a}|g_{12}^{\mu}|\mathbf{b}+\mathbf{1}_i|g_{12}^{\nu}|\mathbf{c})+\gamma(\mathbf{a}|g_{12}^{\mu}|\mathbf{b}|g_{12}^{\nu}|\mathbf{c}+\mathbf{1}_i)\\&=\frac{a_i}{2}(\mathbf{a}-\mathbf{1}_i|g_{12}^{\mu}|\mathbf{b}|g_{12}^{\nu}|\mathbf{c})+\frac{b_i}{2}(\mathbf{a}|g_{12}^{\mu}|\mathbf{b}-\mathbf{1}_i|g_{12}^{\nu}|\mathbf{c})+\frac{c_i}{2}(\mathbf{a}|g_{12}^{\mu}|\mathbf{b}|g_{12}^{\nu}|\mathbf{c}-\mathbf{1}_i).\end{aligned} \tag{3.167}$$

Its application is of a similar nature to that of the two-electron transfer equation (equation 3.85) with computational saving achieved by not looping over the Gaussian geminal exponents for the final angular momentum transfer.

The starting equation for the three-electron transfer equation 3.166 is not obvious. However, one can imagine taking the three Gaussian centres $\vec{A}$, $\vec{B}$ and $\vec{C}$ and transforming them to the basis

$$\vec{P}=\vec{A}+\vec{B}+\vec{C},\qquad \vec{Q}=2\vec{A}-\vec{B}-\vec{C}\qquad\text{and}\qquad \vec{R}=-\vec{A}+2\vec{B}-\vec{C} \tag{3.168}$$

where

$$\vec{A}=\frac{1}{6}(2\vec{P}+3\vec{Q}+2\vec{R}),\qquad \vec{B}=\frac{1}{3}(\vec{P}+\vec{R})\qquad\text{and}\qquad \vec{C}=\frac{1}{6}(2\vec{P}-3\vec{Q}-4\vec{R}). \tag{3.169}$$

Differentiating the integral with respect to P_i must give zero since moving the centre of mass should not alter the value of the integrals. Doing this yields

$$\frac{\partial}{\partial P_i}(\mathbf{a}|\mathbf{b}|\mathbf{c})=\left(\frac{\partial A_i}{\partial P_i}\frac{\partial}{\partial A_i}+\frac{\partial B_i}{\partial P_i}\frac{\partial}{\partial B_i}+\frac{\partial C_i}{\partial P_i}\frac{\partial}{\partial C_i}\right)(\mathbf{a}|\mathbf{b}|\mathbf{c})=0 \tag{3.170}$$

which on substitution of the known differentials yields

$$\frac{\partial}{\partial P_i}(\mathbf{a}|\mathbf{b}|\mathbf{c})=\frac{1}{3}\left(\frac{\partial}{\partial A_i}+\frac{\partial}{\partial B_i}+\frac{\partial}{\partial C_i}\right)(\mathbf{a}|\mathbf{b}|\mathbf{c})=0 \tag{3.171}$$

Integral class J-F

Integral class J-F is defined explicitly as

$$(\mathbf{a}|r_{12}^{-1}|\mathbf{b}|f_{23}|\mathbf{c}) = \int d\vec{r_1} \int d\vec{r_2} \int d\vec{r_3}\, g(\vec{r_1}, \alpha, \mathbf{a}, \vec{A}) r_{12}^{-1}\, g(\vec{r_2}, \beta, \mathbf{b}, \vec{B}) f_{23}\, g(\vec{r_3}, \gamma, \mathbf{c}, \vec{C}). \tag{3.172}$$

As with the F-F integrals the J-F integrals can be represented as a summation over J-G integrals thus

$$(\mathbf{a}|r_{12}^{-1}|\mathbf{b}|f_{23}|\mathbf{c}) = \sum_{\nu} c_\nu (\mathbf{a}|r_{12}^{-1}|\mathbf{b}|g_{23}^{\nu}|\mathbf{c}). \tag{3.173}$$

As in the derivation of the FJ integrals the Gaussian transform of r_{12}^{-1} defined in equation 3.93 is employed such that

$$(\mathbf{a}|r_{12}^{-1}|\mathbf{b}|g_{23}^{\nu}|\mathbf{c}) = \frac{2}{\sqrt{\pi}} \int_0^\infty (\mathbf{a}|g_{12}^{u^2}|\mathbf{b}|g_{23}^{\nu}|\mathbf{c}) du. \tag{3.174}$$

By inspecting the G-G recurrence relations, the J-G recurrence relations prior to integration over the auxiliary variable u can be obtained. All that must be done is to substitute the exponent μ with u^2. This substitution is performed for all three of the G-G recurrence relations giving

$$\begin{aligned}(\mathbf{a}|g_{12}^{u^2}|\mathbf{b}|g_{23}^{\nu}|\mathbf{c}+\mathbf{1}_i) = {} & \frac{\nu(\alpha u^2 \mathrm{AB}_i + (\beta u^2 + \alpha(\beta + u^2))\mathrm{BC}_i)}{\omega} (\mathbf{a}|g_{12}^{u^2}|\mathbf{b}|g_{23}^{\nu}|\mathbf{c}) \\ & + \frac{u^2 \nu a_i}{2\omega} (\mathbf{a}-\mathbf{1}_i|g_{12}^{u^2}|\mathbf{b}|g_{23}^{\nu}|\mathbf{c}) \\ & + \frac{\nu(\alpha+u^2)b_i}{2\omega} (\mathbf{a}|g_{12}^{u^2}|\mathbf{b}-\mathbf{1}_i|g_{23}^{\nu}|\mathbf{c}) \\ & + \frac{(u^2(\beta+\nu) + \alpha(\beta+u^2+\nu))c_i}{2\omega} (\mathbf{a}|g_{12}^{u^2}|\mathbf{b}|g_{23}^{\nu}|\mathbf{c}-\mathbf{1}_i).\end{aligned} \tag{3.175}$$

$$\begin{aligned}(\mathbf{a}|g_{12}^{u^2}|\mathbf{b}+\mathbf{1}_i|g_{23}^{\nu}|\mathbf{c}) = {} & \frac{u^2\alpha(\gamma+\nu)\mathrm{AB}_i - \gamma\nu(u^2+\alpha)\mathrm{BC}_i}{\omega} (\mathbf{a}|g_{12}^{u^2}|\mathbf{b}|g_{23}^{\nu}|\mathbf{c}) \\ & + \frac{u^2(\gamma+\nu)a_i}{2\omega} (\mathbf{a}-\mathbf{1}_i|g_{12}^{u^2}|\mathbf{b}|g_{23}^{\nu}|\mathbf{c}) \\ & + \frac{(u^2+\alpha)(\gamma+\nu)b_i}{2\omega} (\mathbf{a}|g_{12}^{u^2}|\mathbf{b}-\mathbf{1}_i|g_{23}^{\nu}|\mathbf{c}) \\ & + \frac{\nu(u^2+\alpha)c_i}{2\omega} (\mathbf{a}|g_{12}^{u^2}|\mathbf{b}|g_{23}^{\nu}|\mathbf{c}-\mathbf{1}_i).\end{aligned} \tag{3.176}$$

$$\begin{aligned}(\mathbf{a}+\mathbf{1}_i|g_{12}^{u^2}|\mathbf{b}|g_{23}^{\nu}|\mathbf{c}) = &-\frac{u^2((\gamma\nu+\beta(\gamma+\nu))\mathrm{AB}_i+\gamma\nu\mathrm{CB}_i)}{\omega}(\mathbf{a}|g_{12}^{u^2}|\mathbf{b}|g_{23}^{\nu}|\mathbf{c}) \\ &+\frac{(\gamma(\beta+u^2)+\nu(\beta+\gamma+u^2))a_i}{2\omega}(\mathbf{a}-\mathbf{1}_i|g_{12}^{u^2}|\mathbf{b}|g_{23}^{\nu}|\mathbf{c}) \\ &+\frac{u^2(\gamma+\nu)b_i}{2\omega}(\mathbf{a}|g_{12}^{u^2}|\mathbf{b}-\mathbf{1}_i|g_{23}^{\nu}|\mathbf{c}) \\ &+\frac{u^2\nu c_i}{2\omega}(\mathbf{a}|g_{12}^{u^2}|\mathbf{b}|g_{23}^{\nu}|\mathbf{c}-\mathbf{1}_i). \end{aligned} \tag{3.177}$$

Once again an auxiliary integral is introduced

$$(\mathbf{a}|r_{12}^{-1}|\mathbf{b}|e^{-\nu r_{23}^2}|\mathbf{c})^{(m)} = \frac{2}{\sqrt{\pi}}\int_0^{\infty} du\left(\frac{u^2}{u^2+\rho}\right)^m (\mathbf{a}|g_{12}^{u^2}|\mathbf{b}|e^{-\nu r_{23}^2}|\mathbf{c}). \tag{3.178}$$

The choice of ρ is not important but must be greater than zero. For simplicity it is convenient to ensure that the same value of ρ is used for all three recurrence relations. The integration is performed to give

$$
\begin{aligned}
(\mathbf{a}|r_{12}^{-1}|\mathbf{b}|g_{23}^{\nu}|\mathbf{c}+\mathbf{1}_i)^{(m)} &= \frac{\nu}{\eta\rho}\left[\alpha\beta\mathrm{BC}_i(\mathbf{a}|r_{12}^{-1}|\mathbf{b}|g_{23}^{\nu}|\mathbf{c})^{(m)} + (\alpha\rho\mathrm{AB}_i + (\rho(\alpha+\beta)-\alpha\beta)\mathrm{BC}_i)(\mathbf{a}|r_{12}^{-1}|\mathbf{b}|g_{23}^{\nu}|\mathbf{c})^{(m+1)}\right] \\
&+ \frac{\nu a_i}{2\eta}(\mathbf{a}-\mathbf{1}_i|r_{12}^{-1}|\mathbf{b}|g_{23}^{\nu}|\mathbf{c})^{(m+1)} \\
&+ \frac{\nu b_i}{2\eta\rho}\left[\alpha(\mathbf{a}|r_{12}^{-1}|\mathbf{b}-\mathbf{1}_i|g_{23}^{\nu}|\mathbf{c})^{(m)} + (\alpha-\rho)(\mathbf{a}|r_{12}^{-1}|\mathbf{b}-\mathbf{1}_i|g_{23}^{\nu}|\mathbf{c})^{(m+1)}\right] \\
&+ \frac{c_i}{2\eta\rho}\left[\alpha(\beta+\nu)(\mathbf{a}|r_{12}^{-1}|\mathbf{b}|g_{23}^{\nu}|\mathbf{c}-\mathbf{1}_i)^{(m)} - (\alpha(\beta+\nu)-\rho(\alpha+\beta+\nu))(\mathbf{a}|r_{12}^{-1}|\mathbf{b}|g_{23}^{\nu}|\mathbf{c}-\mathbf{1}_i)^{(m+1)}\right],
\end{aligned}
\tag{3.179}
$$

$$
\begin{aligned}
(\mathbf{a}|r_{12}^{-1}|\mathbf{b}+\mathbf{1}_i|g_{23}^{\nu}|\mathbf{c})^{(m)} &= \frac{1}{\eta\rho}\left[-\alpha\gamma\nu\mathrm{BC}_i(\mathbf{a}|r_{12}^{-1}|\mathbf{b}|g_{23}^{\nu}|\mathbf{c})^{(m)} + (\alpha(\gamma+\nu)\mathrm{AB}_i - \gamma\nu(\rho-\alpha)\mathrm{BC}_i)(\mathbf{a}|r_{12}^{-1}|\mathbf{b}|g_{23}^{\nu}|\mathbf{c})^{(m+1)}\right] \\
&+ \frac{(\gamma+\nu)a_i}{2\eta}(\mathbf{a}-\mathbf{1}_i|r_{12}^{-1}|\mathbf{b}|g_{23}^{\nu}|\mathbf{c})^{(m+1)} \\
&+ \frac{(\gamma+\nu)b_i}{2\eta\rho}\left[\alpha(\mathbf{a}|r_{12}^{-1}|\mathbf{b}-\mathbf{1}_i|g_{23}^{\nu}|\mathbf{c})^{(m)} - (\alpha-\rho)(\mathbf{a}|r_{12}^{-1}|\mathbf{b}-\mathbf{1}_i|g_{23}^{\nu}|\mathbf{c})^{(m+1)}\right] \\
&+ \frac{\nu c_i}{2\eta\rho}\left[\alpha(\mathbf{a}|r_{12}^{-1}|\mathbf{b}|g_{23}^{\nu}|\mathbf{c}-\mathbf{1}_i)^{(m)} + (\alpha-\rho)(\mathbf{a}|r_{12}^{-1}|\mathbf{b}|g_{23}^{\nu}|\mathbf{c}-\mathbf{1}_i)^{(m+1)}\right],
\end{aligned}
\tag{3.180}
$$

$$
\begin{aligned}
(\mathbf{a}+\mathbf{1}_i|r_{12}^{-1}|\mathbf{b}|g_{23}^{\nu}|\mathbf{c})^{(m)} &= -\frac{(\gamma\nu+\beta(\gamma+\nu))\mathrm{AB}_i + \gamma\nu\mathrm{BC}_i}{\eta}(\mathbf{a}|r_{12}^{-1}|\mathbf{b}|g_{23}^{\nu}|\mathbf{c})^{(m+1)} \\
&+ \frac{a_i}{2\eta\rho}\left[(\gamma\nu+\beta(\gamma+\nu))(\mathbf{a}-\mathbf{1}_i|r_{12}^{-1}|\mathbf{b}|g_{23}^{\nu}|\mathbf{c})^{(m)} - (\gamma\nu+\beta(\gamma+\nu)-\rho(\gamma+\nu))(\mathbf{a}-\mathbf{1}_i|r_{12}^{-1}|\mathbf{b}|g_{23}^{\nu}|\mathbf{c})^{(m+1)}\right] \\
&+ \frac{(\gamma+\nu)b_i}{2\eta}(\mathbf{a}|r_{12}^{-1}|\mathbf{b}-\mathbf{1}_i|g_{23}^{\nu}|\mathbf{c})^{(m+1)} + \frac{\nu c_i}{2\eta}(\mathbf{a}|r_{12}^{-1}|\mathbf{b}|g_{23}^{\nu}|\mathbf{c}-\mathbf{1}_i)^{(m+1)},
\end{aligned}
\tag{3.181}
$$

where

$$
\rho = \frac{\alpha\beta\gamma + \alpha\nu(\beta+\gamma)}{\eta} \qquad \text{and} \qquad \eta = \gamma(\alpha+\beta) + \nu(\alpha+\beta+\gamma).
\tag{3.182}
$$

As with the F-F class of integrals the transfer equation still holds allowing for an easier and more efficient evaluation of the integrals. In the case of the F-J integrals it also avoids performing the integration over u^2 for building angular momentum. The $(\mathrm{s}|r_{12}^{-1}|\mathrm{s}|g_{23}^{\nu}|\mathrm{s})$ case can now be calculated as follows

$$\begin{aligned}(\mathrm{s}|r_{12}^{-1}|\mathrm{s}|g_{23}^{\nu}|\mathrm{s})^{(m)} &= \frac{2}{\sqrt{\pi}}\int_0^{\infty} du \left(\frac{u^2}{u^2+\rho}\right)^m \int d\vec{r}_1 \int d\vec{r}_2 \int d\vec{r}_3 \\ &\times e^{-\alpha|\vec{r}_1-\vec{A}|^2} e^{-u^2|\vec{r}_1-\vec{r}_2|^2} e^{-\beta|\vec{r}_2-\vec{B}|^2} e^{-\nu|\vec{r}_2-\vec{r}_3|^2} e^{-\gamma|\vec{r}_3-\vec{C}|^2} \qquad (3.183) \\ &= \frac{2\pi^4}{\eta^{3/2}\rho^{3/2}} e^{-|\overline{\mathrm{BC}}|^2\alpha\beta\gamma\nu/\eta\rho} \int_0^{\infty} du \left(\frac{u^2}{u^2+\rho}\right)^m \left(\frac{\rho}{u^2+\rho}\right)^{3/2} \\ &\times \exp\left\{-T\left(\frac{u^2}{u^2+\rho}\right)\right\} \qquad (3.184)\end{aligned}$$

where

$$T = \frac{1}{\eta\rho}\left\{\alpha\gamma\nu\rho|\overline{\mathrm{AC}}|^2 + \alpha\beta\rho(\gamma+\nu)|\overline{\mathrm{AB}}|^2 + \beta\gamma\nu(\rho-\alpha)|\overline{\mathrm{BC}}|^2\right\}. \qquad (3.185)$$

The integral over u can now be performed by transforming variable form u to t

$$t^2 = \frac{u^2}{u^2+\rho}, \qquad (3.186)$$

$$du = \rho^{1/2}(1-t^2)^{-3/2}dt \qquad (3.187)$$

$$\left(\frac{\rho}{u^2+\rho}\right)^{3/2} = (1-t^2)^{3/2} \qquad (3.188)$$

$$\begin{aligned}(\mathrm{s}|r_{12}^{-1}|\mathrm{s}|g_{23}^{\nu}|\mathrm{s})^{(m)} &= \frac{2\pi^4}{\eta^{3/2}\rho^{3/2}} e^{-|\overline{\mathrm{BC}}|^2\alpha\beta\gamma\nu/\eta\rho} \int_0^1 dt\, \rho^{1/2}(1-t^2)^{-3/2} t^{2m}(1-t^2)^{3/2} e^{-Tt^2} \\ &= \frac{2\pi^4}{\eta^{3/2}\rho} e^{-|\overline{\mathrm{BC}}|^2\alpha\beta\gamma\nu/\eta\rho} F_m(T). \qquad (3.189)\end{aligned}$$

The same sort of tests used for the G type integrals also apply to these integrals, applying limits to the Gaussian geminal.

3.3 Summary

In this chapter all of the recurrence relations required to implement the integrals needed for MP2-F12 theories have been derived. Three-electron integral classes for selected integrals have been derived explicitly for evaluating the accuracy of the RI approximation and providing a test for the integral code. The integrals take the majority of the time when running a calculation and similarly when implementing new theories of the kind described here the bulk of the time is spent deriving recurrence relations for integrals and coding them up.

Chapter 4

Implementation

This chapter details the process of implementing the various MP2-F12 methods and the new integral codes into the MOLPRO quantum chemistry package [58].

4.1 Indexing of the integrals

The integral recurrence relationships derived in the integrals chapter were for Cartesian primitives with angular momentum in the range 0–l_{max}. Once constructed there already exist routines for converting to spherical Gaussians, and for contracting and normalising the integrals. Recurrence relations by their very nature have to be able to access integral quantities already constructed, thus indexing of the integrals is of the utmost importance.

The integrals are produced in shells, illustrated in figure 3.1 for a two-electron integral with angular momentum $l = 2$ for both electrons, i.e. a d-d shell. The integral shells are stored in the order by which one would most likely write them down, the rules for which are now defined explicitly.

In the first instance the case of a one-index, one-electron integral will be considered. The first factor in determining the ordering of the integrals is the angular momentum level, thus s-integrals precede p-integrals, p-integrals precede d-integrals and so on ascending until the maximum angular momentum, l_{max}. For Cartesian integrals angular momentum can be spread over three components, x, y, and z. Therefore, within each level of angular momentum the angular momentum can be spread around in variety of ways, with the obvious exception of s-integrals where the angular momentum is zero. In this section l will be used to represent a given level of angular momentum which is defined as $l = i +$

$j+k$ where i, j, and k represent the powers of x, y, and z respectively. The primary order of angular momentum components is defined by i starting with all angular momentum in the i component. Component i is then decremented by one and angular momentum transferred to the j component. The j component defines the secondary ordering of the integral components and angular momentum is decrementally transferred to k for each fixed value of i. This is best illustrated by use of an example, for a one-electron shell of f angular momentum (l_{max}=3) the order is shown in figure 4.1.

index	i	j	k	l
1	0	0	0	0
2	1	0	0	1
3	0	1	0	
4	0	0	1	
5	2	0	0	2
6	1	1	0	
7	1	0	1	
8	0	2	0	
9	0	1	1	
10	0	0	2	
11	3	0	0	3
12	2	1	0	
13	2	0	1	
14	1	2	0	
15	1	1	1	
16	1	0	2	
17	0	3	0	
18	0	2	1	
19	0	1	2	
20	0	0	3	

Figure 4.1: Ordering of one-electron integrals for angular momentum zero to three

When the integrals are stored in this order they can be conveniently accessed through the use of figurate numbers. Figurate numbers in general can be represented by a geometrical pattern of points. The triangular numbers and their d-dimensional generalizations are given by

$$f_d^n = \binom{n+d-1}{d} = \sum_{p=0}^{d} f_p^n. \tag{4.1}$$

For each level of angular momentum there are a fixed number of ways of distributing the angular momentum over the three components, the number of these can be calculated using the expression

$$f_2^{l+1} = (l+1)(l+2)/2. \tag{4.2}$$

The figurate numbers for $d = 1, 2, 3$ are known as the linear, triangular and tetrahedral numbers respectively. The zero-dimensional figurate number is always unity, irrespective of side-length.

For an integral of angular momentum $l = i+j+k$ the location of the integral matching the unique combination of i, j and k in the list is given by

$$\text{index}(i,j,k) = f_3^l + f_2^{j+k} + f_1^k + f_0^0 = f_3^l + f_2^{j+k} + f_1^k + 1. \tag{4.3}$$

The indexing is set up so that $\text{index}(0,0,0) = 1$. The only thing one needs to know in practice, though, is how to get from one element to another. This can easily be determined from the simple figurate recurrence

$$f_d^n = f_d^{n-1} + f_{d-1}^n, \tag{4.4}$$

ie the side length of a figure can be incremented by adding the figure of one fewer dimensions but of the incremented side-length. For example, a side-3 triangle is turned into a side-4 triangle by addition of a side-4 line. Or if one considers the expression on the far right hand side of equation 4.1 then a triangle of side 4 can be composed from a triangle, a line and a point, each of side-length 3.

In all of the recurrence relations derived in the previous chapter the relations required looking up integrals of no more than plus or minus two units of angular momentum. For incrementing one unit of angular momentum the expressions are

$$\begin{aligned}
\text{index}(i+1,j,k) &= \text{index}(i,j,k) + f_2^{l+1} & (4.5)\\
\text{index}(i,j+1,k) &= \text{index}(i,j,k) + f_2^{l+1} + j + k + 1 & (4.6)\\
\text{index}(i,j,k+1) &= \text{index}(i,j,k) + f_2^{l+1} + j + k + 2 & (4.7)
\end{aligned}$$

and for decrementing one unit they are

$$\begin{aligned}
\text{index}(i-1,j,k) &= \text{index}(i,j,k) - f_2^l & (4.8)\\
\text{index}(i,j-1,k) &= \text{index}(i,j,k) - f_2^l - j - k & (4.9)\\
\text{index}(i,j,k-1) &= \text{index}(i,j,k) - f_2^l - j - k - 1. & (4.10)
\end{aligned}$$

For incrementing two units of angular momenta the expressions are

$$\begin{aligned}
\text{index}(i+2,j,k) &= \text{index}(i,j,k) + (l+2)^2 & (4.11)\\
\text{index}(i,j+2,k) &= \text{index}(i,j,k) + (l+2)^2 + 2(j+k) + 3 & (4.12)\\
\text{index}(i,j,k+2) &= \text{index}(i,j,k) + (l+2)^2 + 2(j+k) + 5 & (4.13)
\end{aligned}$$

and for decrementing two units the corresponding expressions are

$$\begin{aligned}
\text{index}(i-2,j,k) &= \text{index}(i,j,k)-l^2 && (4.14)\\
\text{index}(i,j-2,k) &= \text{index}(i,j,k)-l^2-2(j+k)+1 && (4.15)\\
\text{index}(i,j,k-2) &= \text{index}(i,j,k)-l^2-2(j+k)-1. && (4.16)
\end{aligned}$$

Incidentally, the square numbers appear from the fact that $f_2^{l+1}+f_2^{l+2}=(l+2)^2$, ie two triangles differing in side length by one make a square.

The above expressions allow one to move between one-index integrals stored in the list form described previously. However, the integrals that are required are either two- or three-index integrals. In the case of two-index integrals this means that the index is computed from six components; index$(a_i, a_j, a_k, b_i, b_j, b_k)$; and for three-index integrals, from nine components: index$(a_i, a_j, a_k, b_i, b_j, b_k, c_i, c_j, c_k)$.

For the two-index case this means that a matrix of integrals are required demonstrated previously by figure 3.1. In practice because of the way in which MOLPRO assigns its memory it is not possible to efficiently allocate matrices within the Fortran code. Therefore the matrix is assigned as long list with a skip of 1 for one of the electrons and the total number of components of that electron for the other electron. This means that moving between angular momentum will in one case involve multiplying by a fixed factor.

There is a slight complication when making 1 the first index number. Consider the case illustrated in figure 3.1. Assume that $|\mathbf{a})$ runs horizontally as does the indexing, i.e. row one consists of indices 1-10, row two 11-20 etc. Now take the example case index(0,1,0,1,0,1) which corresponds to $(\mathrm{p}_y|\mathrm{d}_{xz})$. By counting the index can be determined to be 63. The expressions for the indices for $|\mathbf{a})$ and $|\mathbf{b})$ are given by

$$\begin{aligned}
\text{index}(0,1,0) &= f_3^1+f_2^1+f_1^0+1=3 && (4.17)\\
\text{index}(1,0,1) &= f_3^2+f_2^1+f_1^1+1=7. && (4.18)
\end{aligned}$$

The skip in $|\mathbf{a})$ is 1 so multiplying by its index above gives $3\times 1=3$ as the $|\mathbf{a})$ index. The skip in $|\mathbf{b})$ is the total number of components there are in $|\mathbf{a})$, i.e. the matrix row size, which is 10. Therefore the $|\mathbf{b})$ index is calculated using its index given above by $7\times 10=70$. Adding together the index numbers give the index of $(\mathrm{p}_y|\mathrm{d}_{xz})$ as 73. This is clearly not correct, and can be seen more clearly when considering the index of (s|s) which is obviously 1 but using the above formula is calculated to be 11. The solution is subtract 1 from the $|\mathbf{b})$ index before multiplying by its skip. This corrects both of the above problems. However, it is not ideal as should one choose to change the order of $|\mathbf{a})$ and $|\mathbf{b})$ then the 1 must be subtracted from $|\mathbf{a})$ not $|\mathbf{b})$. The optimum solution is to remove the 1 from the end of the index expressions of $|\mathbf{a})$ and $|\mathbf{b})$, and $|\mathbf{c})$ in the case of three-electron integrals, then multiply by the appropriate skips and add together. Finally, after adding together a 1 must be added to make the first index be 1, not zero.

4.2 Integral Codes into MOLPRO

Now is perhaps the time to generalise the situation above and take stock of the task in hand. The shell of integrals, be it one-, two- or three-index are to be stored in a piece of memory. They will not necessarily start at a location defined as 0 or 1 so this quantity will be defined as `idx_s`. The skip between integrals are defined as `iskip_a`, `iskip_b` and `iskip_c`. These quantities are intimately related, and it is highly likely that one of the values will be 1, but it need not be.

All the quantities described so far will be known before starting the recurrence relation. When running through the recurrence relation the current index of $|\mathbf{a})$, $|\mathbf{b})$ and $|\mathbf{c})$ will need to be known and these quantities will be termed `idx_a`, `idx_b` and `idx_c`. Thus when the recurrence relation begins the start index will be given by `idx=idx_s` and `idx_a=idx_b=idx_c=0`. From then onward the current location can be obtained by

$$\texttt{idx=idx\_s+idx\_a+idx\_b+idx\_c}. \tag{4.19}$$

The recurrence relations also requires integrals of more or less angular momentum. This could potentially mean looking after six additional indices for each electron, minus 1 in x, y and z direction and plus 1 in x, y and z direction. The situation would become even worse for two units of angular momentum and is analogous to branches of a probability tree. Along with all of the indices mentioned previously this would be a very large number of quantities to take account of. Fortunately there is a way around this and we need only keep track of one index for plus and one for minus for each electron. This might seem strange at first but it comes from the fact that there is some flexibility and choice in the order in which things are calculated. For instance d_{xy} can be calculated by either incrementing p_x in the y direction or p_y in the x direction. This will be further discussed when examining the routine itself. The quantity `idx_ap` indicates the index of $|\mathbf{a}+\mathbf{1}_i)$ and `idx_am` that of $|\mathbf{a}-\mathbf{1}_i)$ where the meaning of i will become clear later on.

The expressions for indices generally involve binomial expressions, and hence factorial quantities to evaluate. These are computationally expensive operations to undertake and the quantity of these must be minimised for an efficient implementation. The best way, if possible, is to calculate integrals in the order in which they will be stored. This is in fact possible and provides the solution used. It will also provide the explanation of why there is only one index for plus and minus angular momentum for each electron.

All of the important concepts about the shell routine structure are contained within the one-electron routine. The two- and three- electron routines are much more lengthy with much care needed to look after the indexing, but they are still based upon the same concepts as the one-electron routine. However, because there are significant simplifications for the one-electron case a two-electron routine will be considered where the angular momentum of $|\mathbf{b})$ is fixed at zero, but still provides a centre and exponent. A pseudo Fortran code for the two-electron G-type integrals for the case just described is now discussed. The syntax of the routine is given by

```
 SUBROUTINE G_integral(α,A⃗,l_a,iskip_a,
>                      β,B⃗,l_b,iskip_b,
>                      idx_s,γ,shell)
 IMPLICIT DOUBLE PRECISION (a-h,o-z)
 DOUBLE PRECISION,                INTENT(IN)  :: α,β
 DOUBLE PRECISION, DIMENSION(3),  INTENT(IN)  :: A⃗,B⃗
 INTEGER,                         INTENT(IN)  :: l_a,l_b
 INTEGER,                         INTENT(IN)  :: iskip_a
 INTEGER,                         INTENT(IN)  :: iskip_b
 INTEGER,                         INTENT(IN)  :: idx_s
 DOUBLE PRECISION,                INTENT(IN)  :: γ
 DOUBLE PRECISION, DIMENSION(*),  INTENT(OUT) :: shell
```

where α, $\vec{A}$ and l_a are the exponent, centre and angular momentum of the Gaussian function and `iskip_a` is the skip between $|\mathbf{a})$ integrals in the destination vector `shell`. The exponent of one of the Gaussian functions comprising the geminal is given by γ and the location of the $(\mathbf{0}|\mathbf{0})$ integral in `shell` is given by `idx_s`. Next the indexing for $|\mathbf{a})$ and

$|\mathbf{b})$ must be defined, along with some constants for convenience.

```
idx_a=idx_s; idx_ap=idx_a+iskip_a; idx_am=idx_a
$\overline{\mathrm{AB}} = \vec{A} - \vec{B}$
$\eta = \alpha\beta + \beta\gamma + \gamma\alpha$
cab=$\frac{\beta\gamma}{\eta}$
camb=$\frac{\beta\gamma}{2\eta}$
```

Finally the actual recurrence relation begins, starting with the special $(\mathbf{0}|\mathbf{0})$ case which is evaluated explicitly and then moving onto the loop structure that builds up the angular momentum

```
 shell(idx)=$\exp\left\{-\frac{|\overline{\mathrm{AB}}|^2\alpha\beta\gamma}{\eta}\right\}\left(\frac{\pi}{\sqrt{\eta}}\right)^3$
 DO ia=0,$l_a$
  shell(idx_ap)=shell(idx_a)*cab*$\mathrm{AB}_1$
>               +ia*camb*shell(idx_am)
  idx_ap=idx_ap+1
  shell(idx_ap)=shell(idx_a)*cab*$\mathrm{AB}_2$
  idx_ap=idx_ap+1
  shell(idx_ap)=shell(idx_a)*cab*$\mathrm{AB}_3$
  idx_ap=idx_ap+1
  idx_a =idx_a +1
  DO ja=1,ia
   shell(idx_ap)=shell(idx_a)*cab*$\mathrm{AB}_2$
>                +ja*camb*shell(idx_am)
   idx_ap=idx_ap+1
   shell(idx_ap)=shell(idx_a)*cab*$\mathrm{AB}_3$
   idx_ap=idx_ap+1
   idx_a =idx_a +1
   DO ka=1,ja
   shell(idx_ap)=shell(idx_a)*cab*$\mathrm{AB}_3$
>                +ka*camb*shell(idx_am)
   idx_ap=idx_ap+1
   idx_a =idx_a +1
```

```
   idx_am=idx_am+1
   ENDDO
  ENDDO
 ENDDO
 RETURN; END SUBROUTINE G_integral
```

The indexing is built up and never has to be explicitly calculated from Cartesian component numbers. The value `idx` is actually disguised within `idx_ap` as it contains `idx_s` and `idx_b=0`. In this case it is simply easier to add in these quantities first rather than add then at every stage. There is no index for incrementing $|\mathbf{b})$ as in this case angular momentum is being built in $|\mathbf{a})$. In this special case there is no index for decrementing $|\mathbf{b})$ as this would be meaningless as it would correspond to negative angular momentum.

A naive loop structure for angular momentum would involve three loops, where only in the inner loop i, j and k are defined. The alternative used here takes into account that if all of the angular momentum is already known to be contained within a single component, for instance i, then the values of j and k are already defined as zero. Because they are defined as zero this leads to simplifications in the expressions containing j and k in the outer loop. With every integral already constructed one has a choice to build integrals with angular momentum increments in the x, y and z direction. However, it is possible to construct certain integrals from a choice of base integrals. By making sure the maximum number of integrals are calculated from each element in the lowest loop the next loop needs to increment in one less direction, thus introducing further simplification. Thus the outer loop increases angular momentum in x, y and z direction, the next loop the y and z direction and in the final loop the z direction only.

The next step is to extend the routine to a general two-electron integral. This is relatively straightforward, although the routine is quite lengthy. The routine described previously builds a row of $|\mathbf{a})$. Thus to build a complete shell using the same efficient manner one must construct the same loop structure looping over the angular momentum of $|\mathbf{b})$. The difference is that instead of producing a single element every time `idx_bp` is incremented, a complete row of $|\mathbf{a})$ is produced. An outline of the situation is

```
idx_bp=idx_s
shell(idx_bp)=row_1 ! (*|s) case
idx_bp=idx_bp+iskip_b
```

```
DO ib=0,$l_b$
 shell(idx_bp)=row_incrementing_x ! $(*|\mathbf{b}+1_x)$
 idx_bp=idx_bp+iskip_b
 shell(idx_bp)=row_incrementing_y ! $(*|\mathbf{b}+1_y)$
 idx_bp=idx_bp+iskip_b
 shell(idx_bp)=row_incrementing_z ! $(*|\mathbf{b}+1_z)$
 idx_bp=idx_bp+iskip_b
 idx_b =idx_b +iskip_b
 DO jb=1,ib
  shell(idx_bp)=row_incrementing_y ! $(*|\mathbf{b}+1_y)$
  idx_bp=idx_bp+iskip_b
  shell(idx_bp)=row_incrementing_z ! $(*|\mathbf{b}+1_z)$
  idx_bp=idx_bp+iskip_b
  idx_b =idx_b +iskip_b
  DO kb=1,jb
   shell(idx_bp)=row_incrementing_z ! $(*|\mathbf{b}+1_z)$
   idx_bp=idx_bp+iskip_b
   idx_b =idx_b +iskip_b
   idx_bm=idx_bm+iskip_b
  ENDDO
 ENDDO
ENDDO
```

Thus there are three do loops for the angular momentum of $|\mathbf{b})$ where the loop structure over $|\mathbf{a})$ is inserted six times. For three-electron integrals all of the above is inserted six times into a loop structure over the angular momentum of $|\mathbf{c})$. In a naive implementation there would then be an additional loop for integrals such as F-type, for each Gaussian function of the geminal. These would then be summed together. As seen in the previous chapter there is an way of significantly reducing the work in the form of the transfer equation.

4.2.1 The transfer equation

The transfer equation is simply another recurrence relation. In that respect it is implemented in much the same fashion as the recurrence relations detailed in the previous section. The saving is that it does not involve the Gaussian geminal exponents and so all of the summations can be done prior to applying the transfer equation. This typically means building up angular momentum in one direction, summing over exponents and then applying the transfer equation in the other direction.

There is a distinct difference from other recurrence relations described previously in that one must take care of angular momentum of both higher and lower indices in the x, y and z direction of the centre from which the angular momentum is being transferred. This entails keeping track of an extra set of indices, and incrementing appropriately.

The centre to which the angular momentum is being transferred as usual only requires a single index for the plus and a single index for the minus angular momentum.

The pseudo code for a transfer equation, where angular momentum in $|\mathbf{a})$ is being transferred from $|\mathbf{b})$, is shown below. Because of simplifications the s and p angular momentum cases are dealt with specifically, and for d and higher angular momentum the general formula is used.

```
SUBROUTINE basis_shell_trans($\alpha$,$l_a$,$\beta$,$l_b$,vec,shell)
IMPLICIT DOUBLE PRECISION (a-h,o-z)
DOUBLE PRECISION,                INTENT(IN)  :: $\alpha$,$\beta$
INTEGER,                         INTENT(IN)  :: $l_a$,$l_b$
DOUBLE PRECISION, DIMENSION(*),  INTENT(IN)  :: vec
DOUBLE PRECISION, DIMENSION(*),  INTENT(OUT) :: shell
$l_{tot} = l_a + l_b$
 get integer vector iq(incc) size $l_{tot} + 1$ and zero
DO i= $1, l_{tot} + 1$ !  calculate some indexing and put in iq(incc)
  iq(incc+i)=i*(i+1)*(i+2)/6
ENDDO
ntot=iq(incc+$l_{tot} + 1$)
naS=iq(incc+$l_a$+1)
 get block of memory q, size naS*ntot , start point idxS and zero the contents
 copy first row of matrix, vec into q(idxS)
```

```
IF($l_a$.GT.0) THEN !  case for building $(\mathbf{p}|*)$
ia0c=idxS
iapc=idxS+1
DO i=$l_{tot}-1$,0,-1
 ib0=naS*iq(incc+i)
 ibmx=ib0-i*(i+1)*naS/2
 ibpx=ib0+(i+1)*(i+2)*naS/2
 ibpy=ibpx+naS
 ibpz=ibpy+naS
 q(iapc+ib0)=$-\frac{\beta}{\alpha}$×q(ia0c+ibpx)+i×$\frac{1}{2\alpha}$×q(ia0c+ibmx)
 iap=iapc+1
 q(iap+ib0)=$-\frac{\beta}{\alpha}$×q(ia0c+ibpy)
 iap=iap+1
 q(iap+ib0)=$-\frac{\beta}{\alpha}$×q(ia0c+ibpz)
 iap=iap+1
 ia0=ia0c+1
 ib0=ib0+naS
 ibmx=ibmx+naS
 ibpx=ibpx+naS
 DO j=1,i
  ibmy=ibmx-j*naS
  ibpy=ibpx+(j+1)*naS
  ibpz=ibpy+naS
  q(iapc+ib0)=$-\frac{\beta}{\alpha}$×q(ia0c+ibpx)+(i-j)×$\frac{1}{2\alpha}$×q(ia0c+ibmx)
  iap=iapc+1
  q(iap+ib0)=$-\frac{\beta}{\alpha}$×q(ia0c+ibpy)+j×$\frac{1}{2\alpha}$×q(ia0c+ibmy)
  iap=iap+1
  q(iap+ib0)=$-\frac{\beta}{\alpha}$×q(ia0c+ibpz)
  iap=iap+1
  ia0=ia0c+1
  ib0=ib0+naS
  ibmx=ibmx+naS
```

```
  ibpx=ibpx+naS
  ibmy=ibmy+naS
  ibpy=ibpy+naS
  DO k=1,j
   ibmz=ibmy-naS
   ibpz=ibpy+naS
   q(iapc+ib0)=$-\frac{\beta}{\alpha}$×q(ia0c+ibpx)+(i-j)×$\frac{1}{2\alpha}$×q(ia0c+ibmx)
   iap=iapc+1
   q(iap+ib0)=$-\frac{\beta}{\alpha}$×q(ia0c+ibpy)+(j-k)×$\frac{1}{2\alpha}$×q(ia0c+ibmy)
   iap=iap+1
   q(iap+ib0)=$-\frac{\beta}{\alpha}$×q(ia0c+ibpz)+k×$\frac{1}{2\alpha}$×q(ia0c+ibmz)
   iap=iap+1
   ia0=ia0c+1
   ib0=ib0+naS
   ibmx=ibmx+naS
   ibpx=ibpx+naS
   ibmy=ibmy+naS
   ibpy=ibpy+naS
  ENDDO
 ENDDO
ENDDO
DO ia=1,$l_a$-1 !  case for building $(\mathbf{d}...|*)$
 iamc=idxS+iq(incc+ia-1)
 ia0c=idxS+iq(incc+ia)
 iapc=idxS+iq(incc+ia+1)
 DO i=$l_{tot}-1$-ia,0,-1
  ib0=naS*iq(incc+i)
  ibmx=ib0-i*(i+1)*naS/2
  ibpx=ib0+(i+1)*(i+2)*naS/2
  ibpy=ibpx+naS
  ibpz=ibpy+naS
  iam=iamc
```

```
   q(iapc+ib0)=$-\frac{\beta}{\alpha}$×q(ia0c+ibpx)+i×$\frac{1}{2\alpha}$×q(ia0c+ibmx)
>              +ia×$\frac{1}{2\alpha}$×q(iam+ib0)
   iap=iapc+1
   q(iap+ib0)=$-\frac{\beta}{\alpha}$×q(ia0c+ibpy)
   iap=iap+1
   q(iap+ib0)=$-\frac{\beta}{\alpha}$×q(ia0c+ibpz)
   iap=iap+1
   ia0=ia0c+1
   DO iya=1,ia
    q(iap+ib0)=$-\frac{\beta}{\alpha}$×q(ia0+ibpy)+iya×$\frac{1}{2\alpha}$×q(iam+ib0)
    iap=iap+1
    q(iap+ib0)=$-\frac{\beta}{\alpha}$×q(ia0+ibpz)
    iap=iap+1
    ia0=ia0+1
    DO iza=1,iya
     q(iap+ib0)=$-\frac{\beta}{\alpha}$×q(ia0+ibpz)+iza×$\frac{1}{2\alpha}$×q(iam+ib0)
     iap=iap+1
     ia0=ia0+1
     iam=iam+1
    ENDDO
   ENDDO
   ib0=ib0+naS
   ibmx=ibmx+naS
   ibpx=ibpx+naS
   DO j=1,i
    ibmy=ibmx-j*naS
    ibpy=ibpx+(j+1)*naS
    ibpz=ibpy+naS
    iam=iamc
    q(iapc+ib0)=$-\frac{\beta}{\alpha}$×q(ia0c+ibpx)+(i-j)×$\frac{1}{2\alpha}$×q(ia0c+ibmx)
>               +ia×$\frac{1}{2\alpha}$×q(iam+ib0)
    iap=iapc+1
```

```
    q(iap+ib0)=$-\frac{\beta}{\alpha}$×q(ia0c+ibpy)+j×$\frac{1}{2\alpha}$×q(ia0c+ibmy)
    iap=iap+1
    q(iap+ib0)=$-\frac{\beta}{\alpha}$×q(ia0c+ibpz)
    iap=iap+1
    ia0=ia0c+1
    DO iya=1,ia
     q(iap+ib0)=$-\frac{\beta}{\alpha}$×q(ia0+ibpy)+iya×$\frac{1}{2\alpha}$×q(iam+ib0)
>                 +j×$\frac{1}{2\alpha}$×q(ia0+ibmy)
     iap=iap+1
     q(iap+ib0)=$-\frac{\beta}{\alpha}$×q(ia0+ibpz)
     iap=iap+1
     ia0=ia0+1
     DO iza=1,iya
      q(iap+ib0)=$-\frac{\beta}{\alpha}$×q(ia0+ibpz)+iza×$\frac{1}{2\alpha}$×q(iam+ib0)
      iap=iap+1
      ia0=ia0+1
      iam=iam+1
     ENDDO
    ENDDO
    ib0=ib0+naS
    ibmx=ibmx+naS
    ibpx=ibpx+naS
    ibmy=ibmy+naS
    ibpy=ibpy+naS
    DO k=1,j
     ibmz=ibmy-naS
     ibpz=ibpy+naS
     iam=iamc
     q(iapc+ib0)=$-\frac{\beta}{\alpha}$×q(ia0c+ibpx)+(i-j)×$\frac{1}{2\alpha}$×q(ia0c+ibmx)
>                  +ia×$\frac{1}{2\alpha}$×q(iam+ib0)
     iap=iapc+1
     q(iap+ib0)=$-\frac{\beta}{\alpha}$×q(ia0c+ibpy)+(j-k)×$\frac{1}{2\alpha}$×q(ia0c+ibmy)
```

```
     iap=iap+1
     q(iap+ib0)=$-\frac{\beta}{\alpha}\times$q(ia0c+ibpz)+k$\times\frac{1}{2\alpha}\times$q(ia0c+ibmz)
     iap=iap+1
     ia0=ia0c+1
     DO iya=1,ia
      q(iap+ib0)=$-\frac{\beta}{\alpha}\times$q(ia0+ibpy)+iya$\times\frac{1}{2\alpha}\times$q(iam+ib0)
>               +(j-k)$\times\frac{1}{2\alpha}\times$q(ia0+ibmy)
      iap=iap+1
      q(iap+ib0)=$-\frac{\beta}{\alpha}\times$q(ia0+ibpz)+k$\times\frac{1}{2\alpha}\times$q(ia0+ibmz)
      iap=iap+1
      ia0=ia0+1
      DO iza=1,iya
       q(iap+ib0)=$-\frac{\beta}{\alpha}\times$q(ia0+ibpz)+iza$\times\frac{1}{2\alpha}\times$q(iam+ib0)
>               +k$\times\frac{1}{2\alpha}\times$q(ia0+ibmz)
       iap=iap+1
       ia0=ia0+1
       iam=iam+1
      ENDDO
     ENDDO
     ib0=ib0+naS
     ibmx=ibmx+naS
     ibpx=ibpx+naS
     ibmy=ibmy+naS
     ibpy=ibpy+naS
    ENDDO
   ENDDO
  ENDDO
 ENDDO
 ENDIF
 Copy the integral into shell and cleanup memory
 RETURN; END SUBROUTINE basis_shell_trans
```

From inspection it is clear that indexing is the key to the transfer equation. The number of operations involving the integrals is significantly less than those involving the indexing. In previous recurrence relations the indices have always been incremented as the integrals are created. For the transfer equation it is optimal to compute some of the indexing prior to the recurrence relation to reduce the number of operations.

4.3 Testing the integrals

There are several tests to check that the integral shell routines implemented are correct, some of which have already been mentioned in the previous chapter. Tests for the various integrals are briefly summarised here. It goes without saying that all of the integrals are, now, correct and these tests have played a significant part in ensuring this to be the case.

In addition to the tests described for each integral the recurrence relations were programmed into the mathematics computer package Mathematica for comparison [75]. Also for some selected cases the exact integrals were calculated to check the integrals were correct and that the recurrence relation was performing to a high degree of accuracy.

4.3.1 Integral type G

The G-type integrals form the base of many of the other recurrence relations so it is critical that they perform correctly. There are two tests that are specific to G-type integrals. Firstly in the limit $\gamma \to \infty$ the G-type integrals become overlap integrals

$$\lim_{\gamma\to\infty} \left(\frac{\gamma}{\pi}\right)^{3/2} (\mathbf{a}|e^{-\gamma r_{12}^2}|\mathbf{b}) = \langle \mathbf{a}|\mathbf{b}\rangle. \tag{4.20}$$

Thus, by increasing the exponent γ and scaling appropriately, the integrals should converge to the value of the overlap integrals. The second test is to apply the opposite limit to γ, that is to say $\gamma \to 0$. Applying this limit gives the following

$$\lim_{\gamma\to 0} (\mathbf{a}|e^{-\gamma r_{12}^2}|\mathbf{b}) = \left[\int d\vec{r}\, \mathbf{a}(\vec{r})\right] \left[\int d\vec{r}\, \mathbf{b}(\vec{r})\right] \tag{4.21}$$

which is the product of two one-electron integrals.

4.3.2 Integral type GJ

The test for the GJ class of integrals is to apply the limit $\gamma \to 0$. Applying this limit yields

$$\lim_{\gamma\to 0} (\mathbf{a}|e^{-\gamma r_{12}^2} r_{12}^{-1}|\mathbf{b}) = (\mathbf{a}|r_{12}^{-1}|\mathbf{b}) \tag{4.22}$$

which is the expression for the J integrals. Therefore the GJ integrals must agree exactly with the J integrals when the Gaussian exponent γ is set to zero.

4.3.3 Integral type F, FJ, FF and FTF

The F, FJ are simply the sum of their G and GJ counterparts respectively. In that respect there is little that can go wrong, however the F integrals can now be directly compared with R integrals when the fitting criterion of the Gaussian geminal function is set to r_{12}. This means that the G integrals are effectively being tested in the whole range 0 to ∞ rather than just the limits as described previously.

In the case of the FJ integrals fitting the Gaussian geminal function to r_{12} should make the FJ integrals converge to

$$(\mathbf{a}|f_{12}r_{12}^{-1}|\mathbf{b}) \approx (\mathbf{a}|r_{12}r_{12}^{-1}|\mathbf{b}) = \left[\int d\vec{r}\,\mathbf{a}(\vec{r})\right]\left[\int d\vec{r}\,\mathbf{b}(\vec{r})\right] \tag{4.23}$$

as the fitting to r_{12} improves with increased number of Gaussians comprising the geminal function.

The FTF integrals are constructed from sums of G-type integrals. Once the G-type integral implementation is confirmed as correct all that must be done is to test the integrals are put together with the right factors and with the correct angular momentum. The integrals should converge to the analogous r_{12} form when f_{12} is fitted to r_{12}.

4.3.4 Integral type G-G and J-G

Tests for these integrals are analogous to those for the G type integrals. For the G-G integrals in the limit $\nu \to \infty$ they reduce to

$$\lim_{\nu\to\infty}\left(\frac{\nu}{\pi}\right)^{3/2}(\mathbf{a}|e^{-\mu r_{12}^2}|\mathbf{b}|e^{-\nu r_{12}^2}|\mathbf{c}) = (\mathbf{a}|e^{-\mu r_{12}^2}|\mathbf{bc}). \tag{4.24}$$

Choosing $\overline{\mathrm{BC}} = 0$ and $\mathbf{c} = 0$ reduces the problem to a two-electron G type integral which can then be tested as described previously. The same can be done to reduce the J-G integrals to two-electron J integrals.

4.4 Intelligent integral generation

Owing to the large number of integral types required for the new methods of this work a more efficient manner for producing them was required. After implementing most of

index	theory	meaning
`o`	$i, j, k, \ldots$	occupied in AO basis
`v`	$a, b, c, \ldots$	unoccupied in AO basis
`a`	$p, q, r, \ldots$	complete AO basis, $\{\texttt{o}, \texttt{v}\}$
`r`	$p', q', r', \ldots$	RI auxiliary basis set
`d`	$A, B, C, \ldots$	DF auxiliary basis set

Table 4.1: List of allowed indices for the automatic integral generator

the integrals classes for the MP2-F12/**2***A' method manually, it became clear that much of the work in ensuring that they were constructed correctly lay with performing the DF transformations correctly and summing together integrals. It would be most convenient to be able to automate this process. The scheme produced allows one to call a single routine with a string argument containing Dirac or Coulomb style notation, for example '`<oo|J|oo>`' or '`(oo|J|d)`'. The routine then breaks down the integral into three-index parts, if appropriate, and calculates them all. It then automatically assembles the three-index integrals via transformations into the target integral. The allowed indices are shown in table 4.1. The allowed operators, for example J, F etc. are essentially those shown in table 3.1 in the previous chapter. The three index-integrals can also be processed using this routine. For example, the integral $\langle ijm|r_{12}r_{23}^{-1}|mno\rangle$ using the RI approximation can be written as $\langle ij|r_{12}|mp'\rangle\langle mp'|r_{12}^{-2}|on\rangle$ which translates to an input of '`<oo|R|or|J|oo>`' using the integrals program.

Using the new program the only work that must be done to implement a new class of integral is to write a new shell routine, the kernel of the integral wrapper routine.

Kinetic energy integrals, and for that matter exchange integrals, are generally calculated one operator, eg. $\hat{t}_1$, at a time. The integrals for electron one and two are then summed together. In some cases where the operators are acting upon the same type of function it is possible to obtain integrals for the other electron by symmetry.

The routine for handling the input of the integrals could easily be extended further, and eventually expanded to take full working equations. The current routine has for this work been invaluable and has also been used in the recent work of others.

Chapter 5

Results

The past two chapters are in the strictest sense also results of this PhD, as they contain the details and implementation of the new class of MP2-F12 theories. In this chapter no new theory is derived and no new methods are implemented; instead the new programs are fully investigated and comparisons made with other, similar theories. Much of the work that will be presented in this chapter has been been the subject of a recent publication [76]. All of the numbers presented, unless otherwise specified, are calculated using the programs of the MOLPRO [58] quantum chemistry package.

The notation VNZ will be used as shorthand for cc-pVNZ, the correlation-consistent basis sets of Dunning [13–18]. The notation VNZ/MP2fit will be used as shorthand for the fitting sets of Weigend *et al.* [77] which will be employed for the DF.

5.1 The test set of molecules and reactions

Throughout this chapter a test set of molecules will be referred to and used in calculations. These 20 molecules are listed in table B.2 with HF energies and table B.3 with their MP2 correlation energies. Their geometries have been taken from the book by Helgaker *et al.* [7]. The molecules contain a variety of chemical bonds including hydrogen to first-row atom bonds and single, double and triple bonds between two first row elements. The molecule list does not include any open-shell molecules as versions of the programs are not implemented for such cases. It also does not include heavier elements and transition-metal compounds where the electrons are placed in a significantly different environment, although they could be treated by the methods provided they were closed shell systems.

All of the molecules contain both dynamic and static correlation. The quantity of static correlation varies significantly, with O_3 having a much larger amount of static correlation than any of the other molecules. The MP2 methods provide a poor description of the dynamic correlation; generally a multi-reference method is required to recover static correlation. Thus when comparing to accurate results, for cases when results for molecules such as O_3 are not as one would otherwise anticipate static correlation may well be the explanation.

A test set of reactions using the test set of molecules just described is also defined and these are listed in table B.4 with HF energies and table B.5 with MP2 energies.

To present some of the data more concisely a probability density function (PDF) will be used. A PDF involves the mean error $\bar{\delta}$ and standard deviation σ of a set of data. Using $\bar{\delta}$ and σ the PDF is constructed as

$$\mathrm{PDF}(\bar{\delta},\sigma) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left\{ -\frac{|\delta-\bar{\delta}|^2}{2\sigma^2} \right\} \tag{5.1}$$

where for completeness

$$\bar{\delta} = \frac{1}{n}\sum_{i=1}^{n} \delta_i \qquad \text{and} \qquad \sigma = \sqrt{\frac{1}{n-1}\sum_{i=1}^{n}(\delta_i-\bar{\delta})^2}. \tag{5.2}$$

The above definition of a PDF includes the normalisation constant, $1/\sigma\sqrt{2\pi}$ which means that all of the functions presented will integrate to 1.

5.2 Density Fitting

The DF approximation is used to increase the speed of the integral evaluation. Calculations on the test set of molecules with increasing DF basis size as well as the corresponding calculations with exact integrals are given in tables B.6 and B.7. The PDFs for the energies using a DF basis set for the integrals compared to the energies using exact integrals are shown in figure 5.1 and figure 5.2. In both sets of figures as the DF basis set is increased the plots become narrower showing a decrease in the error of the fitting. The calculations converge quite quickly with respect to the size of the DF basis. In fact one observes from the numerical tables of data that a DF basis of only one cardinal number higher than the AO basis set is needed for accurate calculations. In practice one should use as large DF basis as possible so that errors from the DF can be disregarded when

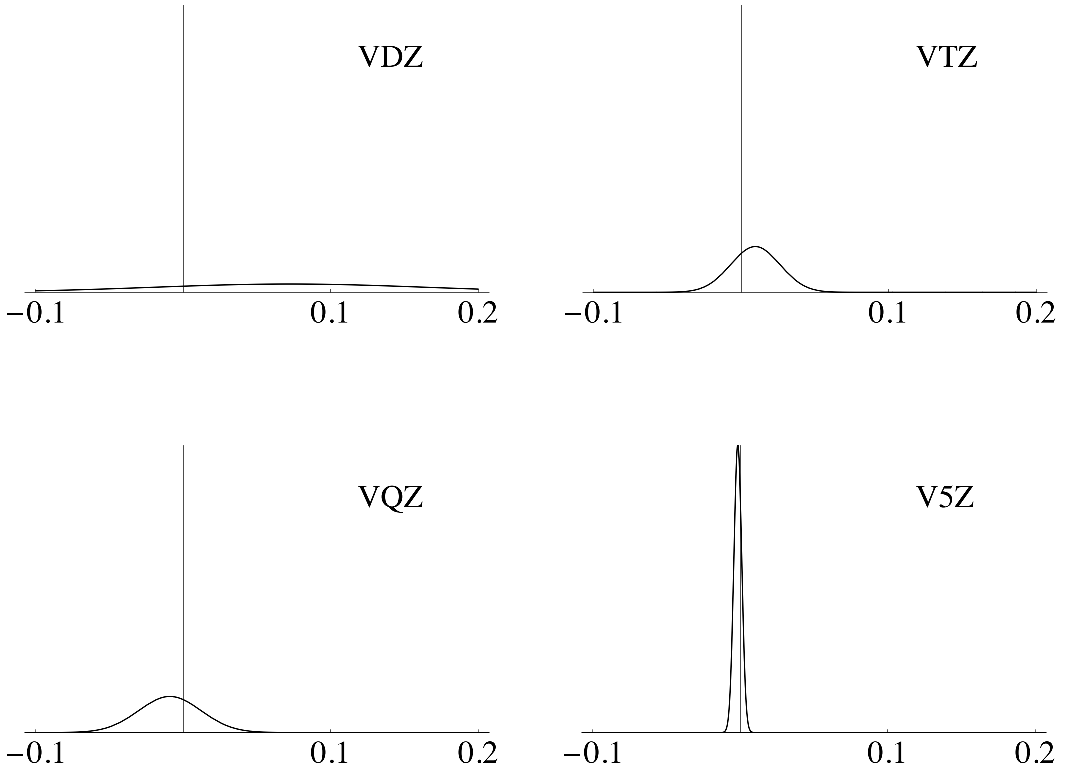

Figure 5.1: DF PDFs for MP2-R12/**2***A' non-invariant energies compared to energies not using the DF approximation for the test set of molecules. In all cases the same horizontal and vertical scales are used with the units of the horizontal length scale millihartree. Calculations use a VDZ AO basis set, an uncontracted VDZ RI basis set and VNZ/MP2fit DF basis set, with N=$\{$D,T,Q,5$\}$.

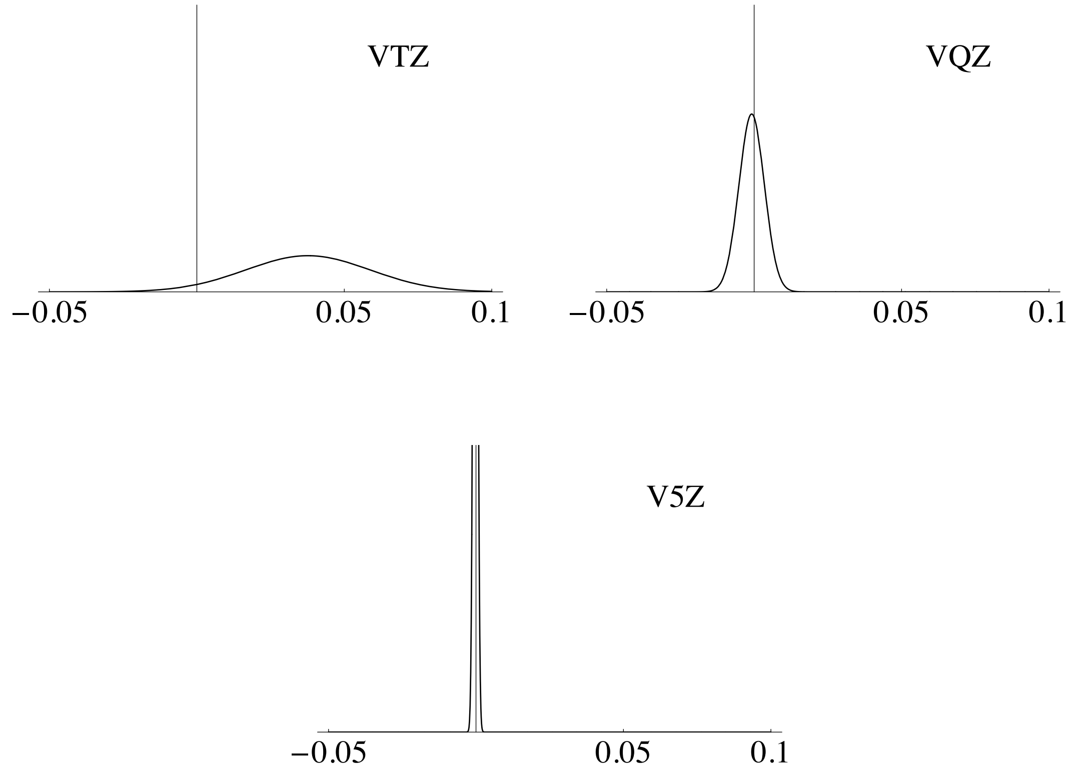

Figure 5.2: DF PDFs for MP2-R12/**2***A’ non-invariant energies compared to energies not using the DF approximation for the test set of molecules. In all cases the same horizontal and vertical scales are used with the units of the horizontal length scale millihartree. Calculations use a VTZ AO basis set, an uncontracted VTZ RI basis set and VNZ/MP2fit DF basis set, with N={T,Q,5}.

considering the overall error in the calculation. The use of DF, for instance, reduces the scaling of the integrals by an order of magnitude, which far outweighs the additional cost of computing integrals in a large DF basis set.

5.3 F12 fitted linearly

When f_{12} is least-squares fitted to r_{12}, the F12 program should give agreement with the R12 program as the number of Gaussian geminal functions becomes sufficient for accurate fitting. For the purposes of comparing the two programs small basis sets are employed as only agreement is needed to verify the program. The results for increasing the number of Gaussian functions comprising the geminal for the MP2-F12/**2***A' method for the neon atom are shown in figure 5.3. The VDZ basis set is used as an AO basis set, uncontracted VDZ is used for the RI basis and V5Z/MP2fit is used for the DF basis set. The Gaussian geminal is centred at 3 and has ratio 3. The value of ω, the exponent needed for the weight function in the least squares fitting is 0.2. From the figure one can see that as the number of Gaussian geminal functions is increased the F12 energy converges smoothly towards the R12 value.

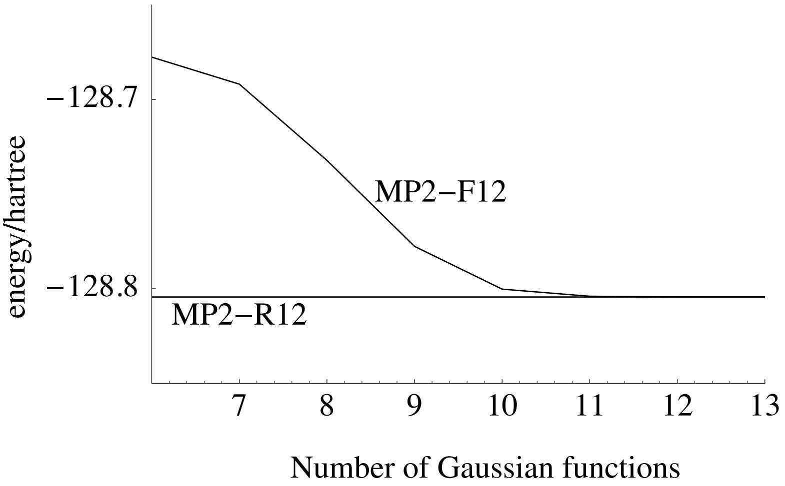

Figure 5.3: Convergence of the MP2-F12 energy to the MP2-R12 energy with respect to the number of Gaussian functions when F12 is fitted to R12 for the neon atom. Details of the calculations can be found in the text.

MP2-F12/**2***A' calculations have been performed on the test set of molecules using geminals comprising six, nine and twelve Gaussian functions. The error between the invariant energies of the MP2-F12/**2***A' method fitted linearly compared to the corresponding MP2-R12/**2***A' values are summarised as PDFs in figure 5.4, with the data in table B.8. The AO basis used is VDZ, the RI basis is uncontracted VDZ and the DF basis is V5Z/MP2fit. The geminal function is constructed as an even tempered basis centred at 3 and ratio 3. The weight function exponent required for the least squares fitting takes the values $\omega = 0.2$.

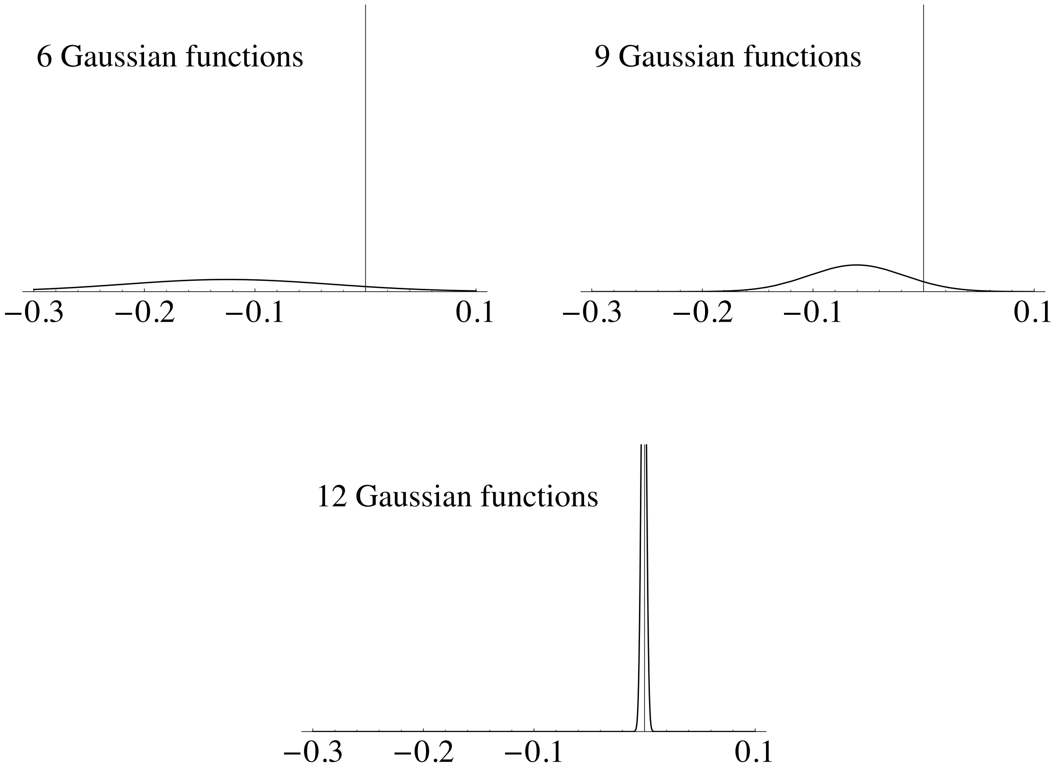

Figure 5.4: PDFs for MP2-F12/**2***A' invariant energies fitted linearly compared to MP2-R12/**2***A' energies. In all cases the same horizontal and vertical scales are used with the units of the horizontal length scale hartree. Details of the calculations can be found in the text.

From the PDFs one can see that by using a geminal function comprising of 12 Gaussian functions it is possible to get almost exact agreement with R12 without optimising the geminal for the given set of problems. Almost all of the error for the 12 geminal calculations can be attributed to the HOF and F_2 molecules. With optimisation it is possible to reduce the quantity of Gaussian functions comprising the geminal to give energies of increased accuracy. The above results confirm that the F12 program agrees with the R12 and is therefore correctly implemented.

5.4 Errors in the methods

In the theory chapter several MP2-R12 and -F12 methods were derived, some of which were subsequently implemented. The most efficient of the methods is the MP2-R12/**2***A' method which has many approximations allowing a fast evaluation. Using this method to perform a calculation on neon using a VTZ basis set for both the AO and RI basis sets and the V5Z/MP2fit for the DF basis gives a correlation energy of -299 millihartree. This energy is significantly lower than the correlation energy of -264 millihartree obtained when one performs a standard MP2 calculation using a VTZ basis set. However the R12 energy is still some way off the basis set limit of -320 millihartree, in fact one third of the remaining correlation energy is unrecovered. This is still a significant improvement on the standard MP2 energy but it is a little depressing that the improvement is not closer to the basis set limit. The obvious question to ask is where the error in the calculation is coming from, assuming that the basis set is large enough to provide a good enough description. As mentioned previously there are a number of approximations associated with evaluation of matrix elements in the various R12 methods. As well as these approximations there are two other sources of error to give three in total:

1. The RI approximation for many-electron integrals,
2. Approximations in evaluating matrix elements,
3. The form of the ansatz for the first-order wavefunction.

The first and second of these sources is obvious: approximations by their very nature contain errors. However, the third source is something that requires careful consideration: is r_{12} necessarily the best correlation factor one could use?

In this chapter all of the errors described above will be analysed to decide upon their importance towards the overall error in a calculation. Results that refer to the aim of using a VTZ basis set to perform accurate quantum chemical calculations are presented and will be fully discussed in the conclusions chapter.

method	GBC	EBC	$[\hat{K}_1, f_{12}] = 0$
1A’	✓	✓	✓
2*A’	✓	✓	✓
2A’	✓	×	✓
2B	✓	×	×

Table 5.1: Approximations used in the MP2-R12 and -F12 methods

5.5 The RI approximation

The work contained in this PhD has focused on developing RI/DF MP2-R12 and -F12 methods. Using these methods one can perform calculations on the test set of molecules using different auxiliary RI basis sets. Calculations using VDZ, VTZ and VQZ AO basis sets on the test set of molecules with uncontracted VTZ, VQZ and V5Z RI basis sets and V5Z/MP2fit DF basis for the MP2-R12/**2***A’ method are shown in tables B.9 and B.10. The differences between correlation energies for the two largest RI basis sets is on the order of a few millihartree. Whilst this error is significant it is small by comparison to the total error in the correlation energy. It is worth noting that the RI basis sets used, uncontracted VTZ, VQZ and V5Z, were not specifically designed for being used in this manner. If an optimised basis set were designed it is reasonable to expect the errors to decrease to an even smaller portion of the total. More accurate RIs such as the RI-DF of Ten-no and Manby [53] and the complementary auxiliary basis set approach of Valeev [51] also exist.

The results of these calculations show that the RI approximation does introduce an error. This error is small by comparison to the total error and can be systematically reduced by increasing the size of the auxiliary RI basis set.

5.6 Approximations in evaluating matrix elements

In the theory chapter several varieties of R12 and F12 methods were presented, some of which were subsequently implemented. These methods use various approximations and a summary is shown in table 5.1. In the previous section is was established that the majority of the error in R12 theory is not due to the RI approximation - here the other approximations are analysed.

5.6.1 Neglect of exchange commutators

The exchange commutators, $[\hat{K}_1, f_{12}] = 0$, are not negligible. Since a program that does not neglect exchange commutators was not implemented the analysis uses the data presented in the paper by Klopper and Samson [50]. The mean difference between the MP2-R12/**2**A' and MP2-R12/**2**B methods is 5.5 millihartree in a VTZ basis set and 2.4 millihartree in a VQZ basis set. Whilst this error is a concern if one wishes to perform accurate calculations, it is not the principal source of error. Recall the error in the neon calculation was in the order of 30 millihartree which is significantly larger than the errors attributed above to the neglect of exchange commutators.

5.6.2 GBC and EBC

The other approximations in these theories are the GBC and EBC. The MP2-R12/**2***A' program employs both the GBC and EBC, whereas the MP2-R12/**2**A' only employs the GBC. However, none of the programs developed or implemented in this work eradicates the use of the GBC. Valeev has produced a program which does not use either the GBC or EBC [51]. Using data from Valeev's program one can see the error introduced by using the GBC or the GBC and EBC approximations. Contributions using a VDZ, VTZ and VQZ AO basis set for calculations on the test set of molecules are displayed in figures 5.5, 5.6 and 5.7 respectively. One can see that the error resulting from introducing the EBC is significant. For a VDZ basis set it is unacceptable, whereas for a VTZ and VQZ basis it is still not accurate enough for chemical accuracy. However, the magnitude of the error introduced by the EBC in a VTZ basis set still does not account for the bulk of the missing correlation energy.

The GBC has a smaller impact, and in a VTZ basis set the errors are all less than a millihartree, which is acceptable.

From the above results one can conclude that the EBC should be avoided if possible. The errors associated with the EBC do not account for the bulk of the missing correlation energy but do not allow calculations at the level of chemical accuracy to be performed. The GBC also introduces an error into calculations. This error is however small enough to allow chemical accuracy level calculations to be conducted in a basis of VTZ or greater.

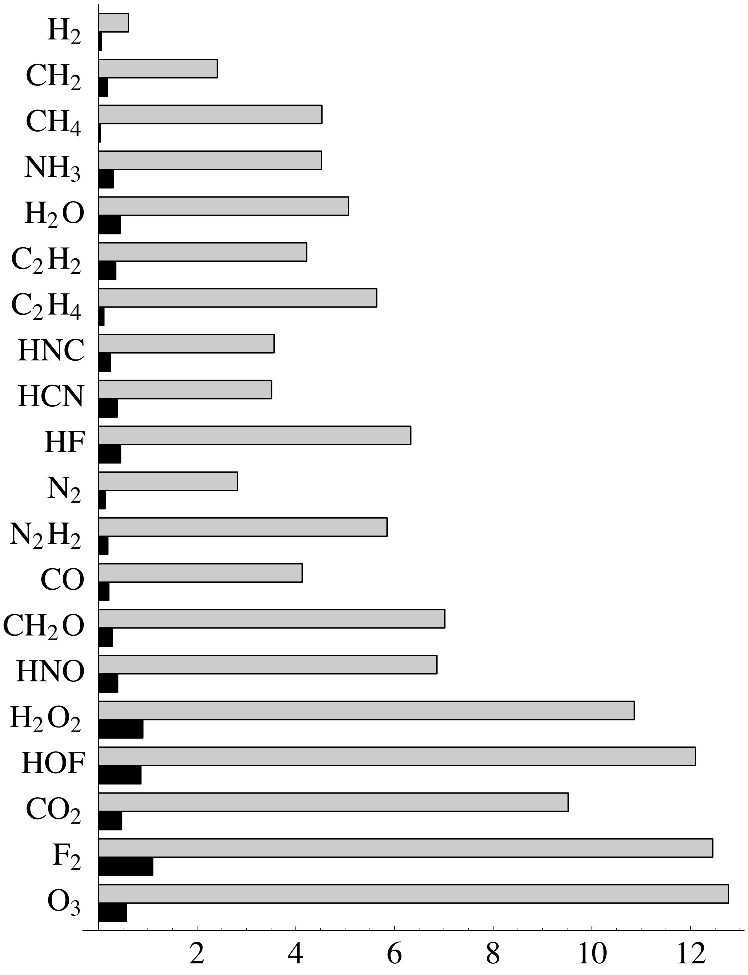

Figure 5.5: Bar chart showing the absolute errors in correlation energies of the test set of molecules in millihartree for the MP2-R12 method in a VDZ AO basis set. GBC errors are shown in black and GBC+EBC errors in grey.

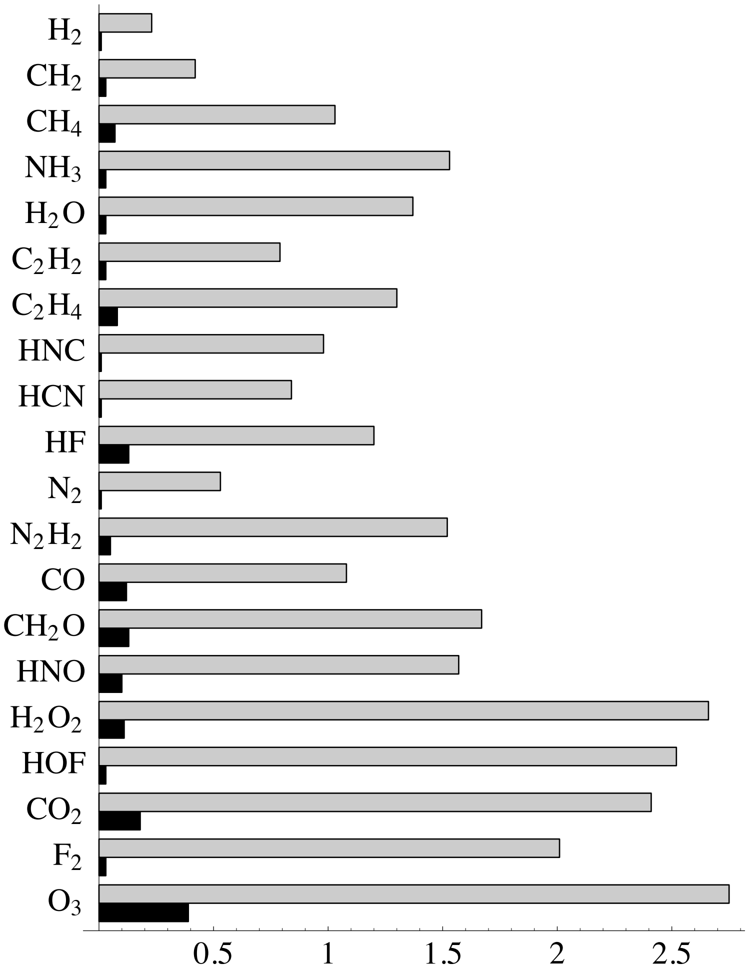

Figure 5.6: Bar chart showing the absolute errors in correlation energies of the test set of molecules in millihartree for the MP2-R12 method in a VTZ AO basis set. GBC errors are shown in black and GBC+EBC errors in grey.

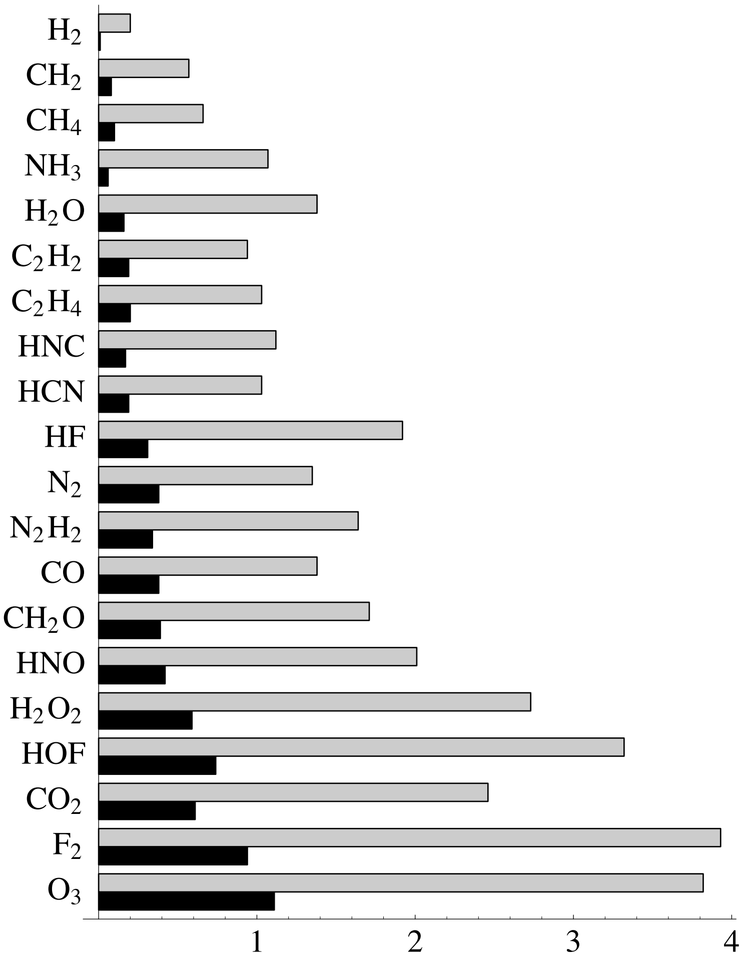

Figure 5.7: Bar chart showing the absolute errors in correlation energies of the test set of molecules in millihartree for the MP2-R12 method in a VQZ AO basis set. GBC errors are shown in black and GBC+EBC errors in grey.

5.7 The form of the correlation factor

5.7.1 A single Gaussian vs. R12

The MP2-F12 programs described previously use a linear combination of Gaussian functions which are then fit using a least squares fit to a function of choice. If only one Gaussian function is provided for the fitting then clearly no matter what the fitting criterion the resulting function will still have a Gaussian shape. This provides an interesting starting position with which to compare with the R12 methods also implemented. Clearly a single Gaussian has no resemblance to R12 and one would therefore expect it to perform poorly by comparison. Plots of correlation energies for the neon atom in different AO basis sets for MP2, MP2-R12 and MP2-F12 are shown in figure 5.8. Clearly the value of the Gaus-

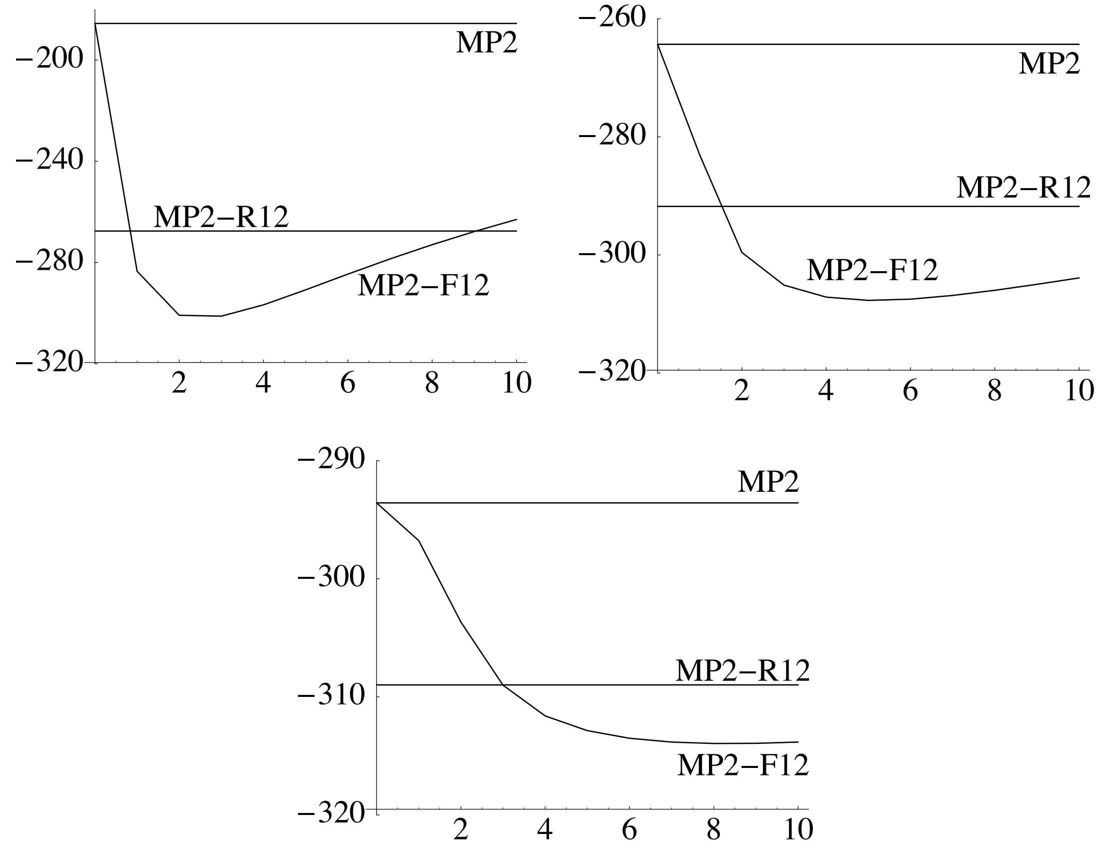

Figure 5.8: Plots of correlation energy vs Gaussian exponent for the neon atom using the MP2, MP2-R12 and MP2-F12 methods. Starting from the top left and working clockwise the AO basis sets are VDZ, VTZ and VQZ. The F12 method uses the **2***A’ ansatz with uncontracted V5Z RI basis and the V5Z/MP2fit DF basis set.

sian function has no effect on the value of the MP2 and MP2-R12 energies and hence they remain invariant on changing this value. As one would expect the MP2-R12 energies are lower than the MP2 values owing to the explicit correlation by including r_{12} in the wavefunction. The extrapolated MP2 V[5,6]Z energy is shown just above the x-axis. It is clear from the graphs that the MP2-F12 ansatz provides significantly lower correlation energies than the corresponding R12 ansatz. This seems odd, especially since r_{12} has always been thought to be the correlation factor that one should be trying to include in the wavefunction. Indeed if one takes the minimum of the F12 curve this approximately corresponds to the correlation energy of the R12 method in the next basis set up, i.e. using a single optimised Gaussian is almost equivalent to the corresponding R12 calculation in the next basis set. Clearly a result of this significance requires further investigation.

The first cautionary note when considering the above result is that the optimum value of the Gaussian exponent ω varied between basis sets. This is a major problem as for a method to be size-consistent this must not be the case. In fact to make the method size-consistent requires imposing the restriction that the value of the Gaussian exponent must remain fixed for all calculations. First it is wise to consider why the optimum value of ω might vary with basis set.

As the size of the basis set increases it is better able to describe electron correlation. The remaining error results from the parts still not correctly described and one can see that a Gaussian function containing an increasing exponent will be needed as the basis set increases in size. Another way of putting this is that the explicitly correlated part of the wavefunction is describing areas closer to $r_{12} = 0$ as the basis set increases. This makes sense if one inspects the plot of the wavefunction in figure 1.3 as it shows the way in which the MP2 methods converge from the top of the correlation hole, thus functions of increasing exponents are needed the more accurate the calculation.

The optimum value of ω is now investigated across the test set of molecules and across the VDZ, VTZ and VQZ basis sets. The results of these calculations are given in table B.11 and summarised in figure 5.9. The optimum values are not similar to that of neon. This is not necessarily that surprising. Neon is a noble gas and as such exists in single atomic form. Molecules on the other hand have bonds where electrons are placed in a very different environment that is not present in atoms. Despite being able to reason the high exponent for neon it does not solve the problem that for the method to be size

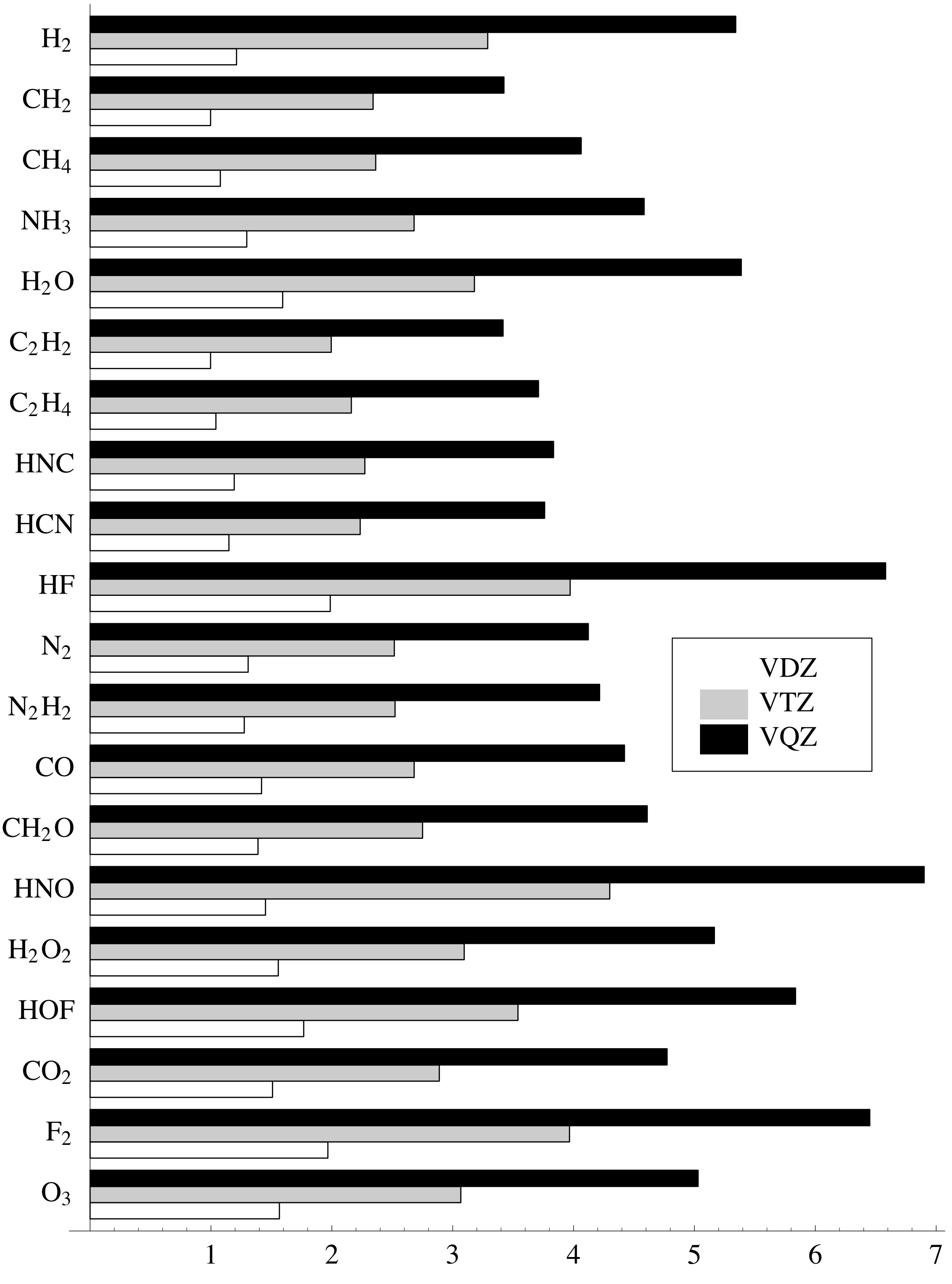

Figure 5.9: Optimum value of ω for the test set of molecules in VDZ, VTZ and VQZ basis sets.

consistent the value of ω must be the same. The calculations are recomputed for the test set of molecules for each basis set using the average optimum Gaussian exponent at the bottom of table B.11 to give correlation energies in table B.12. Comparing correlation energies to the MP2 correlation energies in the V[5,6]Z basis set and doing the same for the corresponding R12 cases gives PDFs shown in figure 5.10. The PDFs show that using a single Gaussian correlation factor is roughly equivalent to performing the R12 calculation in the next highest basis set.

If one had to fix the value of ω for all calculation the optimal value for a VTZ basis should probably be used. The reason for choosing VTZ is that this is the size of basis one would like to be able to perform accurate quantum chemical calculations. A VDZ basis is not complete enough and as such the Gaussian function is likely to be trying to account for basis set incompleteness as well as correlation. One can see that these recomputed values still offer significant improvement over the R12 method even when using the average exponent.

An interesting aside was to perform calculations to find the optimal ω for the elemental hydrides across the first three periods. Results of the optimal exponent for MP2-F12/**2***A' calculations where the geminal comprises of a single Gaussian function only are shown in figure 5.11. The geometries for the molecules not in the molecular test set are given in table B.1 along with their optimal exponents. The AO basis set used is VDZ, the RI basis is uncontracted V5Z and the DF basis is V5Z/MP2fit.

There does appear to be periodicity, most notably the almost uniform increase in optimal exponent across the second period. Across the second period there is increasing charge which can be seen by the bond lengths decreasing, putting the electrons closer and closer together. The optimal function will have steeper gradients the closer the electrons are together, hence the increase in optimal Gaussian exponent. Beyond the second period the periodicity starts to break down. This is most likely due to the increasing number of environments in which the electrons are in. For instance there are core electrons, valence bonding electrons and non-bonding electrons, all of which are interacting with each other at very different inter-electronic distances. The optimal exponent is an average of all of these situations and is the most likely cause of the breakdown of periodicity in the third period.

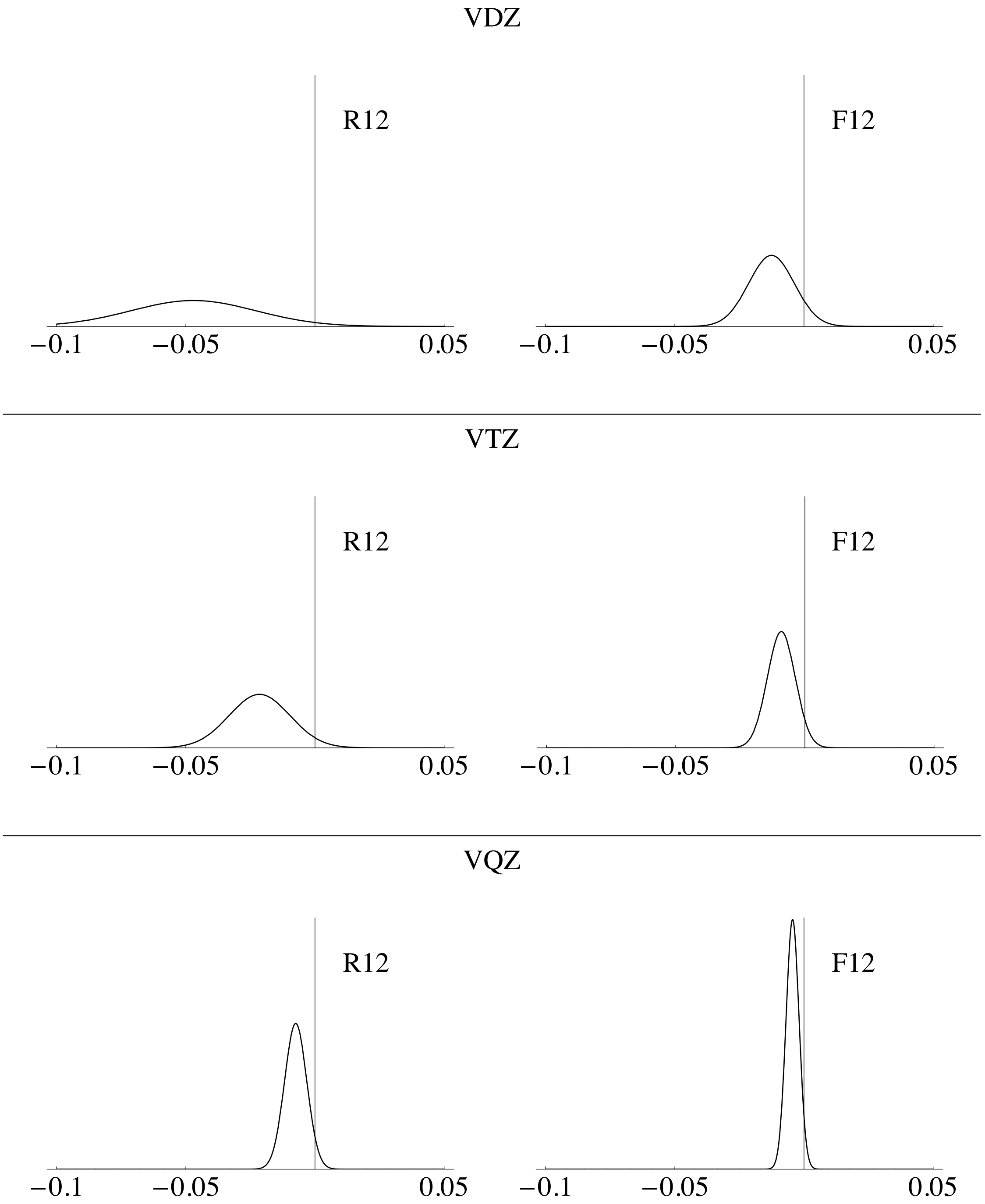

Figure 5.10: PDFs for invariant negative correlation energies MP2-F12/**2***A' using a single Gaussian geminal vs MP2-R12/**2***A' both compared to MP2 correlation energies in a V[5,6]Z basis set. In all cases the same horizontal and vertical scales are used with the units of the horizontal length scale hartree.

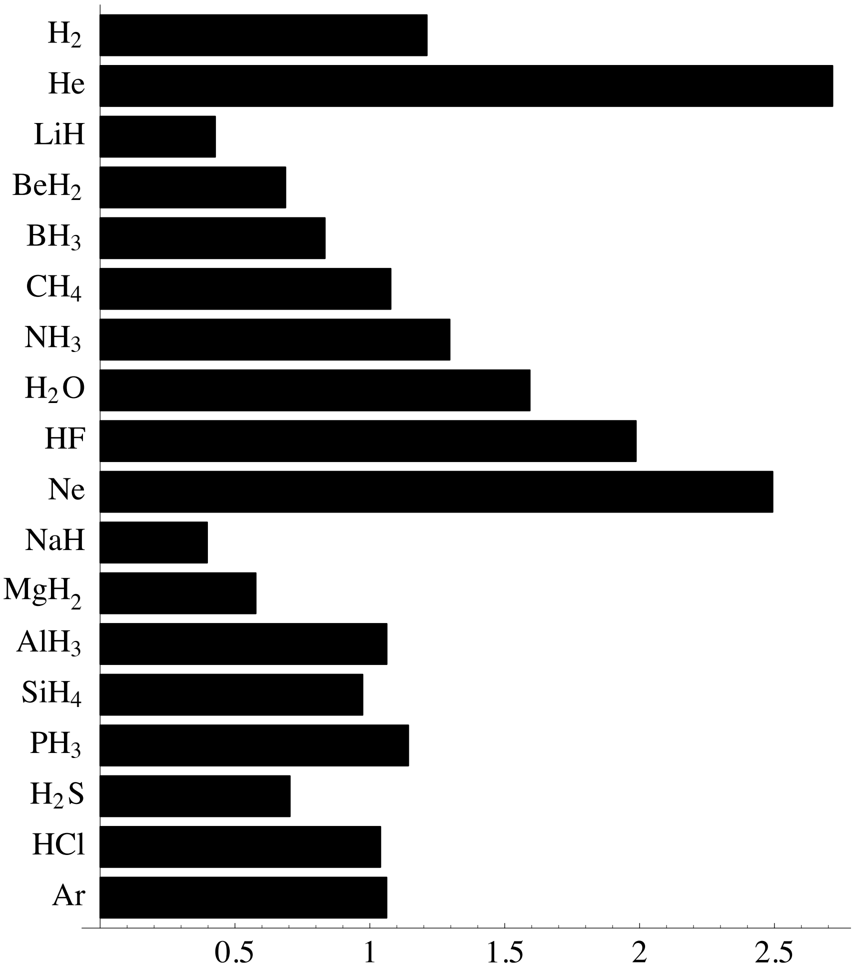

Figure 5.11: Optimum value of ω for the elemental hydrides across the zeroth, first and second periods. Details of the calculations are given in the text.

5.7.2 Other forms for the correlation factor

Having seen the amazing success of using a single Gaussian function as the correlation factor in the previous section a wider range of functions are investigated in this section. Since f_{12} is constructed from a linear combination of Gaussians one can choose any fitting criterion, and hence try almost any function of choice. Initially a series of calculations were performed on helium using Mathematica [75] and the Hamiltonian taken from [78]. These gave an indication of what function types would be worth further investigation and application to the test set of molecules.

So far a linear correlation factor and a Gaussian geminal comprising a single Gaussian function have been investigated. These correlation factors will be compared to the following other functions:

- Slater Function, $\exp\{-\gamma r_{12}\}$
- Gaussian Jastrow,
- Slater Jastrow.

The Gaussian and Slater Jastrow geminal functions are obtained by solving the equation

$$\frac{1}{2}\nabla^2 f(r_{12}) = \frac{g(r_{12})}{r_{12}}, \tag{5.3}$$

where $g(r_{12})$ is either a Gaussian or Slater function. These functions are based upon the work of Ten-no [37].

Calculations using the above fitting criteria are shown in table B.13.

The Slater function has exponent 1 which is fixed for the size consistency reasons discussed in the previous section. One could imagine optimising the value of the Slater exponent in the same manner as the single Gaussian function. Initial work on this has shown that a value close to unity gives good results for a variety of molecules. For the purposes of size extensivity the value will be fixed at unity for all of the calculations.

From the above data it appears that there is not too much to choose between the different functions. The Slater function appears to give the best match. Strikingly though, all of the correlation factors perform significantly better than r_{12}. The error is of the correct magnitude to account for the 30 millihartree error in neon. One can therefore conclude that the use of a Slater function in place of r_{12} is the way forward in explicitly correlated theories [76, 79, 80].

Chapter 6

Conclusions

The expressions for several new explicitly correlated methods have been derived. Recurrence relations for all of the integral classes novel in this work have also been worked out.

Computer implementations of the methods and the integrals they require have been produced and tested thoroughly. The results of these programs have subsequently been published [72].

In the final version of the programs the two-electron integrals are evaluated using the DF approximation and the three-electron integrals are reduced to a sum of products of two-electron integrals by use of the RI approximation.

6.1 Summary of results

One of the original aims of this work was to test the accuracy of the RI approximation, thought by many in the field to be the main source of error in these methods. A good method to do this is to use the DF approximation as a replacement, since the errors associated with the DF approximation are well understood. The three-electron integrals containing the operator r_{12} would not easily factorise under the DF approximation. The way around this was to use a Gaussian geminal operator as a replacement and fit the geminal to the shape of r_{12}. The error in the fitting can be reduced very easily by increasing the number of Gaussians contained in the geminal function [64].

Several three-electron integral classes were implemented by using the DF approximation with Gaussian geminal correlation factor in place of r_{12}. With the integral value converged with respect to the geminal fitting basis the values were in very good agreement with integrals calculated using the RI approximation. This could lead to one of two conclusions, either the RI approximation is a good approximation or both the RI and DF approximations are bad approximations. With DF errors well understood in seemed most likely that the former is the case. Confirmation of this was obtained by calculating a class of integrals very accurately by quadrature [54]. Thus, one of several key conclusions from this work is that the RI approximation is in fact a good approximation and can be used in these methods without fear of introducing severe errors. Of course, the RI approximation by its nature is only approximate and there will be an associated error when using it, but the results show this error to be at least an order of magnitude lower than the total errors introduced in the methods.

The discovery that the RI approximation is a good approximation means that there must be a different reason why R12 methods do not give good results. Within the new methods developed, approximations such as the GBC and EBC are made. The other possibility is that the ansatz of a linear correlation factor, r_{12} is simply not the optimum correlation factor.

The GBC and EBC approximations were examined and shown to have errors of a similar magnitude to those induced by the RI approximation. The EBC contributes consistently higher errors than the GBC which is in line with expectations since the EBC is a less good approximation that the GBC. They are however small errors compared with the total deviation of the MP2-R12 energies from the MP2 basis set limit. For accurate calculations one should avoid using the EBC if possible.

The remaining possibility for the source of the large error in the calculated energies of the new methods is the form of the correlation factor itself. Originally the Gaussian geminal correlation factor was brought in to solve technical problems associated with calculating three-electron integrals by DF. However, the nice side effect of such an implementation is that by simply changing the fitting criterion of the Gaussian geminal one arrives at a method with an entirely new correlation factor. One should of course be careful how the function is fitted and over what range; it is highly likely that one does not require an accurate fit for large values of r_{12} but rather close to $r_{12} = 0$ and the surrounding region.

The programs were run with a variety of correlation factors and the results compared to the results from corresponding calculations using a linear r_{12} correlation factor. It was discovered that an immensely striking improvement could be obtained by using a Gaussian geminal comprising of a sole Gaussian function as a correlation factor. A method with a single Gaussian function as the correlation factor will not be significantly more expensive than a method involving linear r_{12}, indeed only in a few cases where r_{12} cancels with r_{12}^{-1} is extra work involved. The use of f_{12} means that for large molecules screening would be much more effective. This is because f_{12} vanishes in the long range meaning that the integrals decay much more rapidly than for r_{12}. In r_{12} theory non-contributing integrals often have large values which are then subtracted from other large values to give zero.

When developing new methods one is always considering the improvement in accuracy vs the extra cost of computation. At this stage a significant improvement is made at almost no extra computational cost.

Further investigation showed that a variety of other functions can be used that give even better results, most notably a Slater function as fitting target for the Gaussian geminal gives excellent results. Of course there is extra cost involved using a Slater function since the Gaussian geminal must typically comprise of nine Gaussian functions. However, the computational savings of using the transfer equation in evaluating the integrals means that this cost is minimised. The level of improvement is certainly enough to warrant using a Slater over a single Gaussian function. Work in this area has also been done by Ten-no [79] for the Slater function. A more extensive investigation has recently been conducted by Tew and Klopper [80] involving a variety of correlation factors. From their work they also conclude that the Slater function appears to be the optimum correlation factor.

Initial examination of the reaction energy results were not positive. However given the great success of recovering correlation energy of molecules it became clear that something else must be responsible for the less accurate reaction energies. After investigation it was found that the lack of convergence of the HF energy in a VTZ basis set was responsible for the inaccuracy of the reaction energies. Using an AVTZ basis set significantly improves the convergence of the HF energy and the improvement was enough to give good reaction energy results. Therefore, one must always ensure that the HF energy is converged to a high enough degree in order to give accurate reaction energies [72].

One of the conclusions that has been obtained from conducting this work relates to the manner in which one should approach writing computer implementations of such methods. The methods all contain many integral classes over different basis sets. From the experience of writing the programs for this work it seems wise to write code that can automatically deal with as many of the cases as possible. Ideally one should only need to write kernels for each operator and input details for each of the indices. For disk based versions the program needs to store records of which integrals it has already constructed in order to avoid repeating work.

6.2 Future work

One of the obvious areas in which to extend these methods is to apply the local approximations to the new methods. Using the infrastructure developed within this work this has now been successfully implemented and details of the work are found in [81].

The intelligent integrals program could be further improved to make new method implementations even easier. By writing an improved string parser one could envisage inputting a string containing the working equations of the method and the program simply evaluating the energy. The disk based integrals could also be improved. At present the program calculates objects such as `<oo|J|oo>` and `<ao|J|oo>` as entirely independent entities. One can clearly see that the the index `o` is a subset of `a` (because the occupied MOs are a subset of the MOs). Thus the largest case should be evaluated first and all remaining integrals can be extracted from the super-matrix. There may well be some inefficiencies associated with such a method due to a non-contiguous read from the disk but this should be offset by the need to calculate integrals from scratch.

The F12 methods bring real improvements to the convergence of expectation values for molecular systems for the MP2 level of theory so a natural progression would to apply the method to higher levels of theory. Explicitly correlated CC theories and programs already exist using a r_{12} correlation factor, for instance the CC-R12 method [41, 42]. These methods could be adapted to use an f_{12} correlation factor and would hopefully yield the same sorts of improvements as were found for the explicitly correlated MP2 methods. The CCSD-F12 method should be investigated first in order to see that the same sorts of benefits seen in MP2 theory can also be obtained in CC theory. Utilising this method one can construct the CCSD(T)-F12 energy by virtue of

$$E_{\text{CCSD(T)-F12}} = E_{\text{CCSD-F12}} + E_{\text{CCSD(T)}} - E_{\text{CCSD}} \tag{6.1}$$

This method is desirable since the level of theory allows very accurate expectation values and the f_{12} correlation factor would hopefully yield fast convergence of the values with respect to basis set.

An area that could simply yield improved results is spin scaling of the singlet and triplet contributions to the energies using an empirical factor, as can be used in traditional MP2 theory [82]. The same level of improvement for the F12 methods could further reduce the size of basis set required for chemically accurate calculations.

In a similar vein to above, one could consider having two geminals for the F12 methods, one for the single and one for the triple pair integrals. Going a step further one could consider optimising the geminal function for each of the electron pairs. There are several methods one could write down to do this, but one must be careful not to break the size-extensivity of the method. One such proposal would be the ansatz

$$|u_{ij}\rangle = t^{ij}_{ab}|ab\rangle + t^{ij}_{kl\mu}\hat{Q}_{12}e^{-\mu r_{12}^2}|kl\rangle. \tag{6.2}$$

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Appendix A

List of Abbreviations

AO	atomic orbital
BO	Born-Oppenheimer
BSSE	basis set superposition error
cc-pCVXZ	correlation consistent polarised core VXZ
cc-pVXZ	correlation consistent polarised VXZ
CC	coupled cluster
CCSD	CC singles and doubles
CI	configuration interaction
CID	CI doubles
CIS	CI singles
CISD	CI singles and doubles
CP	counterpoise
CPU	central processing unit
DF	density fitting
DFT	density functional theory
DRK	Dupuis Rys King
EBC	extended Brillouin condition
FCI	full CI
GBC	generalised Brillouin condition
GPT	Gaussian product theorem

GTO	Gaussian type orbital
HF	Hartree Fock
LCAO	linear combination of AO
MD	McMurchie Davidson
MO	molecular orbital
MP	Møller-Plesset
MP2	second-order MP
OS	Obara Saika
PDF	probability density function
PT	perturbation theory
PH	Pople Henre
RHF	restricted HF
RI	resolution of identity
SCF	self consistent field
SD	Slater determinant
STO	Slater type orbital
UHF	unrestricted HF
VXZ	valence X-tuple zeta

Appendix B

Tables of data

molecule	E-H	H-E-H	ω
He			2.71571052
LiH	1.619		0.42749123
BeH_2	1.339	180.00	0.68883003
BH_3	1.198	120.00	0.83360047
Ne			2.49667350
NaH	1.918		0.39708817
MgH_2	1.711	180.00	0.57737970
AlH_3	1.585	120.00	1.06288979
SiH_4	1.486	109.47	0.97340256
PH_3	1.418	95.22	1.14299178
H_2S	1.316	180.00	0.70390366
HCl	1.277		1.03948679
Ar			1.06245281

Table B.1: Geometries of some elemental hydrides. Bond lengths denoted by E-H are given in Angstrom and bond angles deonted by H-E-H are given in degrees. The ω column indicates the optimal Gaussian exponent for performing MP2-F12/**2***A' calculations in a VDZ AO basis, uncontracted V5Z RI basis and V5Z/MP2fit DF basis with a geminal comprising of a single Gaussian function only.

molecule	VDZ	VTZ	VQZ	V5Z	V6Z
H_2	−1.12871101	−1.13295914	−1.13345751	−1.13360663	−1.13362394
CH_2	−38.88109657	−38.89237901	−38.89515659	−38.89589150	−38.89601368
CH_4	−40.19864895	−40.21342573	−40.21624827	−40.21699093	−40.21708506
NH_3	−56.19474634	−56.21731345	−56.22260235	−56.22426827	−56.22449329
H_2O	−76.02680787	−76.05718184	−76.06484941	−76.06710490	−76.06742108
C_2H_2	−76.82575349	−76.84938194	−76.85439150	−76.85550972	−76.85565280
C_2H_4	−78.03991676	−78.06378395	−78.06907145	−78.07041381	−78.07058875
HNC	−92.86601970	−92.89226775	−92.89880236	−92.90018716	−92.90038109
HCN	−92.88327035	−92.90808888	−92.91440026	−92.91570667	−92.91587578
HF	−100.01941127	−100.05801143	−100.06768525	−100.07043036	−100.07073833
N_2	−108.95408662	−108.98341154	−108.99102227	−108.99270292	−108.99302418
N_2H_2	−110.00668134	−110.03851151	−110.04699899	−110.04928971	−110.04966872
CO	−112.74931134	−112.78037975	−112.78888414	−112.79064902	−112.79088197
CH_2O	−113.87643216	−113.91197028	−113.92097975	−113.92319936	−113.92347164
HNO	−129.79759943	−129.83586110	−129.84596172	−129.84857950	−129.84896339
H_2O_2	−150.78203104	−150.83355320	−150.84583062	−150.84921482	−150.84964047
HOF	−174.74478156	−174.80405343	−174.81832963	−174.82225007	−174.82270468
CO_2	−187.65110772	−187.70725648	−187.72169477	−187.72494221	−187.72532950
F_2	−198.68566368	−198.75203415	−198.76826334	−198.77272897	−198.77327924
O_3	−224.26557876	−224.34040904	−224.35847179	−224.36320356	−224.36388068

Table B.2: HF energies in hartree for the test set of molecules

molecule	VDZ	VTZ	VQZ	V5Z	V6Z	V[5,6]Z
H_2	26.380 61	31.679 66	33.114 48	33.655 71	33.900 53	34.236 82
CH_2	110.072 51	138.606 38	148.119 11	151.768 39	153.425 65	155.702 11
CH_4	161.041 82	198.239 79	210.049 05	214.322 85	216.283 77	218.977 34
NH_3	186.068 54	234.892 22	251.384 08	257.810 09	260.551 62	264.317 46
H_2O	201.606 97	261.447 45	282.783 94	291.492 80	295.189 58	300.267 57
C_2H_2	255.319 31	309.684 38	329.022 82	336.502 39	339.958 60	344.706 14
C_2H_4	274.703 58	335.517 24	356.185 04	363.965 92	367.672 10	372.763 01
HNC	271.536 60	332.600 79	354.818 27	363.616 86	367.643 11	373.173 67
HCN	284.102 39	345.119 11	367.383 80	376.302 13	380.366 28	385.948 90
HF	201.627 51	271.773 74	297.515 89	308.304 65	312.977 93	319.397 27
N_2	306.387 41	373.764 33	398.828 67	409.194 49	413.902 21	420.368 86
N_2H_2	330.280 88	408.429 45	436.275 79	447.516 69	452.522 28	459.398 09
CO	286.699 04	355.037 11	380.922 14	391.624 05	396.467 80	403.121 30
CH_2O	316.162 31	395.141 35	423.685 65	435.209 66	440.408 19	447.549 03
HNO	350.055 63	436.962 61	468.762 75	481.921 46	487.790 14	495.851 51
H_2O_2	385.611 10	495.985 52	535.454 51	551.795 55	558.908 44	568.678 89
HOF	386.477 41	506.467 71	549.917 58	568.185 29	576.242 80	587.310 81
CO_2	481.286 93	600.763 36	646.181 99	664.850 90	673.259 46	684.809 68
F_2	393.923 13	522.485 52	569.562 64	589.576 57	598.520 61	610.806 38
O_3	634.206 69	778.317 49	832.539 35	855.504 55	865.776 04	879.885 23

Table B.3: MP2 valence negative correlation energies in millihartree for the test set of molecules

reaction	VDZ	VTZ	VQZ	V5Z	V6Z
$CO+H_2 \rightarrow CH_2O$	1.590 19	1.368 61	1.361 90	1.056 29	1.034 27
$HNC \rightarrow HCN$	-17.250 65	-15.821 13	-15.597 90	-15.519 51	-15.494 69
$H_2O+F_2 \rightarrow HOF+HF$	-51.721 27	-52.848 87	-52.902 13	-52.846 56	-52.742 69
$N_2+3H_2 \rightarrow 2NH_3$	-49.273 03	-52.337 94	-53.809 90	-55.013 73	-55.090 58
$N_2H_2 \rightarrow N_2+H_2$	-76.116 29	-77.859 17	-77.480 79	-77.019 84	-76.979 40
$C_2H_2+H_2 \rightarrow C_2H_4$	-85.452 26	-81.442 87	-81.222 44	-81.297 46	-81.312 01
$CO_2+4H_2 \rightarrow CH_4+2H_2O$	-86.312 93	-88.696 37	-90.422 28	-91.832 00	-92.101 96
$CH_2O+2H_2 \rightarrow CH_4+H_2O$	-91.602 64	-92.719 01	-93.202 91	-93.683 21	-93.786 62
$CO+3H_2 \rightarrow CH_4+H2O$	-90.012 45	-91.350 40	-91.841 01	-92.626 92	-92.752 35
$HCN+3H_2 \rightarrow CH_4+NH_3$	-141.242 56	-139.594 01	-139.675 73	-140.252 15	-140.325 44
$H_2O_2+H_2 \rightarrow 2H_2O$	-142.873 69	-147.851 34	-150.410 69	-151.388 35	-151.577 75
$HNO+2H_2 \rightarrow H_2O+NH_3$	-166.532 76	-172.715 91	-174.575 02	-175.580 41	-175.703 10
$C_2H_2+3H_2 \rightarrow 2CH_4$	-185.411 38	-178.592 10	-177.732 51	-177.652 25	-177.645 50
$CH_2+H_2 \rightarrow CH_4$	-188.841 37	-188.087 58	-187.634 17	-187.492 80	-187.447 44
$F_2+H_2 \rightarrow 2HF$	-224.447 84	-231.029 57	-233.649 65	-234.525 12	-234.573 48
$2CH_2 \rightarrow C_2H_4$	-277.723 62	-279.025 93	-278.758 27	-278.630 81	-278.561 39
$O_3+3H_2 \rightarrow 3H_2O$	-428.711 82	-432.259 06	-435.703 91	-437.291 25	-437.510 74

Table B.4: HF energies for the reaction test set in millihartree

reaction	VDZ	VTZ	VQZ	V5Z	V6Z	V[5,6]Z
$CO+H_2 \rightarrow CH_2O$	-1.492 47	-7.055 97	-8.287 13	-8.873 61	-9.005 59	-9.156 63
$HNC \rightarrow HCN$	-29.816 44	-28.339 45	-28.163 43	-28.204 78	-28.217 86	-28.269 92
$H_2O+F_2 \rightarrow HOF+HF$	-44.296 09	-47.157 35	-47.989 02	-48.267 13	-48.253 23	-48.376 82
$N_2+3H_2 \rightarrow 2NH_3$	-35.880 87	-53.319 07	-58.405 95	-60.472 29	-60.590 02	-60.646 17
$N_2H_2 \rightarrow N_2+H_2$	-78.603 43	-74.873 71	-73.148 15	-72.353 35	-72.259 86	-72.186 99
$C_2H_2+H_2 \rightarrow C_2H_4$	-78.455 92	-75.596 07	-75.270 18	-75.105 28	-75.124 98	-75.132 05
$CO_2+4H_2 \rightarrow CH_4+2H_2O$	-63.759 32	-82.349 06	-87.399 30	-89.666 71	-89.903 31	-89.857 49
$CH_2O+2H_2 \rightarrow CH_4+H_2O$	-85.327 90	-93.905 58	-96.121 29	-96.977 78	-97.050 72	-97.008 87
$CO+3H_2 \rightarrow CH_4$+H2O	-86.820 37	-100.961 55	-104.408 42	-105.851 39	-106.056 31	-106.165 50
$HCN+3H_2 \rightarrow CH_4+NH_3$	-137.674 49	-145.086 25	-146.947 15	-147.801 10	-147.816 13	-147.736 10
$H_2O_2+H_2 \rightarrow 2H_2O$	-134.095 92	-143.081 06	-147.409 58	-148.922 69	-149.147 94	-149.197 18
$HNO+2H_2 \rightarrow H_2O+NH_3$	-151.391 42	-168.733 65	-173.751 33	-175.650 42	-175.853 10	-175.962 98
$C_2H_2+3H_2 \rightarrow 2CH_4$	-173.033 88	-170.348 32	-169.464 35	-168.828 43	-168.552 85	-168.183 58
$CH_2+H_2 \rightarrow CH_4$	-213.430 07	-216.041 33	-216.449 63	-216.391 55	-216.405 03	-216.485 85
$F_2+H_2 \rightarrow 2HF$	-207.399 12	-220.411 87	-226.004 31	-227.902 14	-228.108 20	-228.324 82
$2CH_2 \rightarrow C_2H_4$	-332.282 18	-337.330 41	-338.705 09	-339.059 95	-339.382 19	-339.920 18
$O_3+3H_2 \rightarrow 3H_2O$	-320.184 21	-343.244 94	-352.172 94	-355.297 97	-355.601 85	-355.717 77

Table B.5: MP2 energies for the reaction test set in millihartree. Extrapolated energy is added onto the V6Z HF energy.

molecule	exact	VDZ	VTZ	VQZ	V5Z
H_2	30.603 78	30.449 35	30.588 98	30.606 79	30.603 71
CH_2	144.370 80	144.389 78	144.373 26	144.371 16	144.370 24
CH_4	206.421 97	206.440 10	206.427 91	206.421 80	206.421 92
NH_3	250.435 99	250.461 98	250.444 93	250.434 88	250.435 20
H_2O	286.339 29	286.357 88	286.355 20	286.335 91	286.338 69
C_2H_2	332.501 91	332.567 89	332.504 01	332.505 78	332.501 80
C_2H_4	351.789 00	351.796 96	351.800 66	351.788 57	351.788 50
HNC	357.883 08	357.964 32	357.890 78	357.883 74	357.882 97
HCN	370.771 03	370.864 13	370.774 51	370.774 14	370.770 75
HF	309.626 16	309.628 86	309.651 09	309.618 93	309.624 78
N_2	403.868 02	403.981 10	403.849 52	403.870 48	403.865 96
N_2H_2	434.834 47	434.868 92	434.838 12	434.833 13	434.833 36
CO	384.698 49	384.787 29	384.688 45	384.691 63	384.698 15
CH_2O	422.079 18	422.129 75	422.090 33	422.073 17	422.078 55
HNO	473.554 90	473.561 92	473.555 38	473.550 91	473.553 19
H_2O_2	562.353 58	562.506 64	562.397 31	562.350 05	562.352 78
HOF	591.655 07	591.866 35	591.703 38	591.636 76	591.650 93
CO_2	629.878 58	630.057 03	629.880 67	629.864 28	629.878 19
F_2	627.273 90	627.537 94	627.295 32	627.185 74	627.263 73
O_3	853.032 40	853.198 49	853.052 39	852.991 95	853.025 00
$\bar{\delta}$		0.072 25	0.009 53	−0.009 09	−0.001 66
σ		0.092 48	0.016 70	0.021 17	0.002 65

Table B.6: DF-MP2-R12/**2***A’ non-invariant valence negative correlation energies in millihartree with VDZ AO and RI basis sets. The exact column of data does not use the DF approximation and the subscequent columns use the DF basis shown. Mean and standard deviation in millihartree.

molecule	exact	VTZ	VQZ	V5Z
H_2	32.873 47	32.858 16	32.871 36	32.874 40
CH_2	148.115 93	148.121 67	148.112 45	148.115 77
CH_4	210.601 92	210.624 54	210.598 05	210.602 01
NH_3	252.575 10	252.607 70	252.572 61	252.574 32
H_2O	285.227 59	285.254 10	285.228 81	285.227 67
C_2H_2	329.395 85	329.429 07	329.397 75	329.395 68
C_2H_4	355.724 28	355.742 13	355.717 39	355.723 91
HNC	355.462 27	355.512 56	355.464 70	355.462 33
HCN	368.512 50	368.566 40	368.517 85	368.512 27
HF	301.111 75	301.129 55	301.114 94	301.112 56
N_2	399.790 72	399.850 81	399.776 81	399.790 26
N_2H_2	436.086 47	436.131 30	436.083 92	436.085 65
CO	383.033 11	383.076 77	383.035 74	383.033 68
CH_2O	424.468 20	424.511 57	424.465 44	424.468 24
HNO	468.916 01	468.951 44	468.916 98	468.915 76
H_2O_2	537.172 43	537.218 37	537.173 39	537.172 67
HOF	552.682 78	552.732 85	552.685 21	552.684 01
CO_2	642.989 11	643.066 16	642.990 46	642.989 94
F_2	574.120 59	574.167 43	574.118 56	574.122 29
O_3	830.553 50	830.614 45	830.554 52	830.553 84
$\bar{\delta}$		0.037 67	−0.000 83	0.000 18
σ		0.021 10	0.004 29	0.000 66

Table B.7: DF-MP2-R12/**2***A' non-invariant valence negative correlation energies in millihartree with VTZ AO and RI basis sets. The exact column of data does not use the DF approximation and the subscequent columns use the DF basis shown. Mean and standard deviation in millihartree.

molecule	R12	6	9	12
H_2	30.977 27	27.053 43	27.831 05	30.962 74
CH_2	147.927 98	119.674 14	125.893 26	147.890 98
CH_4	211.956 57	171.614 03	180.470 08	211.937 13
NH_3	254.609 83	193.123 46	223.230 92	254.544 12
H_2O	291.737 41	204.365 36	262.128 21	291.677 74
C_2H_2	341.266 58	278.812 15	291.178 75	341.650 78
C_2H_4	365.394 06	295.512 40	310.915 13	365.775 62
HNC	365.824 19	286.940 69	321.906 34	365.914 20
HCN	379.154 69	303.680 93	334.051 23	379.284 65
HF	320.052 86	203.274 53	288.238 89	320.058 40
N_2	415.696 64	323.676 15	370.115 67	415.551 24
N_2H_2	451.597 83	345.324 48	394.093 22	451.685 48
CO	397.239 90	296.801 99	356.165 56	397.180 81
CH_2O	442.137 00	327.782 04	389.871 17	442.272 79
HNO	495.164 46	359.998 09	434.899 77	495.117 87
H_2O_2	619.092 42	393.335 26	507.509 77	618.307 81
HOF	670.493 45	394.018 38	542.282 04	666.438 21
CO_2	681.468 07	495.428 38	611.342 16	681.422 88
F_2	751.046 15	401.637 33	587.140 04	741.823 81
O_3	929.134 27	645.592 78	792.484 11	929.223 67
$\bar{\delta}$		−0.124 72	−0.060 51	−0.000 66
σ		0.094 23	0.042 91	0.002 17

Table B.8: DF-MP2-R12/**2***A' and DF-MP2-F12/**2***A' negative correlation energies for the test set of molecules in -millihartree with six, nine and twelve Gaussian functions comprising the geminal function of the F12 method. The geminal is comprised of an even tempered basis with centre 3 and ratio 3. The weight function has an exponent with value $\omega = 0.2$. The AO basis used is VDZ, the RI basis is uncontracted VDZ and the DF basis V5Z/MP2fit. Mean and standard deviation in hartree.

molecule	VDZ	VTZ	VQZ	V5Z
H_2	30.977 27	30.602 63	30.741 54	30.809 83
CH_2	147.927 98	138.084 94	138.219 03	139.044 97
CH_4	211.956 58	199.090 62	199.645 28	200.515 07
NH_3	254.609 81	234.590 19	233.554 75	235.540 26
H_2O	291.737 40	261.640 92	259.026 89	262.007 37
C_2H_2	341.266 33	311.100 52	310.479 89	312.046 34
C_2H_4	365.394 04	336.834 84	336.496 13	338.647 73
HNC	365.824 19	334.107 41	333.482 70	335.485 58
HCN	379.154 66	345.407 46	346.479 95	348.481 08
HF	320.052 86	275.723 93	270.973 04	273.947 83
N_2	415.696 55	371.687 44	373.992 95	374.776 80
N_2H_2	451.597 83	406.567 92	406.477 59	409.570 27
CO	397.239 89	358.153 25	358.663 79	360.278 91
CH_2O	442.136 97	397.284 15	397.495 59	400.087 25
HNO	495.164 50	436.653 74	438.694 52	438.399 99
H_2O_2	619.092 44	499.635 71	493.929 53	498.115 98
HOF	670.493 45	514.024 10	506.376 07	509.100 23
CO_2	681.468 05	607.219 78	609.917 74	613.203 65
F_2	751.046 15	534.461 48	523.984 91	524.610 01
O_3	929.134 32	789.091 29	779.267 03	780.910 23
$\bar{\delta}$	0.011 74	−0.047 27	−0.048 97	−0.047 08
σ	0.039 34	0.022 19	0.024 55	0.024 17

Table B.9: MP2-R12/**2***A’ invariant negative correlation energies in millihartree for the test set of molecules. The AO basis VDZ, the RI basis is the uncontracted form of the basis given as the column heading. The DF basis is V5Z/MP2fit in all cases. The mean and standard deviation are as compared to the MP2 correlation energies in a V[5,6]Z basis set and are given in hartree.

molecule	VTZ			VQZ	
	VTZ	VQZ	V5Z	VQZ	V5Z
H_2	32.863 70	32.837 60	32.860 32	33.744 54	33.746 44
CH_2	149.149 05	148.219 78	148.128 12	153.334 43	153.223 41
CH_4	211.892 58	211.033 45	211.342 59	216.449 63	216.510 52
NH_3	254.462 40	252.549 70	252.310 45	260.519 57	260.011 55
H_2O	287.341 42	283.956 97	282.911 56	294.876 12	293.972 01
C_2H_2	332.866 59	330.606 46	330.323 96	340.436 89	340.087 97
C_2H_4	360.418 73	357.889 55	357.935 72	367.920 80	367.548 04
HNC	359.739 31	356.645 16	356.667 86	368.057 70	367.730 82
HCN	372.430 52	369.323 89	369.520 62	381.058 61	380.662 62
HF	303.294 09	298.319 44	296.526 40	312.626 96	311.066 50
N_2	404.643 63	400.350 48	400.139 28	414.301 62	413.833 26
N_2H_2	443.600 58	438.537 13	438.017 62	453.155 11	452.229 70
CO	388.519 79	383.818 24	384.190 24	397.334 30	396.812 85
CH_2O	431.392 27	426.166 90	426.356 53	441.143 92	440.384 79
HNO	477.117 97	470.294 79	469.412 30	488.462 30	486.843 35
H_2O_2	549.804 94	538.774 97	537.372 91	559.787 58	556.986 92
HOF	565.083 92	552.901 59	550.057 20	577.452 93	574.297 17
CO_2	659.673 53	651.213 71	652.256 68	675.025 14	673.713 04
F_2	599.504 02	572.246 36	568.787 70	599.307 31	595.779 26
O_3	853.490 60	835.297 15	833.001 61	869.624 48	862.712 40
$\bar{\delta}$	−0.014 50	−0.020 81	−0.021 46	−0.006 13	−0.007 46
σ	0.006 06	0.010 94	0.011 72	0.002 86	0.004 30

Table B.10: MP2-R12/**2***A’ invariant negative correlation energies in millihartree for the test set of molecules. The AO basis is given on the top row, the RI basis is the uncontracted form of the basis given on the second row. The DF basis is V5Z/MP2fit in all cases. The mean and standard deviation are as compared to the MP2 correlation energies in a V[5,6]Z basis set and are given in hartree.

molecule	VDZ	VTZ	VQZ
H_2	1.21171869	3.28980389	5.34170438
CH_2	0.99694996	2.34151354	3.42422357
CH_4	1.07761525	2.36317313	4.06326754
NH_3	1.29640917	2.68057844	4.58380468
H_2O	1.59339757	3.17982296	5.38751937
C_2H_2	0.99674949	1.99511333	3.41684339
C_2H_4	1.04096563	2.16156653	3.70987696
HNC	1.19284888	2.27339692	3.83445323
HCN	1.14880566	2.23474714	3.76078652
HF	1.98695282	3.97197779	6.58184161
N_2	1.30772572	2.51708344	4.12217187
N_2H_2	1.27562791	2.52313874	4.21529166
CO	1.41869983	2.68123508	4.42110400
CH_2O	1.38936964	2.75080974	4.60935513
HNO	1.45130765	4.29940487	6.90055728
H_2O_2	1.55731510	3.09529580	5.16495861
HOF	1.76745368	3.53994850	5.83631770
CO_2	1.50935219	2.88918842	4.77358694
F_2	1.96738597	3.96629394	6.45077054
O_3	1.56645308	3.06718722	5.03006988
$\bar{\delta}$	1.38765519	2.89106397	4.78142524

Table B.11: Optimum value of ω for the test set of molecules. The AO basis used is given as the column heading, the RI basis is uncontracted V5Z and the DF basis is V5Z/MP2fit. The geminal is comprised of a single Gaussian function, exponent ω. Omega is obtained by minimisation with respect to the energy using the Powell method [83].

molecule	VDZ	VTZ	VQZ
H_2	33.974 63	33.748 63	33.952 88
CH_2	152.300 42	152.676 04	154.177 32
CH_4	215.942 39	215.995 36	217.466 00
NH_3	255.426 24	258.570 01	261.510 32
H_2O	286.205 17	291.988 63	296.281 97
C_2H_2	339.091 07	339.490 74	342.004 10
C_2H_4	366.928 30	367.074 38	369.724 59
HNC	365.678 89	366.864 25	370.005 86
HCN	379.071 15	379.858 88	382.878 77
HF	299.865 58	308.104 45	314.142 27
N_2	412.943 50	413.126 55	416.738 71
N_2H_2	449.032 51	450.596 58	454.994 48
CO	393.822 48	395.584 57	399.491 88
CH_2O	436.034 04	438.802 64	443.304 40
HNO	482.399 95	485.219 08	490.696 47
H_2O_2	545.810 47	554.401 29	561.805 03
HOF	559.138 39	570.185 94	579.212 66
CO_2	667.291 31	671.399 93	678.430 10
F_2	578.437 82	591.160 85	601.679 08
O_3	856.179 95	860.165 52	870.316 38
$\bar{\delta}$	−0.012 58	−0.009 11	−0.004 42
σ	0.008 82	0.005 39	0.002 51

Table B.12: Invariant negative correlation energies calculated using the MP2-F12/**2***A' with averaged ω found in table B.11, denoted by $\bar{\delta}$. The AO basis used is given as the column heading, the RI basis is uncontracted V5Z and the DF basis is V5Z/MP2fit. The geminal is comprised of a single Gaussian function, exponent ω. The mean and standard deviation are as compared to the MP2 correlation energies in a V[5,6]Z basis set and are given in hartree.

molecule	Slater	Gaussian Jastrow	Slater Jastrow
H_2	34.200 33	34.175 50	34.085 56
CH_2	155.610 85	155.177 28	154.685 17
CH_4	218.945 89	218.516 51	217.903 82
NH_3	263.553 53	261.619 99	260.888 48
H_2O	298.972 34	295.550 64	294.745 89
C_2H_2	345.002 82	344.715 83	343.742 81
C_2H_4	372.614 73	372.132 87	371.050 32
HNC	373.263 73	371.857 97	370.622 48
HCN	386.169 55	384.879 43	383.707 42
HF	317.906 82	313.183 25	312.547 20
N_2	420.204 08	417.531 00	416.206 06
N_2H_2	458.836 74	456.146 95	454.759 83
CO	403.185 65	400.649 44	399.310 67
CH_2O	447.279 96	444.544 72	443.236 36
HNO	495.164 57	491.253 87	489.812 66
H_2O_2	567.301 77	561.615 69	560.029 53
HOF	585.748 19	578.736 27	577.324 14
CO_2	684.772 36	680.106 59	678.025 87
F_2	609.141 57	600.814 63	599.561 08
O_3	878.226 85	870.513 07	868.231 78

Table B.13: Invariant MP2-F12/**2***A' negative correlation energies in millihartree for the test set of molecules. The AO basis set is VTZ, The RI basis set is uncontracted V5Z and the DF basis set is V5Z/MP2fit. In all cases the Gaussian geminal is constructed from an even tempered basis set comprising of 9 Gaussian functions centred at 8 with ratio 3. The value of ω in all cases is 1