

New model hamiltonians for improved orbital basis
set convergence

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Abstract

The standard approach in quantum chemistry is to expand the eigenfunctions of the non relativistic Born Oppenheimer Hamiltonian in terms of Slater determinants. The quality improvements of such wavefunctions in terms of the underlying one electron basis is frustratingly slow. The error in the correlation energy decreases only with L^{-3} where L is the maximum angular momentum present in the basis. The integral evaluation effort that grows with $O(N^4)$ prevents the use of ever larger bases for obtaining more accurate results. Most of the developments are therefore focused on wavefunction models with explicit correlation to get faster convergence. Although highly successful these approaches are computationally very demanding. A different solution might be provided by constructing new operators which take care of the information loss introduced by truncating the basis. In this thesis different routes towards such new operators are investigated.

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Chapter 1

Introduction

1.1 The Schrödinger Equation

The fundamental quantity in quantum mechanics [10] is a partial differential equation called the Schrödinger Equation named after the Austrian physicist Erwin Schrödinger which takes the form 1.1 for a one particle system. $\Psi(\vec{r}, t)$ is referred to as the wavefunction and \hat{H} is known as the Hamilton operator or Hamiltonian which consists of a kinetic and potential energy part. The quantities \vec{r} and t are variables of space and time.

$$\hat{H}\Psi(\vec{r}, t) = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r}, t) \right] \Psi(\vec{r}, t) = i\hbar \frac{\partial}{\partial t} \Psi(\vec{r}, t) \quad (1.1)$$

If the potential V does not depend on time it is possible to factorise the wavefunction into space and time contributions ($\Psi(\vec{r}, t) = \psi(\vec{r})\xi(t)$). This leads to the time independent Schrödinger Equation 1.2. The solutions of this eigenvalue problem are so called stationary states as the probability density given by $|\Psi^2|$ does not change with time.

$$\hat{H}\psi(\vec{r}) = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r}) \right] \psi(\vec{r}) = E\psi(\vec{r}) \quad (1.2)$$

The generalization to many particle systems is straightforward by replacing the kinetic and potential energy terms in the Hamiltonian with their many body counterparts.

$$\hat{H} = -\frac{1}{2M_A} \sum_{A=1}^M \nabla_A^2 - \frac{1}{2} \sum_{i=1}^N \nabla_i^2 + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} - \sum_{A=1}^M \sum_{i=1}^N \frac{Z_A}{r_{iA}} + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{r_{AB}} \quad (1.3)$$

For a molecular system in the absence of external fields and neglecting relativistic contributions the Hamiltonian in atomic units is given by equation 1.3 where upper and lower case indices denote nuclei and electrons respectively. Although this expression is of the same kind as equation 1.2 it is much more complicated to treat as there are $3M$ nuclear and $3N$ electronic coordinates. There is an additional set of coordinates which enter the wavefunction as a result of the spin properties of the particles. But since the Hamiltonian does not contain any spin coordinates and therefore commutes with the spin angular momentum operators an appropriate wavefunction can be constructed as product of spatial and spin factors.

A simplification may be achieved if one considers the fact that the nuclei are much heavier than the electrons. A proton is almost 2000 times heavier than an electron. Therefore it is expected that the nuclei move much slower than the electrons. This is the motivation behind the Born-Oppenheimer approximation[45] where the nuclear framework is kept fixed. In this way the motion of the electrons and nuclei is artificially separated leading to the electronic Schrödinger equation 1.4. With this approximation the molecular energies depend parametrically on the position of the nuclei and the concept of a potential energy surface is introduced. When solving equation 1.4 the nuclear repulsion term can be omitted as it merely represents an additive constant to the energy.

$$\hat{H}_{el}\Psi_{el} = \left[-\frac{1}{2} \sum_{i=1}^N \nabla_i^2 + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} - \sum_{A=1}^M \sum_{i=1}^N \frac{Z_A}{r_{iA}} \right] \Psi_{el} = E(\vec{r}_A)_{el} \Psi(\vec{r}_i)_{el} \quad (1.4)$$

Despite all the simplifications equation 1.4 is - apart from the most simple systems - still too complicated to be solved analytically as the electron interaction terms prevent any separation of variables. One is therefore left with the task of finding good approximate wavefunctions.

1.2 Approximations

1.2.1 The Variational Principle

The conceptually most simple approach to obtain approximate solutions to the Schrödinger equation is given by the variational principle which states that every trial wavefunction will lead to an energy greater or equal than the energy E_0 of the true lowest eigenfunction.

$$\langle H \rangle = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} \geq E_0 \quad (1.5)$$

The mathematical statement 1.5 can be proven by using the fact that the eigenfunctions 1.6 of the Hamiltonian - being a hermitian operator - form a complete and orthonormal set. The eigenfunctions are assumed to be sorted according to increasing eigenvalues.

$$H|\varphi_n\rangle = E_n|\varphi_n\rangle \quad n \in \mathbb{N}_0 \quad (1.6)$$

The consequence of the completeness property is that any function in the same space can be exactly represented by a linear expansion in eigenfunctions of the Hamiltonian 1.7.

$$\psi = \sum c_n |\varphi_n\rangle \quad c_n = \langle \psi | \varphi_n \rangle \quad (1.7)$$

After inserting expansion 1.7 into equation 1.5 and multiplying by the denominator the result is expression 1.8. As a result of the orthogonality of the basis only quadratic terms in the c_n survive.

$$\langle \psi | H | \psi \rangle = \sum_n |c_n|^2 E_n \geq E_0 \sum_n |c_n|^2 \quad \text{q.e.d.} \quad (1.8)$$

The consequence of the variational theorem is the possibility to construct a trial wavefunction $|\psi(c_i)\rangle$ which depends on some set of undetermined parameters c_i that can be optimised to give the lowest possible energy which will be an upper bound to the true ground state. In the preceding discussion the wavefunctions were assumed to

be complex. Since in practical calculations the wavefunctions are almost always real it seems appropriate at this stage to adopt a real formalism from now on. A special case is the linear parameterisation of the wavefunction as shown in equation 1.9.

$$E = \frac{c_j c_i \langle \chi_j | H | \chi_i \rangle}{c_j c_i \langle \chi_j | \chi_i \rangle} \quad (1.9)$$

The expansion coefficients c_j in equation 1.9 are determined via the variation of the energy 1.10.

$$\frac{\partial E}{\partial c_i} c_j c_k \langle \chi_j | \chi_k \rangle + 2E c_j \langle \chi_j | \chi_i \rangle = 2c_j \langle \chi_j | H | \chi_i \rangle \quad (1.10)$$

Reordering expression 1.10 for the stationary condition $\partial E / \partial c_i = 0$ leads to a general eigenvalue problem 1.11 where H_{ij} and S_{ij} are matrices with elements $H_{ij} = \langle \chi_i | H | \chi_j \rangle$ and $S_{ij} = \langle \chi_i | \chi_j \rangle$. The solution of equation 1.11 leads to the N eigenvalues and eigenvectors which are solutions to N lowest lying eigenstates. It is possible to prove that the upper bound property holds for all of these states under linear parameterisation which is known as the Hylleraas-Undheim-MacDonald[20, 37] theorem.

$$H_{ij} c_j = S_{ij} E c_j \quad (1.11)$$

For nonlinear parametrisations the expansion coefficients are usually much harder to determine. But more importantly only the lowest eigenvalue is guaranteed to be an upper bound to the true ground state.

The variational principle only makes a statement about the energies and gives no information about the quality of the wavefunction. It may therefore happen that properties other than the energy may not be determined as accurately as the energy from a given wavefunction.

1.2.2 Rayleigh-Schrödinger Perturbation Theory

The idea behind perturbation theory[10, 76] is to partition the problem at hand into a major contribution which recovers the essentials of the system under investigation and is easily solved on its own. The components neglected in this simplified treatment are then

recovered subsequently. Put in mathematical terms the perturbative treatment consists of separation of the Hamiltonian into two components as shown in equation 1.12 where $H^{(0)}$ is the simple part and $H^{(1)}$ is the perturbation that is coupled in via the strength parameter λ . For $\lambda = 1$ the full Hamiltonian is recovered.

$$H = H^{(0)} + \lambda H^{(1)} \quad (1.12)$$

The wavefunctions 1.13 and energies 1.14 of the system are expressed as power series in the strength parameter λ . The index i denotes a particular state whose energy and wavefunction are to be corrected by the perturbative treatment. It is also assumed that the eigenvalue $E_i^{(0)}$ of $H^{(0)}$ is not degenerate. For this expansion to work the contributions of $H^{(1)}$ have to be small compared to $H^{(0)}$. As an example application of perturbation theory it is probably helpful to think of a vibrational problem where the potential is only slightly different from a harmonic one. This problem can be tackled by setting $H^{(0)}$ equal to the harmonic contribution and use $H^{(1)}$ for the anharmonic correction.

$$|\psi_i\rangle = \sum_{n=0}^{\infty} \lambda^n |\psi_i^{(n)}\rangle \quad (1.13)$$

$$E_i = \sum_{\lambda=n}^{\infty} \lambda^n E_i^{(n)} \quad (1.14)$$

Combining series expansions 1.13 and 1.14 with expression 1.12 yields eigenvalue equation 1.15. This equation needs to be fulfilled for all orders of λ .

$$\left[H^{(0)} + \lambda H^{(1)} - \sum_{m=0}^{\infty} \lambda^m E_i^{(m)} \right] \sum_{n=0}^{\infty} \lambda^n |\psi_i^{(n)}\rangle = 0 \quad (1.15)$$

Expressions 1.16 to 1.19 show the resulting expressions for various orders of λ . In the present form these relations do not suffice to calculate the corrections to the energies or the wavefunction. The eigenvalue equation 1.16 still holds if $|\psi_i^{(0)}\rangle$ is multiplied by an arbitrary constant. Since all expressions contain a term $(H^{(0)} - E_i^{(0)}) |\psi_i^{(m)}\rangle$ there is an ambiguity for the corrections to the wavefunction as the equations are still satisfied if an unspecified amount of $|\psi_i^{(0)}\rangle$ is added to $|\psi_i^{(m)}\rangle$.

$$\left[H^{(0)} - E_i^{(0)} \right] |\psi_i^{(0)}\rangle = 0 \quad (1.16)$$

$$\left[H^{(0)} - E_i^{(0)} \right] |\psi_i^{(1)}\rangle + \left[H^{(1)} - E_i^{(1)} \right] |\psi_i^{(0)}\rangle = 0 \quad (1.17)$$

$$\left[H^{(0)} - E_i^{(0)} \right] |\psi_i^{(2)}\rangle + \left[H^{(1)} - E_i^{(1)} \right] |\psi_i^{(1)}\rangle - E_i^{(2)} |\psi_i^{(1)}\rangle = 0 \quad (1.18)$$

$$\left[H^{(0)} - E_i^{(0)} \right] |\psi_i^{(m)}\rangle + \left[H^{(1)} - E_i^{(1)} \right] |\psi_i^{(m-1)}\rangle - \sum_{k=0}^{m-2} E_i^{(m-k)} |\psi_i^{(k)}\rangle = 0 \quad (1.19)$$

In order to remove the ambiguities from the equations the unperturbed wavefunction is chosen to be normalised whereas the correction to the eigenvector are defined to be orthogonal to $|\psi_i^{(0)}\rangle$. This convention is referred to as intermediate normalisation and summarised in 1.20.

$$\langle \psi_i^{(0)} | \psi_i^{(0)} \rangle = 1 \quad \langle \psi_i^{(0)} | \psi_i^{(n)} \rangle = 0 \quad (1.20)$$

With these definitions it is now possible to calculate the corrections to the energies and wavefunctions. By projecting equation 1.19 onto the zero order wavefunction from the left an expression for the n-th order energy is readily obtained 1.21.

$$E_i^{(n)} = \langle \psi_i^{(0)} | H^{(1)} | \psi_i^{(n-1)} \rangle \quad (1.21)$$

The projection onto $|\psi_i^{(0)}\rangle$ alone does not use the complete information contained in the equations. In order to determine the corrections to the wavefunctions the remaining parts of the eigenspectrum of $H^{(0)}$ need to be used as well. This ansatz is demonstrated for equation 1.17 by the relations 1.22 and 1.23.

$$\langle \psi_m^{(0)} | \left[H^{(0)} - E_i^{(0)} \right] |\psi_i^{(1)}\rangle + \langle \psi_m^{(0)} | \left[H^{(1)} - E_i^{(1)} \right] |\psi_i^{(0)}\rangle = 0 \quad m \neq i \quad (1.22)$$

$$\langle \psi_m^{(0)} | \psi_i^{(1)} \rangle = c_{i,m}^{(1)} = \frac{\langle \psi_m^{(0)} | H^{(1)} | \psi_i^{(0)} \rangle}{E_m^{(0)} - E_i^{(0)}} \quad (1.23)$$

The higher order corrections to the wavefunction are obtained in a similar fashion but it should be noted that the energy of order $E^{(n)}$ is needed to calculate the wavefunction $|\psi^{(n+1)}\rangle$.

In contrast to the variational principle the calculated energies are no longer guaranteed to be upper bounds. It may be found that the energy corrections $E^{(n)}$ oscillate towards a final value or that the series does not converge at all.

1.3 Wavefunctions

1.3.1 The exact wavefunction

The set of functions that fulfils the Electronic Schrödinger equation 1.4 in a purely mathematical way is too vast to be of physical interest. The true wavefunction is characterised by several properties some of which are given below[74].

- In the Born interpretation $|\psi^2|$ represents a probability density. This implies that the integral $\langle \psi | \psi \rangle$ must exist and be finite.
- Electrons are indistinguishable particles with spin $\frac{1}{2}$. The Pauli antisymmetry requires that the wavefunction changes sign when the coordinates of two electrons are swapped.
- The electronic Hamiltonian 1.4 contains potential terms which rise to infinity as the corresponding radii approach zero. These singularities need to be balanced out by the wavefunction such that the local energy is constant and hence conservation of energy is obeyed. These requirements lead to the nuclear and electronic cusp conditions which will be investigated later.
- Equation 1.4 contains no reference to electron spin and the Hamiltonian commutes with the operators \hat{S}^2 and \hat{S}_z . The wavefunction is therefore a simultaneous eigenfunction of the spin operators and electronic Hamiltonian.
- Under the Born-Oppenheimer approximation the wavefunction provides an irreducible representation for the point group of the Hamiltonian.
- The point group symmetry also requires the states to be eigenfunctions of L^2 and L_z for atoms and of L_z only in case of a linear molecule.

- The true wavefunction fulfils the Hellmann-Feynman theorem.

In actual calculations some of the properties of the true wavefunction have to be ignored in order for the problem at hand to be computationally tractable. The one and N-particle bases that span the vector spaces for a specific problem usually do not obey the cusp conditions. The symmetry properties which include angular momentum arise automatically provided that the basis is invariant under transformations of the point group of the Hamiltonian. But exploitation of symmetry is very important in practice as it allows the reduction of the Hamiltonian to block diagonal form which saves computational resources. Furthermore symmetry constraints may be used to calculate the lowest lying state in a given irreducible representation.

1.3.2 Approximate wavefunctions

A fundamental building block in constructing approximate wavefunctions that fulfil the permutational properties of electrons is the Slater determinant [30] 1.24. The $\chi_i(n)$ are one electron functions called spin orbitals where \vec{x}_n represents the three spatial coordinates and the spin coordinate of electron n . In the current context the orbitals are assumed to form an orthonormal set. As a determinant changes sign when rows or columns are exchanged the antisymmetry is elegantly incorporated.

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\vec{x}_1) & \chi_2(\vec{x}_1) & \dots & \chi_n(\vec{x}_1) \\ \chi_1(\vec{x}_2) & \chi_2(\vec{x}_2) & \dots & \chi_n(\vec{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\vec{x}_n) & \chi_2(\vec{x}_n) & \dots & \chi_n(\vec{x}_n) \end{vmatrix} \quad (1.24)$$

Unfortunately a single Slater determinant is a too simple object to describe a system of interacting particles as the multiplicative nature of its constituent terms corresponds to a non correlated probability distribution. By expanding the wavefunction in several Slater determinants it is nevertheless possible to recover correlation effects. Equation 1.25 illustrates how a function of two variables can be expanded as a product of one electron functions[5] by making the coefficients c_i explicit functions of x_2 .

$$\begin{aligned}
 |F(x_1, x_2)\rangle &= |i(x_1)\rangle \langle i(x_1)|F(x_1, x_2)\rangle = c_i(x_2)|i(x_1)\rangle \\
 &= |j(x_2)\rangle \langle j(x_2)|c_i(x_2)\rangle |i(x_1)\rangle = c_{ij}|j(x_2)\rangle |i(x_1)\rangle
 \end{aligned}
 \tag{1.25}$$

Restricted and unrestricted orbitals

Although nonorthogonal orbitals have very useful and interesting properties[47] most quantum chemical methods are formulated in an orthonormal framework^{1.26}. Orthogonal functions for instance have the advantage of providing very simple equations when projections are involved.

$$\langle p|q\rangle = \delta_{pq} \tag{1.26}$$

In order to fully describe an electron 4 coordinates are needed. Three of those describe the position in space. The fourth coordinate is the spin coordinate. Orbitals are constructed as a product of a spatial and a spin function. The spin functions α and β provide a two dimensional orthonormal basis.

$$\chi(\vec{x}) = \psi(\vec{r})\sigma(s) \quad \sigma = \begin{cases} \alpha(s) \\ \beta(s) \end{cases} \tag{1.27}$$

Given 1.27 and the orthogonality of the spin functions there are two different possibilities to choose the spatial part of the orbitals. One can either choose the same set of orthogonal functions for both α and β spin which are known as restricted orbitals. If different spatial parts are chosen for alpha and beta the set is called unrestricted orbitals. A detailed description of the functional form of the spatial part is given in section 1.7.

Spin Eigenfunctions

The electronic Hamiltonian does not contain any spin dependent part and the wavefunction should also be an eigenfunction of S_z and S^2 . Therefore the electronic wavefunction can be written as a product of a spatial and a spin part. Unfortunately a single Slater determinant is only a spin eigenfunction for closed shell or high spin states¹. Proper spin

¹In a high spin state all unpaired electrons have parallel spins.

eigenfunctions can however be constructed as a linear combination of several Slater determinants when restricted orbitals are used. These linear combinations are known as configuration state functions (CSF's) and shall not be discussed further at this point.

1.4 Second Quantisation

In quantum chemistry N-electron wavefunctions of molecular species are represented as expansions in Slater determinants. The direct manipulation of determinants is rather inconvenient when new models are developed. A further complication is that the determinant and the Hamiltonian both depend explicitly on the number of electrons for a given problem. Second Quantisation[52, 74] is a formalism which remedies all those shortcomings and provides a neat way to handle wavefunctions and operators.

At the heart of second quantisation lies an abstract 2^M -dimensional vector space called the Fock space where M is the number of spin-orbitals present in a chosen basis². Specific configurations are expressed via occupation number vectors. The elements of the occupation number vector are simply ones or zeros depending on whether that particular spin orbital is occupied. The dimensionality 2^M is a result of the definition of the inner product as given in equation 1.28. The vector with zeros only is called the vacuum state as it presents a state with no particle.

$$\langle K|L\rangle = \prod_i \delta_{K_i L_i} \quad (1.28)$$

States with specific occupations are generated by application of operators on the vectors in Fock space. The effect of the creation operators a_p^\dagger is to add an electron to spin orbital p. This is illustrated by equation 1.29. The Kronecker delta ensures that the result is zero if spin orbital p is already occupied. The phase factor Γ ensures antisymmetry.

$$a_p^\dagger|K\rangle = \delta_{K_p 0} \Gamma_p |\dots, K_p = 1, \dots\rangle \quad \Gamma_p = \prod_{i=1}^{p-1} (-1)^{K_i} \quad (1.29)$$

²The term chosen should be understood in a rather abstract manner.

Similarly annihilation operators a_p which remove an electron from orbital p as shown by 1.30 can be defined. The Kronecker delta causes the expression to vanish if p is unoccupied.

$$a_p|K\rangle = \delta_{K_p,1}\Gamma_p|\cdots, K_p = 0, \cdots\rangle \quad (1.30)$$

Although the phase factors Γ_p are necessary for the antisymmetry properties they can be omitted as they lead to the anticommutation relations 1.31, 1.32 and 1.33 which themselves keep track of the exchange properties.

$$[a_p, a_q]_+ = 0 \quad (1.31)$$

$$[a_p^\dagger, a_q^\dagger]_+ = 0 \quad (1.32)$$

$$[a_p^\dagger, a_q]_+ = \delta_{pq} \quad (1.33)$$

With the help of these anticommutators it is now possible to write any electronic state as a string of creation operators 1.34 acting on the vacuum state and the antisymmetry properties hold as expected.

$$a_p^\dagger a_q^\dagger |vac\rangle = -a_q^\dagger a_p^\dagger |vac\rangle \quad (1.34)$$

The usefulness of second quantisation does not stop at generating electronic states from the vacuum. The creation and annihilation may be combined to build excitation operators as shown in 1.35. The effect of these operators is to excite electrons from orbital q to orbital p and so on. This proves useful for the development of correlated theories such as configuration interaction and coupled cluster.

$$\hat{X}_q^p = a_p^\dagger a_q \quad \hat{X}_{qs}^{pr} = a_p^\dagger a_r^\dagger a_s a_q \quad (1.35)$$

1.4.1 Operators

The second quantisation formalism is not complete without the redefinition of the operators. The expressions for one electron operators 1.36 and two electron operators 1.37

are simply tensor elements over the basis functions that form the Fock space times a string of as many creation and annihilation operators as electrons are involved. The elementary operators a_p^\dagger and a_q are in so called vacuum normal order which means that all annihilation operators appear to the right of the creation operators. This property ensures that zero results if an unoccupied orbital is affected.

$$\hat{h} = \sum_{pq} h_{pq} a_p^\dagger a_q \quad h_{pq} = \langle p|h|q \rangle \quad (1.36)$$

$$\hat{g} = \frac{1}{2} \sum_{pqrs} g_{pqrs} a_p^\dagger a_r^\dagger a_s a_q \quad g_{pqrs} = \langle pr|r_{12}^{-1}|qs \rangle = \langle pr|qs \rangle \quad (1.37)$$

It needs to be shown that these operators have the expectation values that are expected from Slater Condon rules [5]. The operator strings in 1.36 and 1.37 can be regarded as excitation operators like the one in 1.35. With the definition of the inner product of the Fock space 1.28 the recipe for evaluating expectation value of second quantisation operators is to single out the “excitations” that lead to non vanishing inner products.

One electron operators

In order to determine the expectation value there are three cases to distinguish.

1. Both ON vectors are equal. This result is obvious considering the definition of the inner product. The only operation the operators a_p^\dagger and a_q are allowed to perform is to map $|k\rangle$ onto itself

$$\langle k|h_{pq}a_p^\dagger a_q|k\rangle = \sum_p h_{pp}k_p \quad (1.38)$$

where k_p is the spin orbital occupation number which can either be zero or one.

2. The ON vectors differ by one spin orbital. In order to generate a non vanishing contribution the elementary operators need to bring $|l\rangle$ in congruence with $\langle k|$. The phase factors are necessary at this stage to obtain the right sign.³

³Most authors refer the phase factor Γ_p^x to $|k\rangle$ but there is some freedom of choice due to associativity and a_p^\dagger can be chosen to work on either $\langle k|$ or $|l\rangle$.

$$\langle k|h_{pq}a_p^\dagger a_q|l\rangle = h_{pq}\Gamma_p^l\Gamma_q^l \quad (1.39)$$

3. The occupation number vectors differ by more than one spin orbital.

$$\langle k|h_{pq}a_p^\dagger a_q|l\rangle = 0 \quad (1.40)$$

In this case it is not possible to change sufficiently many occupation numbers to generate a non vanishing inner product.

Two electron operators

The evaluation of the two electron operator proceeds along the same lines where use is made of the symmetry properties of the kernel r_{12}^{-1} . There are four basic cases to be covered:

1. The ON vectors are equal. Hence the elementary operators need to map $|k\rangle$ onto itself. This means that indices q and s need to refer to the functions p and r . This leads to either $p = q, r = s$ or $p = s, r = q$ where the latter variant is responsible for the exchange term as a result of the antisymmetry properties.

$$\langle k|\frac{1}{2}g_{pqrs}a_p^\dagger a_r^\dagger a_s a_q|k\rangle = \frac{1}{2}\sum_{pq}k_p k_q(g_{ppqq} - g_{pqqp}) \quad (1.41)$$

Alternatively the following shorthand notation for the two electron integrals can be used

$$\frac{1}{2}\sum_{pq}k_p k_q(g_{ppqq} - g_{pqqp}) = \frac{1}{2}\sum_{pq}k_p k_q\langle pq||pq\rangle \quad (1.42)$$

which unifies the coulomb and exchange term in a single object.

2. The ON vectors differ by one spin orbital. The orbitals with different occupation are denoted t and u . There are four different possibilities to bring the vectors to coincide: $(p = t, q = u, r = s)$, $(p = t, s = u, q = r)$, $(r = t, q = u, p = s)$ and $(r = t, s = u, p = q)$.

$$\langle k|\frac{1}{2}g_{pqrs}a_p^\dagger a_r^\dagger a_s a_q|l\rangle = \sum_p k_p \Gamma_t^l \Gamma_u^l (g_{tupp} - g_{tppu}) \quad (1.43)$$

3. The ON vectors differ by two spin orbitals.

$$\langle k | \frac{1}{2} g_{pqrs} a_p^\dagger a_r^\dagger a_s a_q | l \rangle = \Gamma_p^l \Gamma_q^l \Gamma_r^l \Gamma_s^l (g_{pqrs} - g_{psqr}) \quad (1.44)$$

4. The ON vectors differ by more than two spin orbitals. In this case the result is zero because only two orbitals can be modified at a time.

$$\langle k | \frac{1}{2} g_{pqrs} a_p^\dagger a_r^\dagger a_s a_q | l \rangle = 0 \quad (1.45)$$

1.5 Standard models in Quantum Chemistry

1.5.1 The Hartree-Fock Approximation

The most simple approximation to calculate the electronic energy of an atom or molecule is to use a single Slater determinant as trial wavefunction which is the idea behind the Hartree-Fock[17, 78] approach. Using the Slater Condon rule for matrix elements between determinants the energy expression 1.46 is obtained where p and q denote spin orbitals. The functional notation $E_{HF}[\Psi]$ is used to stress the point that the energy depends on the functional form of Ψ which is ultimately determined by the spin orbitals.

$$E_{HF}[\Psi] = \langle p|h|p \rangle + \frac{1}{2} \langle pq||pq \rangle \quad (1.46)$$

It is the goal of the Hartree-Fock approximation to variationally minimise energy by varying the orbitals. Blindly optimising the one electron functions will not have the desired effect when the orbitals are required to remain orthonormal. This constraint can be enforced by setting up the Lagrangian:

$$L_{HF} = \langle p|h|p \rangle + \frac{1}{2} \langle pq||pq \rangle - \epsilon_{pq} (\langle p|q \rangle - \delta_{pq}) \quad (1.47)$$

With the help of the Lagrangian 1.47 it is now possible to apply the functional variation $p \rightarrow p + \delta p$ to all spin orbitals. Of special interest is the first order variation of the Lagrangian δL which is set equal to zero. Since the undetermined multiplier method merely adds zero to the energy equation both equations will have the minimum for the

same variation. The result of the variation is equation 1.48 where cc denotes the complex conjugate of the first half of the expression.

$$\delta L_{HF} = \langle \delta p | h | p \rangle + \langle \delta p q | p q \rangle - \langle \delta p q | q p \rangle - \epsilon_{qp} \langle \delta p | q \rangle + cc = 0 \quad (1.48)$$

The complex conjugate in equation 1.48 does not present an additional degree of freedom therefore the real part is enough to determine the stationary point. From equation 1.48 it is possible to define the so called Fock operator 1.49 whose eigenfunctions are the spin orbitals. The operator \hat{F}_{12} has the effect of swapping the electron labels. The coulomb and exchange operators $J(1)$ and $K(1)$ contain a summation over all occupied orbitals. They represent the average potential seen by electron 1 in orbital $|p\rangle$ which is the reason why Hartree-Fock is classified as mean field theory. The operator J has a purely classical interpretation as it corresponds the interaction energy of an electron and the charge distributions of the remaining electrons⁴. The exchange operator on the other hand is a result of the antisymmetry. $K(1)$ is called a nonlocal operator because the potential depends on the form $|p\rangle$ throughout the whole space.

$$\hat{F}|p\rangle = \left[\frac{1}{2} \nabla_1^2 + V_1 + \sum_q \langle q(x_2) | \frac{1}{r_{12}} (1 - \hat{P}_{12}) | q(x_2) \rangle \right] |p\rangle \quad (1.49)$$

$$= [h(1) + J(1) - K(1)] p \quad (1.50)$$

$$= |q\rangle \epsilon_{qp} \quad (1.51)$$

Equation 1.49 does not look like an ordinary eigenvalue equation. It seems that the application of the operator \hat{F} on a function $|p\rangle$ creates a mixture of various functions. The equation can be brought to standard eigenvalue form by a unitary transformation as shown in 1.52.

$$|q\rangle = |p\rangle U_{pq} \rightarrow \hat{F}|q\rangle = \epsilon_q |q\rangle \quad (1.52)$$

The validity of 1.52 can be proven by showing that the $J(1)$, $K(1)$ and ϵ_{qp} are invariant under unitary transformations. The eigenvalues ϵ_q correspond to the energy of an

⁴The coulomb operator also contains a self-interaction component which is removed by the exchange operator!

electron in orbital $|q\rangle$. An additional interpretation of the eigenvalues is given by Koopmans theorem which equates the negative eigenvalues of occupied orbitals to ionisation energies and the negative eigenvalues of unoccupied to electron affinities.

An interesting feature of the canonical Hartree-Fock equations 1.52 is that given by 1.53 which is known as the Brillouin condition. The matrix element of the Fock operator between an occupied and an unoccupied orbital is zero by construction. It turns out that the individual contributions are exactly those that are given by the Slater Condon rules for Slater determinants which differ in one orbital. This means that the Hamiltonian matrix elements between the Hartree-Fock state and singly excited functions are zero.

$$\langle a|F|i\rangle = \langle a|h|i\rangle + \langle a||ij\rangle = 0 \quad (1.53)$$

The Roothaan Hall equations

With the canonical Hartree-Fock equations 1.52 the problem at hand is still solving a partial differential equation which is notoriously hard to solve numerically in cases where the system is not highly symmetrical e.g. atoms or diatomics. Roothaan [9] recognised that there is a way around this problem by expanding the orbitals in a basis of functions 1.54.

$$|i\rangle = \sum_{\alpha} |\chi_{\alpha}\rangle C_{\alpha i} \quad (1.54)$$

The most simple case is a restricted Hartree-Fock calculation for a closed shell system which has the following Fock operator.

$$F = h_1 + \sum (2J - K) \quad (1.55)$$

Expanding the eigenfunctions of this operators in the basis 1.54 leads to a general eigenvalue problem 1.56. The quantity $P_{\sigma\lambda}$ is called the density matrix.

$$F_{\mu\nu} = h_{\mu\nu} + P_{\sigma\lambda} (g_{\mu\nu\sigma\lambda} - \frac{1}{2} g_{\mu\lambda\sigma\nu}) \quad P_{\sigma\lambda} = C_{\sigma i} 2 C_{i\lambda} \quad (1.56)$$

$$FC = SC\varepsilon \quad (1.57)$$

The Roothaan-Hall equations 1.56, 1.57 have to be solved iteratively because the Fock operator depends on the orbitals which are the eigenvectors of F itself. For a given set of trial orbitals the Fock operator is constructed by evaluating the corresponding density. The eigenvectors of this new Fock operator are then used to define a new density matrix and operator until the energy is stationary. For a calculation to converge a suitable orbital guess for the starting density is needed. There are several possibilities to start a Hartree-Fock calculation where the most simple case is to use a zero density in the first step. The complexity of the Hartree-Fock approach is $O(N^4)$ where N is the number of basis functions and results from the evaluation of the electron repulsion integrals $g_{\mu\nu\sigma\lambda}$.

Open shell Hartree-Fock calculations

Unfortunately many interesting systems are not closed shell. For these cases Hartree-Fock theory is a bit more involved than the closed shell Roothaan Hall equations. The conceptually more simple approach is to allow independent spatial parts for the alpha and beta spin orbitals. This is known as the Unrestricted Hartree-Fock approach which goes back to Pople and Nesbet[26]. In this case it is possible to define individual Fock operators for the α and β electrons. The eigenfunctions of the operators 1.58 and 1.59 cannot be determined independently because they are coupled via the coulomb operators J .

$$F_{\alpha} = h_{\alpha} + J_{\alpha} + J_{\beta} - K_{\alpha} \quad (1.58)$$

$$F_{\beta} = h_{\beta} + J_{\beta} + J_{\alpha} - K_{\beta} \quad (1.59)$$

Finding a set of restricted open shell orbitals is more difficult. Roothaan extended the restricted formalism to open shell systems[15]. For the present work only high spin states shall be of concern with the doubly occupied orbitals i, j, \dots , the singly occupied orbitals s, t, \dots with α -spin and virtuals a, b, \dots . For such a system a Fock operator may be defined as in expression 1.60 [60] where the superscripts denote closed and open shell parts:

$$F = h_1 + 2J^c - K^c + J^o - \frac{1}{2}K^o \quad (1.60)$$

The restricted open shell Hartree-Fock orbitals must fulfil the following constraints:

$$\langle a|F|i\rangle = 0 \quad (1.61)$$

$$\langle s|F + \frac{1}{2}K^o|i\rangle = 0 \quad (1.62)$$

$$\langle a|F - \frac{1}{2}K^o|s\rangle = 0 \quad (1.63)$$

There is no unique way of incorporating these condition into a working program. Specific choices are usually made to permit the efficient formulation of open shell perturbation theory[14] which happens to be less straightforward for restricted than unrestricted orbitals. One way of setting up the Fock matrix is given by[14]:

$$\begin{pmatrix} [F]_{ij} & [F + \frac{1}{2}K^o]_{is} & [F]_{ia} \\ [F + \frac{1}{2}K^o]_{si} & [F]_{st} & [F - \frac{1}{2}K^o]_{sa} \\ [F]_{ai} & [F - \frac{1}{2}K^o]_{as} & [F]_{ab} \end{pmatrix} \quad (1.64)$$

The restricted Hartree-Fock orbitals are somewhat unphysical. For the described high spin state both α and β electrons experience the same coulomb interaction but the exchange contribution that is felt by the α electrons is larger than for the β electrons. By forcing the same functional form for spin up and spin down orbitals in the occupied space the α electrons are subjected to some spurious potential.

1.5.2 Configuration Interaction

The Hartree-Fock approximation cannot provide an exact description of the electronic wavefunction because a single Slater determinant is not an exact wavefunction for interacting fermions. A better description of the electronic problem can be achieved by expanding the N particle state as a linear combination of several Slater determinants 1.65. This is the idea behind the configuration interaction method.

$$|CI\rangle = \sum_K c_K |K\rangle \quad (1.65)$$

The coefficients of expansion 1.65 are determined by inserting the trial wavefunction 1.65 into the Hamiltonian and applying the variational principle 1.66 which leads to a standard eigenvalue problem as shown in section 1.11.

$$\frac{\partial}{\partial c_i} \frac{\langle CI|H|CI\rangle}{\langle CI|CI\rangle} = 0 \quad (1.66)$$

From an N dimensional spatial basis a formidably large number of Slater determinants can be constructed as shown in equation 1.67. When the set of full determinants is used the method is termed “Full Configuration Interaction”. Full CI gives the lowest possible energy for a given N particle vector space. Unless a very small system is investigated and a small basis used the resulting eigenvalue problem is computationally intractable. FCI is however a very important benchmarking tool for all other approximate methods[54].

$$N_{det} = \binom{N}{n_\alpha} \binom{N}{n_\beta} \quad (1.67)$$

The size of the problem can be reduced by selecting a subset of the FCI space. The configurations that enter the FCI wavefunction can be generated in a systematic way by application of the second quantisation formalism and its operators to the Hartree-Fock ground state. The determinants can be classified into singly, doubly, triply and higher excited configurations according to the number of orbitals that are replaced.

$$\begin{aligned} |FCI\rangle &= (c_0 + T_1 + T_2 + \dots + T_N)|0\rangle \\ T_1 &= c_i^a X_i^a = c_i^a a_a^\dagger a_i \\ T_2 &= c_{ij}^{ab} X_{ij}^{ab} = c_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i \\ &\dots \end{aligned} \quad (1.68)$$

The starting point for reducing the variational space is equation 1.69 which shows that the energy can be extracted by projecting onto the Hartree-Fock state. As a result of the Slater Condon rules for matrix elements only contributions up to double excitations need to be evaluated. This suggests that these are the most important configurations and that a suitable approximation is to include only single and double excitations. This is known as the Configuration interaction singles doubles (CISD) method.

$$\langle 0|\hat{H}|CI\rangle = \langle 0|\hat{H}(c_0 + T_1 + T_2 + \underbrace{\cdots + T_N}_{=0})|0\rangle = c_0 E_{CI} \quad |CISD\rangle = (c_0 + T_1 + T_2)|0\rangle \quad (1.69)$$

The singly excited states do not contribute to the energy expression 1.69 directly due to Brillouins theorem. Their inclusion will however modify the coefficients of the doubly excited determinants through the determining equations 1.70. The same is true for other configurations because the Hamiltonian matrix couples all excited determinants in a more or less direct manner. The importance of single excitations lies in the fact that they make an important contribution to the first order density matrix which is important for the first calculation of one electron properties.

$$\langle K|H|CI\rangle = \langle K|H|L\rangle c_L = c_K E_{CI} \quad (1.70)$$

Size extensivity Truncated CI

The truncation of the N particle Hilbert space not only reduces the quality of the calculated energy but also violates the criterion of size extensivity. The term size extensivity means that the total energy of a system of noninteracting particles must be equal to the sum of the individual subsystem energies when calculated as an ensemble.

Equations 1.71 through 1.75 define such a system with two noninteracting particles where the letters *S* and *D* denote the singly and doubly excited parts of the CI wavefunction.

$$H_A|CI_A\rangle = E_A|CI_A\rangle \quad (1.71)$$

$$|CI_A\rangle = |0_A\rangle + |S_A\rangle + |D_A\rangle \quad (1.72)$$

$$H_B|CI_B\rangle = E_B|CI_B\rangle \quad (1.73)$$

$$|CI_B\rangle = |0_B\rangle + |S_B\rangle + |D_B\rangle \quad (1.74)$$

$$\hat{H}_{AB} = \hat{H}_A + \hat{H}_B \quad (1.75)$$

For the wavefunction the term size extensivity implies that the wavefunction of the

supersystem is the product of the subsystem eigenfunctions as shown in the following equations:

$$E_{AB} = \langle \Psi_{AB} | H_{AB} | \Psi_{AB} \rangle \quad (1.76)$$

$$= \langle \Psi_A | \langle \Psi_B | (H_A + H_B) | \Psi_A \rangle | \Psi_B \rangle \quad (1.77)$$

$$= \langle \Psi_A | H_A | \Psi_A \rangle \langle \Psi_B | \Psi_B \rangle + \langle \Psi_B | H_B | \Psi_B \rangle \langle \Psi_A | \Psi_A \rangle \quad (1.78)$$

$$= E_A + E_B \quad (1.79)$$

The product wavefunction for the chosen example is given by 1.80. It can be seen that multiplying the S and D components leads to triple (T) and quadruple (Q) excitations.

$$|\Psi_{AB}\rangle = |CI_A\rangle |CI_B\rangle = |0_{AB}\rangle + |S_{AB}\rangle + |D_{AB}\rangle + |T_{AB}\rangle + |Q_{AB}\rangle \quad (1.80)$$

Within the CISD approximation the wavefunction of the supersystem only contains single and double excitations 1.81. The energy calculated with this wavefunction will therefore differ from the expected answer. This problem exists for all truncation levels and the resulting energies are not size extensive.

$$|CI_{AB}\rangle = |0_{AB}\rangle + |S_{AB}\rangle + |D_{AB}\rangle \neq |CI_A\rangle |CI_B\rangle \quad (1.81)$$

Various schemes to estimate the magnitude of the truncation error have been developed. One approach which tries to restore size extensivity is the Davidson correction[66]:

$$\Delta E = (1 - c_0^2) E_{corr,CISD} \quad (1.82)$$

The Full CI approach is size extensive because it yields “exact” eigenvalues in a given Hilbert space. Pople and coworkers developed the quadratic Configuration interaction approach[25] which provides size extensive energies.

1.5.3 Coupled-Cluster Theory

A method which avoids the size extensivity problem when the excitation operator is truncated at some arbitrary level is the coupled cluster theory[33, 34, 35]. In this ap-

proach the correlated wavefunction is expressed as the reference state times the exponential of an excitation operator 1.83.

$$|CC\rangle = e^{\hat{T}}|0\rangle \quad (1.83)$$

The notion exponential of an operator becomes clear by considering the Maclaurin expansion 1.84 of the exponential function. The object $e^{\hat{T}}$ is known as the cluster operator.

$$e^{\hat{T}} = 1 + \hat{T} + \frac{\hat{T}^2}{2!} + \frac{\hat{T}^3}{3!} + \frac{\hat{T}^4}{4!} + \dots \quad (1.84)$$

Similar to the Full CI expansion 1.68 the excitation operator can be decomposed into various excitation levels, e.g. singles, doubles, etc. An important property of the excitation operators $a_a^\dagger a_i$ for the development of coupled cluster theory is that they commute

$$\left[a_a^\dagger a_i, a_b^\dagger a_j \right] = 0 \quad (1.85)$$

since the contractions between creation and annihilation operators always refer to different subsets. Inserting the single excitations into the exponential 1.86 it becomes obvious that the result of the exponential is to generate higher order excitations such as doubles and triples and indeed all determinants that form the basis of the Hilbert space as products of the lower level excitations:

$$e^{\hat{T}_1} = 1 + \sum_{ai} t_i^a a_a^\dagger a_i + \frac{1}{2} \sum_{ai} \sum_{bj} t_i^a t_j^b a_a^\dagger a_i a_b^\dagger a_j + \dots \quad \hat{T}_1 = \sum_{ai} t_i^a a_a^\dagger a_i \quad (1.86)$$

Although the series expansion of the exponential function is infinite the cluster operator terminates when the maximum possible number of excitations from the reference state is exhausted. Carrying out the expansion with an excitation operator of the form $\hat{T} = \hat{T}_1 + \dots + \hat{T}_N$ and regrouping according to the excitation level

$$\hat{X}_0 = 1 \quad (1.87)$$

$$\hat{X}_1 = \hat{T}_1 \quad (1.88)$$

$$\hat{X}_2 = \hat{T}_2 + \frac{1}{2}\hat{T}_1^2 \quad (1.89)$$

$$\hat{X}_3 = \hat{T}_3 + \hat{T}_1\hat{T}_2 + \frac{1}{6}\hat{T}_1^3 \quad (1.90)$$

$$\vdots \quad (1.91)$$

$$\hat{X}_N = \hat{T}_N + \dots \quad (1.92)$$

further illustrates the appearance of higher order excitations in terms of lower level excitations and shows which terms contribute to a particular excitation level. Product terms such as $\frac{1}{2}\hat{T}_1^2$ are commonly referred to as disconnected clusters whereas the pure terms \hat{T}_N are called connected clusters. The above equations also show that the fraction of connected clusters to a particular excitation level diminishes as the N electron limit is approached which further suggests truncation of the excitation operator although it must be said that the disconnected terms cannot guarantee an appropriate representation of the connected contributions as exemplified by the connected triples which are inadequately represented by disconnected components.

The multiplicative property of the exponential function $e^{x+y} = e^x e^y$ is furthermore responsible for the size extensivity of the coupled cluster ansatz. For two noninteracting systems it is possible to separate the excitation operator into subsystem contributions 1.93. As can be seen from 1.93 the wavefunction can therefore also be factorised.

$$|CC_{AB}\rangle = e^{\hat{T}_A + \hat{T}_B} |O_{AB}\rangle = (e^{\hat{T}_A} |O_A\rangle)(e^{\hat{T}_B} |O_B\rangle) \quad (1.93)$$

In practical calculations the operator \hat{T} is truncated at some excitation level. This is mostly done at the doubly excited level leading to the coupled cluster singles doubles (CCSD) method. Triple excitations are mostly included via a perturbative treatment resulting in the CCSD(T)[41] model.

The difficult part in coupled cluster theory is to determine the wavefunction parameters t . The application of the cluster operator $e^{\hat{T}}$ to the reference state generates the complete set of Full CI configurations even when \hat{T} is truncated. In contrast to the FCI

case the coupled cluster wavefunction depends on the amplitudes t in a nonlinear fashion as shown by equations 1.87 to 1.92. Although it would be desirable to determine the the coupled cluster solution variationally

$$\frac{\partial}{\partial c_i} \frac{\langle CI|H|CI \rangle}{\langle CI|CI \rangle} = 0 \quad \frac{\partial}{\partial t_i} \frac{\langle CC|H|CC \rangle}{\langle CC|CC \rangle} = 0 \quad (1.94)$$

such an approach is not practical because the stationary conditions 1.94 lead to a difficult nonlinear optimisation problem.

$$\langle 0|He^{\hat{T}}|0 \rangle = E_{CC} \quad (1.95)$$

$$\langle K|He^{\hat{T}}|0 \rangle = t_K E_{CC} \quad (1.96)$$

By projecting the coupled cluster energy expression with the reference state 1.95 and all excited determinants 1.96 it is possible to determine the energy and the wavefunction parameters but this comes at the price of losing the upper bound property for the energy. These equations are still not very convenient because the cluster amplitudes t and the energy E_{CC} are coupled. A decoupling can be achieved by exploiting the inverse of the cluster operator as shown in 1.97 and 1.98.

$$\langle 0|e^{-\hat{T}}He^{\hat{T}}|0 \rangle = E_{CC} \quad (1.97)$$

$$\langle K|e^{-\hat{T}}He^{\hat{T}}|0 \rangle = 0 \quad (1.98)$$

An additional benefit of the application of $e^{-\hat{T}}$ is the ability to rewrite $e^{-\hat{T}}He^{\hat{T}}$ as Baker-Campbell-Hausdorff (BCH) series:

$$e^{-\hat{T}}He^{\hat{T}} = H + [H, \hat{T}] + \frac{1}{2!} [[H, \hat{T}], \hat{T}] + \frac{1}{3!} [[[H, \hat{T}], \hat{T}], \hat{T}] + \frac{1}{4!} [[[[H, \hat{T}], \hat{T}], \hat{T}], \hat{T}] + \dots \quad (1.99)$$

As a result of the commutation properties of the excitation operators in \hat{T} the BCH series terminates after the fourth nested commutator because the elementary operators

in the hamiltonian H can lead to a maximum of four contractions. Hence the expansion is at most quartic in the amplitudes.

What has effectively been done in equations 1.97 and 1.98 is a similarity transformation of the Hamiltonian into a new operator $e^{-\hat{T}}He^{\hat{T}}$. An important consequence of this transformation is that the new operator is not hermitian any more and thus the variational principle does not apply. One is therefore left with the task of solving equations 1.97 and 1.98 iteratively. This is the standard approach used in coupled cluster theory.

There have been several attempts to arrive at variational coupled cluster methods. One such approach is the expectation value coupled cluster method XCC(n) of Bartlett and Noga [57] where the infinite order operator $e^{\hat{T}}He^{\hat{T}}$ is truncated based on the contributions that enter the perturbative energies at order n . An alternative approach is to replace \hat{T} in the similarity transformed equations by

$$\sigma = \hat{T} - \hat{T}^\dagger \quad (1.100)$$

which is anti hermitian and leads to a unitary transformation of H . This is the idea behind the unitary coupled cluster approach [58, 43]. Unfortunately the Baker-Campbell-Hausdorff series for σ does not break off at some finite order and some truncation is necessary to make the approach practically viable.

The preceding discourse may give the impression that coupled cluster theory is more of a curse than a blessing for quantum chemistry. But the coupled cluster model is the most successful approach for purely determinantal expansions as it gives the best approximations to the Full CI wavefunction. But the accuracy comes at a cost and the scaling[53] of $O(N^6)$ for CCSD and $O(N^7)$ CCSD(T) becomes prohibitive for large systems. Recent developments however have shown the implementation of linear scaling approaches [46].

1.5.4 Møller-Plesset Perturbation Theory

A different approach in electronic structure calculations that also provides size extensive energies is Møller-Plesset Perturbation theory[13].

$$H = H^{(0)} + \lambda H^{(1)} \quad (1.101)$$

Møller-Plesset perturbation theory is an application of Rayleigh Schrödinger perturbation theory (section 1.2.2) where the Fock operator 1.102 is used as zero order Hamiltonian. The perturbation $H^{(1)}$ in equation 1.101 is expressed as the difference between the full Hamiltonian 1.103 and the $H^{(0)}$. The operator 1.104 is called the fluctuation potential because it introduces fluctuations to the mean field potential of the Fock operator. The operators $H^{(0)}$ and $H^{(1)}$ are sometimes written as F and Φ . Throughout this section use will be made of the summation convention which implies summation over repeated dummy indices.

$$H^{(0)} = (h_{pq} + \langle pi||qi \rangle) a_p^\dagger a_q \quad (1.102)$$

$$H = h_{pq} a_p^\dagger a_q + \frac{1}{2} \langle pr|qs \rangle a_p^\dagger a_r^\dagger a_s a_q \quad (1.103)$$

$$H^{(1)} = H - H^{(0)} = \frac{1}{2} \langle pr|qs \rangle a_p^\dagger a_r^\dagger a_s a_q - \langle pi||qi \rangle a_p^\dagger a_q \quad (1.104)$$

The contributions that can readily be evaluated with the knowledge of the Hartree-Fock state are the zero and first order energies (1.105 and 1.106). It can readily be seen that the sum of both components is equal to the Hartree-Fock energy 1.107. Therefore the first correction comes at second order.

$$E^{(0)} = \langle 0|H^{(0)}|0 \rangle = h_{ii} + \langle ij||ij \rangle \quad (1.105)$$

$$E^{(1)} = \langle 0|H^{(1)}|0 \rangle = \frac{1}{2} \langle ij||ij \rangle - \langle ij||ij \rangle \quad (1.106)$$

$$E^{(0)} + E^{(1)} = h_{ii} + \frac{1}{2} \langle ij||ij \rangle = E_{SCF} \quad (1.107)$$

The first order correction $|1\rangle$ is determined via equation 1.108. The function $|1\rangle$ is expressed as a linear combination of Slater determinants where the expansion coefficients are determined by projecting equation 1.108 from the left with determinants from the N particle space. The SCF state is omitted from the expansion in order to ensure the intermediate normalisation property introduced earlier in section 1.2.2.

$$\left[H^{(0)} - E^{(0)} \right] |1\rangle = \left[E^{(1)} - H^{(1)} \right] |0\rangle \quad (1.108)$$

Not all determinants that span the N particle vector space will contribute the first order correction. Equation 1.108 only contains one and two particle operators which means only single and double excitations need to be considered. Singly excited determinants do not contribute to the first order wavefunction as a result of Brillouin's theorem and the Hartree-Fock conditions. The first order wavefunction $|1\rangle$ thus only consists of double excitations.

$$|1\rangle = \frac{1}{4} t_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i |0\rangle \quad t_{ij}^{ab} = -\frac{\langle ab || ij \rangle}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j} \quad (1.109)$$

The expression for the first order wavefunction is given in 1.109. The formula for the amplitudes t_{ij}^{ab} is obtained by projecting equation 1.108 from the left with all doubly excited determinants. In deriving the expressions for the amplitudes t_{ij}^{ab} use has been made of the fact that all Slater determinants generated from a canonical basis are eigenfunctions of the Fock operator. Inserting $|1\rangle$ into the second order energy expression leads to 1.110. The second order Møller-Plesset energy calculations are among the most popular methods in applied quantum chemistry and recover around 80% of the correlation energy.

$$E_{MP2} = \langle 0 | H^{(1)} | 1 \rangle = -\frac{1}{4} \frac{\langle ab || ij \rangle^2}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j} \quad (1.110)$$

The calculations of higher order contributions proceed along the same lines. From the equation that defines the second order wavefunction 1.111 it can be seen that singly, doubly, triply and quadruply excited determinants will be necessary for the calculation of the third order energy.

$$\left[H^{(0)} - E^{(0)} \right] |2\rangle = E^{(2)} |0\rangle - \left[H^{(1)} - E^{(1)} \right] |1\rangle \quad (1.111)$$

A derivation of the higher order corrections to the energy and the wavefunction will not be carried out as they are more laborious and expected to be of lesser importance. But there remains some level of uncertainty whether the perturbation series will

converge for a given problem. Therefore this aspect has received much attention in research [50]. An interesting feature is that the perturbation series has a finite radius of convergence [32] similar to complex series.

1.6 Electron Correlation

The Hartree-Fock approximation accounts for approximately 98% of the nonrelativistic electronic energy. Although this sounds very promising it is far from satisfactory as the energies involved in chemical processes are usually smaller than the error connected to the self consistent field approximation. The remaining part of the energy is called correlation energy and is associated with the shortcomings of using a single determinant as multi electron wavefunction. It is the aim of this section to give a detailed description of correlation effects.

1.6.1 Static correlation

Although this work focuses on dynamic correlation a discussion of static correlation is needed to give a complete description of correlation effects. Figure 1.1 shows two potential energy curves for the hydrogen molecule obtained from restricted Hartree-Fock (upper curve) and Full CI (lower curve) calculations in a minimal basis. The zero reference energy is chosen for two infinitely separated hydrogen atoms. It is obvious that the Hartree-Fock approach gives a wrong value for the dissociation.

In order to investigate the shortcomings of the Hartree-Fock wavefunction it is necessary to analyse the form of the orbitals. For the minimal basis set the eigenfunctions of the Fock operator which are given by equations 1.112 and 1.113 can be constructed by symmetry arguments where the normalisation constants depend on the inter atomic separation.

$$\sigma_g(r) = \frac{1}{\sqrt{N(R)_g}}(s_A(r) + s_B(r)) \quad (1.112)$$

$$\sigma_u(r) = \frac{1}{\sqrt{N(R)_u}}(s_A(r) - s_B(r)) \quad (1.113)$$

The ground state of the hydrogen molecule is $^1\Sigma_g$ and the σ_g orbital is doubly occupied in the restricted Hartree-Fock wavefunction. After expanding the Slater determinant and grouping together spatial and spin factors equation 1.114 is obtained. A striking fact of expression 1.114 is that the spatial part of the wavefunctions contains terms that localise both electrons at the same nucleus no matter how far the atoms are apart. It is the failure to evenly distribute the two electrons that leads to the wrong dissociation limit.

$$|0\rangle = \frac{1}{\sqrt{2}} \frac{1}{N_g} (s_{Ar_1}s_{Ar_2} + s_{Ar_1}s_{Br_2} + s_{Ar_2}s_{Br_1} + s_{Br_1}s_{Br_2}) \begin{vmatrix} \alpha_1 & \beta_1 \\ \alpha_2 & \beta_2 \end{vmatrix} \quad (1.114)$$

Wavefunction 1.114 is not the only state of gerade symmetry that can be obtained with the orbitals 1.112 and 1.113. There exists also an excited determinant where the orbital of ungerade symmetry is doubly occupied which leads to a totally symmetric wavefunction. Expanding this wavefunction leads to expression 1.115.

$$|K\rangle = \frac{1}{\sqrt{2}} \frac{1}{N_g} (s_{Ar_1}s_{Ar_2} - s_{Ar_1}s_{Br_2} - s_{Ar_2}s_{Br_1} + s_{Br_1}s_{Br_2}) \begin{vmatrix} \alpha_1 & \beta_1 \\ \alpha_2 & \beta_2 \end{vmatrix} \quad (1.115)$$

Although the Slater determinant 1.115 still contains the spurious terms they appear with a different sign. By forming appropriate linear combinations of the two determinants it is possible to describe the wavefunction of the dissociating molecule in a more physical manner. Table 1.6.1 lists the CI coefficients for a minimal basis. Close to the equilibrium the ground state component is dominating as for short separations it is not unlikely to find both electrons near the same nucleus and thus the SCF determinant dominates the wavefunction.

This inability of a single determinant to give a reasonable description of an electronic state is known as static correlation and sometimes also called left right correlation. In the present case the problem is caused by the inflexibility of the restricted orbitals. A UHF would lead to the correct result in the dissociation limit but unrestricted orbitals cannot be used to construct spin eigenfunction and thus a vital part of the physics is ignored. Fortunately most systems of interest are studied near their equilibrium geometry

$\Psi_{CI} = c_0 0\rangle + c_1 K\rangle$		
r [Å]	c_0	c_1
0.50	0.997415976689	-0.071842671480
0.75	0.993413927411	-0.114580839697
1.00	0.984513599364	-0.175308221902
1.50	0.926707105353	-0.375784434069
2.00	0.843746809694	-0.536741391297
2.50	0.770986878717	-0.636851028771
3.00	0.733105811485	-0.680114600025

Table 1.1: CI coefficients for H₂/STO-3G

and their ground states are well separated from other electronic states. Hence a single determinant wavefunction provides a good starting point in most cases.

1.6.2 Dynamic correlation

For the ground state of the helium atom static correlation is not an issue. The complete basis set SCF energy for this state is $-2.86167999E_h$ [16] whereas the true non relativistic energy would be $-2.90372438E_h$ [12]. This difference is caused by the neglect of the Hartree-Fock wavefunction to account for the instantaneous interaction between electrons and is known as dynamical correlation. Figure 1.2 shows the angular probability distribution for the Hartree-Fock and a Hylleraas type wavefunction[2, 65]. The plot is obtained by confining both electrons on a circle with radius R which contains the nucleus in its centre and varying the angle between the electrons. The constant probability distribution belongs to the Hartree-Fock wavefunction. This result is expected as the wavefunction is a simple product of independent probabilities. The cusped curve belongs to an explicitly correlated wavefunction.

By looking at the Hamiltonian 1.116 for the Helium atom it becomes obvious what the shortcomings of the Hartree-Fock wavefunction are. In order to obey conservation of energy the local energy must be constant. But for two coinciding electrons the in-

teraction potential is singular and grows towards infinity. This singularity needs to be balanced somehow. There is no physical rationale which would require the attraction potentials to remove the interaction singularity. Therefore the local kinetic energy at the critical points must be singular with opposite sign to balance the coulomb terms.

$$\hat{H} = \frac{1}{2}\nabla_1^2 + \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \quad (1.116)$$

This requirement leads to the electronic 1.118 and nuclear 1.117 cusp conditions[74]:

$$\left. \frac{\partial \Psi}{\partial r_i} \right|_{r_i=0} = -Z\Psi \quad (1.117)$$

$$\left. \frac{\partial \Psi}{\partial r_{12}} \right|_{r_{12}=0} = \frac{1}{2}\Psi \quad (1.118)$$

Condition 1.118 only holds if Ψ does not vanish for $r_{12} = 0$. The nuclear cusp condition is fulfilled by a Slater type basis function. For coinciding electrons the wavefunction should have the following form:

$$\Psi(r_1, r_2, r_{12}) = \left(1 + \frac{1}{2}r_{12} + O(r_{12}^2) \right) \Psi(r_1, r_2) \quad (1.119)$$

Most quantum chemistry methods expand the nonrelativistic N electron wavefunction in terms of Slater determinants and therefore are not of form 1.119.

$$\Psi_N^{CI} = e^{-\alpha(r_1+r_2)} \sum_{l=0}^{N-1} P_l(\cos \theta_{12}) \sum_{n_1=l+1}^N \sum_{n_2=l+1}^{n_1} C_{n_1 n_2 l} (r_1^{n_1-1} r_2^{n_2-1} + r_2^{n_1-1} r_1^{n_2-1}) \quad (1.120)$$

Equation 1.120 shows one among many possibilities of writing a CI wavefunction for the helium ground state[74]. Where P_l denotes the Legendre polynomial l as a function of the angle between electron one and two and l is the angular momentum. The cosine can be expressed in terms of r_1 , r_2 and r_{12} by application of the cosine rule which leads to 1.121. Equation 1.121 shows that only even powers of r_{12} appear in the CI wavefunction whereas the electronic cusp condition 1.118 demands a linear dependence.

$$\cos \theta_{12} = \frac{1}{2} \frac{r_1^2 + r_2^2 - r_{12}^2}{r_1 r_2} \quad (1.121)$$

Thus the determinantal expansion is an attempt to expand the linear r_{12} behaviour in terms of even powers of the interelectronic distance and such an expansion is expected to converge very slowly. A quantitative analysis of the performance of this expansion is contained in the following section on basis sets.

1.7 Basis sets

In most quantum chemical calculations the spatial part of the orbitals is expanded in a basis of atom centred functions. Like the orbitals of the hydrogen atoms these functions are constructed by combining a radial and an angular part. The radial part is usually represented by a three dimensional Gaussian function although this functional form violates the nuclear cusp condition. Gaussians owe their popularity to the simplicity with which they can be handled. The angular part can either be represented by simple cartesian functions or by spherical harmonics leading to cartesian gaussians 1.122 or spherical harmonic gaussians 1.123 respectively. Cartesian gaussians are used at the heart of all integral programs. The spherical harmonics can be exactly expressed in terms of cartesian functions and a subsequent transformation at the end of the integral evaluation can be carried out. For a given angular momentum l the number of cartesian gaussians is greater or equal to that of spherical harmonic gaussians which means that the transformation leads to a smaller one electron space. Many programs however abstain from such a transformation.

$$G_{\alpha,L,m_x,m_y,m_z} = x^{m_x}y^{m_y}z^{m_z}e^{-\alpha r^2} \quad m_x + m_y + m_z = L \quad (1.122)$$

$$G_{\alpha,L,m} = Y_{l,m}(\theta, \phi)e^{-\alpha r^2} \quad (1.123)$$

A big difficulty when using Gaussian basis functions is achieving the right radial behaviour as they decay much faster than Slater functions. Therefore several gaussians are needed to recover the correct long range behaviour. In order to limit the vector space to reasonable dimensions the primitive gaussians (1.122, 1.123) are contracted to a new set of basis functions that mimic a desired radial behaviour:

$$|i_{L,m}\rangle = \sum_{\alpha} G_{\alpha,L,m} c_{\alpha,i} \quad (1.124)$$

Many different basis sets have been published in literature and are in use today. While some basis sets try to mimic the structure of the atomic SCF orbitals other expansions represent the natural orbitals.

1.7.1 Convergence of the correlation energy

To perform a correlated calculation a basis set is needed that recovers dynamic correlation efficiently. Such a family of basis sets has been developed by Dunning[70, 71, 72, 40, 73]. To understand what inspired the development of these basis sets and find out what the best systematic approach to constructing a basis is an analysis is needed of how the correlation energy depends on the form of the one particle functions. This is best done by looking at the Helium atom in its ground state using natural orbitals as a one particle basis. The natural orbitals are the set of orbitals that diagonalise the first order density matrix and have the property that they lead to faster converging determinantal expansions than the canonical orbitals. The energy increment of a natural orbital on Helium is found to obey the following formula[16]:

$$\Delta E_{nlm} = A \left(n - \frac{1}{2} \right)^{-6} \quad (1.125)$$

Formula 1.125 makes clear that the most efficient way to increase the basis is to add sets of increasing main quantum number n . This procedure is known as principal expansion and stands in contrast to the partial wave expansion where all main quantum numbers n for a given angular momentum l are exhausted before proceeding to the functions with $l + 1$.

Since there are n^2 functions for a given n the error introduced by truncating the basis at a given $n = X$ can be estimated via integration [79] which leads to the well known error formula

$$E(X) = E(\infty) + CX^{-3} \quad (1.126)$$

where higher order exponents have been omitted. This formula is usually employed for extrapolating results to the complete basis set limit [3, 42] with the correlation consistent basis sets cc-pVXZ of Dunning although it is also suited for bases which have been obtained from natural orbitals such as the atomic natural orbital bases by Almlöf and Taylor [27, 28]. The X^{-3} extrapolation only holds for the correlation energy. The convergence behaviour of the Hartree-Fock energy is roughly exponential[4, 21] but extrapolations of SCF results are not very reliable.

Good performance of atomic natural orbitals in correlated calculations is also observed for atoms beyond helium and for molecules. This fact was exploited by Almlöf and Taylor in the development of the atomic natural orbital bases ANO [27, 28]. It was found that the occupation numbers of the natural orbitals follow a similar pattern to the energies with almost equal values for a given main quantum number [27]. A drawback of these ANO bases is that the polarisation functions - functions of angular momentum unoccupied in the atomic SCF ground state wavefunction - are contractions of several primitives which adds to the computational cost. The correlation consistent basis sets by Dunning and coworkers [70, 71, 72, 40, 73] provide a more efficient representation of natural orbitals. Each polarisation function is represented by a primitive Gaussian optimised to recover a maximum amount of electron correlation. Despite this simple structure the cc-pVXZ bases the errors compared to the ANO bases are very small[70]. The only contractions defined in the Dunning bases are the orbitals occupied in the Hartree-Fock determinant for the atom. The functions with same angular momentum as the ones occupied in the atomic Hartree-Fock calculation added for correlation are again single primitive gaussians but are contained in the primitive set of the SCF orbitals. Thus the Dunning bases can be thought of as the set of primitives which exhaust the natural orbital space most efficiently.

1.7.2 Errors in electronic structure calculations

The introduction of a finite basis leads inevitably to errors. As a result of further approximations other kinds of errors are present and it seems therefore worthwhile to give a short summary of errors at this stage.

Quantum chemical calculations are usually performed by ignoring relativistic effects. This is a reasonable approximation as relativistic effects are mostly felt for heavy elements as is for instance seen from the difference in properties between rows 5 and 6 in the periodic table. Furthermore the Born Oppenheimer approximation is introduced and the nuclear framework kept fixed. A rationale for this simplification was given at the start of the introduction. A possible way to reintroduce nuclear motion is to use a perturbative approach. The first order contribution in such a treatment is termed the Born-Oppenheimer diagonal correction (BODC) which is simply the expectation value of the nuclear kinetic energy operator over the electronic wave function but the contribution of the BODC is usually found to be small [48] although its effects can become important if energies of spectroscopic quality are needed [51].

In finding approximate solutions to the nonrelativistic electronic Schrödinger equation two different errors connected to completeness usually arise. The first of these is the one electron error or basis set error which is a result of the finite basis used to represent the orbitals. The N-electron error is a result of restricting the number of Slater determinants used for expanding the wavefunction in the N-particle space and thus is a measure of how good a particular method approximates the Full CI wavefunction which is the exact solution[54] in a given N electron basis. It is very important to distinguish between one and N electron errors as their effects are felt differently. The N electron error is in some way less problematic as coupled cluster models such as CCSD(T) [42] approximate the FCI wavefunction very well. The effects of the finite basis on the other hand are felt more strongly because the determinantal expansion attempts expanding odd powers of r_{12} by means of even powers only.

An important question is what level of accuracy is needed to allow for a reliable comparison between calculation and experiment. For energy differences an error below one kcal/mol would be desirable which is known as chemical accuracy. Translated into atomic units the error should be around $1 mE_h$. In the following a quantitative analysis will be carried out for a single molecule. A more detailed discussion based on a test set of molecules can be found in reference [42]. Table 1.2 lists Hartree-Fock and correlation energies for the nitrogen molecule in its ground state. While the SCF

energies are already within $1mE_h$ for the quintuple zeta basis the correlation energy is still nowhere near the exact value. The desired value accuracy would be reached for a basis with $X = 11$. This is clearly unpractical because the number of basis functions N grows with $O(X^3)$ whereas the number of two electron integrals g_{pqrs} grows with fourth power.

N ₂ , cc-pVXZ, r=2.068a ₀		
X	E_{HF}	E_{corr} (MP2)
2	-108.9545532	-0.30528742
3	-108.9840934	-0.37276967
4	-108.9917353	-0.39786187
5	-108.9934198	-0.40823730
6	-108.9937418	-0.41294793
∞	-108.993826 ^a	-0.4203993 ^b

Table 1.2: SCF and correlation energies for the Nitrogen molecule

a) Numerical Hartree-Fock result from Ref [18]

b) MP2-R12 calculation from Ref [18]

1.8 Explicitly correlated methods

Explicitly correlated methods is the general term used for all models which include the interelectronic distance explicitly to overcome the shortcomings of the determinantal expansion outlined earlier. Hylleraas[19, 75] was the first to realise that the convergence of a CI expansion on the helium atom could be accelerated by incorporating r_{12} -dependent terms into the wavefunction. Despite Hylleraas' great success calculations with explicitly correlated wavefunctions remained limited for many years as the approach becomes extremely laborious for systems with more than two electrons.

A correlation factor also known as Jastrow factor[59] may be written as shown in 1.127 where f denotes an arbitrary function of the interelectronic distance between electron i and j .

$$J = 1 + \sum_{i>j} f(r_{ij}) \quad (1.127)$$

When such a correlating factor is applied to a determinantal wavefunction and inserted into the electronic Hamiltonian of an atom or molecule with more than two electrons difficult three and four body integrals arise 1.128.

$$f(r_{13})\frac{1}{r_{12}} \quad f(r_{13})\frac{1}{r_{12}}f(r_{24}) \quad (1.128)$$

How difficult such integrals may be to calculate is a separate issue. It is their number which is most problematic. The integral evaluation effort for the three electron integrals in the one particle basis is of the order $O(N^6)$ while it is $O(N^8)$ for the four electron integrals. In view of the $O(N^4)$ scaling of the electron repulsion integrals explicit correlation rather adds to the problem than to the solution.

1.8.1 The transcorrelated method

In the 1960s Boys and Handy made an attempt at a new explicitly correlated approach known as the transcorrelated method[49]. They start their ansatz with a very ambitious wavefunction 1.129 where Φ is a Slater determinant. The parameters d_p , d_q as well as the orbitals that enter the Slater determinant are varied in the transcorrelated method.

$$\Psi = C\Phi \quad C = \prod_{i>j} e^{F(r_i, r_j)} \quad (1.129)$$

$$F(r_i, r_j) = \sum_a d_q G_q(r_i, r_j) + \sum_p d_p \{g_p(r_i) + g_p(r_j)\}$$

Inserting the wavefunction just introduced into the Rayleigh-Ritz quotient to calculate an energy would be an almost impossible task as the resulting integrals turn out to be $3N$ -dimensional. In order to simplify the calculation of energies Boys and Handy applied a similarity transformation of the Hamiltonian:

$$C^{-1}HC\Phi = E\Phi \quad (1.130)$$

This approach is similar to the simplification of the coupled cluster equations. Since C is not a unitary the new operator $C^{-1}HC$ is no longer hermitian and the calculated

energies are no longer variational. The integrals that arise after the transformation are at most of three electron type. Therefore in the original publication only very small basis could be used. The transcorrelated method did not find widespread use but has recently received new attention[67].

1.8.2 R12 methods

The most widely used approach to explicit correlation is due to Klopper and Kutzelnigg[81, 82, 84, 83] and can be summarised as R12 methods. The idea behind this approach is to complement the doubles expansion in Slater determinants by terms linear in the interelectronic distance[79]:

$$T_2 = r_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i + r_{ij}^{AB} \langle AB|r_{12}|ij\rangle a_A^\dagger a_B^\dagger a_j a_i \quad (1.131)$$

Although second quantisation is usually thought of as a projection onto a finite vector space equation 1.131 expresses the correlation factor in terms of a basis. This is possible by introducing an abstract complete basis which contains the smaller basis set that is used for a specific calculation[82]. The naming convention for this basis is outlined in figure 1.3.

With the ansatz 1.131 one is still left with difficult integrals of the kind 1.128. Klopper and Kutzelnigg realised that such integrals could be simplified by an approximation which is called resolution of the identity [82]. The identity operator in a finite orthonormal basis can be written as:

$$\hat{1} = \sum_v |v\rangle\langle v| \quad (1.132)$$

Exploiting this relation it is for instance possible to approximate three electron integrals as products of two electron integrals:

$$\langle prt|r_{12}r_{23}^{-1}|qsu\rangle \approx \sum_v \langle pr|r_{12}|qv\rangle \langle vt|r_{12}^{-1}|su\rangle \quad (1.133)$$

It is obvious that this insertion leads to errors and it is crucial to have some understanding of this error. The atomic case is the most simple one to consider. The functions

p, r, t, q, s and u all belong to the finite basis which only contains functions up to some maximum angular momentum. Both kernels r_{12} and r_{12}^{-1} preserve symmetry which means that only functions v are of importance that lead to totally symmetric integrals. Most integrals are therefore expected to have finite L expansions. If all indices on the left hand side of 1.133 refer to s functions then only vectors $|v\rangle$ of the same symmetry are needed in the expansion. The insertion 1.133 can be improved by applying a special fitting basis[80, 69].

Apart from the resolution of the identity Klopper and Kutzelnigg introduced several other approximations. The first of these is the Generalised Brillouin condition (GBC) 1.134 which is equal to the assumption that the Hartree-Fock equations have been solved exactly.

$$f_A^i = 0 \quad (1.134)$$

The generalised Brillouin condition is not a very drastic approximation as the Hartree-Fock energy converges exponentially and it should therefore be possible to find orbitals of reasonable quality. The extended Brillouin condition 1.135 which is also postulated in reference [84] is a bit more drastic as it assumes that the Hartree-Fock equations are also solved exactly in the complete basis.

$$f_A^B = 0 \quad (1.135)$$

An important consequence of the extended and generalised Brillouin conditions is the decoupling of the explicitly correlated and determinantal parts in 1.131 in second order perturbation theory. This leads to an explicitly correlated MP2-R12 ansatz which is essentially the classical MP2 energy expression 1.110 plus correlated parts. Some further approximations are introduced in reference [82] which lead to the variants MP2-R12 A and MP2-R12 B which have an L convergence of $O(L^{-5})$ and $O(L^{-7})$ respectively.

The R12 ansatz has found its way into various orders of perturbation theory [82, 84, 83], coupled cluster theory[31] and even multi reference approaches [62]. The formalisms introduced in the reference [82] can also be applied when correlation factors

other than r_{12} [7]. It has recently been argued[6] that of all technicalities involved in the MP2-R12 calculations the form of the Jastrow factor is most important.

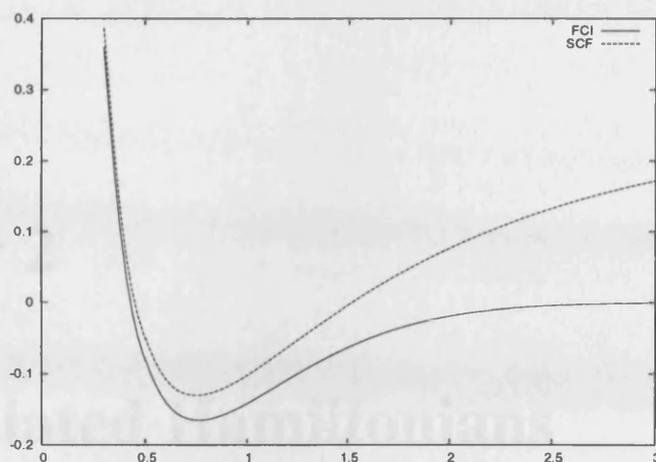


Figure 1.1: Hartree-Fock and FCI potential energy curves of the hydrogen molecule

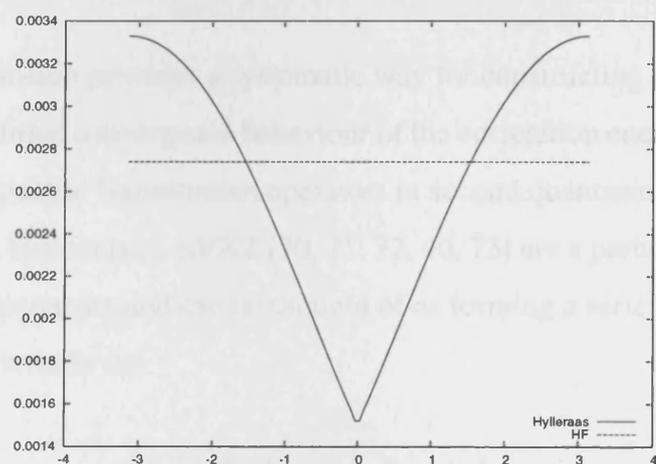


Figure 1.2: Radial probability densities of a Hartree-Fock and a Hylleraas type wavefunction[65] on Helium

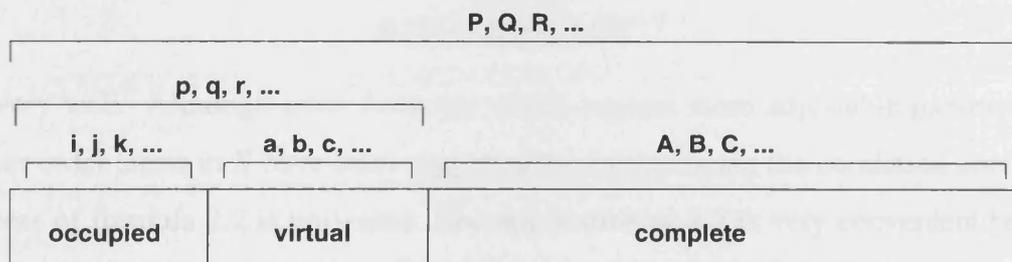


Figure 1.3: Complete and incomplete basis naming convention

Chapter 2

Extrapolated Hamiltonians

2.1 Scaled fluctuation potential

The principal expansion provides a systematic way for constructing a hierarchy of basis sets with a well defined convergence behaviour of the correlation energy. These energies are connected to specific Hamiltonian operators in second quantisation. Dunning's correlation consistent basis sets cc-pVXZ [70, 71, 72, 40, 73] are a particular representative of the principal expansions and can be thought of as forming a series where a particular element is simply written as:

$$\hat{H}^X = h_{pq}^X a_p^\dagger a_q + \frac{1}{2} g_{pqrs}^X a_p^\dagger a_r^\dagger a_s a_q \quad (2.1)$$

A very intriguing feature of this series is its well behaved convergence pattern. The error in the associated correlation energies obey the formula

$$E(X) = E(\infty) + CX^{-3} \quad (2.2)$$

very well. Although other formulae which contain more adjustable parameters or higher order terms in X have been suggested for extrapolating the correlation energy the success of formula 2.2 is unrivaled. The application of 2.2 is very convenient because only two results are needed. Halkier et al. have argued [3] that this simplicity is simultaneously responsible for the good quality of extrapolations to the basis set limit as formulae with more adjustable parameters require more data points where the results

obtained from smaller bases unavoidably introduce larger errors. Bak et al. managed to obtain results of chemical accuracy [42] with triple and quadruple zeta extrapolations of cc-pCVXZ/CCSD(T) calculations for reactions and atomisation energies. In the development of the model chemistries W1 and W2 by Martin and Oliveira[38] where the ambitious goal was set to obtain mean absolute errors below 0.24kcal/mol formula 2.2 was again found to perform best.

The reliability of the X^{-3} formula for extrapolating correlation energies obtained on atoms and molecules suggests that the contributions from a natural orbital is similar in both cases and that the contributions are strongly atomic. This leads to the interesting question whether it is possible to create a modified extrapolated Hamiltonian which gives complete basis set results in a finite basis by exploiting atomic information.

A convenient starting point for constructing such a Hamiltonian is provided by perturbation theory which splits the electronic problem into a zero order and a correlated contribution:

$$H = H^{(0)} + \lambda H^{(1)} \quad (2.3)$$

One way to look at the error in the correlation energy for a truncated basis obtained via perturbation theory is to argue that the corrections introduced by $H^{(1)}$ in equation 2.3 are too weak when λ equals one. This leads to the idea that larger values for λ might be used to recover the exact correlation energy. This can be thought of as balancing the inadequacies of the finite basis representation of $H^{(1)}$ via the strength parameter λ . As the basis is increased the deviations of λ from unity are necessarily expected to decrease with the improved description of the fluctuation potential $H^{(1)}$.

In standard Rayleigh-Schrödinger perturbation theory one usually refers to the Hamiltonian with $\lambda = 1$ as the “physical Hamiltonian”. Following the preceding argument where the variation of λ is employed to recover complete basis set results and $\lambda = 1$ only holds for a complete basis it is possible to interpret the finite space representation Hamiltonian to be unphysical for λ equal to unity.

Equation 2.4 shows a redefinition of the Møller-Plesset Hamiltonian which contains an additional term $(1 - \lambda)E^{(1)}$. This term has been added to ensure that the Hartree-Fock

energy is constant for all values of λ .

$$\hat{H} = \hat{H}^{(0)} + \lambda \hat{H}^{(1)} + (1 - \lambda)E^{(1)} \quad (2.4)$$

This equation forms the basis for the extrapolated Hamiltonian approach. In its present form this equation is too coarse to be used directly as it implies the use of a single λ for a specific system which goes against the idea of incorporating atomic information into the molecular Hamiltonian but more importantly violates the size extensivity constraint. At infinite separation of the constituent atoms the energy of the molecule should be equal to the sum of the energies obtained for the atomic energies. For a single λ this is not the case as all atoms are scaled the same way and not with their appropriate scaling factors. Equation 2.4 is however sufficient to adjust the correlation energies of any atom or homonuclear molecule in the perturbation expansion to the complete basis set limit via:

$$E^{(n)}(\lambda) = \sum_{m=2}^n \lambda^m E^{(m)} = E_{corr}^{(n),CBS} \quad (2.5)$$

For the coupled cluster approach which is also a perturbative treatment the functional dependence on λ is not as straightforward but a value for λ can be obtained iteratively. The methods for determining a suitable λ will be discussed after an implementation for heteronuclear species has been developed in the next section.

Equation 2.4 gives rise to some questions connected to the convergence of the perturbation expansion. It is known that the perturbative approach has a finite radius of convergence similar to a complex series[76].

The radius of convergence is directly connected to the appearance of degeneracies for some value of λ . In standard Møller-Plesset perturbation theory λ is simply taken to be equal to one but for the general case one has to consider λ to be an arbitrary complex number. It can be shown[32] that the perturbation expansion will converge for some range of λ between 0 and R if there is no point λ_D in the complex plane with $|\lambda_D| < R$ where two states of the Hamiltonian become degenerate. In conventional perturbation theory R simply defines the unit circle and a point of degeneracy occurring within the unit circle is referred to as intruder state[32]. Since λ_D is a complex number the intrud-

ers are classified according to their real part $\Re(\lambda_D)$. Depending on the sign of $\Re(\lambda_D)$ the terms front and back door intruder are used where the former are interpreted as interference from low lying excited states and the latter are caused by highly excited states. The back door intruders usually appear in bases which are flexible enough to describe these highly excited states such as example C in reference [32]. Recently the back door intruders have been given new interpretations by Stillinger [22] and subsequently by Goodson et al. [8]. Stillinger has argued that the singularity for $\Re(\lambda) < 0$ corresponds to a phenomenon where the electron dissociate from the nucleus because the electron repulsion will change to an attractive force for small enough λ . This idea has been investigated further by Goodson [8] for the case of finite bases.

The divergence usually only becomes apparent at very high orders of perturbation theory. Helgaker et al. [32] also point out that the divergence does not deny the use of MP2 energies but makes the use of higher order corrections questionable for some systems. Since in the present work values of λ beyond one are used there is the risk of picking up intruder states which remain undiscovered in standard perturbation theory.

2.2 Implementation

As was outlined before simply rescaling the energy components in the perturbation series is too crude. The fluctuation potential in second quantised form provides access to scaling at a much lower level:

$$H^{(1)} = \frac{1}{2} g_{pqrs} a_p^\dagger a_r^\dagger a_s a_q - [g_{pqii} - g_{piqi}] a_p^\dagger a_q \quad (2.6)$$

Since expression 2.6 only contains electron repulsion integrals the task of rescaling the fluctuation potential can be recast into a rescaling of the electron repulsion integrals

$$g(\lambda)_{pqrs} = c_{p\mu} c_{q\nu} c_{r\rho} c_{s\sigma} \lambda_\mu^{1/4} \lambda_\nu^{1/4} \lambda_\rho^{1/4} \lambda_\sigma^{1/4} (\mu\nu|\rho\sigma) \quad (2.7)$$

where each atomic function is scaled by an appropriate scaling factor. For a homonuclear system all λ are equal and the approach reduces to the simple formula 2.4. The

method of calculating a specific scaling factor lambda to be used in equation 2.7 will be discussed later.

The rescaling of the electron repulsion integrals causes some implementational problems as the Fock operator depends directly on the coulomb integrals.

$$F_{\mu\nu} = h_{\mu\nu} + \sum_{\rho\sigma} P_{\rho\sigma} \left[(\mu\nu|\rho\sigma) - \frac{1}{2}(\mu\rho|\nu\sigma) \right] \quad (2.8)$$

This means that the Fock operator changes once the scaling is applied which is problematic as most post SCF programs reconstruct the Fock operator at some point. By introducing an additional one electron potential it is possible to keep the Fock operator constant. This potential is simply the difference between scaled and unscaled integrals contracted with the SCF density matrix:

$$\Delta F_{\mu\nu} = \sum_{\rho\sigma} P_{\rho\sigma} \left\{ \left[(\mu\nu|\rho\sigma) - \frac{1}{2}(\mu\rho|\nu\sigma) \right] - \lambda_{\mu}^{1/4} \lambda_{\nu}^{1/4} \lambda_{\rho}^{1/4} \lambda_{\sigma}^{1/4} \left[(\mu\nu|\rho\sigma) - \frac{1}{2}(\mu\rho|\nu\sigma) \right] \right\} \quad (2.9)$$

Adding this potential to the one electron Hamiltonian guarantees that the Hartree-Fock solution remains unchanged. The above expression only holds for closed shell systems. For open shell systems the approach is similar but slightly more involved as there are several possible ways to perform a perturbative treatment.

Starting from an unrestricted Hartree-Fock determinant where the alpha spin orbitals $|p^{\alpha}\rangle$ and beta spin orbitals $|p^{\beta}\rangle$ are eigenfunctions of the Fock operators

$$F^{\alpha} = h + J^{\alpha} + J^{\beta} - K^{\alpha} \quad (2.10)$$

$$F^{\beta} = h + J^{\alpha} + J^{\beta} - K^{\beta} \quad (2.11)$$

correcting potentials need to be defined for both 2.10 and 2.11 as alpha and beta electrons experience different potentials

$$\Delta F^{\alpha} = \left(J^{\alpha} + J^{\beta} - K^{\alpha} \right) - \left(J(\lambda)^{\alpha} + J(\lambda)^{\beta} - K(\lambda)^{\alpha} \right) \quad (2.12)$$

$$\Delta F^{\beta} = \left(J^{\alpha} + J^{\beta} - K^{\beta} \right) - \left(J(\lambda)^{\alpha} + J(\lambda)^{\beta} - K(\lambda)^{\beta} \right) \quad (2.13)$$

where the shorthand notation $J(\lambda)$ and $K(\lambda)$ implies the scaling of the electron repulsion integrals in the same fashion as in equation 2.9. With F^α and F^β the definition of the zero order operator is trivial

$$H^{(0)} = F^\alpha + F^\beta \quad (2.14)$$

and it is straightforward to apply perturbative corrections. It is well known that perturbation theory applied to UHF wavefunctions is slowly convergent when spin contamination is large [56, 39]. Spin contaminated wave functions are inherently unphysical and it is desirable to eliminate the problem. Methods which limit the effects of spin contamination by projecting out [29, 55, 24] components with wrong $\langle S^2 \rangle$ or by imposing some constraints on the orbitals [60] have been developed but they pose additional implementation difficulties. Therefore only restricted open shell calculations shall be considered in the following.

The main difficulty in implementing a restricted open shell perturbation theory is the definition of the zero order operator $H^{(0)}$. With restricted orbitals where alpha and beta spin orbitals share the same spatial part it is still possible to set up operators F^α and F^β (equations 2.10 and 2.11) but the orbitals are no longer eigenfunctions of these operators. Technically it is easy to set up a zero order operator as a sum of weighted projectors

$$H^{(0)} = |p\rangle \varepsilon_p \langle p| \quad (2.15)$$

where the weights ε_p correspond to the orbital energies. For a closed shell system the choice of ε_p is obvious. For open shell problems there are different possibilities to define the quantities ε_p [14, 61] which are not of concern at this stage. An important consequence of using definition 2.15 is that Brillouin's theorem is no longer obeyed and singles contributions appear in the first order interacting space.

For the scaled fluctuation potential formalism the choice of the zero order system is dictated by the way post Hartree-Fock methods are implemented. The Fock operator employed by MOLPRO [2] has the following structure

$$F = \begin{pmatrix} [F]_{ij} & [F + \frac{1}{2}K^o]_{is} & [F]_{ia} \\ [F + \frac{1}{2}K^o]_{si} & [F]_{st} & [F - \frac{1}{2}K^o]_{sa} \\ [F]_{ai} & [F - \frac{1}{2}K^o]_{as} & [F]_{ab} \end{pmatrix} \quad (2.16)$$

in the MO basis where i, j, \dots, s, t, \dots and a, b, \dots are doubly occupied, singly occupied and unoccupied orbitals respectively. The correcting potential is therefore simply the difference of operator 2.16 with scaled and unscaled two electron integrals:

$$\Delta F = F - F(\lambda) \quad (2.17)$$

2.2.1 Scaling factors

For heteronuclear species it turns out that the simple scaling

$$\lambda_{At(\mu)}^{1/4} \lambda_{At(v)}^{1/4} \lambda_{At(p)}^{1/4} \lambda_{At(\sigma)}^{1/4} (\mu\nu|\rho\sigma) \quad (2.18)$$

where scaling parameters are simply atomic can lead to problems as will be shown in section 2.3.3. This is a result of the non locality of the basis functions. It is therefore more appropriate to construct scaling factors which contain weighted contributions from all constituent atoms:

$$\lambda_\mu = \left(\sum_A w_{\mu A} \lambda_A \right)^{1/4} \quad (2.19)$$

The weight parameter $w_{\alpha A}$ measures the extent of μ 's involvement on atom A . One way to extract this information is via the nuclear attraction potential:

$$w_{\mu A} = \frac{\langle \mu | V_A | \mu \rangle}{\sum_B \langle \mu | V_B | \mu \rangle} \quad \sum_A w_{\mu A} = 1 \quad (2.20)$$

The integrals $\langle \mu | V_A | \mu \rangle$ contain the nuclear charge Z_A which does not contain any spatial information. This suggests that the weight r^{-1} on its own might be enough. In section 2.3.3 it will be shown that better results are obtained by including Z_A .

An important aspect of the extrapolated Hamiltonian or scaled fluctuation potential approach is the choice of the scaling factor λ . One of the main ideas is to transfer

information from atomic calculations onto other species. Hence a scaling factor λ for a specific Dunning basis is determined by adjusting the atomic correlation energy to the complete basis set limit:

$$\lambda_{VXZ,at} \rightarrow E_{corr,at}(VXZ, \lambda) = E_{corr,at}^{CBS} \quad (2.21)$$

Alternatively scaling parameters for a given atom might also be obtained from homonuclear molecules. In section 2.3 these two possibilities will be investigated. For the hydrogen atom the only way to obtain scaling parameters is to resort to H_2 following the idea of Almlöf and Taylor [27] also used by Dunning [70]. This is also true for alkali metals when only the valence electrons are correlated.

An even more important question is how to obtain the complete basis set limit. For atoms it is possible to perform explicitly correlated calculations but many molecules might be out of reach. Ideally the same method to estimate the CBS result should be used for the atoms and molecules in order to be able to assess the transferability. Furthermore MP2-R12 was the only explicitly correlated wavefunction model which was available for this work which would mean a restriction to second order perturbation theory for the extrapolated Hamiltonian. The method of choice is therefore to perform two point extrapolations of the correlation energy on atoms and molecules via the well known formula:

$$E(X) = E_{corr}(\infty) + CX^{-3} \quad (2.22)$$

Having established a calibration procedure for λ and an estimation for the complete basis set the formalism is fully specified.

2.3 Results

2.3.1 Rare gas dimers

The first examples to be studied with the extrapolated hamiltonians are the dimers of Helium, Neon and Argon. The calculated well depths for these systems in μE_h are

listed in table 2.1. The calculations were performed at the singles and doubles coupled cluster[11] level with the doubly augmented Dunning bases [70, 71, 72, 40, 73] and the counterpoise correction. The column headers conventional, scaled and X^{-3} refer to the standard implementation, the extrapolated Hamiltonians and the two point extrapolations with X^{-3} . The complete basis set limit is taken to be the two point extrapolation of the two largest unscaled calculations. The scaling parameters were obtained by adjusting the atomic correlation energies for the d-aug-cc-pVXZ bases to the complete basis set limit which was again taken to be the 5→6 extrapolated energy. The values of the scaling parameters are given in appendix A.1 on page 89.

The calculations for the Helium dimer show that the extrapolated Hamiltonians provide consistent improvements over the conventional calculations but the accuracy and stability of the extrapolation formula remains unrivalled. The dissociation energies for the Neon dimer are also improved by the scaled fluctuation potential although the binding is severely overestimated for the smaller bases and the series of extrapolated Hamiltonian results now converges from below. The triple zeta result shows no net improvement as it deviates by roughly $14\mu E_h$ from the CBS limit which is approximately the error in the unscaled calculation. The well depths obtained for the Argon dimer are substantially improved by the extrapolated Hamiltonians. The triple zeta result is quite far away from the CBS limit but still much better than the conventional d-aug-cc-pVTZ calculation. In general the results obtained for the rare gas dimers provide a first indication that the extrapolated Hamiltonian scheme can be used to improve the description of electron correlation which is the main source of interaction energy between rare gas atoms.

2.3.2 Calibration models

From a chemical standpoint the rare gas dimers are not the most interesting species and the next logical step is therefore to apply the extrapolated Hamiltonians to other problems. Before doing so it seems appropriate to investigate different possibilities for calibrating the scaling parameters. The scaling factor for a given element can either be obtained by adjusting the atomic correlation to the complete basis set value or al-

X	conventional	scaled	X^{-3}
He_2^a			
D	11.40	20.65	
T	24.32	27.75	29.15
Q	27.25	28.64	29.52
5	28.35	29.01	29.47
6	28.83	29.21	29.44
∞	29.44		
Ne_2^b			
d	48.90	125.24	
t	88.45	116.58	104.65
q	100.16	112.14	108.89
5	100.22	106.13	100.87
6	101.28	104.70	102.63
∞	102.63		
Ar_2^a			
d	107.22	337.75	
t	269.30	357.85	339.86
q	294.04	330.92	314.08
5	305.88	326.54	317.47
6	316.62	328.65	330.97
∞	330.97		

^a $r=5.62a_0$, ^b $r=5.86a_0$, ^c $r=7.143a_0$

From tables 5, 8 and 12 of ref. [77]

Table 2.1: Counterpoise corrected well depths of the rare gas dimers He_2 , Ne_2 and Ar_2 in μE_h obtained at the d-aug-cc-pVXZ/CCSD level.

ternatively by applying the same procedure to a molecule that only contains atoms of that specific element. These two variants can then be compared by analysing the errors in the atomisation energies of the homonuclear species. Table 2.2 gives some simple statistics of the two calibration variants for the elements Carbon, Chlorine, Fluorine, Nitrogen and Oxygen. The values are the root mean square error of the dissociation energy for the scaled Hamiltonian in a particular Dunning basis cc-pVXZ compared to the complete basis set limit which was obtained from a quintuple-sextuple zeta extrapolation. The molecular calculations were carried out at the experimental equilibrium distances which are given alongside the scaling parameters in appendix A.1 on page 89. The electronic states of C_2 and O_2 used in the calculations are $^1\Sigma_g^+$ and $^3\Sigma_g^-$. As can be seen from table 2.2 the difference between atomic and molecular calibrations are relatively small but favouring the molecular calibration overall. For the second order Møller-Plesset results the differences are more pronounced than for the Coupled Cluster calculations. The deviations are also more important for the smaller bases which is important because the extrapolated Hamiltonian approach aims to provide high quality results for small bases. It seems therefore justified to use the molecular calibration for the remaining examples in this chapter.

cc-pVXZ	MP2		CCSD[11]	
	atomic	molecular	atomic	molecular
D	0.036699	0.019083	0.020563	0.014427
T	0.009184	0.006319	0.005461	0.004676
Q	0.003792	0.002717	0.002118	0.001848
5	0.001853	0.001359	0.000827	0.000677
6	0.001122	0.000841	0.000472	0.000388

Table 2.2: Root mean square error of the atomisation energies in E_h for different calibration models of the species C_2 , Cl_2 , F_2 , N_2 and O_2 obtained with different calibration models of the extrapolated Hamiltonian approach.

2.3.3 Heteronuclear application

For the heteronuclear case there are different ways to perform the scaling. The simplest variant is to scale each basis function based on the atom it is centred on:

$$\lambda_{At(\mu)}^{1/4} \lambda_{At(\nu)}^{1/4} \lambda_{At(\rho)}^{1/4} \lambda_{At(\sigma)}^{1/4} (\mu\nu|\rho\sigma) \quad (2.23)$$

In table 2.3 second order correlation energies for the hydrogen fluoride molecule at its experimental equilibrium distance are given. The scaling parameters have been obtained via a molecular calibration and are given in appendix A.1. The same naming conventions as before are applied. As can be seen from the second column of table 2.3 the extrapolated Hamiltonian results diverge more strongly from the complete basis set limit with increasing X .

The erratic behaviour leads to the question whether the increased strength parameter leads to a diverging perturbation expansion. Unfortunately it is not simple to give an answer as one would have to evaluate very high orders of perturbation theory. Helgaker et al. have shown [32] a diverging Møller-Plesset series for the hydrogen fluoride with the aug-cc-pVDZ basis¹ which is caused by highly excited intruder states. It does not appear very likely that the bases used in table 2.3 are flexible enough to describe such highly excited states and it is also unlikely that such an effect can be seen already at second order.

A similar behaviour to the one shown in table 2.3 can also be observed in other molecules such as water and carbon monoxide (tables A.4 and A.5 in appendix A.2.1 on page 91). These species are sufficiently different from hydrogen fluoride and it appears reasonable to assume that the divergence in the presented calculations has some other causes. Effective scaling parameters for H_2 , F_2 and HF are given in table 2.4 which can be simply obtained via the formula $\lambda(X) = \sqrt{E(\infty)/E(X)}$ for second order energies. This analysis reveals that the scaling parameters obtained for the Fluorine molecule and Hydrogen fluoride are essentially the same which suggests that the problems might arise from the hydrogen parameters.

Figure 2.1 shows a plot of the correlation energy for Hydrogen fluoride where the

¹See especially figure 9 of reference[32]

Hydrogen fluoride, $r = 0.91480\text{\AA}^a$, MP2			
cc-pVXZ	conventional	scaled	X^{-3}
D	-0.20161883	-0.31081901	
T	-0.27176402	-0.31843343	-0.30129884
Q	-0.29750609	-0.32022988	-0.31629084
5	-0.30829455	-0.32248470	-0.31961358
6	-0.31296766	-0.32502897	-0.31938677
∞	-0.31938677 ^b		

^a From reference [1]

^b $5 \rightarrow 6 X^{-3}$ extrapolation

Table 2.3: Extrapolated Hamiltonian correlation energies for HF in Hartrees

scaling parameter on the Hydrogen atom is varied between 1.024 and 1.036. The straight line corresponds to the complete basis set limit. Intuitively it would be expected that the reduction of the scaling factor on hydrogen atom leads to a decreasing correlation energy which happens to be true only for a certain region. In the actual calculation for the quadruple zeta basis the hydrogen functions were scaled with a factor of 1.017 which is far off the left hand side of the plot.

Even though the hydrogen scaling parameters differ quite drastically from the Fluorine and Hydrogen fluoride parameters for all bases only the larger basis sets seem to be susceptible to this problem. Since the higher order bases contain more diffuse functions the allocation of a specific function to an atom becomes questionable which is a well known phenomenon in the context of the Mulliken population analysis. It seems therefore more appropriate to use a weighting scheme to calculate the contribution of a specific function to an atom. Such a weighting scheme was outlined in section 2.2 and shall be used in the following.

Correlation energies for the hydrogen fluoride molecule are listed in table 2.5 where the scaled Hamiltonian energies have been obtained with the weighted scaling parameters. It can be seen that the scaled fluctuation potential now provides a convergent series of values. The double and triple zeta values are quite far away from the complete basis

cc-pVXZ	H ₂ ^a	F ₂ ^b	HF ^c
2	1.139	1.245	1.259
3	1.040	1.081	1.084
4	1.017	1.036	1.036
5	1.009	1.018	1.018
6	1.005	1.010	1.010

^a $r = 0.74144 \text{ \AA}$

^b $r = 1.41193 \text{ \AA}$

^c $r = 0.91480 \text{ \AA}$

From reference [1]

Table 2.4: Effective MP2 scaling factors for H₂, F₂ and HF

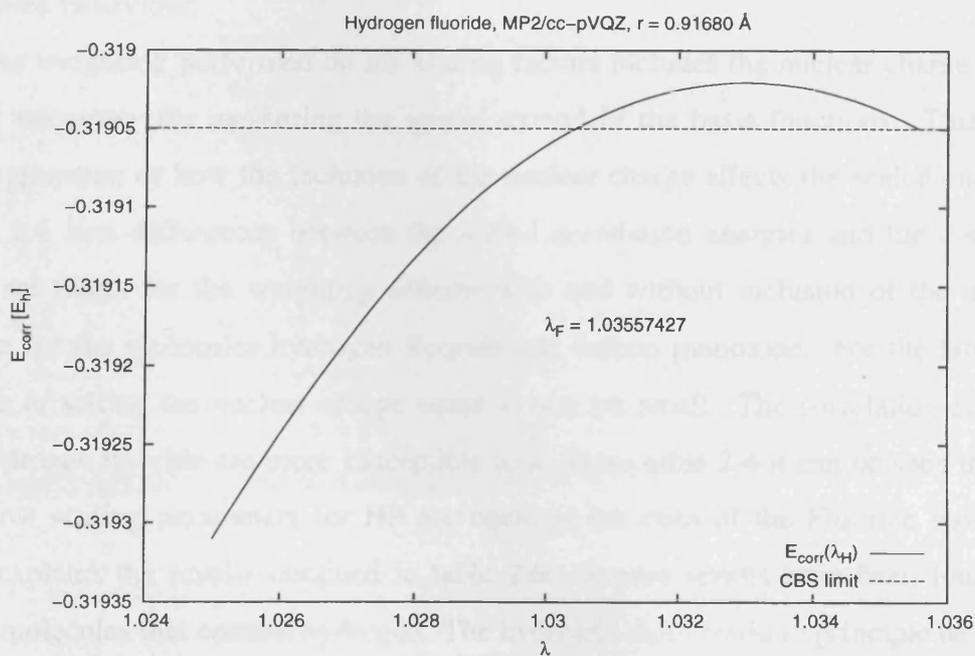


Figure 2.1: Effect of the H scaling parameter on Hydrogen fluoride correlation energy

Hydrogen fluoride, $r = 0.91480\text{\AA}^a$, MP2			
cc-pVXZ	conventional	scaled	X^{-3}
D	-0.20161883	-0.29808677	
T	-0.27176402	-0.31078251	-0.30129884
Q	-0.29750609	-0.31570539	-0.31629084
5	-0.30829455	-0.31778728	-0.31961358
6	-0.31296766	-0.31857131	-0.31938677
∞	-0.31938677 ^b		

^a Data from reference [1]

^b 5 \rightarrow 6 X^{-3} extrapolation

Table 2.5: Extrapolated Hamiltonian correlation energies for HF in Hartrees with weighting

set limit but are much lower than their unscaled counterparts. The corrected energies for water and carbon monoxide are provided in appendix A.2.1 which show the same improved behaviour.

The weighting performed on the scaling factors includes the nuclear charge which is not necessary for measuring the spatial extend of the basis functions. This leads to the question of how the inclusion of the nuclear charge affects the scaled energies. Table 2.6 lists differences between the scaled correlation energies and the complete basis set limits for the weighting scheme with and without inclusion of the nuclear charge for the molecules hydrogen fluoride and carbon monoxide. For the latter the effects of setting the nuclear charge equal to one are small. The correlation energies of Hydrogen fluoride are more susceptible to Z . From table 2.4 it can be seen that the effective scaling parameters for HF are equal to the ones of the Fluorine molecule. This explains the results obtained in table 2.6. Similar results have been found for other molecules that contain hydrogen. The hydrogen atom could in principle be scaled with the same factor as the atom it is bound to without violating the size extensivity requirement as the isolated hydrogen atom does not have a correlation energy. But this could prove problematic for the calculation of potential energy surfaces where a

cc-pVXZ	HF		CO	
	Z	Z = 1	Z	Z = 1
D	0.02130000	0.04682832	0.01444382	0.01764713
T	0.00860426	0.02049906	0.00628937	0.00739871
Q	0.00368138	0.00934852	0.00280882	0.00330160
5	0.00159949	0.00454067	0.00136008	0.00160374
6	0.00081546	0.00261472	0.00057049	0.00071403

Table 2.6: Weighting effect of the nuclear charge relative to the complete basis set limit

proton transfer occurs as there would be a sudden change in scaling parameters. Since one attempts to implement a generally applicable approach using the weighting scheme with the nuclear charge included seems more appropriate.

2.3.4 Atomisation energies

The main aim of the extrapolated Hamiltonian method is to provide high quality correlation energies for finite bases. Although the previous results have shown that the approach cannot fully close the gap between the complete basis set limit and the truncated bases it seems worthwhile to assess the performance of the approach for atomisation energies on a small test set of molecules. The species chosen for the statistics are CO₂, HNO, CH₂O, N₂, C₂H₂, NH₃, H₂O, H₂, HF, F₂, CO, HCN. This is essentially the test set used by Bak et al. [42]. The molecules ethene and methane had to be removed because they were computationally out of reach within the cc-pV6Z basis as the current implementation of the extrapolated Hamiltonian can only handle C₁ symmetry. The geometries were optimised with the cc-pCVXZ basis using CCSD(T) with core correlation.

The root mean square errors in kJ/mol for the mentioned test set are listed in table 2.7. Chemical accuracy would be reached for an error below one kcal/mol which corresponds to approximately to 4.2 kJ/mol. The term chemical accuracy in the present context refers to the deviations from the extrapolated basis set limits and a compari-

VXZ	MP2, kJ mol ⁻¹		
	conventional	scaled	X^{-3}
2	116.925	44.007	
3	42.616	14.112	24.302
4	17.877	5.973	3.430
5	8.967	2.638	0.801
6	5.049	1.778	0.000

Table 2.7: Root mean square error of the atomisation energies of the molecules: CO₂, HNO, CH₂O, N₂, C₂H₂, NH₃, H₂O, H₂, HF, F₂, CO, HCN

son with experimental values might reveal much larger errors which also depend on the choice of the N electron model as outlined in reference [42]. As expected the conventional MP2 atomisation energies differ more than 1 kcal/mol from the complete basis set limit even for the cc-pV6Z basis. Although the scaled results are much better than their unscaled counterparts they are only superior to the extrapolated values up to triple zeta level.

2.3.5 Properties

Although the electronic energy is important to assess the performance of a method derivatives of the energy are of equal importance because they are directly connected to observables. This demands a test of the extrapolated hamiltonians for properties. The equilibrium bond length and harmonic frequencies are very easily obtainable for a diatomic molecule. These properties have been calculated using the conventional MP2, the scaled fluctuation potential and the X^{-3} extrapolation scheme. The parameters have been obtained by fitting a fourth order polynomial to 5 points on the potential energy surface around the equilibrium bond lengths. The points and the spacing between them were chosen in such a way that the frequencies of the SCF contributions determined this way match the values that are obtained with analytical derivatives to within 1 cm⁻¹. The resulting equilibrium bond lengths and vibrational harmonic wavenumbers are given in

X	unscaled	scaled	X^{-3}
Equilibrium bond lengths [Å]			
2	1.1472	1.1648	
3	1.1385	1.1437	1.1372
4	1.1346	1.1368	1.1337
5	1.1341	1.1351	1.1337
6	1.1339	1.1344	1.1337
∞	1.1337		
Vibrational wavenumbers [cm ⁻¹]			
2	2113.4	1972.3	
3	2120.5	2077.6	2126.6
4	2127.5	2109.0	2131.4
5	2127.1	2118.0	2127.2
6	2127.1	2122.4	2127.2
∞	2127.2		

Table 2.8: Equilibrium bond lengths and harmonic wavenumbers of Carbon monoxide obtained at the MP2 level

table 2.8. The 5→6 extrapolations are again taken to be the complete basis set limit.

The equilibrium bond lengths converge quite quickly for the extrapolated calculations and already an extrapolation with triple and quadruple zeta data provide CBS quality. The extrapolated Hamiltonian on the other hand fails quite badly at reproducing the basis set limit. The bond lengths are severely overestimated for the double and triple zeta bases and the convergence is generally very poor. The scaled cc-pV6Z value is even worse than the conventional value. For the vibrational wavenumbers the findings are similar. The extrapolated Hamiltonian completely fails at recovering properties.

2.4 Discussion

Even though the extrapolated Hamiltonian reduces the errors in the calculated correlation energies its application is limited. The X^{-3} extrapolation scheme provides far superior results at estimating complete basis set results even for small bases. Although the scaled fluctuation potential provides improved results compared to conventional calculations the differences to the exact basis set limit are substantial. It is vital for a new description model for electron correlation to perform well for small basis sets in order to be computationally tractable for medium size molecules. The analysis of atomisation energies in table 2.7 has revealed that deviations within chemical accuracy are only possible at the quintuple zeta level whereas the extrapolation scheme already succeeds with a triple quadruple zeta extrapolation. A further complication with the scaled fluctuation potential is that it can only deal with C_1 symmetries. An attempt to prove the invariance of the approach under the transformations of the point group of the Hamiltonian was unsuccessful for the weighted scaling procedure which reduces the efficiency of the approach for small molecules. This is however only a minor drawback as large and flexible molecules will most probably not contain a large number of symmetry elements.

The performance of the extrapolated Hamiltonian for the calculations of properties is especially disappointing. Much chemical insight can be gained from equilibrium structures and vibrational frequencies and it is therefore vital for any method to perform well at these tasks. The failure of the scaled Hamiltonian approach in these cases prevents almost any practical use of the method.

Chapter 3

Completeness Relationships

3.1 Introduction

The algebraic approximation in quantum chemistry implies using a finite basis which is conceptually equivalent to a projection. This insertion replaces operators by tensor elements

$$-\frac{1}{2}\nabla^2 \rightarrow T_{pq} = \langle p | -\frac{1}{2}\nabla^2 | q \rangle \quad (3.1)$$

$$\frac{1}{r_{12}} \rightarrow g_{pqrs} = \langle pr | r_{12}^{-1} | qs \rangle \quad (3.2)$$

$$-\frac{Z_A}{r_{1A}} \rightarrow V_{pq} = \langle p | -Z_A r_{1A}^{-1} | q \rangle \quad (3.3)$$

which obscures their mathematical properties to some extent. Within the space of finite functions the singularity of the kinetic operator is suppressed and the local energy is no longer constant. The projected Hamiltonian thus leads to a wrong energy even when acting on the true wavefunction

$$\frac{\langle \Psi_{true} | \hat{H} | \Psi_{true} \rangle}{\langle \Psi_{true} | \Psi_{true} \rangle} = E_{true} \neq \frac{\langle \Psi_{true} | \hat{P} \hat{H} \hat{P} | \Psi_{true} \rangle}{\langle \Psi_{true} | \hat{P} | \Psi_{true} \rangle} = E_{approx} \quad (3.4)$$

where the projector \hat{P} contains all Slater determinants that can be constructed from a given finite basis. The use of Slater determinants in equation 3.4 generates the tensor elements outlined above and simultaneously guarantees a complete decomposition of the N particle wave function $|\Psi_{true}\rangle$ into finite basis products.

This projection gives rise to the poor convergence of the correlation energy in the determinantal expansion. However much is known about the functional properties of the true wavefunction. The finite basis projector is of course also a known quantity. Exploiting both facts one might be able to gauge and correct the truncation error in an ad hoc fashion for a specific electronic problem by introducing a new operator. This is illustrated in equation 3.5 where the matrix elements M_{pq} are added in order to retrieve the exact energy with the approximate wavefunction $|K\rangle$. This is the idea behind completeness relationships or the projected Hamiltonian approach.

$$\left[h_{pq} a_p^\dagger a_q + \frac{1}{2} g_{pqrs} a_p^\dagger a_r^\dagger a_s a_q + M_{pq} a_p^\dagger a_q \right] |K\rangle = E_{exact} |K\rangle \quad (3.5)$$

In equation 3.5 the new object M is represented as a one particle operator even though a two particle operator would seem more obvious for correlation effects. It is however much more convenient to use a one electron object as the number of matrix elements only grows with $O(N^2)$. It can also be argued that a one electron object is able to capture two electron information via some inherent contraction of higher order density matrices.

3.2 Definition

Given equation 3.5 the important question is how the correlation information should or can be extracted. Although $|\Psi_{exact}\rangle$ is unknown a Slater-Jastrow type wavefunction[59] can provide a reasonable approximation to $|\Psi_{exact}\rangle$. Since the SCF energies converge rapidly to the complete basis set limit it seems appropriate to define the new operator M_{pq} in such a way that it accounts only for electron correlation. Therefore the matrix elements M_{pq} will be calculated once a Hartree-Fock solution has been obtained. The zero order wavefunction also contains important information about a specific system which suggests the substitution of the exact wavefunction by a trial wavefunction which is simply a product of the Hartree-Fock determinant multiplied by a Jastrow factor as shown in 3.6. The Jastrow factor is given in terms of the complete basis second quantised formalism introduced in section 1.8.2 on page 38. The concrete form of the

correlating functions $f(r_{ij})$ will be discussed later

$$|\Psi_{trial}\rangle = J|0\rangle \quad J = 1 + \frac{1}{2}\langle PR|f(r_{ij})|QS\rangle a_p^\dagger a_R^\dagger a_Q a_S \quad (3.6)$$

In Jastrow's original work[59] the correlation factors were N electron functions constructed as products of two electron functions

$$\prod_{i<j} f(r_{ij}) \quad (3.7)$$

which unavoidably lead to $3N$ dimensional integrals. Correlation factors of this complexity are mainly in use in the framework of Quantum Monte Carlo Methods[85, 36]. The linear correlation factor presented in 3.6 can nevertheless be related to more complex variants following the ideas of the transcorrelated method via an exponential representation

$$e^{\sum_{i>j} f(r_{ij})} = 1 + \sum_{i>j} f(r_{ij}) + \frac{1}{2} \left(\sum_{i>j} f(r_{ij}) \right)^2 + \dots \quad (3.8)$$

where the simple linear form can be interpreted as a truncation of the MacLaurin series at the linear term.

What is needed is a formalism that allows to determine the error introduced by the projection or alternatively determine M in such a way that the errors introduced to the finite basis Hamiltonian are minimised. Equation 3.9 gives the difference between a first quantised operator \hat{O} and the new operator M when applied to a wavefunction. It is this error that should be minimised in order to make M recover the properties of \hat{O} in the finite basis.

$$\Delta = \left(\hat{O} - M_{pq} a_p^\dagger a_q \right) |\Psi_{trial}\rangle = \left(\hat{O} - M_{pq} a_p^\dagger a_q \right) J|0\rangle \quad (3.9)$$

Equation 3.9 is not directly suitable for the determination of M as it is not positive definite. For the purpose of minimisation the quadratic error is a much better choice.

$$\min_M \langle 0|J^\dagger \left(\hat{O} - M_{pq} a_p^\dagger a_q \right)^2 J|0\rangle \quad (3.10)$$

To complete the formalism a concrete choice for the first quantised operator \hat{O} has to be made. Inserting the whole Hamiltonian would be rather unpractical as the implementation would probably have an associated complexity similar to other explicitly correlated methods. It can be argued that the coulomb terms are represented correctly in the second quantised Hamiltonian whereas the kinetic energy operator is represented inadequately by the one particle basis as the former still contains the singularity whereas the latter does not. The choice is therefore to replace \hat{O} by the kinetic energy operator T and making 3.10 stationary to variations with respect to M_{pq} :

$$\frac{\partial}{\partial M_{pq}} \langle 0 | J^\dagger \left(T_{vw} a_v^\dagger a_w - M_{pq} a_p^\dagger a_q \right)^2 J | 0 \rangle = \vec{0} \quad T_{vw} = -\frac{1}{2} \langle V | \nabla^2 | W \rangle \quad (3.11)$$

With the previous definitions the second quantised Hamiltonian takes a new form where the matrix M_{pq} replaces the kinetic energy completely:

$$H = M_{pq} a_p^\dagger a_q + V_{pq} a_p^\dagger a_q + \frac{1}{2} g_{pqrs} a_p^\dagger a_r^\dagger a_s a_q \quad (3.12)$$

With this Hamiltonian it is obvious that all post Hartree-Fock approaches do not need any implementational amendment. After calculating the matrix elements M_{pq} it is however necessary to go through a Hartree-Fock step again as the Fock matrix will be no longer diagonal with the new kinetic energy operator. Some care needs to be taken in obtaining M_{pq} as the SCF state should remain unchanged. This issue will be addressed in the next section.

This equation reveals an advantage of the projected Hamiltonian approach: By replacing the kinetic energy operator it will be possible to reuse codes for post Hartree-Fock methods.

The effect of the operator M should undoubtedly be to lower the electronic energy. It might seem counter intuitive that this is possible via a redefinition of the kinetic energy operator as one usually connects the contributions of the kinetic and potential energy operators to the whole electronic energy via the virial theorem. Thus a lower total energy would be associated with an increased kinetic energy. But this is only true if the wave function is “fully relaxed” which is not necessarily true for approximate

wavefunctions[74]. The trial wavefunctions outlined above do not belong to this category. Table 3.1 lists virial coefficients for different wavefunctions on the helium atom. It can be seen that the minimal basis SCF wavefunction is the only one to exactly fulfil the virial theorem. Even the variationally optimised r_{12} dependent wavefunction deviates from the expected value. This discrepancy would disappear if the exponent α was simultaneously optimised. It can also be seen that the expectation values of the kinetic energy is lowered by the introduction of the correlation factor which justifies the choice.

$ \Psi\rangle$	$\langle T \rangle$	$\langle V \rangle$	virial
$ 0\rangle$	2.848	-5.695	2.00
$(1 + 1/2r_{12}) 0\rangle$	2.297	-5.150	2.242
$(c_0 + c_1r_{12}) 0\rangle$	2.536	-5.411	2.134
$ 0\rangle = e^{-\alpha(r_1+r_2)}, \alpha = 27/16$			

Table 3.1: Virial coefficients for different wavefunctions

3.3 Configuration space of the Jastrow factor

As outlined before the new operator M should only account for correlation effects. In other words only the matrix elements M_{ab} should be different from the true kinetic energy operator in order to leave the Hartree-Fock energy unchanged. But the trial wavefunction introduced contains large components outside the virtual space. First there is the constant factor one but it is also expected that important components will arise from integrals such as $\langle ij|f(r_{ij})|ij\rangle$ in:

$$|\Psi_{trial}\rangle = \left(1 + \frac{1}{2} \langle PR|f(r_{ij})|QS\rangle a_P^\dagger a_R^\dagger a_S a_Q \right) |0\rangle \quad (3.13)$$

It is therefore necessary to constrain the problem in such a way that the matrix elements of M which contain indices in the occupied space remain unchanged. The most simple way to enforce this property is to introduce Lagrangian multipliers:

$$\frac{\partial}{\partial M_{pq}} \left[\langle \Psi_{trial} | (T_{TU} - M_{pq})^2 | \Psi_{trial} \rangle + \lambda_{pi}(M_{pi} - T_{pi}) \right] = 0 \quad (3.14)$$

$$\frac{\partial}{\partial \lambda_{pi}} \left[\langle \Psi_{trial} | (T_{TU} - M_{pq})^2 | \Psi_{trial} \rangle + \lambda_{pi}(M_{pi} - T_{pi}) \right] = 0 \quad (3.15)$$

The simplicity of this approach is certainly tempting. But this approach remains slightly unsatisfactory as the wavefunction still contains the occupied contributions which are expected to find their way into the virtual part. These contributions might be quite large because the Hartree-Fock energy is roughly 99% of the whole electronic energy and the virial theorem is well obeyed. An alternative method to obtain a purely virtual formalism is to use the strong orthogonality projector

$$\hat{P}_{SO} = (1 - |i\rangle\langle i|)(1 - |j\rangle\langle j|) \quad (3.16)$$

which removes all occupied components from the Jastrow factor and the problem can be recast in the following form:

$$\frac{\partial}{\partial M_{ab}} \langle 0 | J_{SO}^\dagger (T_{TU} - M_{ab})^2 J_{SO} | 0 \rangle \quad (3.17)$$

Introducing the shorthand notation R for the integrals over the correlating function $f(r_{ij})$ the strongly orthogonal Jastrow factor J_{SO} takes the form:

$$J_{SO} = R_{PQRS} a_p^\dagger a_r^\dagger a_s a_Q - R_{iQRS} a_i^\dagger a_r^\dagger a_s a_Q - R_{PQis} a_p^\dagger a_i^\dagger a_s a_Q + R_{iQjs} a_i^\dagger a_j^\dagger a_s a_Q \quad (3.18)$$

Although both approaches yield the desired properties the strong orthogonality version turns out to be favourable. In appendix B.3 a proof is given that only two electron contributions have to be evaluated in the strong orthogonality framework whereas the Lagrangian multiplier leads to six electron contributions. The term contribution here refers to the number of occupied indices that arise from the evaluation of the expectation value of the SCF Slater determinant. Both approaches lead to the same complex many electron integrals that have to be simplified.

The Lagrangian multiplier method as well as the strong orthogonality approach have been implemented in MOLPRO [2]. In the following the focus will be on the strong orthogonality implementation but results for both variants will be given later.

3.4 Evaluation of the quadratic error

The implementation process of the strong orthogonality and the Lagrangian multiplier variant are very similar. The differences are mainly in the linear system that determines the actual matrix elements which in the latter case has a higher dimensionality due to the constraints. The steps involved in obtaining concrete expressions for the quadratic error are:

- Normal ordering of the second quantised operators
- Contracting equal expressions
- Evaluation of the expectation value
- Reduction of multi centre integrals

All of the above steps can be performed within a computer program which allows the rapid implementation of both the strong orthogonality and Lagrangian multiplier method. Details on the employed methods for code generation are given in appendix B.5. A derivation of the strong orthogonality expressions is carried in the next section to illustrate the types of expressions that have to be dealt with and to support arguments in later sections. The explicit equations arising from the Lagrangian multiplier formalism are omitted because they turn out to be too numerous. There are around 100 second quantised operators and 3700 expectation values to be handled in the Lagrangian approach.

3.4.1 Derivation of the strong orthogonality expressions

A useful starting point for the derivation is to bring the quadratic term $(T - M)^2$ into normal order:

$$\begin{aligned}
\left(T_{TU}a_T^\dagger a_U - M_{ab}a_a^\dagger a_b\right)^2 &= M_{ab}M_{cd}a_a^\dagger a_c^\dagger a_d a_b & (3.19) \\
&+ M_{ab}M_{cd}\delta_{bc}a_a^\dagger a_b \\
&- T_{TU}M_{ab}\delta_{Ua}a_T^\dagger a_b \\
&- M_{ab}T_{TU}\delta_{bT}a_a^\dagger a_U \\
&- 2T_{TU}M_{ab}a_T^\dagger a_a^\dagger a_b a_U \\
&\dots
\end{aligned}$$

The terms quadratic in the true kinetic energy operator T have been omitted as they will drop out once the derivatives with respect to M_{ab} are taken. The next step is to put the above terms between the Jastrow factor

$$\begin{aligned}
J_{SO} &= \frac{1}{4}R_{PQRS}a_P^\dagger a_R^\dagger a_S a_Q - \frac{1}{4}R_{iQRS}a_i^\dagger a_R^\dagger a_S a_Q \\
&\quad - \frac{1}{4}R_{PQis}a_P^\dagger a_i^\dagger a_S a_Q + \frac{1}{4}R_{iQjs}a_i^\dagger a_j^\dagger a_S a_Q & (3.20)
\end{aligned}$$

and its hermitian adjoint J_{SO}^\dagger . The matrix elements $\langle PR|f(r_{ij})|QS\rangle$ have been replaced by R_{PQRS} and a factor $\frac{1}{4}$ has been included which corresponds to a correlation factor of $\frac{1}{2}r_{12}$. The factors have been included to maintain consistency with appendix B.2 which lists the complete strong orthogonality expressions but they could have been omitted as the determining equations are only unique up to an arbitrary multiplier.

The derivation proceeds by multiplying the terms quadratic in M with J_{SO} from the right and by J_{SO}^\dagger from the left:

$$J_{SO}^\dagger M_{ab}a_a^\dagger a_b M_{cd}a_c^\dagger a_d J_{SO} = \dots \quad (3.21)$$

The development can be simplified by ignoring all terms in J_{SO} that contain occupied indices in a first step. Normal ordering then leads to:

$$\left(\frac{1}{4}R_{VWXY}a_V^\dagger a_X^\dagger a_Y a_W\right) \left(M_{ab}a_a^\dagger a_b\right) \left(M_{cd}a_c^\dagger a_d\right) \left(\frac{1}{4}R_{PQRS}a_P^\dagger a_R^\dagger a_S a_Q\right) = \\ \frac{1}{4}R_{VaXc}M_{ab}M_{cd}R_{bQdS}a_V^\dagger a_X^\dagger a_S a_Q + \frac{1}{4}R_{VaXT}M_{ab}M_{bd}R_{dQTS}a_V^\dagger a_X^\dagger a_S a_Q + \dots \quad (3.22)$$

In the preceding equation a factor of four arises in both terms on the r.h.s. as a result of the possible contractions of the elementary operators and leads to the overall factor of 1/4. The terms with particle rank greater than two have been omitted as they do not contribute to the determining equation when a Hartree-Fock reference determinant is used. In order to preserve strong orthogonality the normal ordering has to be repeated with the other terms that are obtained by multiplying out $J_{SO}^\dagger M_{ab}a_a^\dagger a_b M_{cd}a_c^\dagger a_d J_{SO}$. It is however simpler to analyse directly where contributions arising from the occupied space have to be eliminated and it is obvious that the following term needs to be added

$$-\frac{1}{4}R_{VaXi}M_{ab}M_{bd}R_{dQis}a_V^\dagger a_X^\dagger a_S a_Q \quad (3.23)$$

in order to remove single excitations. For the mixed contributions between M and T there are three different contributions (from equation 3.19)

$$-2M_{ab}T_{TU}a_a^\dagger a_T^\dagger a_U a_b \quad -M_{ab}T_{bU}a_a^\dagger a_U \quad -T_{Ta}M_{ab}a_T^\dagger a_b \quad (3.24)$$

where the second and third term are simply adjoint expressions. Evaluating the two electron expression analogous to 3.22 yields:

$$\left(\frac{1}{4}R_{VWXY}a_V^\dagger a_X^\dagger a_Y a_W\right) \left(-2M_{ab}T_{TU}a_a^\dagger a_T^\dagger a_U a_b\right) \left(\frac{1}{4}R_{PQRS}a_P^\dagger a_R^\dagger a_S a_Q\right) = \\ -\frac{1}{2}R_{VTXa}M_{ab}T_{TU}R_{UQbs}a_V^\dagger a_X^\dagger a_S a_Q + \dots \quad (3.25)$$

An inspection of the contracted indices reveals that the following projector terms are needed as well:

$$\frac{1}{2}R_{ViXa}M_{ab}T_{iU}R_{UQ}b_s a_v^\dagger a_x^\dagger a_s a_Q \quad (3.26)$$

$$\frac{1}{2}R_{VTXa}M_{ab}T_{Ti}R_{iQ}b_s a_v^\dagger a_x^\dagger a_s a_Q \quad (3.27)$$

$$-\frac{1}{2}R_{ViXa}M_{ab}T_{ij}R_{jQ}b_s a_v^\dagger a_x^\dagger a_s a_Q \quad (3.28)$$

The operator contraction $-M_{ab}T_{bU}a_a^\dagger a_U$ results in:

$$\left(\frac{1}{4}R_{VWXY}a_v^\dagger a_x^\dagger a_Y a_W\right) \left(-M_{ab}T_{bU}a_a^\dagger a_U\right) \left(\frac{1}{4}R_{PQRS}a_p^\dagger a_r^\dagger a_s a_Q\right) = \\ -\frac{1}{4}R_{VaXU}M_{ab}T_{bT}R_{TQU}a_v^\dagger a_x^\dagger a_s a_Q + \dots \quad (3.29)$$

The corresponding terms to remove occupied components are:

$$\frac{1}{4}R_{VaXT}M_{ab}T_{bi}R_{iQT}a_v^\dagger a_x^\dagger a_s a_Q \quad (3.30)$$

$$\frac{1}{4}R_{VaXi}M_{ab}T_{bT}R_{TQi}a_v^\dagger a_x^\dagger a_s a_Q \quad (3.31)$$

$$-\frac{1}{4}R_{VaXj}M_{ab}T_{bi}R_{iQj}a_v^\dagger a_x^\dagger a_s a_Q \quad (3.32)$$

The terms involving form $T_{Ta}M_{ab}$ can be obtained by forming the adjoint of the last four expressions.

3.4.2 Resolution of the identity

The expressions obtained in the previous section contain summations over the complete basis sets. These terms need to be modified to allow an efficient computation. One example is the following expression quadratic in the new operator:

$$R_{PaRT}M_{ab}M_{bd}R_{dQTS} = M_{ab}M_{bd}\langle PRd|f(r_{12})f(r_{23})|aSQ\rangle \quad (3.33)$$

The three electron integral can be avoided by using the Resolution of the identity approximation[82] leading to a product of two electron operators:

$$\langle PRd|f(r_{12})f(r_{23})|aSQ\rangle \approx \langle PR|f(r_{12})|ap\rangle \langle pd|f(r_{12})|SQ\rangle \quad (3.34)$$

When evaluating expressions that contain both the true and the new kinetic energy operator slightly more care has to be taken. Replacing the summation over U in the following term would only lead to matrix elements M_{ab} which are equal to T_{ab} .

$$R_{PaRT}M_{ab}T_{bU}R_{UQTS} \quad (3.35)$$

Letting the Laplacian in T act directly on the correlating function leads to:

$$T_{bU}R_{UQTS} = TR_{bQTS} = -\frac{1}{2}\langle bT|\nabla_1^2 f(r_{12})|QS\rangle \quad (3.36)$$

Expression 3.35 now reads

$$R_{PaRT}M_{ab}TR_{bQTS} \quad (3.37)$$

which still contains a three electron contribution which can be simplified by replacing the index T with a function of the finite basis. For the adjoint of equation 3.35 the only difference is the appearance of the following type of integral:

$$RT_{PQRS} = -\frac{1}{2}\langle PR|f(r_{12})\nabla_1^2|QS\rangle \quad (3.38)$$

There is a second type of three electron integral where both indices of the true kinetic energy operator are in the complete basis 3.39. In this case resolution of the identity has to be applied with more care.

$$R_{PTRa}T_{TU}M_{ab}R_{UQbs} \quad (3.39)$$

It seems tempting to only replace the index T with the finite basis to arrive at a product of two electron operator because it is the term $\nabla_1^2 r_{12}$ which gives rise to the singularity in the kinetic energy. It turns out however that the right way to approximate expression 3.39 is by introducing the finite basis projection in a symmetrised way:

$$R_{PTRa}T_{TU}M_{ab}R_{UQbs} \approx \frac{1}{2} (RT_{PpRa}M_{ab}R_{pQbs} + R_{PpRa}M_{ab}TR_{pQbs}) \quad (3.40)$$

The underlying reason behind this insertion is that an asymmetric approximation will lead to determining equations where M is no longer hermitian and thus $M_{ab} \neq M_{ba}$ which is shown in appendix B.4 on page 101.

3.4.3 Linear System

With the second quantised expressions of the previous sections expectation values for a closed shell Hartree-Fock determinant can easily be obtained and this step shall be omitted. It is therefore assumed that closed shell expressions such as

$$R_{iajc}M_{ab}M_{cd}R_{bidj} - \frac{1}{2}R_{iajc}M_{ab}M_{cd}R_{bjdi} \quad (3.41)$$

are already available. Thus the next step is to take the derivatives with respect to M :

$$\frac{\partial}{\partial M_{ab}} \langle 0 | J_{SO}^\dagger \left(T_{TU} a_T^\dagger a_U - M_{ab} a_a^\dagger a_b \right)^2 J_{SO} | 0 \rangle = 0 \quad (3.42)$$

This expression is slightly too general because the off diagonal elements M_{ab} are related via the hermitian constraint which leads to $\frac{1}{2}N(N+1)$ degrees of freedom instead of N^2 . If the resolution of the identity is applied in the symmetric fashion discussed previously the correct result is obtained even when taking the derivatives with respect to M_{ab} and M_{ba} at the same time. For the sake of computational efficiency and mathematical elegance it is better to employ the relation $M_{ab} = M_{ba}$ to reduce the size of the linear system which then reads:

$$A_{cd,ab}M_{ab} = B_{cd} \quad a \geq b \quad c \geq d \quad (3.43)$$

This equation has a solution if the matrix $A_{cd,ab}$ is non-singular. This turns out to be the case in all calculations that were carried out. A close investigation of the terms that contribute to the matrix A reveals that under most circumstances the matrix A should in fact be singular as a result of the symmetry properties as will be shown below.

The true kinetic energy operator is a symmetry conserving operator which means that integrals over functions belonging to different irreducible representations i and j vanish:

$$\langle p^{(i)}|T|q^{(j)}\rangle\delta_{ij} \rightarrow M_{p^{(i)}q^{(j)}}\delta_{ij} \quad (3.44)$$

The projected Hamiltonian M is required to have the same property otherwise some symmetry breaking would be introduced which is clearly unphysical. Therefore the matrix A should have whole rows and columns equal to zero where the respective indices belong to different symmetries. This leads to the question which terms lead to such symmetry forbidden contributions. Expression 3.45 gives one such term where the correlating functions are symmetry conserving operators.

$$R_{iajc}M_{ab}M_{cd}R_{bidj} = \langle ij|f(r_{12})|ac\rangle M_{ab}M_{cd}\langle bd|f(r_{12})|ij\rangle \rightarrow A_{ab,cd} \quad (3.45)$$

The most illustrative example of how the symmetry forbidden contributions arise is an analysis of the helium ground state where the product $|ij\rangle$ is totally symmetric. This means that the products $|ac\rangle$ and $\langle bd|$ need to be totally symmetric as well in order to add to the matrix which is fulfilled if $a = c$ and $b = d$. Setting $a = 2s$ and $b = 2p_z$ leads to:

$$\langle 1s1s|f(r_{12})|2s2s\rangle\langle 2p_z2p_z|f(r_{12})|1s1s\rangle M_{2s2p_z}M_{2s2p_z} \quad (3.46)$$

The integrals over the correlation function in this expression are totally symmetric. The matrix elements M_{2s2p_z} should be zero but are also the unknown quantities at this stage. This explains why singular matrices have not been observed. Other terms quadratic in M also lead to such contaminations.

In the performed calculations no symmetry forbidden terms were ever observed as the vector B in 3.43 does not contain any spurious terms. The vector therefore acts as a driver and removes these symmetry forbidden elements. The appearance of these terms is however disturbing. These contributions can be removed by exploiting the symmetry information included in the overlap matrix. Tests have shown however that there is no change in the computed matrix elements when this extra step is used.

Technically it will still be possible to find a solution for the linear system even when A becomes singular. By application of the singular value decomposition[86] it should be possible to get a reasonable set of matrix elements.

3.5 Form of the correlation factor

So far the form of the correlating function has been left unspecified and in this section different choices of the correlation factor are discussed. From the electronic cusp condition it is known that the wavefunction should behave as:

$$|\Psi\rangle = (1 + \frac{1}{2}r_{12} + O(r_{12}^2) + \dots)|0\rangle \quad (3.47)$$

This suggests substituting $f(r_{12})$ with $\frac{1}{2}r_{12}$ and neglecting higher order terms in a first approximation. As long as the interelectronic distance is small the linear term will dominate the expansion. But as the separation between the electrons increases the linear term grows which means that the electrons still feel strong correlation effects at long distances which is conceptually wrong. A more physical behaviour can be achieved by introducing a Slater type correlation factor:

$$e^{-\alpha r_{12}} = 1 - \alpha r_{12} + \alpha^2 r_{12}^2 + \dots \quad (3.48)$$

In this way good correlation energies can be obtained [68]. Unfortunately integrals over Slater functions are usually difficult to handle. Gaussian geminals $e^{-\zeta r_{12}^2}$ on the other hand lead to analytically tractable expressions. Although this functional form also violates the cusp condition several studies have attempted to fit a linear expansion of Gaussian geminals to specific correlation factors to mimic the desired functional form. In this work Slater type correlation factors are represented by a frozen contraction of Gaussian geminals

$$e^{-\alpha r_{12}} \approx \sum_i c_i e^{(-\gamma_i r_{12}^2)} \quad (3.49)$$

as was recently suggested in references [7] and [6]. Calculations with both linear and Slater type correlation factors have been carried out and the results are presented in section 3.6.

3.5.1 Integrals

In the section on resolution of the identity 3.4.2 the following integrals were introduced:

$$TR_{pqrs} = \langle pr | T_1 f(r_{12}) | qs \rangle \quad (3.50)$$

$$RT_{pqrs} = \langle pr | f(r_{12}) T_1 | qs \rangle \quad (3.51)$$

On the other hand the integrals provided by R12 theory are:

$$R_{pqrs} = \langle pr | f(r_{12}) | qs \rangle \quad (3.52)$$

$$U_{pqrs} = \langle pr | [(T_1 + T_2), f(r_{12})] | qs \rangle \quad (3.53)$$

It would be very convenient to reuse as many contributions from R12 theory as possible for the new projected Hamiltonian approach. If it were possible to symmetrise the expressions obtained between electron one and two the following kernels would be needed where only the first one requires an additional implementation effort.

$$Q_{pqrs} = \langle pr | f(r_{12}) (T_1 + T_2) | qs \rangle \quad (3.54)$$

$$L_{pqrs} = \langle pr | [(T_1 + T_2), f(r_{12})] | qs \rangle + Q_{pqrs} \quad (3.55)$$

Unfortunately such a symmetrisation of the expression turns out to be impossible as will be shown hereafter. The terms involving no projections in the occupied space are:

$$\frac{1}{4} R_{PaRT} M_{ab} T_{bU} R_{UQTS} a_P^\dagger a_R^\dagger a_S a_Q \quad (3.56)$$

$$\frac{1}{4} R_{PTRU} T_{Ta} M_{ab} R_{bQU} S a_P^\dagger a_R^\dagger a_S a_Q \quad (3.57)$$

$$\frac{1}{2} R_{PaRT} M_{ab} T_{TU} R_{bQU} S a_P^\dagger a_R^\dagger a_S a_Q \quad (3.58)$$

These terms can be symmetrised without any problems if the third expression is used evenly to complement the first two terms the following expressions are obtained:

$$\frac{1}{4} R_{PaRT} M_{ab} L_{bQTS} a_P^\dagger a_R^\dagger a_S a_Q \quad (3.59)$$

$$\frac{1}{4} Q_{PaRT} M_{ab} R_{bQTS} a_P^\dagger a_R^\dagger a_S a_Q \quad (3.60)$$

The inability to achieve the symmetrisation results from the terms involving projectors onto the occupied space:

$$\frac{1}{4}R_{PaRi}M_{ab}T_{bT}R_{TQi}S_a^\dagger a_R^\dagger a_S a_Q \quad (3.61)$$

$$\frac{1}{4}R_{PTRi}T_{Ta}M_{ab}R_{bQi}S_a^\dagger a_R^\dagger a_S a_Q \quad (3.62)$$

$$\frac{1}{2}R_{PaRi}M_{ab}T_{iT}R_{bQT}S_a^\dagger a_R^\dagger a_S a_Q \quad (3.63)$$

$$\frac{1}{2}R_{PaRT}M_{ab}T_{Ti}R_{bQi}S_a^\dagger a_R^\dagger a_S a_Q \quad (3.64)$$

The latter two equations cannot be used to symmetrise the first two because they appear with different prefactors. One is therefore left with having to implement the integrals with kernels¹ $\nabla_1^2 f(r_{12})$ and $f(r_{12})\nabla_1^2$. The necessary expressions for these integrals are given in appendix B.1 on page 93

3.6 Results

3.6.1 R12 calculations

Helium

Singles and doubles configuration interaction correlation energies obtained with different kinetic energy operators for the helium atom are listed in the upper half of table 3.2. The column M_{pq} refers to the Lagrangian multiplier method whereas M_{ab} is used to denote the strong orthogonality approach. The complete basis set reference energy is obtained by a two point extrapolation with the X^{-3} formula. Results for the projected hamiltonians could only be obtained up to the quintuple zeta level because the integral routines have not been tuned to full efficiency and use too much memory in the current implementation.

The second column in table 3.2 which lists the Lagrangian multiplier results looks quite promising for the double zeta basis as the correlation energy is brought within mE_h of the estimated exact result. The triple zeta value however presents a step back

¹The integrals over the two kernels are related via Green's theorem!

as it moves further away from the complete basis set limit. What causes this erratic behaviour is not clear and the quadruple and quintuple zeta calculations again provide results that are closer to the extrapolated result. They fail however to significantly close the gap. The quintuple zeta results are particularly disappointing as the improvement is marginal. For the biggest basis it is also reasonable to expect that the errors connected to the resolution of the identity are small.

The strong orthogonality CISD results in the third column of table 3.2 look less promising than their Lagrangian multiplier counterparts apart from the quintuple zeta value which is of comparable quality. This suggests that the removal of the reference determinant and the single excitations from the trial wavefunction has quite severe effects.

VXZ	T_{pq}	M_{pq}^a	M_{ab}^b
CISD			
2	-0.03243435	-0.04122574	-0.03598012
3	-0.03907882	-0.04002438	-0.03975032
4	-0.04089665	-0.04159455	-0.04126243
5	-0.04152705	-0.04162476	-0.04161644
∞	-0.04207797 ^c		
MP2			
2	-0.02582834	-0.03102289	-0.02818721
3	-0.03313756	-0.03392970	-0.03368198
4	-0.03547800	-0.03615359	-0.03597884
5	-0.03640651	-0.03658329	-0.03657579
∞	-0.03735764 ^c		

^a Lagrangian multiplier variant

^b Strong orthogonality method

^c $5 \rightarrow 6 X^{-3}$ extrapolation

Table 3.2: Projected Hamiltonian correlation energies for Helium in E_h

In second part of table 3.2 correlation energies obtained from second order Møller-

Plesset calculations are given for the helium atom. The first point to note is that the series of Lagrangian multiplier results M_{pq} show a more systematic behaviour with the triple zeta result now well in between cc-pVDZ and cc-pVQZ. The values obtained with strong orthogonality are again less accurate for the smaller bases but ultimately both approaches fail to reach the extrapolated result.

Hydrogen

It is useful at this stage to evaluate the performance of the projected Hamiltonian for another two electron system. Table 3.3 lists CISD and MP2 correlation energies for the Hydrogen molecule where the same conventions as before apply. Comparing the columns for the lagrangian multiplier and strong orthogonality implementations reveals that now both approaches lead to results of similar quality but fail at reproducing the CBS value.

Since the results for the Helium atom show a different behaviour for configuration interaction and MP2 (table 3.2) it is useful to compare different methods for the hydrogen molecule as well. The values obtained for the two different implementations are again similar. Both series show a systematic behaviour which is also true for the CI results.

What caused the deviating triple zeta CISD result in table 3.2 is not clear. Similar effects have been observed in other cases. It is important to remember that in the Lagrangian multiplier approach the wavefunction still contains contributions of the occupied space which might have a strong influence due to their magnitude although the major component should be removed by restricting the matrix elements in the occupied space. For the remaining part only strong orthogonality results shall be presented as it stands on more solid conceptual grounds.

VXZ	T_{pq}	M_{pq}^a	M_{ab}^b
CISD			
2	-0.03460429	-0.03820311	-0.03837126
3	-0.03931928	-0.03998924	-0.03981949
4	-0.04028254	-0.04045644	-0.04043254
∞	-0.04081213 ^c		
MP2			
2	-0.02633528	-0.02845302	-0.02856090
3	-0.03166112	-0.03223212	-0.03210147
4	-0.03309783	-0.03330692	-0.03329354
∞	-0.03422133 ^c		

^a Lagrangian multiplier variant

^b Strong orthogonality method

^c 5→6 X^{-3} extrapolation

Table 3.3: Projected Hamiltonian correlation energies for H₂ in E_h

VXZ	T_{pq}	M_{ab}^a
2	-0.19280699	-0.22388603
3	-0.26847498	-0.27348523
4	-0.29947759	-0.30319462
∞	-0.32496535 ^b	

^a strong orthogonality

^b 5→6 X^{-3} extrapolation

Table 3.4: Projected Hamiltonian MP2 correlation energies for Neon in E_h using the MWB effective core potential

The neon atom

The application of the projected Hamiltonian approach for many electron systems requires special attention as it is common practice to only subject the valence electrons to a correlated treatment which can create some problems for the calculation of the matrix elements of M . For the Lagrangian multiplier approach where the wavefunction is simply written as

$$|\Psi_{trial}\rangle = (1 + \frac{1}{2} \sum_{i>j} r_{ij})|0\rangle \quad (3.65)$$

it is not clear how to perform the separation between core and valence electrons. The most straightforward way to avoid this problem is replace the core electrons via the introduction of an effective core potential.

The strong orthogonality approach should be less problematic in this respect as it only contains two electron contributions which suggests that it can be treated as a simple pair theory such as MP2. Since the implementation has not been carried out to discriminate between core and valence electrons effective core potential are also used in the framework of the strongly orthogonal model. The correlation energies of the Neon atom in the cc-pVXZ Dunning bases when using the MWB core potential are given in table 3.4. Although the correlation energies are lowered by the projected Hamiltonian the improvements are not significant.

X	T_{pq}	M_{ab}^a
2	-0.02582834	-0.02373901
3	-0.03313756	-0.03306279
4	-0.03547800	-0.03588046
5	-0.03640651	-0.03650733
∞	-0.03735764 ^b	

^a strong orthogonality

^b 5 \rightarrow 6 X^{-3} extrapolation

Table 3.5: Projected Hamiltonian MP2 correlation energies in E_h for Helium with Gaussian geminals

3.6.2 Gaussian geminals

As was seen in the previous section the projected Hamiltonian approach fails to bridge the gap between the truncated bases and the complete basis set limit. Especially the corrections for large bases are very small. In these cases it is reasonable to assume that the errors introduced by the resolution of the identity are small[6]. Which suggest that the Jastrow factor is the main source of error and this fact shall be addressed in this section.

In accordance with paper[6] the exponent of the Slater function is chosen to be one. This Slater type geminal is expanded in nine even tempered Gaussians with ratio 3 and centre 8. The coefficients are determined in a least squares approach. The Mathematica input file for this procedure was kindly provided by Dr. F. Manby. The correlation energies obtained with this new correlation factor for Helium are given in table 3.5. It is obvious that the projected Hamiltonian fails completely at improving the correlation energies.

VXZ	r_{12}	geminal
D	6.40	2.02
T	288.65	79.92
Q	3415.45	744.21
5	25454.73	3762.40

Table 3.6: Condition numbers of the linear system for the Helium calculation in the strong orthogonality implementation

3.7 Discussion

The correlation energies obtained with the projected Hamiltonians are disappointing. In the remaining part of this chapter an analysis of this failure will be given. There are several approximations in the projected Hamiltonian that lead to errors. The replacement of the exact wavefunction by a Slater Jastrow type wavefunction is an approximation which can hardly be avoided whereas the resolution of the identity and the form of the correlation factor are parameters that can be controlled.

Before analysing these errors the attention shall be turned towards the linear system. Of special interest is the question whether the the matrix A is ill conditioned. The condition number of a matrix is simply given as the ratio[23]

$$K(A) = \frac{\max[\lambda(A)]}{\min[\lambda(A)]} \quad (3.66)$$

where $\lambda(A)$ is the set of eigenvalues of A . Most mathematics texts on this subject state that a matrix is ill conditioned if $K(A)$ is too high. A more tangible criterion is given in reference [86] which classifies a matrix as ill conditioned if the inverse of $K(A)$ is of the order of the machine precision. All calculations have been carried out in double precision where a critical value would be in the area of 10^{-12} . The condition numbers for the linear system in the strong orthogonality case for helium are given in table 3.6. The condition numbers are all in a range where no numerical problems are expected. It is therefore safe to assume that there must be another source of error.

The resolution of the identity has received much attention[80, 6] in the framework

of the R12 methods. It is usually found that the errors are only relevant for small bases. This has inspired the development of methods where special bases are used to perform the RI insertion[80]. In recent investigation of errors in explicitly correlated second order Møller-Plesset theory it has been shown for MP2-R12 calculations in a cc-pVQZ basis² that the increase of the RI basis does not lead to very large improvements. Since the performance of the projected Hamiltonian is particularly poor for large bases it seems justified to assume that the problems are not caused by the resolution of the identity.

The fact that an improved correlation factor leads to worse energies is quite puzzling. The quality of the Slater type correlation factor represented by Gaussians has been shown in reference [6]. It was shown in table 3.1 on page 65 that the kinetic energy is reduced by the introduction of the Jastrow factor. The introduction of the factor $1 + 1/2r_{12}$ reduced the kinetic energy by roughly 20% and this difference is far greater than the true correlation energy of helium. In table 3.7 an analysis is carried out how the introduction of a correlation factor $(3/2 - 1/2e^{-r_{12}})$ affects expectation values. The kinetic contribution to the correlation energy is quite substantial and corresponds to almost five times the true kinetic energy. The kinetic part is balanced by an increase in potential energy which leads to a correlation energy $-0.028084763 E_h$. Although the Hartree-Fock wavefunction used in this analysis is very simple it would nevertheless be expected that the projected Hamiltonian leads to a significant lowering of the kinetic energy.

Having shown the huge discrepancy between the expected effect of introducing a correlation factor and the actual results obtained with the projected Hamiltonian leads to the question which components of the trial wavefunction are recovered by the matrix elements M and which are neglected. The MP2-R12 wavefunction

$$|MP2 - R12\rangle = \left(t_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i + t_{IJ}^{AB} \langle AB | f(r_{12}) | ij \rangle a_A^\dagger a_B^\dagger a_j a_i \right) |0\rangle \quad (3.67)$$

provides a convenient way to perform such an analysis as it contains a conventional CI-like part and an explicitly correlated component. In R12 theory there are different ansätze to enforce the strong orthogonality conditions of the explicitly correlated part.

²See figure 2 of ref. [6]

	$ 0\rangle$	$(\frac{3}{2} - \frac{1}{2}e^{-r_{12}}) 0\rangle$
$\langle E \rangle$	-2.847656249	-2.875741012
$\langle T \rangle$	2.847656249	2.643825617
$\langle V \rangle$	-5.695312498	-5.519566629
$\langle E_{corr} \rangle$		-0.028084763
$\langle T_{corr} \rangle$		-0.203830632
$\langle V_{corr} \rangle$		0.175745869

$|0\rangle = e^{-\alpha(r_1+r_2)}, \alpha = 27/16$

Table 3.7: Slater type geminal energy contributions for Helium

$$\hat{P}_{SO}^1 = (1 - |p\rangle\langle p|)(1 - |q\rangle\langle q|) \quad (3.68)$$

$$\hat{P}_{SO}^2 = (1 - |i\rangle\langle i|)(1 - |j\rangle\langle j|) \quad (3.69)$$

The first approach chosen by Klopper and Kutzelnigg [82] uses a strong orthogonality projector of form 3.68 which makes the r_{12} dependent part orthogonal to all determinants in the finite basis. More recent implementations [80] of R12 theory use a less restrictive projector of type 3.69 which make the explicitly correlated contribution orthogonal to the reference state and singly excited determinants only. The projectors 3.68 and 3.69 are known as ansatz 1 and ansatz 2 respectively[80]. For the present discussion ansatz 1 is more useful as the conventional and explicitly correlated parts are orthogonal to each other.

Evaluating the quadratic error expression

$$\langle MP2 - R12 | \left(T_{TU} a_T^\dagger a_U - M_{ab} a_a^\dagger a_b \right)^2 | MP2 - R12 \rangle \quad (3.70)$$

leads to the following expressions:

$$\langle MP2 - R12 | T_{PQ} a_P^\dagger a_Q T_{RS} a_R^\dagger a_S | MP2 - R12 \rangle \quad (3.71)$$

$$+ 4t_{ij}^{ac} M_{ab} M_{cd} t_{kl}^{bd} a_i^\dagger a_j^\dagger a_l a_k \quad (3.72)$$

$$+ 4t_{ij}^{ac} M_{ab} M_{bd} t_{kl}^{dc} a_i^\dagger a_j^\dagger a_l a_k \quad (3.73)$$

$$- 4t_{ij}^{cd} T_{ca} M_{ab} t_{kl}^{bd} a_i^\dagger a_j^\dagger a_l a_k \quad (3.74)$$

$$- 4t_{ij}^{ad} M_{ab} T_{bc} t_{kl}^{cd} a_i^\dagger a_j^\dagger a_l a_k \quad (3.75)$$

$$- 8t_{ij}^{ac} M_{ab} T_{cd} t_{kl}^{bd} a_i^\dagger a_j^\dagger a_l a_k \quad (3.76)$$

The quadratic term in T has not been evaluated since it is removed when taking the derivatives with respect to M_{ab} . In deriving the other terms use has been made of the properties that the sets of functions a, b, \dots and A, B, \dots are orthogonal to each other by virtue of ansatz 1. The terms involving the new operator M only contains components in the incomplete basis which implies that the resulting matrix elements M_{ab} will be equal to T_{ab} . Hence in the quadratic error expressions double excitations into the complete basis are removed. The new matrix elements are therefore only determined by excitations of type t_{ij}^{Ab} which are far less important than the contributions t_{ij}^{AB} as can be seen from MP2-R12 calculations. This is the reason behind the failure of the projected Hamiltonian approach.

This problem would not exist if T would be replaced by a two electron operator. It is possible to set up the quadratic error expression by using the coulomb operator:

$$\langle MP2 - R12 | \left(g_{PQRS} a_P^\dagger a_R^\dagger a_S a_Q - M_{ab} a_a^\dagger a_b \right)^2 | MP2 - R12 \rangle \quad (3.77)$$

With this approach it is no longer clear what meaning should be attached to the one electron quantity M . Hence there is no straightforward way to use this object in a correlated calculation. This could be remedied by introducing a unknown two electron quantity M_{abcd} :

$$\langle MP2 - R12 | \left(g_{PQRS} a_P^\dagger a_R^\dagger a_S a_Q - M_{abcd} a_a^\dagger a_c^\dagger a_d a_b \right)^2 | MP2 - R12 \rangle \quad (3.78)$$

Computationally such an approach is very punishing because the following system has to be solved:

$$A_{efgh,abcd}M_{abcd} = B_{efgh} \quad (3.79)$$

The matrix A in this case has a memory footprint of $O(v^8)$. Thus such an approach is computationally not viable.

Chapter 4

Concluding remarks

The purpose of this thesis was to investigate possible routes to recover the one electron error resulting from the application of a finite atomic basis set by constructing new operators. In doing so the conventional paradigm of developing more elaborate wavefunction models to improve the description of correlation effects was abandoned. The reasons behind this approach are the steep increase in computational cost when extending the one electron basis and the complexity of explicitly correlated wavefunction models both in a computational and implementational sense.

The extrapolated Hamiltonian approach introduced in chapter 2 attempts to use atomic information about basis set completeness for improving correlation energies on molecules. The conceptual basis for this approach is given by the convergence behaviour of the principal expansion. This inspired a redefinition of the perturbative treatment by using strength parameters greater than one. Although the correlation energies could be improved the method cannot rival X^{-3} two point extrapolations in quality. The results obtained for the calculation of properties that are expressed in terms of derivatives of the energy turned out to be particularly disappointing. There appears to be no way to rectify the shortcomings of the extrapolated Hamiltonian approach as the scaling parameters offer a limited amount of degrees of freedom. The stability of the X^{-3} extrapolation however leaves the question open whether it is possible to estimate the complete basis set limit from a single calculation with the use of some atomic heuristic.

The completeness relationships or projected Hamiltonians (Chapter 3) attempt a re-

definition of the kinetic energy operator which is inspired by the fact that the singularity of the kinetic energy operator is suppressed in the finite basis. New matrix elements for the kinetic energy operator are obtained by using an explicitly correlated trial wavefunction and minimizing the error between the true and projected kinetic energy operator. The method fails because it neglects a major fraction of the double excitations involving the complete basis. If a two electron first quantised operator was used the full set of double excitations could be recovered but the new operator then necessarily would have to be a two electron quantity as well. This however makes the approach intractable because the memory requirements scale as $O(N^8)$. From a theoretical perspective it might still be interesting to investigate such an approach to analyse the validity of the assumptions made. In the atomic case with full exploitation of symmetry the calculation of new matrix elements might be possible for basis sets of reasonable size.

With the time available it was clearly not possible to investigate all conceivable approaches to develop new operators. The efforts in this thesis have concentrated on improving post Hartree-Fock calculations. A different route towards new operators might be the construction of a “correlated” Hartree-Fock approach where one constructs an operator in such a way that a single Slater determinant can deliver a result close to the exact wavefunction.

Appendix A

Extrapolated Hamiltonians

A.1 Calibration data

A.1.1 MP2 calibration data

Atomic

cc-pVXZ					
	D	T	Q	5	6
C	1.22413458	1.07011113	1.03006129	1.01522246	1.00872296
F	1.31155031	1.09705247	1.04197411	1.02090669	1.01193919
N	1.26725856	1.07676731	1.03229271	1.01601031	1.00916898
O	1.30110192	1.09126949	1.03910608	1.01943904	1.01111008

Table A.1: Atomic scaling factors for MP2

Molecular

cc-pVXZ					
	D	T	Q	5	6
C ₂ (¹ Σ _g ⁺)	1.24048415	1.08039550	1.03161960	1.01606269	1.00920174
F ₂	1.24522367	1.08122264	1.03557427	1.01784533	1.01021146

H ₂	1.13914811	1.03957028	1.01680262	1.00859519	1.00494714
N ₂	1.17139870	1.06053167	1.02665629	1.01356547	1.00778343
O ₂ (³ Σ _g ⁻)	1.35501708	1.10575113	1.04530017	1.02253847	1.01285915

$r(\text{C}_2) = 1.2425 \text{ \AA}$, $r(\text{F}_2) = 1.41193 \text{ \AA}$, $r(\text{H}_2) = 0.74144 \text{ \AA}$, $r(\text{N}_2) = 1.09768 \text{ \AA}$

$r(\text{O}_2) = 1.20752 \text{ \AA}$, from reference [1]

Table A.2: Molecular scaling factors for MP2

A.1.2 CCSD

d-aug-cc-pVXZ					
	D	T	Q	5	6
He	1.10020830	1.03022416	1.01182302	1.00550469	1.00317987
Ne	1.22251408	1.07147226	1.02932985	1.01441701	1.00828122
Ar	1.25400473	1.07673247	1.03155519	1.01757518	1.01009360

Table A.3: Rare gas CCSD scaling factors

A.2 Additional data

A.2.1 Simple atomic scaling

H ₂ O ^a , MP2			
VXZ	conventional	scaled	X ⁻³
D	-0.20248326	-0.28563442	
T	-0.26233477	-0.29825750	-0.28753541
Q	-0.28366041	-0.30114776	-0.29922236
5	-0.29238236	-0.30420281	-0.30153326
6	-0.29608765	-0.30643687	-0.30117733
∞	-0.30117733 ^b		

^a r(OH) = 0.968565 Å, α(HOH) = 103.999825

^b 5→6 X⁻³ extrapolation

Table A.4: Scaled Hamiltonian results for H₂O

CO, r=1.128323 Å ^a , MP2			
VXZ	conventional	scaled	X ⁻³
D	-0.28675617	-0.39502497	
T	-0.35508996	-0.39939728	-0.38386208
Q	-0.38097268	-0.40192326	-0.39986007
5	-0.39167409	-0.40389567	-0.40290180
6	-0.39651766	-0.40839195	-0.40317093
∞	-0.40317093 ^b		

^a from reference [1]

^b 5→6 X⁻³ extrapolation

Table A.5: Scaled Hamiltonian results for CO

A.2.2 Weighted atomic scaling

H ₂ O ^a , MP2			
VXZ	conventional	scaled	X ⁻³
D	-0.20248326	-0.27598934	
T	-0.26233477	-0.29113089	-0.28753541
Q	-0.28366041	-0.29690446	-0.29922236
5	-0.29238236	-0.29931091	-0.30153326
6	-0.29608765	-0.30014598	-0.30117733
∞	-0.30117733 ^b		

^a r(OH) = 0.968565 Å, α(HOH) = 103.999825

^b 5→6 X⁻³ extrapolation

Table A.6: Scaled Hamiltonian results for H₂O

CO, r=1.128323 Å ^a , MP2			
VXZ	conventional	scaled	X ⁻³
D	-0.28675617	-0.38872711	
T	-0.35508996	-0.39688156	-0.38386208
Q	-0.38097268	-0.40036211	-0.39986007
5	-0.39167409	-0.40181085	-0.40290180
6	-0.39651766	-0.40260044	-0.40317093
∞	-0.40317093 ^b		

^a from reference [1]

^b 5→6 X⁻³ extrapolation

Table A.7: Scaled Hamiltonian results for CO

Appendix B

Completeness Relationships

B.1 Integrals

For the implementation of the projected Hamiltonians some special integrals involving the correlation factors are needed which are given by equations B.1, B.2 and B.3 where f_{12} is a generic correlation factor. The factor $-\frac{1}{2}$ included in the kinetic energy operator has been omitted from equations B.2 and B.3. The standard integrals of R12 theory are not sufficient due to an asymmetry in the expressions that determine the new matrix elements. Integrals B.2 and B.3 are related to each other but explicit expressions for both will be given in this section.

$$\langle ac|f_{12}|bd\rangle \tag{B.1}$$

$$\langle ac|\nabla_1^2 f_{12}|bd\rangle = \langle ac|\{\nabla_1^2 f_{12}\} + 2\{\vec{\nabla}_1 f_{12}\}\vec{\nabla}_1 + f_{12}\nabla_1^2|bd\rangle \tag{B.2}$$

$$\langle ac|f_{12}\nabla_1^2|bd\rangle \tag{B.3}$$

The integrals discussed in this section involve Cartesian Gaussians of the form B.4 where B denotes the point at which the Gaussian is centred. The derivatives of this type of function are given in terms of the very useful recurrence relations B.5 and B.6. Since in all the expression only one Cartesian component will be affected at a time the short hand notations B.7 and B.8 are introduced. With the help of these recurrence relations the integrals B.2 and B.3 can be expressed in terms of integrals of type B.1.

$$b = x_b^{l_{x,b}} y_b^{l_{y,b}} z_b^{l_{z,b}} e^{-\alpha_b r_B^2} \quad x_b = (x_1 - X_B) \quad (\text{B.4})$$

$$\frac{\partial}{\partial x_1} b = (l_{x,b} x_b^{l_{x,b}-1} - 2\alpha_b x_b^{l_{x,b}+1}) y_b^{l_{y,b}} z_b^{l_{z,b}} e^{-\alpha_b r_B^2} \quad (\text{B.5})$$

$$\frac{\partial^2}{\partial x_1^2} b = (l_{x,b}(l_{x,b}-1)x_b^{l_{x,b}-2} - 2\alpha_b(2l_{x,b}+1)x_b^{l_{x,b}} + 4\alpha_b^2 x_b^{l_{x,b}+2}) y_b^{l_{y,b}} z_b^{l_{z,b}} e^{-\alpha_b r_B^2} \quad (\text{B.6})$$

$$\frac{\partial}{\partial x_1} b = l|b(-1)\rangle - 2\alpha|b(+1)\rangle \quad (\text{B.7})$$

$$\frac{\partial^2}{\partial x_1^2} b = l(l-1)|b(-2)\rangle - 2\alpha(2l+1)|b\rangle + 4\alpha^2|b(+2)\rangle \quad (\text{B.8})$$

Equation B.9 gives an alternative definition of the vector \vec{r}_{12} . This definition is used in the following to properly generate higher angular momenta of the basis functions where products involving $x_1 - x_2$ occur.

$$x_1 - x_2 = (x_1 - X_B) - (x_2 - X_D) + (X_B - X_D) \quad \vec{r}_{12} = \vec{r}_B - \vec{r}_D + (\vec{R}_B - \vec{R}_D) \quad (\text{B.9})$$

B.1.1 r_{12} Kernels

The additional integrals needed for a correlation factor proportional to r_{12} are given by equations B.10 and B.11. Integrals with kernel r_{12} and r_{12}^{-1} are already implemented in MOLPRO [2]. Integral B.10 contains one term which corresponds to B.11. Therefore only the second and third term of B.10 need to be treated. Only the terms need for the x_1 component are given here.

$$LR = \langle ac | \nabla_1^2 r_{12} | bd \rangle = \langle ac | \frac{2}{r_{12}} + 2 \frac{\vec{r}_{12}}{r_{12}} \vec{\nabla}_1 + r_{12} \nabla_1^2 | bd \rangle \quad (\text{B.10})$$

$$RL = \langle ac | r_{12} \nabla_1^2 | bd \rangle \quad (\text{B.11})$$

$$\begin{aligned} RL = \langle ac | r_{12} \frac{\partial^2}{\partial x_1^2} | bd \rangle &= l(l-1) \langle ac | r_{12} | b(-2)d \rangle \\ &\quad - (4\alpha l + 2\alpha) \langle ac | r_{12} | bd \rangle \\ &\quad + 4\alpha^2 \langle ac | r_{12} | b(+2)d \rangle \end{aligned} \quad (\text{B.12})$$

$$\begin{aligned}
\langle ac | \frac{x_1 - x_2}{r_{12}} \frac{\partial}{\partial x_1} | bd \rangle &= l \langle ac | r_{12}^{-1} | bd \rangle & (B.13) \\
&- 2\alpha_b \langle ac | r_{12}^{-1} | b(+2)d \rangle \\
&- l \langle ac | r_{12}^{-1} | b(-1)d(+1) \rangle \\
&+ 2\alpha_b \langle ac | r_{12}^{-1} | b(+1)d(+1) \rangle \\
&+ l(X_B - X_D) \langle ac | r_{12}^{-1} | b(-1)d \rangle \\
&- 2\alpha_b(X_B - X_D) \langle ac | r_{12}^{-1} | b(+1)d \rangle
\end{aligned}$$

B.1.2 Geminal kernels

The integrals needed for a correlation factor expanded in geminals are given by equations B.14 and B.15. Expression B.15 is part of the first equation so only the three terms in B.14 need to be evaluated.

$$\langle ac | \nabla_1^2 g_{12} | bd \rangle = \langle ac | (\nabla_1^2 g_{12}) + 2\vec{\nabla}_1 g_{12} \vec{\nabla}_1 + g_{12} \nabla_1^2 | bd \rangle \quad (B.14)$$

$$\langle ac | g_{12} \nabla_1^2 | bd \rangle \quad (B.15)$$

In order to get recurrence relations for the different integral kernels the derivatives of a simple Gaussian geminal B.16 are needed. These are given by B.17 and B.18. For the integral evaluation the difference $(x_1 - x_2)$ is replaced by B.9.

$$g_{12} = e^{-\beta r_{12}^2} \quad (B.16)$$

$$\frac{\partial}{\partial x_1} e^{-\beta r_{12}^2} = -2\beta(x_1 - x_2)e^{-\beta r_{12}^2} \quad (B.17)$$

$$\frac{\partial^2}{\partial x_1^2} e^{-\beta r_{12}^2} = (4\beta^2(x_1 - x_2)^2 - 2\beta)e^{-\beta r_{12}^2} \quad (B.18)$$

The integral terms are given for the component x_1 only.

$$\begin{aligned}
\langle ac | \left(\frac{\partial^2}{\partial x_1^2} g_{12} \right) | bd \rangle &= -2\beta \langle ac | g_{12} | bd \rangle & (B.19) \\
&- 8\beta^2 \langle ac | g_{12} | b(+1)d(+1) \rangle \\
&+ 8(X_B - X_D)\beta^2 \langle ac | g_{12} | b(+1)d \rangle \\
&- 8\beta^2(X_B - X_D) \langle ac | g_{12} | bd(+1) \rangle \\
&+ 4\beta^2 \langle ac | g_{12} | b(+2)d \rangle \\
&+ 4\beta^2 \langle ac | g_{12} | bd(+2) \rangle \\
&+ 4\beta^2(X_B - X_D)^2 \langle ac | g_{12} | bd \rangle
\end{aligned}$$

$$\begin{aligned}
\langle ac | \left(\frac{\partial}{\partial x_1} g_{12} \right) \frac{\partial}{\partial x_1} | bd \rangle &= -2l\beta \langle ac | g_{12} | bd \rangle & (B.20) \\
&+ 4\beta\alpha \langle ac | g_{12} | b(+2)d \rangle \\
&+ 2l\beta \langle ac | g_{12} | b(-1)d(+1) \rangle \\
&- 4\beta\alpha \langle ac | g_{12} | b(+1)d(+1) \rangle \\
&- 2l(X_B - X_D)\beta \langle ac | g_{12} | b(-1)d \rangle \\
&- 4(X_B - X_D)\beta\alpha \langle ac | g_{12} | b(+1)d \rangle
\end{aligned}$$

$$\begin{aligned}
\langle ac | g_{12} \frac{\partial^2}{\partial x_1^2} | bd \rangle &= l(l-1) \langle ac | g_{12} | b(-2)d \rangle & (B.21) \\
&- (4\alpha l + 2\alpha) \langle ac | g_{12} | bd \rangle \\
&+ 4\alpha^2 \langle ac | g_{12} | b(+2)d \rangle
\end{aligned}$$

B.2 Strong orthogonality expressions

This section lists the two electron expressions of the projected Hamiltonian for a strongly orthogonal wavefunction. The Jastrow factor is given by equation B.22. The expression is obtained by applying a strong orthogonality projector $(1 - |i\rangle\langle i|)(1 - |j\rangle\langle j|)$ to $J = 1 + 1/2r_{12}$. Expressions for other correlation functions lead to the same form of equations although different factors may appear.

$$J_{SO} = \frac{1}{4}R_{PQRS}a_P^\dagger a_R^\dagger a_S a_Q - \frac{1}{4}R_{iQRS}a_i^\dagger a_R^\dagger a_S a_Q \\ - \frac{1}{4}R_{PQis}a_P^\dagger a_i^\dagger a_S a_Q + \frac{1}{4}R_{iQjs}a_i^\dagger a_j^\dagger a_S a_Q \quad (\text{B.22})$$

The expressions are grouped in sections that are obtained by expanding and normal ordering of $(T - M)^2$ and subsequent application of J_{SO} and J_{SO}^\dagger on those terms. Terms with particle rank greater than two have been omitted as they vanish when a Hartree-Fock reference state is used.

$$M_{ab}M_{cd}a_a^\dagger a_b a_c^\dagger a_d$$

$$J_{SO}^\dagger M_{ab}M_{cd}a_a^\dagger a_b a_c^\dagger a_d J_{SO} = \frac{1}{4}R_{PaRc}M_{ab}M_{cd}R_{bQds}a_P^\dagger a_R^\dagger a_S a_Q \\ + \frac{1}{4}R_{PaRT}M_{ab}M_{bd}R_{dQTS}a_P^\dagger a_R^\dagger a_S a_Q \\ - \frac{1}{4}R_{PaRi}M_{ab}M_{bd}R_{dQis}a_P^\dagger a_R^\dagger a_S a_Q \\ + \dots$$

$$-M_{ab}T_{bU}a_a^\dagger a_U$$

$$-J_{SO}^\dagger M_{ab}T_{bU}a_a^\dagger a_U J_{SO} = -\frac{1}{4}R_{PaRU}M_{ab}T_{bT}R_{TQU}a_P^\dagger a_R^\dagger a_S a_Q \\ + \frac{1}{4}R_{PaRT}M_{ab}T_{bi}R_{iQTS}a_P^\dagger a_R^\dagger a_S a_Q \\ + \frac{1}{4}R_{PaRi}M_{ab}T_{bT}R_{TQi}a_P^\dagger a_R^\dagger a_S a_Q \\ - \frac{1}{4}R_{PaRj}M_{ab}T_{bi}R_{iQjs}a_P^\dagger a_R^\dagger a_S a_Q \\ + \dots$$

$$-T_{Ta}M_{ab}a_T^\dagger a_b$$

$$\begin{aligned} -J_{SO}^\dagger T_{Ta}M_{ab}a_T^\dagger a_b J_{SO} &= -\frac{1}{4}R_{PTRU}T_{Ta}M_{ab}R_{bQU}S a_P^\dagger a_R^\dagger a_S a_Q \\ &+ \frac{1}{4}R_{PiRU}T_{ia}M_{ab}R_{bQU}S a_P^\dagger a_R^\dagger a_S a_Q \\ &+ \frac{1}{4}R_{PTRi}T_{Ta}M_{ab}R_{bQi}S a_P^\dagger a_R^\dagger a_S a_Q \\ &- \frac{1}{4}R_{PiRj}T_{ia}M_{ab}R_{bQj}S a_P^\dagger a_R^\dagger a_S a_Q \\ &+ \dots \end{aligned}$$

$$-2T_{TU}M_{ab}a_T^\dagger a_a^\dagger a_b a_U$$

$$\begin{aligned} -2J_{SO}^\dagger T_{TU}M_{ab}a_T^\dagger a_a^\dagger a_b a_U J_{SO} &= -\frac{1}{2}R_{PTRa}M_{ab}T_{TU}R_{UQb}S a_P^\dagger a_R^\dagger a_S a_Q \\ &+ \frac{1}{2}R_{PiRa}M_{ab}T_{iU}R_{UQb}S a_P^\dagger a_R^\dagger a_S a_Q \\ &+ \frac{1}{2}R_{PTRa}M_{ab}T_{Ti}R_{iQb}S a_P^\dagger a_R^\dagger a_S a_Q \\ &- \frac{1}{2}R_{PiRa}M_{ab}T_{ij}R_{jQb}S a_P^\dagger a_R^\dagger a_S a_Q \\ &+ \dots \end{aligned}$$

B.3 Two electron proof

In this section it will be proven that only two electron terms are needed in the strong orthogonality framework when the reference state is a the Hartree-Fock wavefunction. In order to shorten the notation where necessary an alternative notation for second quantisation expressions is introduced to replace terms such as $h_{pq}a_p^\dagger a_q$ by either $h_{pq}\hat{X}_{pq}$ or simply h_{pq} .

$$\begin{aligned} \langle 0 | J_{so}^\dagger (T_{TU} - M_{ab})^2 J_{so} | 0 \rangle \\ J_{SO} = \frac{1}{4}R_{PQRS} - \frac{1}{4}R_{iQRS} - \frac{1}{4}R_{PQiS} + \frac{1}{4}R_{iQjS} \end{aligned} \quad (\text{B.23})$$

Expanding the the central term $(T_{TU} - M_{ab})^2$ one obtains the following one and two electron terms where the quadratic term in T was omitted as it will drop out under differentiation. The signs are ignored for simplicity.

one electron	two electron
$M_{ab}M_{cd}\delta_{bc}a_a^\dagger a_d$	$M_{ab}M_{cd}a_a^\dagger a_c^\dagger a_d a_b$
$T_{TU}M_{ab}\delta_{Ua}a_T^\dagger a_b$	$2T_{TU}M_{ab}a_a^\dagger a_T^\dagger a_U a_b$
$M_{ab}T_{TU}\delta_{bT}a_a^\dagger a_U$	

In a first step it will be shown that the terms in M_{ab} can only generate two electron contributions. Use is made of the fact that $\langle a|i\rangle = 0$. This means that the only non vanishing contributions arise from terms where the virtual indices are picked up by the complete basis functions in the Jastrow factor. Hence the two electron component $M_{ab}M_{cd}$ can only generate two electron terms. Therefore it remains to show what happens when $M_{ab}M_{cd}\delta_{bc}$ is involved in a three electron term where a and d are picked up by J_{SO} and J_{SO}^\dagger . These terms are listed in table B.1 and a close inspection reveals that although II.1 and II.2 exist on their own they clearly cancel and the same is true for III.1 and III.2 in table B.1. However cancellation only occurs due to the fact that a Hartree-Fock determinant is used to compute the expectation values.

$J_{SO}^\dagger \times M_{ab}M_{cd}\delta_{bc} \times J_{SO}$			
$M_{ab}M_{cd}\delta_{bc} \times J_{SO}$			
I.1		$\frac{1}{2}M_{ab}M_{cd}R_{PQRS}\delta_{bc}\delta_{dP}$	$\frac{1}{4}R_{PQRS}$
I.2		$-\frac{1}{2}M_{ab}M_{cd}R_{PQIS}\delta_{bc}\delta_{dP}$	$-\frac{1}{2}R_{PQIS}$
$J_{SO}^\dagger \times \text{I.1}$			
II.1	$\frac{1}{4}R_{VWXY}$	$\frac{1}{4}R_{VWXY}M_{ab}M_{cd}R_{PQRS}\delta_{Wa}\delta_{bc}\delta_{dP}\hat{X}_{VQ,XY,RS}$	
II.2	$-\frac{1}{2}R_{VWXj}$	$-\frac{1}{4}R_{VWXj}M_{ab}M_{cd}R_{PQRS}\delta_{Wa}\delta_{bc}\delta_{dP}\hat{X}_{VQ,Xj,RS}$	
$J_{SO}^\dagger \times \text{II.2}$			
III.1	$\frac{1}{4}R_{VWXY}$	$-\frac{1}{4}R_{VWXY}M_{ab}M_{cd}R_{PQIS}\delta_{Wa}\delta_{bc}\delta_{dP}\hat{X}_{VQ,XY,iS}$	
III.2	$-\frac{1}{2}R_{VWXj}$	$\frac{1}{4}R_{VWXj}M_{ab}M_{cd}R_{PQIS}\delta_{Wa}\delta_{bc}\delta_{dP}\hat{X}_{VQ,Xj,iS}$	

Table B.1: Three electron terms in M^2

For the terms involving T_{TU} and M_{ab} the situation is slightly more complex. For the true kinetic energy operator contributions involving the occupied functions exist but all occurrences where T_{TU} does not act on the Jastrow factor J_{SO} have to be eliminated

from the start in order to retain the strong orthogonality imposed. A direct consequence of this is that one only has to consider the three electron terms created by $T_{TU}M_{ab}\delta_{Ua}$ and $M_{ab}T_{TU}\delta_{bT}$. Where only a proof for the former will be conducted as the result for the latter becomes obvious by investigating the symmetry of the equations.

Table B.2 shows the terms obtained by applying J_{SO} to $T_{TU}M_{ab}\delta_{Ua}$. The relevant blocks are II and III. By restricting the indices of the excitation operators $\hat{X}_{EF,GB,CD}$ to the occupied part of the vector space it becomes clear that the terms in both blocks cancel.

$J_{SO}^\dagger \times T_{TU}M_{ab}\delta_{Ua} \times J_{SO}$			
$T_{TU}M_{ab}\delta_{Ua} \times J_{SO}$			
I.1		$\frac{1}{2}T_{TU}M_{ab}R_{PQRS}\delta_{Ua}\delta_{bP}$	$\frac{1}{4}R_{PQRS}$
I.2		$-\frac{1}{2}T_{TU}M_{ab}R_{PQis}\delta_{Ua}\delta_{bP}$	$-\frac{1}{2}R_{PQis}$
$J_{SO}^\dagger \times I.1$			
II.1	$\frac{1}{4}R_{VWXY}$	$\frac{1}{4}R_{VWXY}T_{TU}M_{ab}R_{PQRS}\delta_{YT}\delta_{Ua}\delta_{bP}\hat{X}_{VW,XQ,RS}$	
II.2	$-\frac{1}{2}R_{VkXY}$	$-\frac{1}{4}R_{VkXY}T_{TU}M_{ab}R_{PQRS}\delta_{YT}\delta_{Ua}\delta_{bP}\hat{X}_{Vk,XQ,RS}$	
II.3		$-\frac{1}{4}R_{VkXY}T_{TU}M_{ab}R_{PQRS}\delta_{kT}\delta_{Ua}\delta_{bP}\hat{X}_{VQ,XY,RS}$	
II.4	$\frac{1}{4}R_{VkXl}$	$\frac{1}{4}R_{VkXl}T_{TU}M_{ab}R_{PQRS}\delta_{kT}\delta_{Ua}\delta_{bP}\hat{X}_{VQ,Xl,RS}$	
$J_{SO}^\dagger \times II.2$			
III.1	$\frac{1}{4}R_{VWXY}$	$-\frac{1}{4}R_{VWXY}T_{TU}M_{ab}R_{PQis}\delta_{YT}\delta_{Ua}\delta_{bP}\hat{X}_{VW,XQ,is}$	
III.2	$-\frac{1}{2}R_{VkXY}$	$\frac{1}{4}R_{VkXY}T_{TU}M_{ab}R_{PQis}\delta_{YT}\delta_{Ua}\delta_{bP}\hat{X}_{Vk,XQ,is}$	
III.3		$\frac{1}{4}R_{VkXY}T_{TU}M_{ab}R_{PQis}\delta_{kT}\delta_{Ua}\delta_{bP}\hat{X}_{VQ,XY,is}$	
III.4	$\frac{1}{4}R_{VkXl}$	$-\frac{1}{4}R_{VkXl}T_{TU}M_{ab}R_{PQis}\delta_{kT}\delta_{Ua}\delta_{bP}\hat{X}_{VQ,Xl,is}$	

Table B.2: Allowed three electron terms in T and M

B.4 Hermitian constraint

Being hermitian is crucial for the projected Hamiltonian. In order to compute the matrix elements some difficult integrals are approximated by the use of the resolution of the identity. How the resolution of the identity is applied determines whether the matrix elements form a symmetric matrix or whether symmetry has to be enforced. Equation B.24 contains two indices in the complete basis¹. One of those indices has to be replaced with RI. In the case of a correlation factor of r_{12} it is tempting to only replace the index T with the finite set of functions because this generates the singularity that is missing in the principal wave expansion. It will be shown in the following however that one needs to insert the resolution of the identity in a symmetrised fashion in order to preserve hermiticity.

$$R_{iT ja} T_{TU} M_{ab} R_{Uibj} - R_{iT ja} T_{TU} M_{ab} R_{Ujbi} \quad (\text{B.24})$$

In order to show the effects of RI it is necessary to investigate the properties of the integral kernels $f_{12} \nabla_1^2$ and $\nabla_1^2 f_{12}$. Both of these terms are related to each other. This will be shown in the following by using Greens theorem[23]:

$$\int_V u \nabla^2 v d\tau = \int_S u \vec{\nabla} v d\sigma - \int_V (\vec{\nabla} u) (\vec{\nabla} v) d\tau \quad (\text{B.25})$$

The analysis is carried out in equation B.26 through B.28 for a generic correlation factor f_{12} . By applying Greens theorem[23] twice and making use of the fact that the integral over the surface is zero as a result of the boundary conditions a relation is established which in the finite basis takes the form of B.29.

$$\int u \nabla_1^2 \{f_{12} v\} d\tau = \underbrace{\int u [\vec{\nabla}_1 f_{12} v] d\sigma}_0 - \int [\vec{\nabla}_1 u] [\vec{\nabla}_1 f_{12} v] d\tau \quad (\text{B.26})$$

$$= - \underbrace{\int [\vec{\nabla}_1 v] [f_{12} v] d\tau}_0 + \int [\nabla_1^2 u] [f_{12} v] d\tau \quad (\text{B.27})$$

$$= \int v f_{12} \nabla_1^2 u d\tau \quad (\text{B.28})$$

¹All expressions in this section are in given in spin orbital form.

$$\langle pr | \nabla_1^2 r_{12} | qs \rangle = \langle qs | r_{12} \nabla_1^2 | pr \rangle \quad (\text{B.29})$$

B.4.1 Non symmetric RI

Equation B.30 shows expression B.24 after resolution of the identity was applied to the index T .

$$R_{ipja} M_{ab} T R_{pibj} - R_{ipja} M_{ab} T R_{pjbi} \quad (\text{B.30})$$

In order to show that in this way one receives a non symmetric matrix one needs to consider the vector elements for M_{ab} and M_{ba} . These are given by equations B.31 and B.32 which are obviously different as there is no way to rearrange them to be equal.

$$M_{ab} \rightarrow R_{ipja} T R_{pibj} - R_{ipja} T R_{pjbi} \quad (\text{B.31})$$

$$M_{ba} \rightarrow R_{ipjb} T R_{piaj} - R_{ipjb} T R_{pjai} \quad (\text{B.32})$$

B.4.2 Symmetric RI

Equations B.33 and B.34 show symmetrised variants of the coulomb and exchange terms of equation B.30.

$$\frac{1}{2} R_{ipja} M_{ab} T R_{pibj} + \frac{1}{2} R T_{ipja} M_{ab} R_{pibj} \quad (\text{B.33})$$

$$-\frac{1}{2} R_{ipja} M_{ab} T R_{pjbi} - \frac{1}{2} R T_{ipja} M_{ab} R_{pjbi} \quad (\text{B.34})$$

The terms that determine M_{ab} and M_{ba} are given by B.35 and B.36.

$$M_{ab} \rightarrow \frac{1}{2} R_{ipja} T R_{pibj} + \frac{1}{2} R T_{ipja} R_{pibj} \quad (\text{B.35})$$

$$-\frac{1}{2} R_{ipja} T R_{pjbi} - \frac{1}{2} R T_{ipja} R_{pjbi}$$

$$M_{ba} \rightarrow \frac{1}{2} R_{ipjb} T R_{piaj} + \frac{1}{2} R T_{ipjb} R_{piaj} \quad (\text{B.36})$$

$$-\frac{1}{2} R_{ipjb} T R_{pjai} - \frac{1}{2} R T_{ipjb} R_{pjai}$$

By application of B.29 the coulomb term in B.36 can be converted to the corresponding expression in B.35 as shown by equation B.37

$$\frac{1}{2}R_{ipjb}TR_{piaj} + \frac{1}{2}RT_{ipjb}R_{piaj} = \frac{1}{2}R_{ipja}TR_{pibj} + \frac{1}{2}RT_{ipja}R_{pibj} \quad (\text{B.37})$$

The equivalence for the exchange terms is slightly more complicated. First the index labels i and j are swapped in B.38. Then B.29 is applied in B.39 which yields B.40.

$$-\frac{1}{2}R_{ipjb}TR_{pjai} - \frac{1}{2}RT_{ipjb}R_{pjai} \quad \sum_{ij} : i \leftrightarrow j \quad (\text{B.38})$$

$$-\frac{1}{2}R_{jpib}TR_{piaj} - \frac{1}{2}RT_{jpib}R_{piaj} \quad \rightarrow \text{B.29} \quad (\text{B.39})$$

$$-\frac{1}{2}RT_{ipja}R_{pjbi} - \frac{1}{2}R_{ipja}TR_{pjbi} \quad (\text{B.40})$$

With this the proof is completed as both the coulomb and exchange terms of B.36 have been turned into the same expressions as the ones in B.35.

B.5 Automatic code generation

The implementation of the projected Hamiltonian or completeness relationships was greatly assisted by an automated code generation procedure. It would have been very hard to implement the Lagrangian multiplier variant without this tool. Although the strongly orthogonal expressions are much more manageable the availability of the automatic code generation tool meant that several ideas could be tested with ease. In the following some insight into the employed techniques will be given.

B.5.1 Normal ordering

This section describes an algorithm for the normal ordering of strings of creation and annihilation operators such as $a_p^\dagger a_q a_r^\dagger a_s$. A normal ordered string is one which has all annihilation operators to the right and all creation operators to the left. The described procedure was implemented in a C++ program. To simplify the notation the a^\dagger and a are expressed as C and A respectively.

The algorithm is also illustrated in figure B.1. In the first step the operators are put into an array and a pointer is set to the leftmost element. This pointer is moved to the right until an annihilation operator is encountered which has a creation operator to its right. At this stage two new strings are generated which have the operators swapped and resolved into a Kronecker delta. At this stage the procedure is repeated on both of the new strings. If the pointer hits the last element in the list the string is sorted.

B.5.2 Contracting equivalent expressions

The normal ordering of second quantisation expressions will usually lead to many terms which are not necessarily distinct. It is therefore of central importance to reduce these expressions. Investigation of the underlying combinatorics of normal ordering reveals the extent of the problem. By multiplying an n and an m electron operator one gets terms of $\max(n, m)$ up to $(n + m)$ electron type while there will be for instance $\max(n, m)! / |n - m|!$ ($\max(n, m)$)-electron terms. This example clearly shows that the number of terms grows very rapidly.

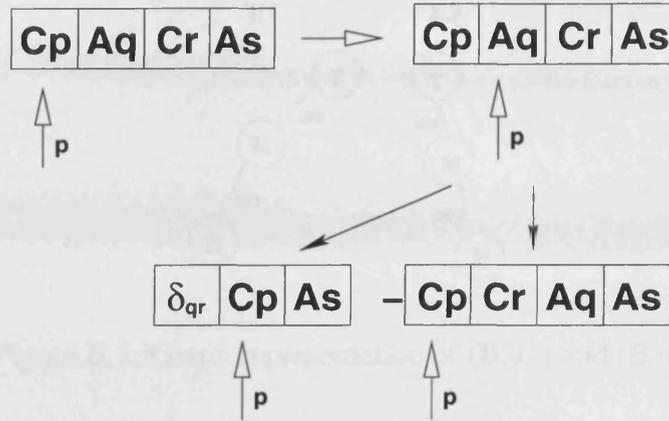


Figure B.1: Normal ordering procedure

$$E1 = T_{TU}M_{pq}R_{PQRS}\delta_{Up}\delta_q p a_T^\dagger a_R^\dagger a_S a_Q \tag{B.41}$$

$$E2 = T_{TU}M_{pq}R_{PQRS}\delta_{Up}\delta_q r a_T^\dagger a_P^\dagger a_Q a_S \tag{B.42}$$

Expressions (B.41) and (B.42) are clearly equal. The problem is to find a representation which can easily be handled in a computer program to determine equality. It was realised that a possible solution to this problem is the representation of these expressions as directed graphs[64]. The tensor elements in (B.41) and (B.42) are represented as vertices where the name of the tensor defines the colour of the vertex. Arcs are inserted to represent the Kronecker deltas. The arcs need to be weighted as not all Kronecker deltas are equal. δ_{Up} refers to the incomplete space for instance where δ_{UP} would refer to the complete space. A simplified graph representation for (B.41) and (B.42) is given in figure B.2 which makes the equality obvious. If there are some elementary operators which do not refer to arbitrary function as in (B.41) and (B.42) additional vertices have to be added in order to allow for a unique representation of these properties as well.

A graph isomorphism algorithm was implemented from scratch which tries to bring the weighted adjacency matrices of two graphs to congruence. It was however realised that for these small graphs it is very likely that there exists some invariant which would allow more efficient isomorphism testing². Although the used algorithm relies on brute

²Most of the graphs are in fact directed trees

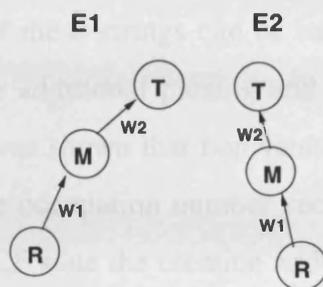


Figure B.2: Graph representation of (B.41) and (B.42)

force permutation generation inside subclasses of vertices [44] there is almost no time spent in isomorphism testing as all graphs are very small.

B.5.3 Expectation values

Once a suitable set of expressions is obtained the remaining step is to evaluate the expectation values of the second quantisation terms between occupation number vectors[74]. This is easily done in the case of one and two electron operators but requires a little bit more work for contributions with higher particle rank. This section focuses on the generation of expectation values of a closed shell Hartree-Fock determinant. However spin orbital expressions for differing ON vectors can be readily obtained by following the same approach and generating the appropriate permutations for the bra and the ket vectors.

In their book Szabo and Ostlund [5] point out that an expectation value for the Hartree-Fock case can be obtained by restricting the indices of the elementary operators to the occupied space and subsequent reversal of normal ordered expression as shown in equation (B.43). It is obvious that the second term yields zero as a_i^\dagger attempts to create an electron in an already occupied orbital and the familiar expression results. For an N electron operator reversing would yield $N!$ terms involving only Kronecker deltas where the index combinations are determined by all possible permutations.

$$\langle 0|h_{ij}a_i^\dagger a_j|0\rangle = \langle 0|h_{ij}\delta_{ij} - a_j a_i^\dagger|0\rangle = h_{ii} \quad [5] \quad (\text{B.43})$$

Although the reordering of these strings can be easily performed³ it is somewhat inefficient as it requires some additional parsing and generates many terms that are not needed. In section 1.4 it was shown that non vanishing terms only arise when the elementary operators bring the occupation number vectors to congruence. Since both bra and ket are equal to the SCF state the creation and annihilation operators must act on the same set of indices. The task is therefore to generate all permutations of these indices. The Johnson-Trotter⁴ algorithm was implemented according to reference [63] and used to create the necessary permutations. The generation scheme is illustrated in table B.3.

$\langle 0 \hat{O}_{pqrstu} a_p^\dagger a_r^\dagger a_t^\dagger a_u a_s a_q 0 \rangle$					
<i>p</i>	<i>r</i>	<i>t</i>	<i>q</i>	<i>s</i>	<i>u</i>
<i>ijk</i>	<i>ijk</i>	$\langle ijk \hat{O} ijk \rangle$	<i>ijk</i>	<i>kji</i>	$-\langle ijk \hat{O} kji \rangle$
<i>ijk</i>	<i>jik</i>	$-\langle ijk \hat{O} jik \rangle$	<i>ijk</i>	<i>kij</i>	$\langle ijk \hat{O} kij \rangle$
<i>ijk</i>	<i>jki</i>	$\langle ijk \hat{O} jki \rangle$	<i>ijk</i>	<i>ikj</i>	$-\langle ijk \hat{O} ikj \rangle$

Table B.3: Expectation value generation

The next task is to translate the spin orbital formulae into expressions which contain only the spatial orbitals. The sums in (B.44) show how one would proceed to eliminate the electron spin from the expectation values. It was realised that combinations of alpha and beta spin patterns in the functions corresponds to the n -bit long binary strings (B.45) from 0 to $2^n - 1$ where the i -th bit corresponds to the spin function associated with orbital i . By reordering the bit string according to the permutation of the bra and the ket two signatures are created. If both patterns are equal the term is spin allowed otherwise spin forbidden. An example is provided in table B.4 for a two particle operator.

$$\sum_{i=1}^N \sum_{j=1}^N ij \rightarrow \sum_{i=1}^{N/2} \sum_{j=1}^{N/2} (i + \bar{i})(j + \bar{j}) \rightarrow \sum_{i=1}^{N/2} \sum_{j=1}^{N/2} ij + i\bar{j} + \bar{i}j + \bar{i}\bar{j} \quad [5] \quad (\text{B.44})$$

$$ij + i\bar{j} + \bar{i}j + \bar{i}\bar{j} \rightarrow \{00, 01, 10, 11\} \quad (\text{B.45})$$

³This is just the opposite case of normal ordering.

⁴Sometimes also referred to as Steinhaus-Johnson-Trotter algorithm.

	$\frac{1}{2} \langle ij ij \rangle$	$-\frac{1}{2} \langle ij ji \rangle$
ij	$0 = \alpha$	$1 = \beta$
00	$\langle 00 00 \rangle$	$\langle 00 00 \rangle$
01	$\langle 01 01 \rangle$	$\langle 01 10 \rangle = 0$
10	$\langle 10 10 \rangle$	$\langle 10 01 \rangle = 0$
11	$\langle 11 11 \rangle$	$\langle 11 11 \rangle$
	$2 \langle ij ij \rangle$	$-\langle ij ji \rangle$

Table B.4: Spatial orbital resolution

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