AWESOME TITLE

by

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Abstract

This is an abstract text.

To someone

This is a dedication to my cat.

Acknowledgements

I acknowledge my acknowledgements.

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Theory

Chapter 1

From quantum mechanics to higher scales

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Many-body theory

This chapter discusses the basic quantum mechanics of identical fermions. First the Hamiltian is introduced, and the fundamental properties of fermionic wave functions are examinded. Then the reference energy, that is, the expectation value of the Hamiltonian calculated on the basis of some chosen reference Slater determinant, is derived. The chapter ends with a review of second quantization.

2.1   The Hamiltonian

Our task is to solve the time independent Schrödinger equation:

$$H|\Psi\rangle = E|\Psi\rangle, \tag{2.1}$$

where H is the Hamiltonian of the system and E is the energy. For atomic systems consisting of N electrons and K nuclei the Hamiltonian of the electrons is given by

$$H = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 - \sum_{i=1}^{N}\sum_{n=1}^{K}\frac{Z_n}{|\mathbf{R}_n - \mathbf{r}_i|} + \frac{1}{2}\sum_{\substack{i,j=1 \\ i\neq j}}^{n}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}, \tag{2.2}$$

where $\mathbf{r}_i$ and $\mathbf{R}_n$ are the positions of the electrons and nuclei, respectively, and Z_n are the charges of the nuclei, all in atomic units. The terms represent the kinetic energy of the electrons, the potential energy due to the interaction between the nuclei and electrons and the potential energy due to the interaction between the electrons, respectively. If the total energy of the whole system is of interest, the kinetic energy of the nuclei and the potential energy due to the interaction between the nuclei should be added. However,

the first of these is most often neglected because the nuclei move much slower than the electrons. This is the so-called Born-Oppenheimer approximation. We shall stick to it in this thesis.

The Hamiltonian (2.2) is often split into a one-body part, H_1, and a two-body part, H_2:

$$H = H_1 + H_2 \tag{2.3}$$

where

$$H_1 = \sum_{i=1}^{N} h(\mathbf{r}_i) = \sum_{i=1}^{N} \left[-\frac{1}{2}\nabla_i^2 - \sum_{n=1}^{K} \frac{Z_n}{|\mathbf{R}_n - \mathbf{r}_i|} \right], \tag{2.4}$$

$$H_2 = \frac{1}{2}\sum_{\substack{i,j=1 \\ i\neq j}}^{N} g(\mathbf{r}_i, \mathbf{r}_j) = \frac{1}{2}\sum_{\substack{i,j=1 \\ i\neq j}}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}. \tag{2.5}$$

If we neglect the term H_2, the Schrödinger equation is separable and easy to solve. One possible solution is the so-called Hartree wave function, Ψ_H, which is defined as:

$$\Psi_H(\mathbf{x}_1, \ldots, \mathbf{x}_N) = \psi_1(\mathbf{x}_1) \cdots \psi_N(\mathbf{x}_N), \tag{2.6}$$

where $\psi_i(\mathbf{x})$ is the single-particle wave function, named spinorbital, which solves the single-particle Schrödinger equation

$$\left(-\frac{1}{2}\nabla^2 - \sum_{i=1}^{N} \frac{Z_n}{|\mathbf{R}_n - \mathbf{r}|} \right)\psi_i(\mathbf{x}) = \varepsilon_i\psi_i(\mathbf{x}). \tag{2.7}$$

The total energy of the system is then $E = \sum_{i=1}^{N} \varepsilon_i$.

The spinorbitals $\psi_k(\mathbf{x})$ are functions of both spatial and spin coordinates, that is $\mathbf{x} = (\mathbf{r}, s)$, hence the name. In this thesis we will assume that the spinorbitals can be written as a product of a spatial part and a spin part:

$$\psi_k(\mathbf{x}) = \phi_k(\mathbf{r})\xi_k(s), \tag{2.8}$$

where $\xi_k(s)$ is either $\alpha(s)$ or $\beta(s)$. The spin functions are defined by

$$\alpha(s) = \begin{cases} 1 & \text{if} \quad s = \uparrow \\ 0 & \text{if} \quad s = \downarrow \end{cases}, \tag{2.9}$$

and

$$\beta(s) = \begin{cases} 0 & \text{if} \quad s = \uparrow \\ 1 & \text{if} \quad s = \downarrow \end{cases}. \tag{2.10}$$

The spinorbitals are assumed to be normalized:

$$\int d\mathbf{x}\,\psi_k^*(\mathbf{x})\psi_k(\mathbf{x}) = 1, \tag{2.11}$$

where integration over $\mathbf{x}$ is defined as

$$\int d\mathbf{x} = \sum_{s=\uparrow\downarrow}\int d\mathbf{r}. \tag{2.12}$$

Unfortunately, the term H_2 must be taken into account, and this makes the Schrödinger equation considerably more difficult to solve. In fact, except for a few simple systems, no analytical solution is known and approximative methods are needed. Chapter xxx gives a survey of some of the most popular methods.

2.2 The fermionic many-particle wave function

For the simple case where $H = H_1$, the Hartree wave function, Ψ_H, in equation (2.6) solves the Schrödinger equation. However, it is still not a physically valid solution. Why? Because the solution does not reflect the fact that we are dealing with *identical* particles. To see what is wrong with the solution, let us consider a system of N identical particles in the state $|\Psi\rangle$. Suppose we want to calculate the expectation value $\langle B \rangle$ of some observable B. Since the particles are identical, $\langle B \rangle$ should not change if we were to switch the coordinates of two particles i and j, say. If P_{ij} is the operator which changes the coordinates of particles i and j we must therefore have

$$\langle P_{ij}\Psi|B|P_{ij}\Psi\rangle = \langle\Psi|B|\Psi\rangle, \tag{2.13}$$

which means that

$$P_{ij}^\dagger B P_{ij} = B. \tag{2.14}$$

Multiplying this equation from the right by P_{ij} gives

$$P_{ij}^\dagger B = B P_{ij}, \tag{2.15}$$

since $P_{ij}^2 = I$. For the special case where $B = I$ this means that $P_{ij}^\dagger = P_{ij}$. From this we can draw the following interesting conclusions:

1. The permutation operator is Hermitian, i.e. $P_{ij}^\dagger = P_{ij}$.

2. The permutation operator is unitary, i.e. $P_{ij}^\dagger = P_{ij}^{-1}$.

3. The permutation operator commutes with any observable B,
   i.e. $[P_{ij}, B] = 0$. This means that it is possible to find states which diagonalize both P_{ij} and B.

It is now possible to determine what the eigenvalue of P_{ij} must be. Suppose that it is some number p. Then the eigenvalue of P_{ij}^2 is p^2. But we know that $p^2 = 1$ (since $P_{ij}^2 = I$). This, together with the fact that P_{ij} is Hermitian[1], implies that $p = \pm 1$. This means that the state $|\Psi\rangle$ is either symmetric or antisymmetric with respect to particle interchange. Particles with a symmetric state are called bosons, and particles with an antisymmetric state are called fermions. This thesis deals with fermions only. The fact that the wave function of fermions is antisymmetric with respect to the exchange of particle coordinates is called the Pauli principle.

It is now obvious why (2.6) cannot be a physically correct solution; it is neither symmetric nor antisymmetric. However, we can make it antisymmetric by applying the antisymmetrization operator $\mathcal{A}$. It is defined by

$$\mathcal{A} = \frac{1}{N!} \sum_P (-1)^p P, \qquad (2.16)$$

where P is a permutation operator, p is the number of interchanges in P and the sum is over all permutations. The permutation operator P can always be written as

$$P = P_{ij} P_{kl} \cdots P_{ps}. \qquad (2.17)$$

Because each operator in the product is Hermitian, so is the permutation operator P.

A solution of the Schrödinger equation which also satisfies the antisymmetry requirement is given by

$$\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N) = \sqrt{N!}\, \mathcal{A}\, \Psi_H(\mathbf{x}_1, \ldots, \mathbf{x}_N). \qquad (2.18)$$

Another common way of writing this is through the determinant

$$\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\mathbf{x}_1) & \ldots & \psi_N(\mathbf{x}_1) \\ \vdots & & \vdots \\ \psi_1(\mathbf{x}_N) & \ldots & \psi_N(\mathbf{x}_N) \end{vmatrix} \qquad (2.19)$$

The wave function in (2.18) and (2.19) is called a Slater determinant. From the last equation it is seen that if two single-particle wave functions are equal,

---

[1]Recall that the eigenvalues of a Hermitian operator are real.

the total wave function vanishes. This means that two identical fermions cannot occupy the same single-particle state. The total wave function also vanishes if the coordinates of two particles are the same. This translates to the fact that two fermions with equal spins cannot be located at the same point in space.

It i useful to illustrate these last remarks with an example of two electrons. Assume that the electrons occupy the spinorbitals $\{\psi_i(\mathbf{x}) = \phi_i(\mathbf{r})\xi_i(s)\}_{i=1}^2$, where $\{\phi_i(\mathbf{r})\}_{i=1}^2$ are the spatial parts and $\{\xi(s)\}_{i=1}^2$ are the spin parts, and let us construct the Slater determinant from these spinorbitals. Consider now the probability density $\rho(\mathbf{x}_1, \mathbf{x}_2)$ to observe one of the particles with coordinate $\mathbf{x}_1$ and the other with coordinate $\mathbf{x}_2$:

$$
\begin{aligned}
\rho(\mathbf{x}_1, \mathbf{x}_2) &= \langle \Psi | \Psi \rangle \\
&= \frac{1}{2}|\psi_1(\mathbf{x}_1)\psi_2(\mathbf{x}_2) - \psi_2(\mathbf{x}_1)\psi_1(\mathbf{x}_2)|^2 \\
&= \frac{1}{2}\Big[|\psi_1(\mathbf{x}_1)|^2|\psi_2(\mathbf{x}_2)|^2 + |\psi_2(\mathbf{x}_1)|^2|\psi_1(\mathbf{x}_2)|^2 \\
&\quad - \psi_1^*(\mathbf{x}_1)\psi_2^*(\mathbf{x}_2)\psi_2(\mathbf{x}_1)\psi_1(\mathbf{x}_2) - \psi_2^*(\mathbf{x}_1)\psi_1^*(\mathbf{x}_2)\psi_1(\mathbf{x}_1)\psi_2(\mathbf{x}_2)\Big].
\end{aligned}
\tag{2.20}
$$

In order to find the probability density $\rho(\mathbf{r}_1, \mathbf{r}_2)$ to observe the particles at *spatial positions* $\mathbf{r}_1$ and $\mathbf{r}_2$, we need to integrate with respect to the spin coordinates s_1 and s_2. However, the result of this integration depends upon the specific spin configuration of the particles.

Let us first assume that the particles have the same spatial orbital, but opposite spins, i.e. that $\phi_1 = \phi_2 = \phi$ and $\xi_1 \neq \xi_2$. The last two negative terms of the above equation will then vanish, and we are left with

$$
\rho(\mathbf{r}_1, \mathbf{r}_2) = |\phi(\mathbf{r}_1)|^2|\phi(\mathbf{r}_2)|^2.
\tag{2.21}
$$

This expression shows explicitly that the positions of the two electrons are uncorrelated, that is to say, the probability distribution of one electron has no effect on the probability distribution of the other. In fact, the expression above is the statistical definition of uncorrelated probability distributions.

Next, consider the case where the electrons have different spatial orbitals, but equal spins, i.e. that $\phi_1 \neq \phi_2$ and $\xi_1 = \xi_2$. Integrating over the spin coordinates then gives

$$
\begin{aligned}
\rho(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2}\Big[&|\phi_1(\mathbf{r}_1)|^2|\phi_2(\mathbf{r}_2)|^2 + |\phi_2(\mathbf{r}_1)|^2|\phi_1(\mathbf{r}_2)|^2 \\
&- \phi_1^*(\mathbf{r}_1)\phi_2^*(\mathbf{r}_2)\phi_2(\mathbf{r}_1)\phi_1(\mathbf{r}_2) - \phi_2^*(\mathbf{r}_1)\phi_1^*(\mathbf{r}_2)\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)\Big].
\end{aligned}
\tag{2.22}
$$

The positions of the two electrons are now obviously correlated. Furthermore, it is seen that the probability to find the two electrons at the same position is equal to zero. This means that there is some kind of "force" acting between the particles which pushes them away from each other. This "force" is often referred to as the exchange force. It is not a force in the classical sense, but a statistical effect which arises due to the antisymmetry of the wave function.

This discussion illustrates a point which will become important later when we discuss Hartree-Fock theory: The exchange force, which pushes electrons apart, is only acting between electrons with opposite spins.

2.3   The reference energy

Even though the Slater determinant in (2.18) and (2.19) does not solve the Schrödinger equation of the full Hamiltonian (2.3), it can nevertheless be used as an anzats to estimate the energy. We call this energy the reference energy.

Although we thus far have assumed that the single-particle wave functions are eigenfunctions of H_1 (see equation (2.4)), this is not necessary; they can for example be the eigenfunctions of the Fock operator $\mathcal{F}$, which will improve the value of the reference energy. The Hartree-Fock equations are discussed in chapter xxx.

As stated above, the reference energy is simply the expectation value of the Hamiltonian calculated on the basis of some assumed reference Slater determinant $|\Psi\rangle$:

$$E_{ref} = \langle \Psi | H | \Psi \rangle. \tag{2.23}$$

Inserting the Slater determinant (2.18) yields

$$E_{ref} = N! \int d\mathbf{x}_1 \dots d\mathbf{x}_N (\mathcal{A}\Psi_H(\mathbf{x}_1 \cdots \mathbf{x}_N))^* H \mathcal{A}\Psi_H(\mathbf{x}_1 \cdots \mathbf{x}_N). \tag{2.24}$$

By using the fact that $\mathcal{A}$ is Hermitian and commutes with H as well as the fact that $\mathcal{A}^2 = \mathcal{A}$ this can be simplified to

$$E_{ref} = N! \int d\mathbf{x}_1 \dots d\mathbf{x}_N \Psi_H^*(\mathbf{x}_1 \cdots \mathbf{x}_N) H \mathcal{A}\Psi_H(\mathbf{x}_1 \cdots \mathbf{x}_N). \tag{2.25}$$

The contributions from H_1 and H_2 are

$$\langle \Psi | H_1 | \Psi \rangle = \sum_{i=1}^{N} \int d\mathbf{x}\, \psi_i^*(\mathbf{x})\, h(\mathbf{x})\, \psi_i(\mathbf{x}) = \sum_{i=1}^{N} \langle i|h|i \rangle \tag{2.26}$$

and

$$\langle\Psi|H_2|\Psi\rangle = \frac{1}{2}\sum_{\substack{i,j=1\\i\neq j}}^{N}\int d\mathbf{x}\,d\mathbf{x}'[\psi_i^*(\mathbf{x})\,\psi_j^*(\mathbf{x}')\,g(\mathbf{r},\mathbf{r}')\times$$
$$[\psi_i(\mathbf{x})\,\psi_j(\mathbf{x}') - \psi_j(\mathbf{x})\,\psi_i(\mathbf{x}')] \qquad (2.27)$$

$$\langle\Psi|H_2|\Psi\rangle = \frac{1}{2}\sum_{i,j=1}^{N}[\langle ij|g|ij\rangle - \langle ij|g|ji\rangle]. \qquad (2.28)$$

Equation (2.26) results from the fact that all permutations of the orbitals vanish. When calculating the contribution from H_2, however, the interchange of two coordinates $\mathbf{x}_i$ and $\mathbf{x}_j$ will give a non-zero result for the cases where $\mathbf{r}_i$ and $\mathbf{r}_j$ are the arguments of g. Notice that in equation (2.28) the restriction $i \neq j$ has been removed since the two terms automatically cancel in this case.

The total reference energy is thus

$$E_{ref} = \sum_{i=1}^{N}\langle i|h|i\rangle + \frac{1}{2}\sum_{i,j=1}^{N}[\langle ij|g|ij\rangle - \langle ij|g|ji\rangle]. \qquad (2.29)$$

2.4   Second quantization

We will now briefly discuss the so-called second quantization. Second quantization is an alternative way to express quantum mechanical operators and Slater determinants. An attractive feature of the formalism is that it makes no reference to the number of particles of the system. Most important for us, however, is the fact that it provides a compact notation and an efficient way of manipulating operators. It will prove to be especially useful when we later discuss perturbation theory.

To begin with, we assume that there exists a basis of orthonormal single-particle spinorbitals $\{\psi_i\}_{i=1}^{\infty}$. As discussed above, these can typically be eigenfunctions of H_1 or the Fock operator $\mathcal{F}$. From them different Slater determinants can be constructed. A Slater determinant is written as

$$|\Psi\rangle = |pqr\cdots z\rangle, \qquad (2.30)$$

where the indices inside the ket indicate the various spinorbitals that are occupied by particles. Because (2.30) represents a Slater determinant, which is necessarily antisymmetric, changing the order of two indices introduces a minus sign. It is customary to let the indices be ordered lexicographically and let the Slater determinant be positive in this case. The physical vacuum state, in which no single-particle states are occupied, is written $|0\rangle$.

Next, we define the creation and annihilation operators $a_p^\dagger$ and a_p, respectively. They are defined through the relations

$$a_p^\dagger |qr\cdots z\rangle = |pqr\cdots z\rangle$$
$$a_p |pqr\cdots z\rangle = |qr\cdots z\rangle \qquad (2.31)$$

and

$$a_p^\dagger |pqr\cdots z\rangle = 0$$
$$a_p |qr\cdots z\rangle = 0. \qquad (2.32)$$

The fact that these operators are each others adjoints is not self evident, but can be realised by considering the quantity $\langle\Psi'|a_p^\dagger|\Psi\rangle$. Obviously, this will have the value 0 or ± 1. By letting the creation operator act on the ket we see that the answer can be nonzero only if the orbital ψ_p is unoccupied in $|\Psi\rangle$ and occupied in $\langle\Psi'|$. Also, all other occupancies must be identical. If we let the operator act on the bra instead we should get the same answer. This is only possible if a_p removes the occupancy of ψ_p. Hence, the annihilation operator is the adjoint of the creation operator and vice versa.

Note that any Slater determinant $|pqr\cdots z\rangle$ can be written as a sequence of creation operators acting on the vacuum state:

$$|pqr\ldots z\rangle = a_p^\dagger a_q^\dagger a_r^\dagger \cdots a_z^\dagger |0\rangle \qquad (2.33)$$

Fundamental to the second quantization formalism are the anti-commuation relations of the creation and annihilation operators. By considering how they operate on general Slater determinants it is not difficult to derive the following relations

$$[a_p^\dagger,\ a_q^\dagger]_+ = 0$$
$$[a_p,\ a_q]_+ = 0 \qquad (2.34)$$
$$[a_p^\dagger,\ a_q]_+ = \delta_{pq},$$

where $[A,\ B]_+ = AB + BA$. See Shavitt and Bartlett [4] for a derivation.

2.4.1   The Hamiltonian in second quantization

The creation and annihilation operators are used to construct other operators. The one- and two-particle operators (2.4) and (2.5) are in second quantization written as

$$H_1 = \sum_{pq} \langle p|h|q\rangle a_p^\dagger a_q \qquad (2.35)$$

$$H_2 = \frac{1}{2}\sum_{pqrs} \langle pq|g|rs\rangle a_p^\dagger a_q^\dagger a_s a_r. \qquad (2.36)$$

The sums in equations (2.35) and (2.36) are over all single-particle states. Because $a_s^\dagger a_r^\dagger = -a_r^\dagger a_s^\dagger$, H_2 can alternatively be written as

$$H_2 = \frac{1}{4} \sum_{pqrs} \langle pq||rs \rangle a_p^\dagger a_q^\dagger a_s a_r, \tag{2.37}$$

where $\langle pq||rs \rangle = \langle pq|g|rs \rangle - \langle pq|g|sr \rangle$.

2.4.2   Particle-hole formulation

Instead of referring all Slater determinants to the physical vacuum, it is more useful to operate with a reference Slater determinant

$$|c\rangle = |ijk\ldots n\rangle, \tag{2.38}$$

which is called the Fermi vacuum. For a system of N particles, it is build up of the N lowest eigenfunctions of some operator (most often H_1 or the Fock operator $\mathcal{F}$). The spinorbitals included in the Fermi vacuum are called hole states, and all others are called particle states. When using creation and annihilation operators, $a_p^\dagger$ and a_p, it is common to let indices $(i, j, k, \ldots)$ indicate hole states, $(a, b, c, \ldots)$ indicate particle states and $(p, q, r, \ldots)$ indicate both hole and particle states. Thus, other Slater determinants relative to the Fermi vacuum can be created as

$$|\Psi_i^a\rangle = a_a^\dagger a_i |c\rangle = a_a^\dagger a_i |ijk\ldots n\rangle = |ajk\ldots n\rangle \tag{2.39}$$

$$|\Psi_{ij}^{ab}\rangle = a_a^\dagger a_b^\dagger a_j a_i |c\rangle = a_a^\dagger a_b^\dagger a_j a_i |ijk\ldots n\rangle = |abk\ldots n\rangle. \tag{2.40}$$

Recall that any annihilation operator acting to the right on the physical vacuum gives zero. However, this is not the case when operating relative to the Fermi vacuum. It is desired to retain this property also for the Fermi vacuum. In order to achieve this, we introduce the so-called pseudo creation and pseudo annihilation operators $b_p^\dagger$ and b_p, respectively. They are defined as

$$b_i^\dagger = a_i, \qquad b_i = a_i^\dagger, \tag{2.41}$$

$$b_a^\dagger = a_a^\dagger, \qquad b_a = a_a. \tag{2.42}$$

From this it is clear that any pseudo annihilation operator acting on the Fermi vacuum gives zero.

In the remainder of this text we will always operate with the Fermi vacuum.

2.4.3   Normal order, contractions and Wick's theorem

The normal ordering of a product of operators, written $\{AB\ldots Z\}$, is the rearrangement of all operators such that all pseudo creation operators are to the left of all pseudo annihilation operators times the factor $(-1)^\sigma$, where σ is equal to the number of interchanges made in order to obtain the rearrangement. As an example, consider the normal ordering of the product $a_a a_i a_b^\dagger a_j^\dagger$:

$$\{a_a a_i a_b^\dagger a_j^\dagger\} = \{b_a b_i^\dagger b_b^\dagger b_j\} = (-1)^2\, b_i^\dagger b_b^\dagger b_a b_j = a_i a_b^\dagger a_a a_j^\dagger \qquad (2.43)$$

The normal ordering is not unique since the following is also correct:

$$\{a_a a_i a_b^\dagger a_j^\dagger\} = -a_i a_b^\dagger a_j^\dagger a_a. \qquad (2.44)$$

Note also that the vacuum expectation value of a normal ordered product of operators is equal to zero.

The *contraction* of two operators A and B is defined as

$$\overset{\frown}{AB} = AB - \{AB\}. \qquad (2.45)$$

It will always be equal to zero or one. This is easily seen by considering all four possible contractions:

$$
\begin{aligned}
\overset{\frown}{b_p b_q} &= b_p b_q - b_p b_q = 0,\\
\overset{\frown}{b_p^\dagger b_q^\dagger} &= b_p^\dagger b_q^\dagger - b_p^\dagger b_q = 0,\\
\overset{\frown}{b_p^\dagger b_q} &= b_p^\dagger b_q - b_p^\dagger b_q = 0,\\
\overset{\frown}{b_p b_q^\dagger} &= b_p b_q^\dagger + b_q^\dagger b_p = [b_p, b_q^\dagger]_+ = \delta_{pq}.
\end{aligned}
\qquad (2.46)
$$

Contractions can occur between operators within a normal ordered product:

$$\{ABC\cdots \overset{\frown}{R}\cdots \overset{\frown}{S}\cdots T\} = (-1)^\sigma \overset{\frown}{RS}\{ABC\cdots T\}, \qquad (2.47)$$

where σ is the number of interchanges needed to bring the operators R and S next to each other.

Finally we state *Wick's theorem*:

A product of a string of creation and annihilation operators is equal to their normal product plus the sum of all possible normal products with contractions:

$$AB\cdots Z = \{AB\cdots Z\} + \sum\{\overset{\frown}{AB}\cdots Z\} + \sum\{\overset{\frown}{AB}\cdots Z\} + \ldots \qquad (2.48)$$

Wick's theorem is especially useful when calculating vacuum expectation values of operators because all terms except the fully contracted ones are equal to zero.

A corollary of Wick's theorem, often referred to as Wick's generalised theorem, will also prove to be useful. It says that a general product of creation and annihilation operators in which some strings of operators are already normal ordered is equal to the overall normal product plus the sum of all possible normal products with contractions between operators which are not within the same normal product to begin with:

$$\{A_1 A_2 \cdots\}\{B_1 B_2 \cdots\}\{C_1 C_2 \cdots\} \cdots$$

$$= \{A_1 A_2 \cdots B_1 B_2 \cdots C_1 C_2 \cdots\} + \sum{}' \{A_1 A_2 \cdots B_1 B_2 \cdots C_1 C_2 \cdots\}, \quad (2.49)$$

where the sum has been labeled with a prime to indicate that contractions between operators which belong to the same original normal product shall be omitted.

2.4.4 Normal ordered operators

As pointed out in the previous section, normal ordered operators are very useful when calculating vacuum expectation values. We will therefore show what the normal ordered one- and two-particle operators in (2.35) and (2.37) look like.

Let us first consider the one-particle operator. Using Wick's theorem we find that

$$\begin{aligned}
a_p^\dagger a_q &= \{a_p^\dagger a_q\} + \{\overline{a_p^\dagger a_q}\} \\
&= \{a_p^\dagger a_q\} + \delta_{pq \in I}.
\end{aligned} \quad (2.50)$$

The subindex $pq \in I$ signifies that p and q must be hole states. From this we arrive at the operator:

$$H_1 = \sum_{pq} h_{pq}\{a_p^\dagger a_q\} + \sum_i h_{ii}. \quad (2.51)$$

Wick's theorem applied on the two-particle operator gives:

$$a_p^\dagger a_q^\dagger a_s a_r = \{a_p^\dagger a_q^\dagger a_s a_r\} + \{\overline{a_p^\dagger a_q^\dagger} a_s a_r\} + \{\overline{a_p^\dagger a_q^\dagger a_s a_r}\}$$

$$+ \{a_p^\dagger \overline{a_q^\dagger a_s} a_r\} + \{a_p^\dagger \overline{a_q^\dagger a_s a_r}\} + \{\overline{a_p^\dagger a_q^\dagger a_s a_r}\}$$

$$+ \quad \{a_p^\dagger a_q^\dagger a_s a_r\}$$

$$
\begin{aligned}
a_p^\dagger a_q^\dagger a_s a_r = &\{a_p^\dagger a_q^\dagger a_s a_r\} - \{a_q^\dagger a_r\}\delta_{ps\in I} + \{a_q^\dagger a_s\}\delta_{pr\in I} \\
&+ \{a_p^\dagger a_r\}\delta_{qs\in I} - \{a_p^\dagger a_s\}\delta_{qr\in I} + \delta_{pr\in I}\delta_{qs\in I} \\
&- \delta_{ps\in I}\delta_{qr\in I}.
\end{aligned}
\tag{2.52}
$$

Inserting this into equation (2.37) gives:

$$
\begin{aligned}
H_2 = &\frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle\{a_p^\dagger a_q^\dagger a_s a_r\} \\
&+ \frac{1}{4}\sum_{pqi}\Big[-\langle ip||qi\rangle + \langle ip||iq\rangle + \langle pi||qi\rangle - \langle pi||iq\rangle \Big]\{a_p^\dagger a_q\} \\
&+ \frac{1}{4}\sum_{ij}\Big[\langle ij||ij\rangle - \langle ij||ji\rangle\Big].
\end{aligned}
\tag{2.53}
$$

By using the fact that $\langle pq||rs\rangle = \langle qp||sr\rangle$ and $\langle pq||rs\rangle = -\langle pq||sr\rangle$ this can be written as

$$
H_2 = \frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle\{a_p^\dagger a_q^\dagger a_s a_r\} + \sum_{pqi}\langle pi||qi\rangle\{a_p^\dagger a_q\} + \frac{1}{2}\sum_{ij}\langle ij||ij\rangle
\tag{2.54}
$$

Thus the total Hamiltonian can be expressed as

$$
H = \sum_{pq}[\langle p|h|q\rangle + \langle pi||qi\rangle]\{a_p^\dagger a_q\} + \frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle\{a_p^\dagger a_q^\dagger a_s a_r\} + E_{ref}.
\tag{2.55}
$$

2.5   A basis for the fermionic wave function

We end this chapter by stating a very important theorem:

If the basis $\{\psi_i\}_{i=1}^\infty$ is complete in the Hilbert space of single-particle wave functions, then the set of all Slater determinants constructed from this basis is also complete in the Hilbert space of antisymmetric many-particle functions.

In particular, this means that with the particle-hole formulation introduced above, any state $|\Psi\rangle$ can be written as

$$
|\Psi\rangle = C_0|c\rangle + \sum_{ia} C_i^a|\Psi_i^a\rangle + \sum_{ijab} C_{ij}^{ab}|\Psi_{ij}^{ab}\rangle + \ldots
\tag{2.56}
$$

Chapter 3

Hartree-Fock

3.1 Introduction

The Hartree-Fock method is a popular method for calculating the ground state and ground state energy of many-particle systems. It is a variational method which aims to find the minimum of the expectation value of the Hamiltonian. However, instead of searching through the space of all possible wavefunctions, the method restricts itself to the set of all Slater determinants.

The Hartree-Fock equations are given by

$$\mathcal{F}\psi_k = \varepsilon_k \psi_k, \tag{3.1}$$

where $\mathcal{F}$ is the Fock operator, defined as

$$\mathcal{F}\psi_k = \Big[-\frac{1}{2}\nabla^2 - \sum_{i=1}^{N}\frac{Z_n}{|\mathbf{R}_n - \mathbf{r}|}\Big]\psi_k(\mathbf{x}) + \sum_{l=1}^{N}\int d\mathbf{x}'|\psi_l(\mathbf{x}')|^2\frac{1}{|\mathbf{r} - \mathbf{r}'|}\psi_k(\mathbf{x})$$
$$- \sum_{l=1}^{N}\int d\mathbf{x}'\psi_l^*(\mathbf{x}')\frac{1}{|\mathbf{r} - \mathbf{r}'|}\psi_k(\mathbf{x}')\psi_l(\mathbf{x}). \tag{3.2}$$

These are a set of coupled one-electron eigenvalue equations for the spinorbitals ψ_k. The eqations are non-linear because the orbitals we are seeking are actually needed in order to obtain the operator $\mathcal{F}$ which determine them. They are therefore often referred to as self consistent field (SCF) equations and must be solved iteratively. The procedure goes along the following lines. First make an initial guess for the spinorbitals ψ_k and calculate the Fock operator $\mathcal{F}$. Then, solve the Hartree-Fock equations to obtain a new set of spinorbitals and use these as input to calculate a new Fock operator. The process continues like this until a convergence criterium is reached.

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The terms in the square brackets are the same as those in equation (2.7). The two extra sums are due to the interactions between the electrons. The first of these represent the Coulomb potential from the mean field set up by the electrons of the system. The last is similar to the first except that the indices of two orbitals have been switched. This is a direct consequence of the fact that, in the derivation of the equations, the state was assumed to be a Slater determinant. Note that due to the last sum, the Fock operator is non-local, that is to say, the value of $\mathcal{F}\psi_k(\mathbf{x})$ depends on the value of $\psi_k(\mathbf{x}')$ at all coordinates $\mathbf{x}' \in \mathbb{R}^3 \bigotimes \{\uparrow, \downarrow\}$.

As stated in section 2.5, any state $|\Psi\rangle$ can be written as a linear combination of Slater determinants

$$|\Psi\rangle = C_0|c\rangle + \sum_{ia} C_i^a |\Psi_i^a\rangle + \sum_{ijab} C_{ij}^{ab} |\Psi_{ij}^{ab}\rangle + \dots \qquad (3.3)$$

The most crude approximation is to neglect all terms except the reference Slater $|c\rangle$. The Hartree-Fock method answers the following problem: Given the approximation $|\Psi\rangle = |c\rangle$, what is the optimal set of spinorbitals to choose as constituents of $|c\rangle$ and what is the resulting approximation for the energy, E_{HF}? The energy E_{HF} is defined as the energy found from an *exact* solution of the Hartree-Fock equations, which requires an infinite single-particle basis. Contrary to what one might guess, it is not the sum of the energies ε_k, but given by

$$E_{HF} = \sum_{i=1}^N \varepsilon_i - \frac{1}{2}\sum_{i,j=1}^N \langle ij||ij\rangle. \qquad (3.4)$$

In most cases the Hartree-Fock methods provides an excellent first approximation to the wave function and energy of the system. Often the method accounts for about 99% of the total energy, which in many cases might fall within the required accuracy. However, in quantum chemistry an even higher degree of precision is sometimes needed. In such cases, the solution of the Hartree-Fock equations is a very good starting point to use as input for other so-called *post-Hartree-Fock methods*. The other methods discussed in this thesis can be considered to belong to this class of methods.

The difference between the exact energy E and the Hartree-Fock energy E_{HF} is referred to as the correlation energy ΔE_{corr}:

$$\Delta E_{corr} = E - E_{HF}. \qquad (3.5)$$

3.2   Derivation of the Hartree-Fock equations

For a given Slater determinant, the reference energy is given by equation (2.29). We thus aim to find the set of spinorbitals that minimizes this energy:

$$\delta(E_{ref} - \sum_{k=1}^{N} \varepsilon_k \langle \psi_k | \psi_k \rangle) = 0. \tag{3.6}$$

The parameters $\{\varepsilon_k\}_{k=1}^{N}$ are Lagrange multipliers which make sure that the spinorbitals are normalised.

When taking the variation of this expression, we get variations of the spinorbitals in both the bras end kets. However, it can be shown that it is necessary to vary only one of these. In the following only the bras will be varied.

Taking the variation of the energy yields:

$$
\begin{aligned}
\delta E_{ref} &= \sum_{k=1}^{N} \langle \delta\psi_k | h | \psi_k \rangle \\
&\quad + \frac{1}{2} \sum_{k,l=1}^{N} [\langle \delta\psi_k\psi_l | g | \psi_k\psi_l \rangle + \langle \psi_k\delta\psi_l | g | \psi_k\psi_l \rangle \\
&\qquad - \langle \delta\psi_k\psi_l | g | \psi_l\psi_k \rangle - \langle \psi_k\delta\psi_l | g | \psi_l\psi_k \rangle] \\
&= \sum_{i=1}^{N} \langle \delta\psi_k | h | \psi_k \rangle \\
&\quad + \frac{1}{2} \sum_{k,l=1}^{N} [\langle \delta\psi_k\psi_l | g | \psi_k\psi_l \rangle + \langle \delta\psi_l\psi_k | g | \psi_l\psi_k \rangle \\
&\qquad - \langle \delta\psi_k\psi_l | g | \psi_l\psi_k \rangle - \langle \delta\psi_l\psi_k | g | \psi_k\psi_l \rangle] \\
&= \sum_{i=1}^{N} \langle \delta\psi_k | h | \psi_k \rangle + \sum_{k,l=1}^{N} [\langle \delta\psi_k\psi_l | g | \psi_k\psi_l \rangle - \langle \delta\psi_k\psi_l | g | \psi_l\psi_k \rangle] \quad (3.7)
\end{aligned}
$$

We next define two operators J_k and K_k as follows:

$$J_k(\mathbf{x})\psi(\mathbf{x}) = \left[\int d\mathbf{x}' \psi_k^*(\mathbf{x}')g(\mathbf{r},\mathbf{r}')\psi_k(\mathbf{x}') \right]\psi(\mathbf{x}) \tag{3.8}$$

$$K_k(\mathbf{x})\psi(\mathbf{x}) = \left[\int d\mathbf{x}' \psi_k^*(\mathbf{x}')g(\mathbf{r},\mathbf{r}')\psi(\mathbf{x}') \right]\psi_k(\mathbf{x}). \tag{3.9}$$

We further define

$$J \;=\; \sum_{k=1}^{N} J_k \qquad\qquad (3.10)$$

$$K \;=\; \sum_{k=1}^{N} K_k \qquad\qquad (3.11)$$

Using this the variation of the energy can be written as

$$\delta E_{ref} = \sum_{k=1}^{N} \langle \delta\psi_k | h + J - K | \psi_k \rangle \qquad\qquad (3.12)$$

The operator $\mathcal{F} = h + J - K$ is called the Fock operator. Equation (3.6) can now be written as

$$\sum_{k=1}^{N} \langle \delta\psi_k | \mathcal{F} - \varepsilon_k | \psi_k \rangle = 0. \qquad\qquad (3.13)$$

Because all the kets $\langle \delta\psi_k |$ can be varied independently, this leads to the Hartree-Fock equations

$$\mathcal{F}|\psi_k\rangle = \varepsilon_k |\psi_k\rangle. \qquad\qquad (3.14)$$

A peculiar thing about the Hartree-Fock equations is that one needs to know the spinorbitals in order to set up the equations which determine them. The usual way around this is to start with a set of trial functions in order to calculate the operator $\mathcal{F}$. From this operator a new set of spinorbitals is found and the process is continued until a convergence criterium is reached.

The reference energy (2.29) can be written in therms of the operators J and K in the following way:

$$E_{ref} = \sum_{k=1}^{N} \langle \psi_k | h + \frac{1}{2}(J - K) | \psi_k \rangle. \qquad\qquad (3.15)$$

From this it is clear that the eigenvalues of the HF equations (3.14) do not add up to the ground state energy; the term $(J - K)$ in the Fock operator is a factor of two too large. This can be accounted for in the following two equivalent ways:

$$E_{ref} = \frac{1}{2}\sum_{k=1}^{N}[\varepsilon_k + \langle \psi_k | h | \psi_k \rangle] = \sum_{k=1}^{N}[\varepsilon_k - \frac{1}{2}\langle \psi_k | J - K | \psi_k \rangle] \qquad (3.16)$$

3.3   Open- and closed-shell systems

In a closed-shell system every level (Fock-level) is occupied by two electrons with opposite spin, whereas in an open-shell system one or more levels are occupied by one electron only. Closed-shell systems are the easiest to handle because in such systems two and two electrons have identical spatial orbitals. This means that the spinorbitals can be written as

$$\{\psi_{2k}(\mathbf{x}),\, \psi_{2k+1}(\mathbf{x})\} = \{\phi_k(\mathbf{r})\alpha(s),\, \phi_k(\mathbf{r})\beta(s)\}, \qquad (3.17)$$

where $\phi_k(\mathbf{r})$ is the spatial part and $\alpha(s)$ and $\beta(s)$ are the spin parts. The HF equations that result from this assumption are referred to as restricted Hartree Fock (RHF) equations. RHF is appropriate to use on closed-shell systems.

Let us say that we have solved the HF equations for some particular system so that the occupied spinorbitals and Fock-energies are known. What can we say about the degeneracy of the Fock-energies? Well, since each spatial orbital can at least be occupied by two electrons and since the Fock operator contains no explicit spin dependence, each level must *at least* be doubly degenerate. If this is the case, and if there is an even number of electrons, the system is closed-shell. However, it is important to note that an even number of electrons does not imply that the system is closed-shell. If degeneracies apart from that due to spin are present, some levels might be occupied by one electron only. Some closed- and open-shell systems are illustrated in figure ...

Although an even number of electrons does not imply that the system is closed-shell, it is easy to realise that an odd number of electrons does imply that the system is open-shell. Open-shell systems are often more appropriately treated by the unrestricted Hartree-Fock (UHF) equations, in which the restriction (3.17) is not assumed.

In the following two subsections the RHF- and UHF-equations are developed.

3.4 Restricted Hartree-Fock (RHF)

In the RHF equations it is assumed that the spinorbitals can be written as in equation (3.17). Inserting this into the Fock operator gives:

$$
\begin{aligned}
\mathcal{F}\psi_k &= (h + J - K)\psi_k(\mathbf{x})\\
&= h\,\psi_k(\mathbf{x}) + \Big[\sum_{l=1}^{N}\int d\mathbf{x}'\psi_l^*(\mathbf{x}')g(\mathbf{r},\mathbf{r}')\psi_l(\mathbf{x}')\Big]\psi_k(\mathbf{x})\\
&\quad - \Big[\sum_{l=1}^{N}\int d\mathbf{x}'\psi_l^*(\mathbf{x}')g(\mathbf{r},\mathbf{r}')\psi_k(\mathbf{x}')\Big]\psi_l(\mathbf{x})\\
&= h\,\phi_k(\mathbf{r})\xi_k(s) + 2\Big[\sum_{l=1}^{N/2}\int d\mathbf{r}'\phi_l^*(\mathbf{r}')g(\mathbf{r},\mathbf{r}')\phi_l(\mathbf{r}')\Big]\phi_k(\mathbf{r})\xi_k(s)\\
&\quad - \Big[\sum_{l=1}^{N/2}\int d\mathbf{r}'\phi_l^*(\mathbf{r}')g(\mathbf{r},\mathbf{r}')\phi_k(\mathbf{r}')\Big]\phi_l(\mathbf{r})\xi_k(s).
\end{aligned}
$$

In the last two lines the integration over the spin coordinates has been carried out. Here $\xi_k(s)$ is the spin function of $\psi_k(\mathbf{x})$ which can be either $\alpha(s)$ or $\beta(s)$. This factor shows up on both sides of the Hartree-Fock equations and can therefore be omitted. The RHF equations can now be written as

$$
\hat{\mathcal{F}}\phi_k(\mathbf{r}) = \varepsilon_k \phi_k(\mathbf{r}), \tag{3.18}
$$

where

$$
\hat{\mathcal{F}} = h + 2\hat{J} - \hat{K}, \tag{3.19}
$$

$$
\hat{J}(\mathbf{r})\phi_k(\mathbf{r}) = \sum_{l=1}^{N/2}\Big[\int d\mathbf{r}'\phi_l^*(\mathbf{r}')g(\mathbf{r},\mathbf{r}')\phi_l(\mathbf{r}')\Big]\phi_k(\mathbf{r}), \tag{3.20}
$$

$$
\hat{K}(\mathbf{r})\phi_k(\mathbf{r}) = \sum_{l=1}^{N/2}\Big[\int d\mathbf{r}'\phi_l^*(\mathbf{r}')g(\mathbf{r},\mathbf{r}')\phi_k(\mathbf{r}')\Big]\phi_l(\mathbf{r}). \tag{3.21}
$$

Note that the sums in equations (3.20) and (3.21) run from 1 to $N/2$ since each (spatial) orbital is occupied by two electrons. The factor of two in front of $\hat{J}\phi_k$ is due to the fact that all spinorbitals in the integrand of $J\psi_k$ have parallel spins. However, it is not present in front of $\hat{K}\phi_k$ because the spinorbitals in the integrand of $K\psi_k$ are alternately parallel and antiparallel.

The energy is now given by

$$
E_{ref} = 2\sum_{k=1}^{N/2}[\langle\phi_k|h + \hat{J} - \tfrac{1}{2}\hat{K}|\phi_k\rangle \tag{3.22}
$$

In order to actually solve the HF equations (3.18) it is customary to express the orbitals $\phi_k(\mathbf{r})$ in terms of some other known set of basis functions $\chi_p(\mathbf{r})$:

$$\phi_k(\mathbf{r}) = \sum_p C_{pk}\chi_p(\mathbf{r}). \qquad (3.23)$$

Inserting this into equation (3.18), multiplying by $\chi_p^*(\mathbf{r})$ and integrating with respect to $\mathbf{r}$ leads to the following set of eigenvalue equations

$$\mathbf{FC_k} = \varepsilon_k \mathbf{SC_k} \qquad (3.24)$$

where the elements of the Fock matrix $\mathbf{F}$ are

$$F_{pq} = \langle p|h|q \rangle + \sum_l \sum_{rs} (2\langle pr|g|qs \rangle - \langle pr|g|sq \rangle) C_{rl}^* C_{sl} \qquad (3.25)$$

and the elements of the overlap matrix $\mathbf{S}$ are

$$S_{pq} = \langle p|q \rangle. \qquad (3.26)$$

It is convenient to introduce the density matrix $P_{rs} = 2\sum_l C_{rl}^* C_{sl}$. The Fock matrix is then written more compactly as

$$F_{pq} = \langle p|h|q \rangle + \frac{1}{2}\sum_{rs} P_{rs}(2\langle pr|g|qs \rangle - \langle pr|g|sq \rangle). \qquad (3.27)$$

The energy is given by

$$E_{ref} = \sum_{pq} P_{pq}\langle p|h|q \rangle + \frac{1}{2}\sum_{pqrs} P_{pq}P_{rs}(\langle pr|g|qs \rangle - \frac{1}{2}\langle pr|g|sq \rangle) \qquad (3.28)$$

3.5   Unrestricted Hartree-Fock (UHF)

In the UHF equations the restriction of equation (3.17) is no longer assumed. Instead particles of opposite spins are allowed to have different spatial orbitals:

$$\{\psi_{k_+}(\mathbf{x}),\, \psi_{k_-}(\mathbf{x})\} = \{\phi_{k_+}(\mathbf{r})\alpha(s),\, \phi_{k_-}(\mathbf{r})\beta(s)\}. \qquad (3.29)$$

However, the spatial orbitals $\phi_{k+}(\mathbf{r})$ and $\phi_{k-}(\mathbf{r})$ are still expressed in terms of the same basis:

$$\psi_{k_+}(\mathbf{r}) = \sum_p C_{pk_+}\chi_p(\mathbf{r}),$$

$$\psi_{k_-}(\mathbf{r}) = \sum_p C_{pk_-}\chi_p(\mathbf{r}). \qquad (3.30)$$

This assumption will lead to two sets of equations:

$$
\begin{aligned}
\mathcal{F}\psi_{k_+}(\mathbf{x}) &= \varepsilon_{k_+}\psi_{k_+}(\mathbf{x}), \\
\mathcal{F}\psi_{k_-}(\mathbf{x}) &= \varepsilon_{k_-}\psi_{k_-}(\mathbf{x}).
\end{aligned}
\tag{3.31}
$$

We start by calculating how the operators J and K act on the spinorbitals:

$$
\begin{aligned}
J\phi_{k_\pm}(\mathbf{r}) = \Big[\sum_{l_\pm} \int d\mathbf{r}'\phi_{l_\pm}^*(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}\phi_{l_\pm}(\mathbf{r}') \\
+ \sum_{l_\mp} \int d\mathbf{r}'\phi_{l_\mp}^*(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}\phi_{l_\mp}(\mathbf{r}')\Big]\phi_{k_\pm}(\mathbf{r}),
\end{aligned}
\tag{3.32}
$$

$$
K\phi_{k_+}(\mathbf{r}) = \Big[\sum_{l_\pm} \int d\mathbf{r}'\phi_{l_\pm}^*(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}\phi_{k_\pm}(\mathbf{r}')\Big]\phi_{l_\pm}(\mathbf{r}).
\tag{3.33}
$$

For convenience the equtions for ϕ_{k_+} and ϕ_{k_-} have been grouped together. Just as for the RHF case, because all integrals over spinorbitals with opposite spins vanish, we get twice as many terms in J as in K. Inserting (3.30) in (3.31), multiplying by $\chi_p^*(\mathbf{r})$ and integrating with respect to $\mathbf{r}$ leads to the equations:

$$
\mathbf{F}^\pm\mathbf{C}_{k_\pm} = \varepsilon_{k_\pm}\mathbf{S}\mathbf{C}_{k_\pm},
\tag{3.34}
$$

where the elements of the Fock matrices $\mathbf{F}^\pm$ are

$$
\begin{aligned}
F_{pq}^\pm = h_{pq} + \sum_{l_\pm}\sum_{rs} \Big[\langle pr|g|qs\rangle - \langle pr|g|sq\rangle\Big]C_{rl_\pm}^*C_{sl_\pm} \\
+ \sum_{l_\mp}\sum_{rs}\langle pr|g|qs\rangle C_{rl_\mp}^*C_{sl_\mp}.
\end{aligned}
\tag{3.35}
$$

Note that in the UHF case there are two sets of coupled linear equations which has to be solved: One set for the spin-up particles and one set for the spin-down particles.

3.6   Basis functions

The choice of basis functions is critical when doing Hartree-Fock calculations. What basis functions to choose is primarily dictated by the following two criteria:

1. The functions should make physically sense, i.e. they should be large where the electrons are likely to be and small elsewhere.

2. It should be possible to integrate the functions efficiently.

A set of basis functions which is very popular in atomic quantum mechanical calculations are the so-called Slater type orbitals (STOs):

$$\chi(\mathbf{r}) = r^{n-1} P_l(x, y, z) e^{-ar}. \qquad (3.36)$$

Here n and l are the principal and angular momentum quantum numbers, respectively, and $P_l(x, y, z)$ is a polynomial in x, y and z of degree l. The exponent a can be determined according to a simple set of rules developed by Slater. The main attractive features of the STOs are that they have the correct exponential decay with increasing r and that the angular component is hydrogenic. For this reason, they are often used in atomic Hartree-Fock calculations. When doing molecular calculations, however, they have the disadvantage that the two-particle integrals $\langle pr|g|qs\rangle$ occuring in the Fock matrix F_{pq} have no known analytical expression. This is because integrals of products of exponentials centered on different nuclei are difficult to handle. They can of course be calculated numerically, but for large molecules this is very time consuming.

A clever way around this problem is to replace the exponential term e^{-ar} with e^{-ar^2}, i.e. to use Gaussian functions. This greatly simplifies the integrals because the product of two Gaussians centered on different nuclei with positions $\mathbf{R}_A$ and $\mathbf{R}_B$ is equal to *one* Gaussian centered on some point $\mathbf{R}_p$ on the line between them:

$$\exp(-a|\mathbf{r} - \mathbf{R}_A|^2) \cdot \exp(-b|\mathbf{r} - \mathbf{R}_B|^2) = K_{AB} \exp(-p|\mathbf{r} - \mathbf{R}_p|^2), \quad (3.37)$$

where

$$K_{AB} = \exp\left(-\frac{ab}{a+b}|\mathbf{R}_A - \mathbf{R}_B|^2\right), \qquad (3.38)$$

$$\mathbf{R}_p = \frac{a\mathbf{R}_A + b\mathbf{R}_B}{a+b}, \qquad (3.39)$$

$$p = a+b. \qquad (3.40)$$

This is the so-called Gaussian product theorem. It is illustrated in the one-dimensional case in figure 3.1.

The general functional form of a normalised Gaussian type orbital (GTO) centered at $\mathbf{R}_A$ is given by

$$G_a = G_{ijk}(a, \mathbf{r}_A) = \left(\frac{2\alpha}{\pi}\right)^{3/4} \left[\frac{(8\alpha)^{i+j+k} i!j!k!}{(2i)!(2j)!(2k)!}\right] x_A^i y_A^j z_A^k e^{-ar_A^2}, \qquad (3.41)$$

where $\mathbf{r}_A = \mathbf{r} - \mathbf{R}_A$ and the integers i, j, k determine the angular momentum quantum number $l = i + j + k$. The greatest drawback with Gaussians,
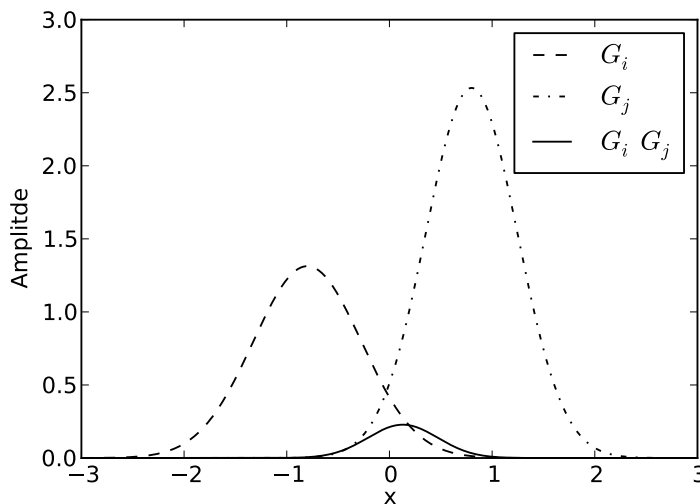
Figure 3.1: Illustrations of the Gaussian product theorem which says that the product of two Gaussians with centers at points A and B is another Gaussian with center somewhere between A and B.

however, is that they do not have the proper exponential radial decay. This can be remedied by expressing each STO as a linear combination of GTOs, which leads to the co-called STO-MG basis sets, where M refers to the number of Gaussians used in the linear combination. A very common choice is $M = 3$. Figure 3.2 shows how the $1s$ STO for Hydrogen is approximated by 3 GTOs. In this plot the exponents a_i and coefficients d_i have been set so that the linear combination of the Gaussians lie as close to the STO as possible, see table 3.1. It is important to note that the parameters (α_i, d_i) are static and that the linear combination of these Gaussians constitute *one single* basis function. The individual Gaussians are called *primitive* basis functions and the linear combination is called a *contracted* basis function. Throughout this text the word basis function will always refer to a contracted basis function.

STO-3G basis sets have been developed for most of the atoms in the periodic table.

Note that the GTOs and STOs do not have any radial nodes as the hydrogenic functions do. This means that no single GTO or STO can mimic the $2s$ hydrogenic orbital for example. With contractions, however, this problem is eliminated; nodes can be introduced by using a combination of positive and negative coefficients d_i.
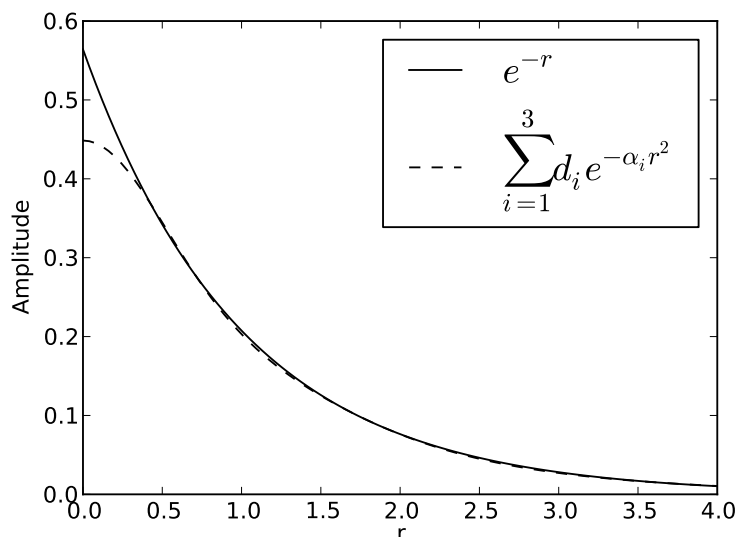
Figure 3.2: The whole line shows the 1s STO basis function, while the broken line shows a linear combination of three Gaussians.

Table 3.1: Coefficients and exponents used in the STO-3G basis shown in figure 3.2.

i	1	2	3
d_i	0.1543	0.5353	0.4446
α_i	3.4252	0.6239	0.1688

The STO-MG basis sets are examples of what is called *minimal basis sets*. As the name suggests, such basis sets contain no more than the minimum number of basis functions needed. The STO-3G basis sets for the Hydrogen and Helium atoms for example, contain only one (contracted) basis function for the $1s$ atomic orbital. This contracted basis is, as explained above, composed of a linear combination of three primitives. For the atoms Lithium through Neon the STO-3G basis sets contain 5 (contracted) basis functions; one for each of the atomic orbitals $1s$, $2s$, $2p_x$, $2p_y$ and $2p_z$.

The reader might be asking herself why the coefficients d_i in the linear combination of the STO-MGs are static. Shouldn't the accuracy of our results actually improve if we let the coefficients vary? The answer to this is yes. However, the linear system to be solved (the Hartree-Fock equations) will then be larger. Thus there is a trade off between accuracy and compu-

tational efficiency which must be considered.

However, basis sets where the STO-MG sets have been "decontracted" as described above have actually been used. They belong to the family of ζ-basis sets. The double-ζ and triple-ζ basis sets have two and three (contracted) basis functions, respectively, for each atomic orbital. As an example, if we were to create a double-ζ from the STO-3G basis set for Hydrogen, we could contract the two first primitives and let the third primitive stand alone. Similarly, the triple-ζ constructed from the STO-3G basis set for Hydrogen will be fully decontracted; each primitive is now a basis function.

Note that the double-ζ and triple-ζ basis sets are not minimal basis sets as they contain more basis functions than are strictly needed.

Let us for a moment assume that we use the triple-ζ constructed from the STO-3G basis set to do Hartree-Fock calculations on atomic Oxygen. What will the orbitals obtained from the calculations (i.e. the eigenfunctions of the Fock operator) look like? The answer is that the lowest orbital, $1s$, will be very close to the contracted $1s$-basis of the STO-3G set. This is hardly surprising as latter function was indeed constructed so that it would closely resemble the $1s$ STO-orbital.

What if we use the same triple-ζ basis set, but now apply it to calculations on the CO molecule? In this case we would probably also find an orbital which would resemble the $1s$ orbital of the STO-3G basis for Oxygen. This is not very surprising; it is mostly the valence electrons which contribute in the bonding between atoms, and the core electrons are more or less unaffected. Thus the decontraction of the basis functions corresponding to the core atomic orbitals will generally not pay off, but will merely increase the computational load. Therefore, basis sets have been constructed where only the basis functions corresponding to the valence atomic orbitals are decontracted: the so-called *split-valence* basis sets. An example of a split-valence basis set is the 3-21G basis set. The number before the hyphen (in this case 3) tells how many primitives that compose the basis functions for the core atomic orbitals. The fact that there are two numbers after the hyphen signifies that there are two basis functions for each valence atomic orbital. The numbers themselves (in this case 2 and 1) indicate that the first of these two basis functions consist of two primitives, while the second consist of one primitive. As an example, the 3-21G basis set for the Oxygen atom has one single basis function for the $1s$ orbital (since this is the core orbital), and this basis function consists of three primitives. Furthermore, it has two basis functions for the $2s$, $2p_x$, $2p_y$ and $2p_z$ atomic orbitals (since these are the valence orbitals). One of these basis functions consists of two primitives, while the other consists of only one primitive. In sum the Oxygen atom thus has 9 contracted basis functions which are built up from a total of 15 primitives.

Other examples of split-valence basis sets are 4-31G, 6-31G and 6-311G.

In many molecular calculations, the split-valence basis sets mentioned thus far do not provide enough flexibility to describe the chemistry appropriately. This is often fixed by adding functions corresponding to atomic orbitals with angular momentum $l_{max} + 1$, where l_{max} is the highest angular momentum of the atom. Such functions are called *polarization functions*. The polarization functions for the Oxygen atom are the d-functions. Asterisks (*) are added to the name of the basis set to indicate that polarization functions are included. One asterisk (as in 3-21G*) indicate that d-functions are added to polarize the p-functions. Two asterisks (as in 3-21G**) are added to show that also p-functions are added to ploarize the s-functions of Hydrogen and Helium.

It should be noted that the list of basis sets mentioned here is in no way exhaustive. There is a flora of basis sets out there.

3.7   Integral evaluation

As discussed in the previous section, using contractions of Gaussians as basis functions significantly improves the speed of the integrations. This section summarises how the integration is actually performed. Many clever tricks are used in order to optimize the speed. This is vital if one wants to run calculations on heavier molecules. The theory behind the integration techniques presented here is taken from Helgaker et al [3].

3.7.1   Overlap integral S_{ij}

We will start by showing how to calculate the overlap integral

$$
\begin{aligned}
S_{ab} &= \langle G_a | G_b \rangle \\
&= \langle G_{ikm}(a, \mathbf{r}_A) | G_{jln}(b, \mathbf{r}_B) \rangle
\end{aligned}
\tag{3.42}
$$

between two Gaussians centered at the points $\mathbf{R}_A$ and $\mathbf{R}_B$. The first thing to notice is that the Gaussians factorise in their Cartesian components:

$$
G_{ikm}(a, \mathbf{r}_A) = G_i(a, x_A) \, G_k(a, y_A) \, G_m(a, z_A),
\tag{3.43}
$$

where

$$
G_i(a, x_A) = x_A^i \exp(-a \, x_A^2),
\tag{3.44}
$$

and the other factors are defined similarly. This means that the integrals over x, y and z can be calculated independently. The integration over x, for

example, is

$$S_{ij} = \int dx\, G_i(a, x_A)\, G_j(b, x_B) = K_{AB,X} \int dx\, x_A^i x_B^j \exp(-p x_p^2), \quad (3.45)$$

where

$$K_{AB,X} = \exp\left(-\frac{ab}{a+b} X_{AB}^2\right) \tag{3.46}$$

$$X_{AB} = A_x - B_x \tag{3.47}$$

$$x_p = x - P_x \tag{3.48}$$

$$P_x = \frac{aA_x + bB_x}{a+b} \tag{3.49}$$

$$p = a + b \tag{3.50}$$

The integral (3.45) has been transformed from a two-center integral to a one-center integral. However, the integral is still not straightforward to calculate because of the powers x_A^i and x_B^j. A smart way to deal with this is to express the Cartesian Gaussians in terms of the so-called Hermite Gaussians. The Hermite Gaussian is defined as

$$\Lambda_{tuv}(a, \mathbf{r}_p) = \left(\frac{\partial}{\partial P_x}\right)^t \left(\frac{\partial}{\partial P_y}\right)^u \left(\frac{\partial}{\partial P_z}\right)^v \exp(-p\,\mathbf{r}_p). \tag{3.51}$$

The Hermite Gaussians also factorise as the Cartesian Gaussians:

$$\Lambda_{tuv}(a, \mathbf{r}_p) = \Lambda_t(a, x_p)\, \Lambda_u(a, y_p)\, \Lambda_v(a, z_p), \tag{3.52}$$

where

$$\Lambda_t(a, x_p) = \left(\frac{\partial}{\partial P_x}\right)^t \exp(-p\, x_p), \tag{3.53}$$

and the other factors are defined similarly. Note that the differentiation $(\partial/\partial P_x)^t$ in (3.53) will result in a polynomial of order t in x multiplied by the exponential function. In equation (3.45) the polynomial is of order $i + j$. This means that we can express the product of Cartesian Gaussians in (3.45) in terms of the Hermite Gaussians in (3.53) in the following way:

$$G_i(a, x_A)\, G_j(b, x_B) = \sum_{t=0}^{i+j} E_t^{ij} \Lambda_t(p, x_p). \tag{3.54}$$

This is the expression we want to integrate over all $\mathbb{R}$, which now turns out to be extremely easy; the only term that survives the integration is the term

for $t = 0$:

$$\int dx \, \Lambda_t(p, x_p) = \int dx \left(\frac{\partial}{\partial P_x}\right)^t \exp(-p \, x_p), \tag{3.55}$$

$$= \left(\frac{\partial}{\partial P_x}\right)^t \int dx \, \exp(-p \, x_p), \tag{3.56}$$

$$= \sqrt{\frac{\pi}{p}} \, \delta_{t0}. \tag{3.57}$$

We have used Leibniz' rule, which says that the differentiation of an integrand with respect to a variable which is not an integration variable can be moved outside the integral. Thus the integral in (3.45) is simply

$$S_{ij} = E_0^{ij} \sqrt{\frac{\pi}{p}}. \tag{3.58}$$

The exact same procedure can be used for the integrals with respect to y and z, which means that the total overlap integral is

$$S_{ab} = E_0^{ij} \, E_0^{kl} \, E_0^{mn} \left(\frac{\pi}{p}\right)^{3/2}. \tag{3.59}$$

This is all very good, but so far nothing has been said about how to actually determine the coefficients E_t^{ij}. First observe that when $i = j = 0$ in equation (3.54) we obtain

$$E_0^{0,0} = K_{AB,X}. \tag{3.60}$$

The other coefficients can be found via the following recurrence relations (derived in appendix A):

$$\begin{aligned}
E_t^{i+1,j} &= \frac{1}{2p} E_{t-1}^{ij} + X_{PA} E_t^{ij} + (t+1) E_{t+1}^{ij} \\
E_t^{i,j+1} &= \frac{1}{2p} E_{t-1}^{ij} + X_{PB} E_t^{ij} + (t+1) E_{t+1}^{ij}.
\end{aligned} \tag{3.61}$$

3.7.2   Kinetic integral T_{ij}

Next we turn to the evaluation of the kinetic integral:

$$\begin{aligned}
T_{ab} &= -\frac{1}{2} \langle G_a | \nabla^2 | G_b \rangle \\
&= -\frac{1}{2} \langle G_{ikm}(a, \mathbf{r}_A) | \nabla^2 | G_{jln}(b, \mathbf{r}_B) \rangle \\
&= -\frac{1}{2} (T_{ij} \, S_{kl} \, S_{mn} + S_{ij} \, T_{kl} \, S_{mn} + S_{ij} \, S_{kl} \, T_{mn}),
\end{aligned} \tag{3.62}$$

where

$$T_{ij} = \int dx\, G_i(a, x_A) \frac{\partial^2}{\partial x^2} G_j(b, x_B), \tag{3.63}$$

and the other factors are defined in the same way. Performing the differentiation yields

$$T_{ij} = 4b^2\, S_{i,j+2} - 2b(2j+1)S_{i,j} + j(j-1)S_{i,j-2}. \tag{3.64}$$

Thus we see that the kinetic integrals are calculated easily as products of the overlap integrals.

3.7.3   Coulomb integral V_{ab}

We now turn to the Coulomb integral due to the interaction between the electrons and the nuclei:

$$\begin{aligned}
V_{ab} &= \langle G_a | \frac{1}{r_C} | G_b \rangle \\
&= \langle G_{ikm}(a, \mathbf{r}_A) | \frac{1}{r_C} | G_{jln}(b, \mathbf{r}_B) \rangle \\
&= \sum_{tuv} E_t^{ij} E_u^{kl} E_v^{mn} \int d\mathbf{r}\, \frac{\Lambda_{tuv}(p, \mathbf{r}_p)}{r_C} \\
&= \sum_{tuv} E_{tuv}^{ab} \int d\mathbf{r}\, \frac{\Lambda_{tuv}(p, \mathbf{r}_p)}{r_C}
\end{aligned} \tag{3.65}$$

In this integral other terms beside Λ_{000} will survive due to the factor $1/r_C = 1/|\mathbf{r} - \mathbf{R}_C|$. Let us nonetheless start with the integral

$$V_p = \int d\mathbf{r}\, \frac{\Lambda_{000}(p, \mathbf{r}_p)}{r_C} = \int d\mathbf{r}\, \frac{e^{-p\, r_p^2}}{r_C}. \tag{3.66}$$

We will show that this three-dimensional integral can actually be converted to a one-dimensional one. The trick is to observe that the factor $1/r_C$ can be replaced by an integral:

$$\frac{1}{r_C} = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} dt\, e^{-r_C^2\, t^2}. \tag{3.67}$$

Inserting this into the integral V_p and using the Gaussian product rule gives

$$\begin{aligned}
V_p &= \frac{1}{\sqrt{\pi}} \int \exp(-p\, r_P^2) \Big(\frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} \exp(-r_C^2\, t^2)\, dt \Big)\, d\mathbf{r} \tag{3.68} \\
&= \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} \int \exp\Big(-\frac{pt^2}{p + t^2} R_{PC}^2 \Big) \exp[-(p + t^2)r_S^2] d\mathbf{r}\, dt. \tag{3.69}
\end{aligned}$$

Here the value of $\mathbf{R}_S$ in r_S does not matter. Doing the integral over the spatial coordinates reveals this:

$$V_p = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} \exp\left(-\frac{pt^2}{p+t^2}R_{PC}^2\right)\left(\frac{\pi}{p+t^2}\right)^{3/2} dt \tag{3.70}$$

$$= 2\pi \int_0^{\infty} \exp\left(-\frac{pt^2}{p+t^2}R_{PC}^2\right)\frac{dt}{(p+t^2)^{3/2}}. \tag{3.71}$$

Next we change integration variable from t to u by defining

$$u^2 = \frac{t^2}{p+t^2}. \tag{3.72}$$

This will change the range of integration from $[0,\infty\rangle$ to $[0,1]$. This is beneficial because the final integral at which we arrive will be calculated numerically. The change of variables leads to

$$V_p = \frac{2\pi}{p} \int_0^1 \exp(-p\,R_{PC}^2\,u^2)\,du \tag{3.73}$$

$$= \frac{2\pi}{p}F_0(p\,R_{PC}^2). \tag{3.74}$$

$F_n(x)$ is the so-called Boys function defined as

$$F_n(x) = \int_0^1 \exp(-xt^2)\,t^{2n}\,dt. \tag{3.75}$$

How to actually evaluate the Boys function numerically will be discussed in section 3.8.

We have now a tremendously simplified way of calculating the integral of Λ_{000}/r_C. However, we need to integrate Λ_{tuv}/r_C for general values of t, u and v. These integrals are actually not that hard to do once the Boys function is calculated:

$$V_{ab} = \sum_{tuv} E_{tuv}^{ab} \int d\mathbf{r}\, \frac{\Lambda_{tuv}(p,\mathbf{r}_p)}{r_C} \tag{3.76}$$

$$= \sum_{tuv} E_{tuv}^{ab} \frac{\partial^{t+u+v} F_0(-pR_{PC}^2)}{\partial P_x^t \partial P_y^u \partial P_z^v} \tag{3.77}$$

$$= \sum_{tuv} E_{tuv}^{ab} R_{tuv}(p,\mathbf{R}_{PC}). \tag{3.78}$$

So we need to know how to calculate $R_{tuv}(p,\mathbf{R}_{PC})$, which are the derivatives of the Boys function. In a similar manner as the coefficients E_t^{ij}, these

are found through some recurrence relations. Before presenting these, we introduce the so-called auxiliary Hermite integrals

$$R_{tuv}^n(p, \mathbf{R}_{PC}) = (-2p)^n \frac{\partial^{t+u+v} F_n(-pR_{PC}^2)}{\partial P_x^t \partial P_y^u \partial P_z^v}. \tag{3.79}$$

By starting with the source term $R_{000}^n(p, \mathbf{R}_{PC}) = F_n(p, R_{PC}^2)$ we can reach the target $R_{tuv}^0(p, \mathbf{R}_{PC}) = R_{tuv}(p, \mathbf{R}_{PC})$ through the following recurrence relations (derived in appendix A)

$$\begin{aligned}
R_{t+1,u,v}^n &= tR_{t-1,u,v}^{n+1} + (P_x - C_x)R_{tuv}^{n+1} \\
R_{t,u+1,v}^n &= tR_{t,u-1,v}^{n+1} + (P_y - C_y)R_{tuv}^{n+1} \\
R_{t,u,v+1}^n &= tR_{t,u,v+1}^{n+1} + (P_z - C_z)R_{tuv}^{n+1}.
\end{aligned} \tag{3.80}$$

From these relations it is clear that in order to calculate the values of $R_{tuv}(p, \mathbf{R}_{PC})$ needed in (3.78), the Boys function $F_n(p, R_{PC}^2)$ has to be evaluated for $n \in \{0, \ldots, \max(t_{max}, u_{max}, v_{max})\}$.

3.7.4   Coulomb integral g_{acbd}

Finally we show how to calculate the Coulomb integral due to the interaction between the electrons. It is given by[1]

$$\begin{aligned}
g_{acbd} &= \langle G_a G_c | \frac{1}{r_{12}} | G_b G_d \rangle \\
&= \sum_{tuv} \sum_{\tau\nu\phi} E_{tuv}^{ab} E_{\tau\nu\phi}^{cd} \int \int \frac{\Lambda_{tuv}(p, \mathbf{r}_{1P}) \Lambda_{\tau\nu\phi}(q, \mathbf{r}_{2Q})}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 \\
&= \sum_{tuv} \sum_{\tau\nu\phi} E_{tuv}^{ab} E_{\tau\nu\phi}^{cd} \frac{\partial^{t+u+v}}{\partial P_x^t \partial P_y^u \partial P_z^v} \frac{\partial^{\tau+\nu+\phi}}{\partial Q_x^\tau \partial Q_y^\nu \partial Q_z^\phi} \\
&\qquad\qquad \int \int \frac{\exp(-pr_{1P}^2) \exp(-qr_{1Q}^2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2,
\end{aligned} \tag{3.81}$$

where $p = a + b$, $q = c + d$, $\mathbf{r}_{1P} = \mathbf{r}_1 - \mathbf{R}_P$ and $\mathbf{r}_{2Q} = \mathbf{r}_2 - \mathbf{R}_Q$. Thus we need to evaluate the integral

$$V_{pq} = \int \int \frac{\exp(-pr_{1P}^2) \exp(-qr_{2Q}^2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2. \tag{3.82}$$

---

[1] Here G_a is combined with G_b and G_c combined with G_d using the Gaussian product rule. In many books on quantum chemistry this is written as
$g_{abcd} = \langle G_a(1)G_b(1)|r_{12}^{-1}|G_c(2)G_d(2)\rangle = \int \int d\mathbf{r}_1 d\mathbf{r}_2 G_a(\mathbf{r}_1)G_b(\mathbf{r}_1)r_{12}^{-1}G_c(\mathbf{r}_2)G_d(\mathbf{r}_2)$. However, since this departs from the usual notation of quantum physics, it will not be used in this thesis.

By first integrating over $\mathbf{r}_1$ and using equation (3.73) this can be written as

$$V_{pq} = \int \left(\frac{2\pi}{p}\int_0^1 \exp(-p\,R_{2P}^2\,u^2)\,du\right)\exp(-qr_{2Q}^2)d\mathbf{r}_2. \qquad (3.83)$$

Next we change the order of integration and use the Gaussian product rule to get

$$\begin{aligned}V_{pq} &= \frac{2\pi}{p}\int_0^1\int \exp(-\frac{pqu^2}{pu^2+q}R_{PQ}^2)\exp[-(pu^2+q)r_{2S}^2]d\mathbf{r}_2 du \\ &= \frac{2\pi}{p}\int_0^1 \exp(-\frac{pqu^2}{pu^2+q}R_{PQ}^2)\left(\frac{\pi}{pu^2+q}\right)^{3/2}du.\end{aligned} \qquad (3.84)$$

Again, the value of $\mathbf{R}_S$ in r_{2S}^2 is immaterial. If we now make the change of variable

$$\frac{v^2}{p+q} = \frac{u^2}{pu^2+q}, \qquad (3.85)$$

we get the result

$$V_{pq} = \frac{2\pi^{5/2}}{pq\sqrt{p+q}}F_0\left(\frac{pq}{p+q}R_{PQ}^2\right). \qquad (3.86)$$

From this we get the final answer

$$\begin{aligned}g_{acbd} &= \frac{2\pi^{5/2}}{pq\sqrt{p+q}}\sum_{tuv}\sum_{\tau\nu\phi}(-1)^{\tau+\nu+\phi}E_{tuv}^{ab}E_{\tau\nu\phi}^{cd} \\ &\qquad\qquad \frac{\partial^{t+u+v+\tau+\nu+\phi}}{\partial P_x^{t+\tau}\partial P_y^{u+\nu}\partial P_z^{v+\phi}}F_0\left(\frac{pq}{p+q}R_{PQ}^2\right) \\ &= \frac{2\pi^{5/2}}{pq\sqrt{p+q}}\sum_{tuv}\sum_{\tau\nu\phi}(-1)^{\tau+\nu+\phi}E_{tuv}^{ab}E_{\tau\nu\phi}^{cd}R_{t+\tau,u+\nu,v+\phi}(\alpha,\mathbf{R}_{PQ}),\end{aligned} \qquad (3.87)$$

where $\alpha = pq/(p+q)$. The term $(-)^{\tau+\nu+\phi}$ arises due to the fact that

$$\frac{\partial}{\partial Q_x}F_0\left(\frac{pq}{p+q}R_{PQ}^2\right) = -\frac{\partial}{\partial P_x}F_0\left(\frac{pq}{p+q}R_{PQ}^2\right). \qquad (3.88)$$

3.8   Evaluation of the Boys function

As shown in the previous section, calculating the Coulomb integrals boils down to evaluating the Boys function (3.75). Doing this real time by standard numerical procedures is compuationally expensive and should therefore

be avoided. This section describes one possible way to calculate the Boys function efficiently.

First note that if x is very large, the function value will hardly be affected by changing the upper limit of the integral from 1 to ∞. Doing this is beneficial because then the integral can be calculated exactly. Thus, we have the following approximation for the Boys function for large x:

$$F_n(x) \approx \frac{(2n-1)!!}{2^{n+1}} \sqrt{\frac{\pi}{x^{2n+1}}}. \qquad (x \text{ large}) \qquad (3.89)$$

For small values of x there seems to be no escape from numerical calculation. However, instead of doing the integral real time, computational effort can be saved by pretabulating the function at regular values of x. For values between the tabulated ones, the function can be calculated by a Taylor expansion centered at the nearest tabulated point x_t:

$$F_n(x_t + \Delta x) \approx \sum_{k=0}^{\infty} \frac{F_{n+1}(x_t)(-\Delta x)^k}{k!}. \qquad (x \text{ small}) \qquad (3.90)$$

Computational cost can be reduced even further by calculating the Boys function according to the description above only for the highest values of n needed; for lower values of n the function can be found via the recursion relation

$$F_n(x) = \frac{2xF_{n+1}(x) + e^{-x}}{2n+1}. \qquad (3.91)$$

This relation can be proved by integrating the Boys function by parts.

Chapter 4

Perturbation theory

4.1 Formal perturbation theory

The basic starting point of perturbation theory is to divide the total Hamiltonian H into two parts: One part, H_0, of which we are able to find the eigenstates and eigenvalues and the remaining part, V, which is called the perturbation:

$$H = H_0 + V. \tag{4.1}$$

When $V = 0$, the known solutions to the Schrödinger equation are given by

$$H_0|\Psi_i^{(0)}\rangle = E_i^{(0)}|\Psi_i^{(0)}\rangle, \tag{4.2}$$

where the superindices indicate that the solutions are with respect to H_0. Most often we will be interested in the ground state. Of course, $|\Psi_0^{(0)}\rangle$ is not the actual ground state, but merely an approximation. To obtain the exact ground state $|\Psi_0\rangle$, an (unknown) correction term $|\gamma\rangle$ must be added:

$$|\Psi_0\rangle = |\Psi_0^{(0)}\rangle + |\gamma\rangle. \tag{4.3}$$

The same is true for the energy:

$$E_0 = E_0^{(0)} + \Delta E. \tag{4.4}$$

In perturbation theory, the goal is to estimate the corrections $|\gamma\rangle$ and ΔE order by order in terms of the perturbation V.

It will be assumed that $\langle\Psi_0^{(0)}|\gamma\rangle = 0$, i.e. that there is no overlap between the unperturbed solution and the correction. Furthermore, we will let the unperturbed solution be normalized, which means that the overlap between the unperturbed and excact solution is equal to unity:

$$\langle\Psi_0^{(0)}|\Psi_0\rangle = \langle\Psi_0^{(0)}|\big(|\Psi_0^{(0)}\rangle + |\gamma\rangle\big) = 1 + 0 = 1. \tag{4.5}$$

This is often referred to as intermediate normalisation.

The general expression for the energy correction ΔE can be derived from the Schrödinger equation as follows:

$$(H_0 + V)|\Psi_0\rangle = E_0|\Psi_0\rangle,$$
$$\langle\Psi_0^{(0)}|(H_0 + V)|\Psi_0\rangle = E_0\langle\Psi_0^{(0)}|\Psi_0\rangle,$$
$$\langle\Psi_0^{(0)}|H_0|\Psi_0\rangle + \langle\Psi_0^{(0)}|V|\Psi_0\rangle = E_0, \qquad (4.6)$$
$$\langle H_0\Psi_0^{(0)}|\Psi_0\rangle + \langle\Psi_0^{(0)}|V|\Psi_0\rangle = E_0,$$
$$E_0^{(0)} + \langle\Psi_0^{(0)}|V|\Psi_0\rangle = E_0,$$

so that

$$\Delta E = \langle\Psi_0^{(0)}|V|\Psi_0\rangle. \qquad (4.7)$$

Once we have an order by order expansion of $|\Psi_0\rangle$, this will give us an order by order expansion also of ΔE.

To make further progress, we define the projection operators P and Q:

$$P = |\Psi_0^{(0)}\rangle\langle\Psi_0^{(0)}|, \qquad (4.8)$$

$$Q = \sum_{i=1}^{\infty} |\Psi_i^{(0)}\rangle\langle\Psi_i^{(0)}|. \qquad (4.9)$$

When acting on the state $|\Psi\rangle$, P picks out the part which is parallel with $|\Psi_0^{(0)}\rangle$. This is easily shown by expressing $|\Psi\rangle$ in the basis $\left\{|\Psi_i^{(0)}\rangle\right\}_0^{\infty}$:

$$P|\Psi\rangle = |\Psi_0^{(0)}\rangle\langle\Psi_0^{(0)}| \sum_{j=0}^{\infty} C_j|\Psi_j^{(0)}\rangle = C_0|\Psi_0^{(0)}\rangle. \qquad (4.10)$$

Similarly, Q picks out the part which is orthogonal to $|\Psi_0^{(0)}\rangle$ since $PQ = QP = 0$. Note also that $P^2 = P$, $Q^2 = Q$ and $P + Q = I$. Furthermore, P commutes with H_0:

$$H_0 P|\Psi\rangle = H_0 P \sum_{i=0}^{\infty} C_i|\Psi_i^{(0)}\rangle = H_0 C_0|\Psi_0^{(0)}\rangle = C_0 E_0^{(0)}|\Psi_0^{(0)}\rangle,$$
$$PH_0|\Psi\rangle = PH_0 \sum_{i=0}^{\infty} C_i|\Psi_i^{(0)}\rangle = P \sum_{i=0}^{\infty} C_i E_i^{(0)}|\Psi_i^{(0)}\rangle = C_0 E_0^{(0)}|\Psi_0^{(0)}\rangle.$$
$$(4.11)$$

Also, since $Q = I - P$, Q commutes with H_0 also.

We now have the ingredients necessary to find a perturbative expansion of $|\Psi_0\rangle$. The starting point is a slight rewrite of the Schrödinger equation:

$$(\zeta - H_0)|\Psi_0\rangle = (V - E_0 + \zeta)|\Psi_0\rangle, \qquad (4.12)$$

where ζ is a hitherto unspecified parameter. Different choises of ζ will lead to different perturbation schemes. Two very common choices are $\zeta = E_0$ and $E_0^{(0)}$ which lead to Brillouin-Wigner and Rayleigh-Schrödinger perturbation theory, respectively. Acting from the left with the operator Q on both sides, and using the fact that $Q^2 = Q$ and $[Q, H_0] = 0$ leads to

$$Q(\zeta - H_0)Q|\Psi_0\rangle = Q(V - E_0 + \zeta)|\Psi_0\rangle. \tag{4.13}$$

We now need an expression for the inverse of $Q(\zeta - H_0)Q$. As long as ζ is not equal to any of the eigenvalues $\{E_i^{(0)}\}_{i=1}^\infty$, this exists and is equal to

$$R_0(\zeta) = \frac{Q}{\zeta - H_0} = \sum_{i=1}^\infty \sum_{j=1}^\infty |\Psi_i^{(0)}\rangle\langle\Psi_i^{(0)}|(\zeta - H_0)^{-1}|\Psi_j^{(0)}\rangle\langle\Psi_j^{(0)}|, \tag{4.14}$$

which is called the resolvent of H_0. Writing $R_0(\zeta)$ as the fraction above is justified by the fact that Q commutes with H_0.

Acting with $R_0(\zeta)$ from the left on both sides of our last equation gives

$$Q|\Psi_0\rangle = R_0(\zeta)(V - E_0 + \zeta)|\Psi_0\rangle, \tag{4.15}$$

and using the fact that $(P + Q)|\Psi_0\rangle = |\Psi_0\rangle$ leads to

$$|\Psi_0\rangle = |\Psi_0^{(0)}\rangle + R_0(\zeta)(V - E_0 + \zeta)|\Psi_0\rangle. \tag{4.16}$$

This equation will give us the perturbative expansion we are after. Substituting this expression for $|\Psi_0\rangle$ into itself gives

$$\begin{aligned}
|\Psi_0\rangle = |\Psi_0^{(0)}\rangle &+ R_0(\zeta)(V - E_0 + \zeta)|\Psi_0^{(0)}\rangle \\
&+ [R_0(\zeta)(V - E_0 + \zeta)]^2|\Psi_0\rangle,
\end{aligned} \tag{4.17}$$

and repeating this process yields the expression we are seeking:

$$|\Psi_0\rangle = \sum_{n=0}^\infty [R_0(\zeta)(V - E_0 + \zeta)]^n|\Psi_0^{(0)}\rangle. \tag{4.18}$$

The corresponding expansion for the energy is found by inserting this into equation (4.7):

$$\Delta E = \sum_{n=0}^\infty \langle\Psi_0^{(0)}|V[R_0(\zeta)(V - E_0 + \zeta)]^n|\Psi_0^{(0)}\rangle. \tag{4.19}$$

4.2   Rayleigh-Scrhödinger perturbation theory

Rayleigh-Schrödinger perturbation theory is obtained by setting $\zeta = E_0^{(0)}$, which gives

$$\Delta E = \sum_{n=0}^{\infty} \langle \Psi_0^{(0)} | V [R_0(E_0^{(0)})(V - \Delta E)]^n | \Psi_0^{(0)} \rangle. \tag{4.20}$$

Writing out the first three terms explicitly:

$$
\begin{aligned}
\Delta E =& \langle \Psi_0^{(0)} | V | \Psi_0^{(0)} \rangle \\
&+ \langle \Psi_0^{(0)} | V R_0 (V - \Delta E) | \Psi_0^{(0)} \rangle \\
&+ \langle \Psi_0^{(0)} | V R_0 (V - \Delta E) R_0 (V - \Delta E) | \Psi_0^{(0)} \rangle + \ldots
\end{aligned} \tag{4.21}
$$

were the dependence of R_0 on $E_0^{(0)}$ has been supressed. This is still not a proper perturbative expansion since ΔE is present also on the right side of the equation. We get the correct expression by inserting the expression itself into every occurence of ΔE on the right hand side. Doing this, and noting that $R_0 |\Psi_0^{(0)}\rangle = 0$, we get

$$
\begin{aligned}
\Delta E =& \langle \Psi_0^{(0)} | V | \Psi_0^{(0)} \rangle \\
&+ \langle \Psi_0^{(0)} | V R_0 V | \Psi_0^{(0)} \rangle \\
&+ \langle \Psi_0^{(0)} | V R_0 (V - \langle \Psi_0^{(0)} | V | \Psi_0^{(0)} \rangle) R_0 V | \Psi_0^{(0)} \rangle + \cdots
\end{aligned} \tag{4.22}
$$

The three lines are the first, second and third order corrections, respectively, to the zero order energy.

4.3   Møller-Plesset perturbation theory

To make further progress, it is necessary to specify the zero order Hamiltonian H_0. Setting it equal to the Fock operator,

$$H_0 = \sum_{pq} \langle p | \mathcal{F} | q \rangle a_p^\dagger a_q, \tag{4.23}$$

yields the so-called Møller-Plesset perturbation thoery, after Møller and Plesset in 1935 (need reference). If we choose the eigenfunctions of the Fock operator as our single-particle basis, then H_0 simplifies to

$$H_0 = \sum_{pq} \langle p | \varepsilon_q | q \rangle a_p^\dagger a_q = \sum_{pq} \varepsilon_q \delta_{pq} a_p^\dagger a_q = \sum_p \varepsilon_p a_p^\dagger a_p. \tag{4.24}$$

Furthermore, any Slater determinant is now an eigenstate of H_0. Consider for example $|\Psi_0^{(0)}\rangle$ which is composed of the spinorbitals corresponding to the N lowest eigenvalues of $\mathcal{F}$:

$$H_0|\Psi_0^{(0)}\rangle = \sum_p \varepsilon_p a_p^\dagger a_p |123\ldots N\rangle = \sum_{i=1}^N \varepsilon_i |\Psi_0^{(0)}\rangle. \tag{4.25}$$

Thus the zero order energy of the Hamiltonian is

$$E_0^{(0)} = \sum_{i=1}^N \varepsilon_i. \tag{4.26}$$

Next we show how this choice of H_0 determines the perturbation V:

$$H = H_0 + (H_1 - H_0 + H_2). \tag{4.27}$$

This means that

$$\begin{aligned}
V &= H_1 - H_0 + H_2 \\
&= \sum_{pq}[\langle p|h|q\rangle - \langle p|\mathcal{F}|q\rangle]a_p^\dagger a_q + \frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle a_p^\dagger a_q^\dagger a_s a_r \\
&= -\sum_{pq}\langle p|(J-K)|q\rangle a_p^\dagger a_q + \frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle a_p^\dagger a_q^\dagger a_s a_r.
\end{aligned} \tag{4.28}$$

This form of V seems to suggest that it has a one-body as well as a two-body part. However, normal ordering the operator with respect to $|\Psi^{(0)}\rangle$ as the Fermi vacuum reveals that the one-body part of V cancels out. Doing exactly the same calculations as in section 2.4.4 leads to

$$\begin{aligned}
V = &-\sum_{pq}\langle p|(J-K)|q\rangle\{a_p^\dagger a_q\} - \sum_i \langle i|(J-K)|i\rangle \\
&+ \frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle\{a_p^\dagger a_q^\dagger a_s a_r\} + \sum_{pq}\sum_i \langle pi||qi\rangle\{a_p^\dagger a_q\} \\
&+ \frac{1}{2}\sum_{ij}\langle ij||ij\rangle
\end{aligned} \tag{4.29}$$

Noting that $\langle p|(J-K)|q\rangle = \langle pi||qi\rangle$, the one-body parts now cancel, and we arrive at

$$V = \frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle\{a_p^\dagger a_q^\dagger a_s a_r\} - \frac{1}{2}\sum_{ij}\langle ij||ij\rangle. \tag{4.30}$$

This form of the perturbation makes it easier to evaluate the energy corrections. The first order correction is:

$$\Delta E^{(1)} = \langle \Psi_0^{(0)} | V | \Psi_0^{(0)} \rangle = -\frac{1}{2} \sum_{ij} \langle ij || ij \rangle, \qquad (4.31)$$

since the expectation of the normal product is equal to zero. Comparing equations (4.26) and (4.31) with equation (3.4) shows that the Hartree-Fock energy is in fact accurate up to first order perturbation theory.

The expression for the second order correction is somewhat more complicated. It is given by

$$\Delta E^{(2)} = \langle \Psi_0^{(0)} | V R_0 V | \Psi_0^{(0)} \rangle. \qquad (4.32)$$

Because of the resolvent R_0, only the normal product of equation (4.30) survives. The resolvent R_0 is given by:

$$R_0 = \frac{Q}{E_0 - H_0} = \sum_{i=1}^{\infty} \frac{|\Psi_i^{(0)}\rangle\langle\Psi_i^{(0)}|}{E_0 - E_i^{(0)}}, \qquad (4.33)$$

where the states $|\Psi_i^{(0)}\rangle$ include all eigenstates of the zero order Hamiltonian H_0 except the ground state $|\Psi_0^{(0)}\rangle$. In terms of particle- and hole-states, the resolvent can be written as

$$R_0 = \sum_{ia} \frac{|\Psi_i^a\rangle\langle\Psi_i^a|}{\varepsilon_i - \varepsilon_a} + \sum_{i<j,a<b} \frac{|\Psi_{ij}^{ab}\rangle\langle\Psi_{ij}^{ab}|}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} + \cdots \qquad (4.34)$$

We will use Wick's generalised theorem to calculate the second order correction. From the theorem it follows that only the two-particle-two-hole states will give non-zero terms. This means that

$$\Delta E^{(2)} = \frac{1}{16} \sum_{pqrs} \sum_{tuvw} \sum_{i<j,a<b} \frac{\langle pq||rs\rangle\langle tu||vw\rangle}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} \langle \Psi_0^{(0)} | \{a_p^\dagger a_q^\dagger a_s a_r\}\{a_a^\dagger a_b^\dagger a_j a_i\} | \Psi_0^{(0)} \rangle$$
$$\langle \Psi_0^{(0)} | \{a_i^\dagger a_j^\dagger a_b a_a\}\{a_t^\dagger a_u^\dagger a_w a_v\} | \Psi_0^{(0)} \rangle. \qquad (4.35)$$

The only non-zero contractions are those between creation and annihilation operators. Thus

$$\Delta E^{(2)} = \frac{1}{16} \sum_{pqrs} \sum_{tuvw} \sum_{i<j,a<b} \frac{\langle pq||rs\rangle\langle tu||vw\rangle}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} \langle \Psi_0^{(0)} | \{a_p^\dagger a_q^\dagger a_s a_r\}\{a_a^\dagger a_b^\dagger a_j a_i\} |\Psi_0^{(0)}\rangle$$

$$\langle \Psi_0^{(0)} | \{a_i^\dagger a_j^\dagger a_b a_a\}\{a_t^\dagger a_u^\dagger a_w a_v\} |\Psi_0^{(0)}\rangle + 15 \text{ more terms} \qquad (4.36)$$

The 15 other terms are due to the fact that there are four possible ways of contracting the first as well as the second vacuum expectation, resulting in a total of 16 terms. Each change of order in the contractions introduces a minus sing which in turn can be compensated for by using the antisymmetry of the matrix elements. This means that all the terms are actually equal, and we get

$$\Delta E^{(2)} = \frac{1}{4} \sum_{i,j} \sum_{a,b} \frac{|\langle ij||ab\rangle|^2}{\varepsilon_{ij}^{ab}}, \qquad (4.37)$$

where $\varepsilon_{ij}^{ab} = \varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b$. Note that a factor of $1/4$ has been introduced by removing the restrictions $i < j$ and $a < b$. The sums over the hole states range from 0 to the number of particles N, and the sums over the particle states range from $N + 1$ to the number of basis functions M.

Clearly, the calculations become more and more laborious as we increase the order of correction. In practice, diagrammatic notation is used to evaluate higher order terms. It will not be introduced here, and the interested reader is referred to Shavitt and Bartlett [4]. In any case, only second order Møller-Plesset perturbation theory (MP2) will be considered in this thesis.

4.4   MP2 in the RHF-case

In the case of RHF, the spinorbitals are assumed to be on the from

$$\{\psi_{2k}(\mathbf{x}),\ \psi_{2k+1}(\mathbf{x})\} = \{\phi_k(\mathbf{r})\alpha(s),\ \phi_k(\mathbf{r})\beta(s)\}. \qquad (4.38)$$

Inserting this in equation (4.37) results in

$$\begin{aligned}
\Delta E^{(2)} =& \frac{1}{4} \sum_{i,j} \sum_{a,b} \frac{1}{\varepsilon_{ij}^{ab}} \Big[|\langle(\phi_i\alpha)(\phi_j\alpha)||(\phi_a\alpha)(\phi_b\alpha)\rangle|^2 \\
& + |\langle(\phi_i\beta)(\phi_j\beta)||(\phi_a\beta)(\phi_b\beta)\rangle|^2 + |\langle(\phi_i\alpha)(\phi_j\alpha)||(\phi_a\alpha)(\phi_b\alpha)\rangle|^2 \\
& + |\langle(\phi_i\beta)(\phi_j\alpha)||(\phi_a\beta)(\phi_b\alpha)\rangle|^2 + |\langle(\phi_i\alpha)(\phi_j\beta)||(\phi_a\beta)(\phi_b\alpha)\rangle|^2 \\
& + |\langle(\phi_i\beta)(\phi_j\alpha)||(\phi_a\alpha)(\phi_b\beta)\rangle|^2 \Big].
\end{aligned}$$

$$(4.39)$$

Terms which are automatically zero due to spin have not been included. Integrating out spin now yields

$$
\begin{aligned}
\Delta E^{(2)} =& \frac{1}{4} \sum_{i,j=1}^{N/2} \sum_{a,b=N/2+1}^{M/2} \frac{1}{\varepsilon_{ij}^{ab}} \Big[|\langle \phi_i \phi_j || \phi_a \phi_b \rangle|^2 \\
& + |\langle \phi_i \phi_j || \phi_a \phi_b \rangle|^2 + |\langle \phi_i \phi_j | g | \phi_a \phi_b \rangle|^2 \\
& + |\langle \phi_i \phi_j | g | \phi_a \phi_b \rangle|^2 + |\langle \phi_i \phi_j | g | \phi_b \phi_a \rangle|^2 \\
& + |\langle \phi_i \phi_j | g | \phi_b \phi_a \rangle|^2 \Big].
\end{aligned}
\tag{4.40}
$$

Note that the first two terms in the sum have both the direct term and the exchange term, whereas in the rest of the terms only one of these (direct or exchange) survives. Collecting equal terms finally gives

$$
\Delta E^{(2)} = \sum_{i,j=1}^{N/2} \sum_{a,b=N/2+1}^{M/2} \frac{\langle ij|g|ab \rangle \big(2\langle ab|g|ij \rangle - \langle ab|g|ji \rangle \big)}{\varepsilon_{ij}^{ab}}.
\tag{4.41}
$$

Note that in this expression the explicit appereance of ϕ has been supressed. This might lead to confusion about whether the sum is over spinorbitals or merely spatial orbtials (which it is in this case). In this thesis we shall let explicit indication of summation ranges mean that the sums are over spatial orbitals. Otherwise, the sums are over spinorbitals.

4.5   MP2 in the UHF-case

In the case of UHF, the spinorbitals are assumed to be on the form

$$
\{\psi_{k_+}(\mathbf{x}), \psi_{k_-}(\mathbf{x})\} = \{\phi_{k_+}(\mathbf{r})\alpha(s), \phi_{k_-}(\mathbf{r})\beta(s)\}.
\tag{4.42}
$$

Inserting this in equation (4.37) and integrating out spin in the same manner as above yields

$$
\begin{aligned}
\Delta E^{(2)} =& \frac{1}{4} \sum_{i,j=1}^{N/2} \sum_{a,b=N/2+1}^{M/2} \Big[\frac{|\langle i_+ j_+ || a_+ b_+ \rangle|^2}{\varepsilon_{i_+ j_+}^{a_+ b_+}} \\
& + \frac{|\langle i_- j_- || a_- b_- \rangle|^2}{\varepsilon_{i_- j_-}^{a_- b_-}} + \frac{|\langle i_+ j_- | g | a_+ b_- \rangle|^2}{\varepsilon_{i_+ j_-}^{a_+ b_-}} \\
& + \frac{|\langle i_- j_+ | g | a_- b_+ \rangle|^2}{\varepsilon_{i_- j_+}^{a_- b_+}} + \frac{|\langle i_+ j_- | g | b_+ a_- \rangle|^2}{\varepsilon_{i_+ j_-}^{a_- b_+}} \\
& + \frac{|\langle i_- j_+ | g | b_- a_+ \rangle|^2}{\varepsilon_{i_- j_+}^{a_+ b_-}} \Big].
\end{aligned}
\tag{4.43}
$$

Notice that in the UHF-case there are twice as many spatial hole-states to sum over since both i_+ and i_i range from 1 to $N/2$.

Chapter 5

Other many-body methods

5.1 Configuration interaction (CI)

5.2 Density functional theory (DFT)

5.3 Variational Monte Carlo (VMC)

5.4 Diffusion Monte Carlo (DMC)

Part II

Implementation

Part III

Results

Appendix A

Integral evaluation

A.1 Recurrence relation for E_t^{ij}

In this section we will show the recurrence relation in equation (3.61). We start by considering the fact that the product $G_{i+1}(a, x_A)G_j(b, x_B)$ can be expressed in terms of the Hermite Gaussians in two different ways. The most obvious way is

$$G_{i+1}(a, x_A)G_j(b, x_B) = \sum_{t=0}^{i+j+1} E_t^{i+1,j}\Lambda_t(p, x_P). \tag{A.1}$$

The other way is

$$
\begin{aligned}
G_{i+1}(a, x_A)G_j(b, x_B) &= x_A G_i(a, x_A)G_j(b, x_B) \\
&= [(x - P_x) + (P_x - A_x)] \sum_{t=0}^{i+j} E_t^{ij}\Lambda_t \\
&= \sum_{t=0}^{i+j} [x_P + X_{PA}]E_t^{ij}\Lambda_t.
\end{aligned}
\tag{A.2}
$$

Next we use the relation (shown below)

$$x_P\Lambda_t = \frac{1}{2p}\Lambda_{t+1} + t\Lambda_{t-1}. \tag{A.3}$$

Inserting this, we obtain

$$
\begin{aligned}
G_{i+1}(a, x_A)G_j(b, x_B) &= \sum_{t=0}^{i+j} [\frac{1}{2p}\Lambda_{t+1} + t\Lambda_{t-1} + X_{PA}\Lambda_t]E_t^{ij} \\
&= \sum_{t=0}^{i+j} [\frac{1}{2p}E_{t-1}^{ij} + X_{PA}E_t^{ij} + (t+1)E_{t+1}^{ij}]\Lambda_t
\end{aligned}
\tag{A.4}
$$

Comparing this with the first expansion yields the desired result.

We now show the relation (A.3):

$$
\begin{aligned}
\Lambda_{t+1}(p, x_P) &= \left(\frac{\partial}{\partial P_x}\right)^t \frac{\partial}{\partial P_x} e^{-px_P^2} \\
&= \left(\frac{\partial}{\partial P_x}\right)^t 2px_P e^{-px_P^2} \\
&= 2p[-t\left(\frac{\partial}{\partial P_x}\right)^{t-1} + x_P\left(\frac{\partial}{\partial P_x}\right)^t] e^{-px_P^2} \\
&= 2p[-t\Lambda_{t-1} + x_P\Lambda_t].
\end{aligned}
\tag{A.5}
$$

A.2   Recurrence relation for R_{tuv}^n

This following proves the recurrence relations (3.80):

$$
R_{t+1,u,v}^n = (-2p)^n \frac{\partial^{t+u+v}}{\partial P_x^t \partial P_y^u \partial P_z^v} \frac{\partial}{\partial P_x} F_n(pR_{PC}^2)
\tag{A.6}
$$

$$
= (-2p)^n \frac{\partial^{t+u+v}}{\partial P_x^t \partial P_y^u \partial P_z^v} [-2p(P_x - C_x)F_{n+1}(pR_{PC}^2)]
\tag{A.7}
$$

$$
= (-2p)^{n+1} \frac{\partial^{u+v}}{\partial P_y^u \partial P_z^v} \left[\frac{\partial^t}{\partial P_x^t}(P_x - C_x)F_{n+1}(pR_{PC}^2)\right]
\tag{A.8}
$$

$$
= (-2p)^{n+1} \frac{\partial^{u+v}}{\partial P_y^u \partial P_z^v} \left[t\frac{\partial^{t-1}}{\partial P_x^{t-1}} + (P_x - C_x)\frac{\partial^t}{\partial P_x^t}\right] F_{n+1}(pR_{PC}^2)
\tag{A.9}
$$

$$
= tR_{t-1,u,v}^{n+1} + (P_x - C_x)R_{tuv}^{n+1}.
\tag{A.10}
$$

In the derivation it was used that $F_n'(x) = -F_{n+1}(x)$.

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