

Chapter 7

The Hartree-Fock Method

7.1 Introduction

There are many problems of interest, for example in solid state physics, and indeed, the whole of chemistry, where we need to consider the quantum mechanical behaviour of many interacting electrons. This is a very difficult problem. In earlier lectures, we discussed how to solve the Schrödinger equation for a single electron in various ways, e.g. Numerov integration of the time independent equation, special techniques for solving the time dependent equation, and various variational approaches. We shall now turn our attention to solving the many-electron problem.

There is, of course, a hierarchy of techniques that can be used to solve this problem, which differ in the approximations used. There is usually a trade-off between computational speed and accuracy. For example, we have classical molecular dynamics which neglects the existence of individual electrons altogether and considers the interaction between atoms with some empirically derived potential. Then there are the *semi-empirical* methods, which start with a more or less rigorous treatment of the quantum mechanics, but then replace many of the terms in the equations with parameters derived from experiments. Finally, there are the *ab initio* (from first principles) methods, which require no experimental input, but can still differ in the approximations made and so have varying cost and accuracy.

The two most widespread *ab initio* methods are the *Hartree-Fock* method and *Density Functional Theory*. Traditionally, Hartree-Fock (HF) was used by chemists and Density Functional Theory (DFT) was used by physicists. This is because for many years chemists were primarily interested in predicting the structure and spectra of molecules to high accuracy, whereas physicists were more concerned with predicting the more general features of band structures in solids. However, there have been many technical improvements in the implementation of DFT over the last 10-15 years, which has meant that more chemists are starting to use DFT in preference to HF.

We shall start by discussing some of the basics that underly the HF method, before discussing the method itself. We shall leave a discussion of DFT until the next lecture. There are also Quantum Monte Carlo methods that can be used to solve this problem which we will discuss at the end of this lecture course.

7.2 Born-Oppenheimer approximation

Obviously, when considering the study of atoms, molecules, solids, etc. we should consider the whole system as an interacting QM whole. For example, each electron is moving in the electric field generated by all the other electrons and all the nuclei. Therefore, we have a large numbers of interacting degrees of freedom. The most obvious approximation is to consider the electrons as moving in the classical field generated by static nuclei, as each electron is much lighter, and therefore moves much faster, than any nucleus. (The mass of the proton is 1835 times the mass of the electron.) This therefore decouples the nuclear and electronic degrees of freedom, and the remaining problem is then how to solve for the *electronic structure* of the system. This approximation, known as the *Born-Oppenheimer approximation*, is almost universally used. The total energy of the system is now the sum of the energy of the electrons and the nuclei. We often also neglect the QM of the nuclei, and instead just use the electrostatic energy of the nuclei. Note that the positions of the nuclei can be varied in a quasi-static manner in order to find the minimum energy of the combined system, in which case we consider the electrons to be moving on the *potential energy surface* given by the nuclei (also known as the *Born-Oppenheimer surface*). This is not always a valid approximation - see my own research for more details!

7.3 Many-electron Hamiltonian

We can now write down the Born-Oppenheimer Hamiltonian for the electrons in atomic units:

$$\hat{H} = \sum_{i=1}^N \frac{\hat{p}_i^2}{2} + \frac{1}{2} \sum_{i,j=1;i \neq j}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{n=1}^K \sum_{i=1}^N \frac{Z_n}{|\mathbf{r}_i - \mathbf{R}_n|} \quad (7.1)$$

where the indices i and j refer to one of the N electrons, and the n index refers to one of the K nuclei. The electrons are at positions \mathbf{r}_i and the nuclei at \mathbf{R}_n . The first term then represents the kinetic energy of the electron, the second the Coulomb repulsion between different electrons, and the third term represents the Coulomb attraction between electrons and nuclei.

The curious thing is that although we can write down the exact many-body Hamiltonian, we do not know the form of the corresponding exact

many-body wavefunction! The difficulty in solving the many-body Schrödinger equation is primarily the second term in equation 7.1 which contains the interactions between all the electrons. The simplest way around this problem is therefore to approximate this term in a manner that decouples the interactions. This is the basis of the *independent particle* approximation.

7.4 Independent particle approximation

The independent particle approximation effects the two fundamental parts of the problem - the Hamiltonian and the wavefunction. We replace the electron-electron repulsion term with one that only depends on repulsion between an electron and the *average* position of all the other electrons. We can then combine the second and third terms in equation 7.1 to yield:

$$\hat{H} \simeq \sum_{i=1}^N \left(\frac{\hat{p}_i^2}{2} + V_{eff}(\mathbf{r}_i) \right) \quad (7.2)$$

where $V_{eff}(\mathbf{r})$ is the *effective potential*, which depends on the position of all the nuclei $\{\mathbf{R}\}$ and also on the wavefunction ψ that the Hamiltonian is acting upon! The other part of the approximation is to assume that we can write down the basic form of ψ in terms of *one-electron wavefunctions*, such as the atomic orbitals of an isolated Hydrogen atom.

We therefore have to solve this problem *self-consistently*: that is, given a set of nuclear coordinates $\{\mathbf{R}\}$ and a guess at ψ we calculate V_{eff} , form \hat{H} , and solve to get a new ψ . We then use this new ψ to make a new V_{eff} , etc and repeat until there is no further change in ψ , whereupon we have the self-consistent solution.

The Born-Oppenheimer and the independent particle approximation are the basic ingredients of many *ab initio* approaches - the differences arise in the form of V_{eff} and ψ chosen.

7.5 Hartree method

One of the oldest methods is the Hartree method. In this, the N -electron wavefunction is chosen to be a simple product of one-electron wavefunctions ϕ_k (otherwise known as *orbitals*):

$$\Psi(\mathbf{r}_1, \mathbf{r}_2 \dots \mathbf{r}_N) = \phi_1(\mathbf{r}_1) \phi_2(\mathbf{r}_2) \dots \phi_N(\mathbf{r}_N) \quad (7.3)$$

and the corresponding Hamiltonian is:

$$\hat{H} = -\frac{1}{2}\nabla^2 + \sum_{i=1}^N \int |\phi_i(\mathbf{r}')|^2 \frac{1}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' - \sum_n \frac{Z_n}{|\mathbf{r} - \mathbf{R}_n|} \quad (7.4)$$

where this form for the second term is known as the *Hartree potential*.

The simple product form of the many-electron wavefunction is called *uncorrelated*, because the probability of finding an electron at \mathbf{r}_1 and another one at \mathbf{r}_2 is uncorrelated as it can be written as the product of two one-electron probabilities. Note that we are not saying that the two electrons are not interacting - there is still the $\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}$ term in the Hamiltonian, but that this interaction has been taken into account in an average way. It is the average charge distribution of \mathbf{r}_2 that interacts with the electron at \mathbf{r}_1 . This neglect of correlations can lead to unphysical results - the most famous of which is that it predicts that an H_2 molecule will dissociate (as the $H - H$ bond length is increased) into a state where both electrons sit on the same atom. The other major flaw with this form of the many-electron wavefunction is that it is not anti-symmetric under particle *exchange* as required by the *Pauli Exclusion Principle* for fermions.

We know, for example, that when dealing with a two particle system that the overall wavefunction is not just the product of the two individual wavefunction - we need to form a proper symmetrised combination. In general, if particle 1 is in state $\alpha(\mathbf{r}_1)$ and particle two is in state $\beta(\mathbf{r}_2)$ then the overall wavefunction is:

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} (\alpha(\mathbf{r}_1)\beta(\mathbf{r}_2) - \alpha(\mathbf{r}_2)\beta(\mathbf{r}_1)) \quad (7.5)$$

as the electrons are indistinguishable, and the overall wavefunction must be anti-symmetric (i.e. changes sign) under particle exchange. If we include spin, then it is the overall product of space*spin that must be antisymmetric - for example, for two electrons that can each be either spin-up or spin-down, we know that there are 4 possible results - 3 states making a triplet with net spin $1\hbar$ and a singlet with net spin $0\hbar$. We therefore find that the basic Hartree method neglects all effects of exchange and correlation.

There is also a flaw in the Hartree potential, in that it contains the interaction of any given orbital with itself, as the summation in the charge density runs over all such functions. This is an example of a spurious *self-interaction*, which must be corrected.

Both of these deficiencies are remedied in the Hartree-Fock method.

7.6 Hartree-Fock method

The two major flaws in the Hartree method can be cured by writing the N -electron wavefunction as an anti-symmetrised product of orbitals, which

can be expressed most concisely as a *Slater determinant*:

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(1) & \phi_1(2) & \cdots & \phi_1(N) \\ \phi_2(1) & \phi_2(2) & \cdots & \phi_2(N) \\ \vdots & & \ddots & \\ \phi_N(1) & & & \phi_N(N) \end{vmatrix} \quad (7.6)$$

which has the useful side-effect of also making the resulting wavefunction *correlated*. The result is that every electron is surrounded by an “*exchange hole*” within which there is only a very small probability of finding another electron.

Note that the term “correlated” is used in various ways in electronic structure theory. The term “correlation effect” is usually taken to refer to correlations other than those due to exchange, for example dynamic correlations due to Coulomb repulsion between electrons. As such, the Hartree-Fock method is usually considered to neglect correlation but to treat exchange exactly.

The Hartree-Fock method may be derived by applying the variational principle to equation 7.1, using a single Slater determinant wavefunction and minimising the expectation value of the energy w.r.t. the orbitals. The result is:

$$\hat{F}\phi_k = (\hat{h} + \hat{J} - \hat{K})\phi_k \quad (7.7)$$

where \hat{F} is known as the *Fock operator*, and

$$\hat{h}\phi_k = \left(-\frac{1}{2}\nabla^2 - \sum_{n=1}^K \frac{Z_n}{|\mathbf{r} - \mathbf{R}_n|} \right) \phi_k \quad (7.8)$$

$$\hat{J}\phi_k = \sum_{l=1}^N \int |\phi_l(\mathbf{r}')|^2 \frac{1}{|\mathbf{r} - \mathbf{r}'|} \phi_k(\mathbf{r}) d\mathbf{r}' \quad (7.9)$$

$$\hat{K}\phi_k = \sum_{l=1}^N \int \phi_l^*(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \phi_k(\mathbf{r}') \phi_l(\mathbf{r}) d\mathbf{r}' \quad (7.10)$$

where \hat{J} is known as the Coulomb operator, and \hat{K} as the exchange operator.

The Hartree method can be considered as $(\hat{h} + \hat{J})$, but the exchange operator is the new addition due to Fock. It looks like the Coulomb operator, but with the two orbital labels k and l interchanged. This is an example of a *non-local operator*, that is, the effect on $\phi_k(\mathbf{r})$ is determined by the assumed values for $\phi_k(\mathbf{r}')$ at all positions \mathbf{r}' . The exchange term vanishes for orthogonal states $\phi_k(\mathbf{r})$ and $\phi_l(\mathbf{r})$ so that two electrons with the same quantum numbers but different spins do not feel this term - as required by the exclusion principle. Note that the exchange term also cancels the self-energy term in the Hartree potential as a result of the anti-symmetry. Note

also that the exchange term has a negative sign - that is, exchange lowers the total energy of the system, due to the tendency to keep two electrons with the same spin apart.

As in the Hartree method, this equation must also be solved by the self-consistent approach. A subtlety is that the total energy of the system is not merely the sum of the eigenvalues of the Fock operator, ε_k , but rather is given by:

$$\langle E \rangle = \sum_{l=1}^N \left(\varepsilon_k - \frac{1}{2} \int \phi_k^*(\mathbf{r}) (\hat{J} - \hat{K}) \phi_k(\mathbf{r}) d\mathbf{r} \right) \quad (7.11)$$

where the second term is subtracted off the sum of the eigenvalues, to prevent double counting certain integrals.

The most time consuming part of the problem is the calculation of all the integrals in the Coulomb and exchange operators, which are known as *two-electron integrals*. Remember that in order to calculate ε_k we need to evaluate

$$\varepsilon_k = \int \phi_k^*(\mathbf{r}) \hat{F} \phi_k(\mathbf{r}) d\mathbf{r} \quad (7.12)$$

which therefore contains many integrals of the general form:

$$\int \int \phi_p^*(\mathbf{r}) \phi_q^*(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \phi_s(\mathbf{r}') \phi_t(\mathbf{r}) d\mathbf{r}' d\mathbf{r} \quad (7.13)$$

where the different labels p, q, r, s vary according to whether calculating Hartree or exchange terms, with some symmetry of labels as appropriate. Note that if we expand each orbital in terms of some basis functions, with M basis functions in total, then there will be approximately $\frac{M^4}{8}$ of these two-electron integrals to perform. For example, a small system, with say 6 atoms and 12 basis functions per atom, will require approximately 3.4 million two-electron integrals per iteration towards self-consistency! The results of all these integrals are then used to form the Fock matrix, which then must be diagonalized, which as mentioned before is an $O(M^3)$ operation. Therefore, a lot of effort has been devoted over the years towards minimising the size of the basis set required (as discussed earlier in the lecture on Basis Sets), and to approximating or even neglecting various subsets of these integrals.

7.7 Approximate Hartree-Fock

It used to be quite common practice to neglect various subsets of the two-electron integrals. The crudest such approximation was to neglect all integrals which involved the overlap of Gaussians from different atoms - an approach known as Complete Neglect of Differential Overlap (CNDO). This is drastic! Whilst such integrals may be small, there are many of them and their overall effect is not insignificant. Therefore, other less drastic schemes were

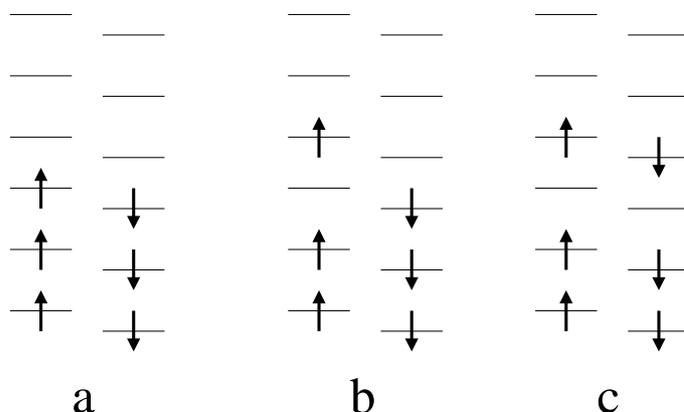


Figure 7.1: Schematic of some of the different Slater determinants in a Configuration Interaction calculation. (a) shows the reference spin-polarized HF ground state, (b) shows a sample single excitation, (c) shows a sample double excitation. This can be extended to higher multiplicities. In a full CI calculation, all such determinants are included.

devised, such as Intermediate Neglect of Differential Overlap (INDO), and Modified Intermediate Neglect of Differential Overlap (MINDO) and others. In these schemes, some of the integrals are replaced by semi-empirical parameterizations, whilst others are done analytically. Obviously, such approaches are significantly quicker than Hartree-Fock, but are severely compromised in accuracy and reliability, and are not much used nowadays.

7.8 Improving the Hartree-Fock approach

Whilst the Hartree-Fock method has many strengths, it has some weaknesses, such as the neglect of Coulomb correlations. This can be remedied in a systematic way by improving upon the form of the many-body wavefunction used. Instead of considering just a single Slater determinant, consider a linear combination of determinants, where each determinant is constructed from the ground state by exciting electrons. See figure 7.1 for an example. The resulting wavefunction must produce a lower ground state energy as it contains more basis functions. This approach is known as the *Configuration Interaction* (CI) method. Obviously, it is only possible to consider a limited number of additional determinants as the cost of the calculation rises dramatically. However, it is possible to extrapolate results from a sequence of calculations with progressively more determinants, to the “full CI” limit. Such results are in principle exact (within the Born-Oppenheimer approximation) but in practice will be limited by the finite basis set size used for each determinant. Note that the total number of determinants is $M!$ where M is the size of the basis set in each determinant.

Other, more complex schemes, such as Møller-Plesset, attempt to include the effect of correlations using perturbation analysis, at differing levels: MP2 corresponds to a second-order perturbation theory (where Hartree-Fock is actually the first-order theory) and adds the correlation between pairs of electrons. Similarly, MP3 adds the interaction between pairs of pairs of electrons, and so on for higher orders. Whilst Hartree-Fock scales as M^4 , MP2 scales as M^5 , MP3 as M^6 , etc. Very few calculations go beyond MP4, and even that is only for very small molecules containing at most 10-20 electrons.

7.9 Results

Using the analytic expressions for the Hamiltonian and the orbitals, it is possible to calculate expressions for the forces, i.e. the first derivative of the total energy. This gives higher accuracy than numerical differencing, and can be used to great effect in calculating the equilibrium geometry of the system, i.e. the arrangement of atoms which minimizes both the energy and the forces on the atoms. It has also more recently become possible to calculate the second-derivatives of the total energy, which then makes it possible to calculate vibrational frequencies and locate saddle-points of the potential energy surface (e.g. transition states of chemical reactions).

The many-body wavefunction found can be used to calculate many electronic and optical properties, such as the electron charge density, polarizabilities, etc. and the one-electron orbitals can be used in an approximate way to interpret photo-emission spectra using *Koopman's Theorem*.

In situations where the Hartree-Fock method works, such as for organic molecules, or clusters of atoms from the main group of the periodic table, it produces results of high precision (as many of the computations are done pseudo-analytically), and with a reasonable accuracy. For example, bond lengths are generally correct to within $\pm 0.003 \text{ \AA}$, angles to within $\pm 3^\circ$, and relative energies can be as good as 0.05 eV/atom. However, it typically overestimates vibrational frequencies by about 10%, and underestimates binding energies by as much as 50%.

Whilst the basic cost of calculating the matrix elements of the Hamiltonian is $O(M^4)$, in practice a large number of these integrals can be justifiably neglected for sufficiently large systems, and the computational cost is then dominated by diagonalizing the Hamiltonian, which therefore means that the overall cost scales as $O(M^3)$. Calculations of individual molecules containing a few hundred atoms have been performed, but the inclusion of correlation with multiple determinants reduces the accessible system size to a few tens of atoms. There have also been developments in applying the method to solids but it has been found to be unsatisfactory for metallic systems and works best for high-symmetry insulators.

7.10 Final comments

A few final points to highlight:

- The Hartree-Fock method is most often applied to the study of molecules.
- It gives an exact treatment of the effects of electron exchange by using a Slater determinant form for the many-body wavefunction.
- It is most often used with a Gaussian basis set.
- It does not include any effects of dynamic correlation.
- Such effects can be included by more complex schemes, such as CI, but are exceedingly expensive.

7.11 Further reading

- Hartree-Fock theory in “Methods of Electronic Structure Calculations” by M. Springborg, Chapter 9
- Hartree-Fock theory in “Computational Physics” by J.M. Thijssen, chapter 4

