

Physics 514 – Hartree Fock and Extensions

Emanuel Gull

December 3, 2015

Draft – Please report mistakes!

Chapter 1

Hartree Fock and Extensions

1.1 Introduction

Hartree Fock is the first of two fundamental theories for the electronic structure problem: Hartree Fock theory and density functional theory. Both of these methods are in wide use in quantum chemistry and condensed matter physics, and they build the foundations on which many of the more accurate theories are built.

The Hartree Fock method can be viewed as a variational method where the one *single* Slater determinant is found which minimizes the energy of the system. Slater determinants form a basis of the Fock space, thus a general vector in Fock space is a *linear combination* of Slater determinants. The Hartree Fock approximation consists of selecting only one of these many determinants.

Hartree Fock theory can also be seen as a *mean field* method, and is in fact often called *mean field* or *Hartree Fock mean field* in the condensed matter context. We shall see that it consists of solving a single-particle Schrödinger

equation in an averaged background potential caused by all other particles.

1.2 Born Oppenheimer approximation

We start from the general electronic structure Hamiltonian

$$H = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m} + \sum_{n=1}^K \frac{\mathbf{p}_n^2}{2M_n} + \sum_{i<j}^N \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i=1}^N \sum_{n=1}^K \frac{Z_n e^2}{|\mathbf{r}_i - \mathbf{R}_n|} + \sum_{m<n}^K \frac{Z_n Z_m e^2}{|\mathbf{R}_m - \mathbf{R}_n|} \quad (1.1)$$

where K is the number of nuclei, N the number of electrons, e the elementary charge, m the electron mass and M_n the nuclear mass.

The nuclei are at least $2000\times$ heavier than the electrons, implying a separation of scales: electronic motion is much faster than nuclear motion.

The Born Oppenheimer approximation uses this to approximate the nuclei as static, and instead solve the Hamiltonian

$$H_{BO} = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m} + \sum_{i<j}^N \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_n^K \sum_i^N \frac{Z e^2}{|\mathbf{r}_i - \mathbf{R}_n|}. \quad (1.2)$$

with a classical Coulomb potential given by the location of the nuclei. This neglects all quantum fluctuations of the nuclei.

Even in this approximation, solving the Schrödinger equation is a daunting task. In a typical condensed matter system there are on the order of 10^{26} electrons, by

far too many for an exact treatment. This means that further approximations are necessary.

The electronic structure problem would get much simpler if – instead of solving for a many-body problem – we could solve a system of coupled single-particle problems:

$$H_{\text{indep. particles}} = \sum_i^N \left(\frac{\mathbf{p}_i^2}{2m} + V(\mathbf{r}_i) \right), \quad (1.3)$$

where $V(\mathbf{r}_i)$ incorporates the potential of the nuclei as well as some effective potential caused by the influence of all other particles in the system, but is *only* dependent on the position of a single particle, rather than of all other particles.

Both the Hartree Fock method and the density functional theory are based on such a mapping of the system to a ‘non-interacting’ single-particle system.

1.3 The Helium atom

To illustrate Hartree Fock we start with the Helium atom in the Born Oppenheimer approximation and make the ansatz

$$\Psi(\mathbf{r}_1, \sigma_1; \mathbf{r}_2, \sigma_2) = \phi(\mathbf{r}_1)\phi(\mathbf{r}_2) \frac{1}{\sqrt{2}} \left(\alpha(\sigma_1)\beta(\sigma_2) - \alpha(\sigma_2)\beta(\sigma_1) \right) \quad (1.4)$$

where $\alpha(s)$ denotes one spin direction (e.g. ‘spin up’), $\beta(s)$ the other (‘spin down’), and ϕ denotes an orbital wave function. The Hamiltonian in reduced units is

$$H_{BO} = \frac{-1}{2} \left(\nabla_1^2 + \nabla_2^2 \right) + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} - \frac{2}{|\mathbf{r}_1|} - \frac{2}{|\mathbf{r}_2|}. \quad (1.5)$$

Writing down the Schrödinger equation and separating out the spin part, we are left with

$$\left[\frac{-1}{2}(\nabla_1^2 + \nabla_2^2) + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} - \frac{2}{|\mathbf{r}_1|} - \frac{2}{|\mathbf{r}_2|} \right] \phi(\mathbf{r}_1)\phi(\mathbf{r}_2) = E\phi(\mathbf{r}_1)\phi(\mathbf{r}_2). \quad (1.6)$$

after multiplication with $\phi^*(\mathbf{r}_2)$ and integration over \mathbf{r}_2 ,

$$\left[\frac{-1}{2}\nabla_1^2 - \frac{2}{|\mathbf{r}_1|} + \int d^3\mathbf{r}_2 \frac{|\phi(\mathbf{r}_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \right] \phi(\mathbf{r}_1) = E'\phi(\mathbf{r}_1) \quad (1.7)$$

where E' absorbed all of the integration constants. The term on the right hand side is the Coulomb energy of electron 1 moving in the potential background created by the second electron – and it has the form of Eq. 1.3, *i.e.* of an electron moving in a background potential.

Note that the ϕ appears both in the effective potential and in the eigenvalue equation. This means that this equation is best solved self-consistently: starting from an initial guess for ϕ , solve the eigenvalue problem, then replace ϕ in the potential, and iterate to convergence.

It is obvious here that ϕ is *uncorrelated*: $P(\mathbf{r}_1, \mathbf{r}_2) = p(\mathbf{r}_1)p(\mathbf{r}_2)$; or $p(\mathbf{r}_1)$, the probability of finding an electron at position \mathbf{r}_1 , is independent of the location of the second electron. It is not the actual position of that second electron that matters, rather its averaged charge distribution. This is why Hartree Fock is a ‘mean field’ theory, very similar to other ‘mean field’ theories in statistical physics.

1.4 Failure of Hartree-Fock – the stretched limit of H_2

We can apply the ansatz Eq. 1.4 to the Hydrogen molecule H_2 , with a symmetric $1s$ orbital wave function centered around the nuclei:

$$\phi(\mathbf{r}) = u(\mathbf{r} - \mathbf{R}_A) + u(\mathbf{r} - \mathbf{R}_B) \quad (1.8)$$

The Hartree Fock wave function Ψ then contains contributions of both electrons on the same nucleus, as well as contributions of both electrons on different nuclei.

As H_2 is stretched, the physically expected solution will have one electron on one atom, and the other one on the other atom. Hartree Fock fails because the electron 1 only feels the average potential of electron 2, which is symmetrically distributed. A more accurate wave function would incorporate this:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2} \left(u(\mathbf{r}_1 - \mathbf{R}_A)u(\mathbf{r}_2 - \mathbf{R}_B) + u(\mathbf{r}_2 - \mathbf{R}_A)u(\mathbf{r}_1 - \mathbf{R}_B) \right) \quad (1.9)$$

but this wave function is not of the form of our ansatz.

If you still need a project or if you are interested: Try coding Hartree Fock for the H_2 and the helium problem!

1.5 General case – Many-electron picture

We start from the Hamiltonian

$$H = \sum_i h(i) + \frac{1}{2} \sum_{i \neq j} g(i, j) \quad (1.10)$$

with

$$g(i, j) = \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}, \quad (1.11)$$

$$h(i) = \frac{-1}{2} \nabla_i^2 - \sum_n \frac{Z_n}{|\mathbf{r}_i - \mathbf{R}_n|} \quad (1.12)$$

$h(i)$ contains all single-particle terms, and $g(i, j)$ contains all two-particle interactions. We search for a single Slater determinant as the solution. A short exercise (do it!) will show that, for any Slater determinant Ψ_{AS} ,

$$\Psi_{AS}(\mathbf{r}_1, \dots, \mathbf{r}_k) = \frac{1}{\sqrt{N}} \begin{vmatrix} \psi_1(r_1) & \psi_2(r_1) & \cdots & \psi_k(r_1) \\ \psi_1(r_2) & \ddots & \ddots & \vdots \\ \vdots & \ddots & \ddots & \vdots \\ \psi_1(r_k) & \psi_2(r_k) & \cdots & \psi_k(r_k) \end{vmatrix} \quad (1.13)$$

$$\langle \Psi_{AS} | \sum_i h(i) | \Psi_{AS} \rangle = \sum_k \langle \psi_k | h | \psi_k \rangle = \sum_k \int d^3\mathbf{r} \psi_k^*(\mathbf{r}) h(\mathbf{r}) \psi_k(\mathbf{r}) \quad (1.14)$$

The two-particle term becomes

$$\langle \Psi_{AS} | \sum_{ij} g(i, j) | \Psi_{AS} \rangle = \sum_{kl} \langle \psi_k \psi_l | g | \psi_k \psi_l \rangle - \langle \psi_k \psi_l | g | \psi_l \psi_k \rangle, \quad (1.15)$$

where

$$\langle \psi_k \psi_l | g | \psi_m \psi_n \rangle = \iint d^3\mathbf{r} d^3\mathbf{r}' \psi_k^*(\mathbf{r}) \psi_l^*(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \psi_m(\mathbf{r}) \psi_n(\mathbf{r}') \quad (1.16)$$

Thus

$$E = \sum_k \langle \psi_k | h | \psi_k \rangle + \frac{1}{2} \sum_{kl} \left(\langle \psi_k \psi_l | g | \psi_k \psi_l \rangle - \langle \psi_k \psi_l | g | \psi_l \psi_k \rangle \right) \quad (1.17)$$

We define the two operators J_k and K_k as:

$$J_k(\mathbf{x})\psi(\mathbf{x}) = \int \psi_k^*(\mathbf{x}') \frac{1}{|\mathbf{x} - \mathbf{x}'|} \psi_k(\mathbf{x}') \psi(\mathbf{x}) d^3\mathbf{x}' \quad (1.18)$$

$$K_k(\mathbf{x})\psi(\mathbf{x}) = \int \psi_k^*(\mathbf{x}') \frac{1}{|\mathbf{x} - \mathbf{x}'|} \psi(\mathbf{x}') \psi_k(\mathbf{x}) d^3\mathbf{x}' \quad (1.19)$$

and $J = \sum_k J_k$, $K = \sum_k K_k$. J is called the ‘Coulomb’ operator, K the ‘exchange’ operator. With the definition of these operators, the energy functional 1.17 simplifies to

$$E = \sum_k \langle \psi_k | h + \frac{1}{2}(J - K) | \psi_k \rangle \quad (1.20)$$

This is the energy functional of a single Slater determinant. We need to minimize it, under the constraint that the wave function stays normalized and orthogonal (we will relax the orthogonality constraint later):

$$\langle \psi_k | \psi_l \rangle = \delta_{kl}. \quad (1.21)$$

This implies

$$\delta E - \sum_{kl} \Lambda_{kl} \left[\langle \delta \psi_k | \psi_l \rangle - \langle \psi_k | \delta \psi_l \rangle \right] = 0 \quad (1.22)$$

with

$$\begin{aligned} \delta E = & \sum_k \langle \delta\psi_k | h | \psi_k \rangle + h.c. \\ & + \frac{1}{2} \sum_{kl} \left(\langle \delta\psi_k \psi_l | g | \psi_k \psi_l \rangle + \langle \psi_l \delta\psi_k | g | \psi_l \psi_k \rangle \right. \\ & \left. - \langle \delta\psi_k \psi_l | g | \psi_l \psi_k \rangle - \langle \psi_l \delta\psi_k | g | \psi_k \psi_l \rangle \right) + h.c. \end{aligned} \quad (1.23)$$

using the symmetry of the matrix element, $\langle \psi_k \psi_l | g | \psi_m \psi_n \rangle = \langle \psi_l \psi_k | g | \psi_n \psi_m \rangle$ we obtain

$$\delta E = \sum_k \langle \delta\psi_k | \mathcal{F} | \psi_k \rangle + \langle \psi_k | \mathcal{F} | \delta\psi_k \rangle \quad (1.24)$$

with $\mathcal{F} = h + J - K$ the ‘Fock’ operator. Combining terms, we obtain

$$\langle \delta\psi_k | \mathcal{F} | \psi_k \rangle + \langle \psi_k | \mathcal{F} | \delta\psi_k \rangle + \sum_l \Lambda_{kl} \left(\langle \delta\psi_k | \psi_l \rangle - \langle \psi_l | \delta\psi_k \rangle \right) = 0, \quad (1.25)$$

and since $\delta\psi$ is arbitrary, this corresponds to the equation

$$\mathcal{F}\psi_k = \sum_l \Lambda_{kl} \psi_l \quad (1.26)$$

Since the basis functions ψ_k form an orthonormal set, we replace $\Lambda_{kl} = \epsilon_k \delta_{kl}$ and thus

$$\mathcal{F}\psi_k = \epsilon_k \psi_k \quad (1.27)$$

This looks similar to the Schrödinger equation, but the ϵ_k are in fact not eigen energies but the Lagrange multiplier coefficients (or the eigenvalues of the Fock operator). We

can compute the energies from

$$E = \frac{1}{2} \sum_k \left(\epsilon_k + \langle \psi_k | h | \psi_k \rangle \right) = \sum_k \epsilon_k - \frac{1}{2} \langle \psi_k | J - K | \psi_k \rangle. \quad (1.28)$$

The Hartree Fock approximation often yields unsatisfactory results. This is because the approximation of using a single Slater determinant is just not good enough: it neglects all Coulomb correlations. This becomes especially important in stretched geometries and for atoms and molecules that are more complex than hydrogen and helium.

There is a straightforward way of improving on Hartree Fock: instead of using a single Slater determinant, we minimize the energy in a space spanned by a set of Slater determinants.

$$\Psi = \sum_n \alpha_n \Psi_{AS}^{(n)}(\mathbf{x}_1, \dots, \mathbf{x}_n) \quad (1.29)$$

and obtain a linear combination of Slater determinants as a solution. The energy of this procedure will be lower than (or equal to) Hartree Fock but higher than (or equal to) the ground state and the wave function more accurate. By systematically increasing the number of Slater determinants considered, we can converge the energy to the true ground state. This is the general principle behind Configuration-Interaction (CI) methods which are frequently used in quantum chemistry.

Starting from the Hartree Fock ground state (in second

quantized notation, in the HF eigenbasis)

$$|\Psi_{HF}\rangle = \sum_{\mu=1}^N c_{\mu}^{\dagger} |0\rangle \quad (1.30)$$

we construct additional Slater determinants by replacing one or two of the c_{μ}^{\dagger} by other orbitals c_i^{\dagger} :

$$|\psi_0\rangle = \left(1 + \sum_{i\mu} \alpha_{\mu}^i c_i^{\dagger} c_{\mu} + \sum_{i<j, \mu<\nu} \alpha_{\mu\nu}^{ij} c_i^{\dagger} c_j^{\dagger} c_{\mu} c_{\nu} \right) |\Psi_{HF}\rangle \quad (1.31)$$

If all possible combinations of Slater determinants are considered, we obtain the exact solution: a linear combination of Slater determinants in the space of all possible determinants. In Chemistry, this method is called ‘Full CI’. In Physics, it is generally known as ‘Exact Diagonalization’ (ED) or ‘Full Diagonalization’.

The solution to the ED problem is obtained by diagonalizing the eigenvalue problem $H\Psi = E\Psi$ in the full Hilbert space.

While ED is limited to a few basis states (typically 36 to 38 spins or 18 fermionic sites) and scales exponentially, Hartree Fock can be applied to thousands of electrons, as it only scales polynomially (the self-consistent solution of the eigenvalue problem of the Fock operator is the limiting step). Modern Hartree Fock implementations scale very well and ensure that the self-consistency / minimization procedure does not get stuck in local minima; they are commercially available or open source (e.g. VASP, NWChem, MOLPRO, CRYSTAL) as part of quantum chemistry packages. Use these packages rather than writing your own code!

1.6 Basis functions

So far we did not specify the set of basis functions ψ_k for the single-particle wave functions. Several popular choices which are adapted to different physical situations exist:

1.6.1 The electron gas

For the free electron gas with Hamiltonian

$$H = - \sum_i^N \frac{-\hbar^2}{2m} \nabla^2 + \sum_{i < j}^N \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (1.32)$$

the ideal choice for the basis functions are plane waves:

$$\psi_{\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{k}\mathbf{r}) \quad (1.33)$$

Such plane wave basis functions are also commonly used for band structure calculations of periodic crystals. One of their advantages is that it is easy to systematically reduce basis errors by adding more basis states.

At low density the electron gas forms a ‘Wigner’ crystal. Then a better choice of basis functions are eigenfunctions of harmonic oscillators centered around the classical equilibrium positions.

1.6.2 Atoms and molecules, STO and GTO

Which functions should be used as a basis function for atoms and molecules? The *Slater-type orbitals* or STO basis functions are inspired by the exact solution of the Hydrogen atom:

$$f_{inlm}(r, \theta, \phi) \propto r^{n-1} e^{-\zeta r} Y_{lm}(\theta, \phi). \quad (1.34)$$

These wave functions have the correct asymptotic radial dependence and the correct angular dependence. The values ζ_i are optimized so that the eigenstates of isolated atoms are reproduced as accurately as possible. The main disadvantage of STOs becomes apparent when trying to evaluate the matrix elements in the Coulomb equation for basis functions centered around two different nuclei at position R_A and R_B . There we have to evaluate the integrals containing terms like

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} e^{-\zeta_i |\mathbf{r} - \mathbf{R}_A|} e^{-\zeta_j |\mathbf{r} - \mathbf{R}_B|}, \quad (1.35)$$

which cannot be solved in a closed form.

The Gauss-Type Orbitals or GTO

$$f_{ilmn}(\mathbf{r}) \propto x^l y^m z^n e^{-\zeta_i r^2} \quad (1.36)$$

simplify the evaluation of matrix elements, as Gaussian functions can be integrated easily and the product of Gaussian functions centered at two different nuclei is again a single Gaussian function:

$$e^{-\zeta_i |\mathbf{r} - \mathbf{R}_A|^2} e^{-\zeta_j |\mathbf{r} - \mathbf{R}_B|^2} = K e^{-\zeta |\mathbf{r} - \mathbf{R}|^2} \quad (1.37)$$

with

$$K = \exp \left(- \frac{\zeta_i \zeta_j}{\zeta_i + \zeta_j} |\mathbf{R}_A - \mathbf{R}_B|^2 \right) \quad (1.38)$$

$$\zeta = \zeta_i + \zeta_j \quad (1.39)$$

$$\mathbf{R} = \frac{\zeta_i \mathbf{R}_A + \zeta_j \mathbf{R}_B}{\zeta_i + \zeta_j} \quad (1.40)$$

Also, the term $\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$ can be rewritten as an integral over

a Gaussian function:

$$\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} = \frac{2}{\sqrt{\pi}} \int_0^\infty dt e^{-t^2(\mathbf{r}_i - \mathbf{r}_j)} \quad (1.41)$$

and thus all the integrals reduce to purely Gaussian integrals which can be performed analytically. The resulting speed-up more than outweighs the larger number of GTO orbitals needed in comparison to STOs.

As there are $O(L^4)$ Coulomb integrals, quantum chemistry codes typically scale at least as $O(N^4)$. Modern algorithms reduce the effort to around $O(N)$ in simple cases, as the overlap of basis functions at large distances becomes negligibly small.

Independent of whether one chooses STOs or GTOs, extra care must be taken to account for the non-orthogonality of these basis functions.

1.6.3 Pseudo-potentials

The electrons in the inner, fully occupied, shells do not contribute to the chemical bonds. To simplify the calculations they are often replaced by pseudo-potentials which are designed to model the inner shells. Only the outer shells (including the valence shells) are then modeled using basis functions. The pseudo-potentials are chosen such that calculations for isolated atoms are as accurate as possible.