

1 Hartree-Fock Approximation

We have a system of N interacting fermions with a Hamiltonian

$$H = \sum_{i=1}^N h(i) + \sum_{i<j}^N V_{\text{int}}(i, j) \quad . \quad (1)$$

Here, $h(i)$ is the “single-particle Hamiltonian” for the particle- i and $V_{\text{int}}(i, j)$ is the part of the Hamiltonian describing the interaction between particles i and j . By the “single-particle Hamiltonian” we mean the terms that would be present if there were only one fermion in the system. For the case of N electrons in an atom with proton number Z at the nucleus, these terms would be

$$h(i) = \frac{\mathbf{p}_i^2}{2m} - \frac{Ze^2}{r_i} \quad ,$$
$$V_{\text{int}}(i, j) = \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \quad .$$

Again we ignored the rest of the terms like spin-orbit interaction which would introduce spin-dependent terms into the Hamiltonian. Note that in Eq. (1), the interaction part is summed over each particle pair only once. As a result, there are

$$\binom{N}{2} = \frac{N(N-1)}{2}$$

terms in the last sum.

Such problems cannot be solved exactly in general (there are a few uninteresting exceptions). As a result, we need a general approximation procedure for solving such many-body equations. Obviously, what we want to calculate is important in choosing the approximation procedure. Hence, there are various methods developed to cope with different aspects of such kind of problems. The very first step should be obtaining a “feel” for the energy levels for those problems. That certainly means that we don’t need accurate numerical values.

Independent particle picture is this first step in visualizing the energy levels of most of the many-body problems. This is the language used in describing the electronic states of atoms in Atomic Physics courses. When we are saying that in Lithium, there are two electrons in the 1s orbital and

one electron in the 2s orbital, we are using that language. However, we say, in those atoms, the orbital wavefunctions and their energies are different than those of the hydrogenic atoms. Our purpose in here is to formalize those kind of statements.

Therefore, the question we would like to answer is “What is the best independent-particle approximation for an interacting system of fermions?” And the answer can be provided by the variational theory. We should form a many-body wavefunction of the atom as a Slater determinant using some one-particle states $\varphi_1, \dots, \varphi_N$. And, we should choose these one-particle states as the ones that minimize the expectation value of the Hamiltonian in Eq. (1). This is the Hartree-Fock approximation.

2 Expectation Values

Let us suppose that we have N arbitrary one-particle states $\varphi_1, \dots, \varphi_N$. We should choose them as an orthonormal set, since this will make the calculation of expectation values easier. So, we have

$$\langle \varphi_i | \varphi_j \rangle = \delta_{i,j} \quad i, j = 1, \dots, N. \quad (2)$$

As a result, we have N^2 equations giving us a restriction on the one-particle states. (Some may notice that, there are only $N(N + 1)/2$ equations in Eq. (2), but the number of real quantities fixed to a certain value is N^2 . So, there are N^2 real equations.)

We form the Slater determinant from these N states as

$$\Psi(1, 2, \dots, N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(1) & \varphi_1(2) & \dots & \varphi_1(N) \\ \varphi_2(1) & \varphi_2(2) & \dots & \varphi_2(N) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_N(1) & \varphi_N(2) & \dots & \varphi_N(N) \end{vmatrix} .$$

By using the many-body wavefunction thus formed, we will calculate the expectation value of the Hamiltonian, H , as

$$\langle \Psi | H | \Psi \rangle = N \langle \Psi | h(1) | \Psi \rangle + \binom{N}{2} \langle \Psi | V_{\text{int}}(1, 2) | \Psi \rangle .$$

These quantities were calculated before, so we just reproduce the results in here

$$\langle \Psi | H | \Psi \rangle = \sum_{i=1}^N E_i + \sum_{i < j} (C_{ij} - E_{ij}) \quad , \quad (3)$$

where

$$\begin{aligned} E_i &= \langle \varphi_i | h | \varphi_i \rangle \quad , \\ C_{ij} &= \langle \varphi_i \varphi_j | V_{\text{int}} | \varphi_i \varphi_j \rangle \quad , \\ E_{ij} &= \langle \varphi_j \varphi_i | V_{\text{int}} | \varphi_i \varphi_j \rangle \quad . \end{aligned}$$

Here, C_{ij} is usually called as the Coulomb integral for the orbitals φ_i and φ_j (specifically considering electrons in atoms and molecules), and E_{ij} is called the exchange integral. We note that in Eq. (3) sum over Coulomb and exchange integrals is over pairs of states. That sum can be written in another way. We just need to note that $C_{ij} = C_{ji}$ and $E_{ij} = E_{ji}$. It can also be noticed that, by the definition of Coulomb and exchange integrals, we have the relation $C_{ii} = E_{ii}$. Keep in mind that C_{ii} is not physically meaningful (interaction of an electron with itself?). But, in order to simplify the Eq. (3), those terms are frequently used. By using these relations, Eq. (3) can be rewritten as,

$$\langle \Psi | H | \Psi \rangle = \sum_{i=1}^N E_i + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N (C_{ij} - E_{ij}) \quad . \quad (4)$$

3 Effective Hamiltonian

Now, all we have to do is to minimize the expectation value in Eq. (4) with the restrictions in Eq. (2). We can use the Lagrange multiplier method to carry out this minimization. As a result the quantity,

$$A = \langle \Psi | H | \Psi \rangle - \sum_{i=1}^N \sum_{j=1}^N \Lambda_{ij} \langle \varphi_i | \varphi_j \rangle \quad (5)$$

should be minimized, where Λ_{ij} are the Lagrange multipliers. The Lagrange multipliers in this expression can take on complex values, but you should not be concerned about this. Obviously, only real valued functions can be minimized, hence the expression in Eq. (5) should be real valued. This implies that the Λ matrix is hermitian. If you are concerned about the presence of complex numbers in a real-valued expression, you should derive Eq. (5) starting from the real-valued forms of the expressions in Eq. (2).

Now, we can consider the variations in each element of the one-particle state set $\varphi_1, \dots, \varphi_N$. In effect, what we will be doing is evaluating the functional derivatives and equating them to zero. Since we are using the Lagrange multiplier method, we can vary each φ_i in an arbitrary way. That means, we will make sure that the replacement $|\varphi_i\rangle \rightarrow |\varphi_i\rangle + |\delta\varphi_i\rangle$, where $|\delta\varphi_i\rangle$ is an arbitrary infinitesimal state, will not change the expression in Eq. (4) up to first order. (To be precise, we will set $|\delta\varphi_i\rangle = \epsilon |\psi\rangle$ where $|\psi\rangle$ is an arbitrary one-particle state and we will equate the order ϵ term of the variation in Eq. (4) to 0.)

Now, the first order variation of real-valued expressions that depend on a quantum mechanical state (say $|\varphi_i\rangle$) are of the form

$$\langle \delta\varphi_i | \alpha \rangle + \langle \alpha | \delta\varphi_i \rangle$$

for some (perhaps complicated) “state” $|\alpha\rangle$. This expression is then set equal to 0 at the extrema. Since $|\delta\varphi_i\rangle$ is arbitrary, this will only imply that $|\alpha\rangle = 0$ (show). If we keep this in mind, we can quickly find the conditions for minimum in our calculation. As a result we find,

$$\begin{aligned} \delta A = & \sum_{i=1}^N \langle \delta\varphi_i | h | \varphi_i \rangle \\ & + \sum_{i,j=1}^N \left(\langle \delta\varphi_i \varphi_j | V_{\text{int}} | \varphi_i \varphi_j \rangle - \langle \delta\varphi_i \varphi_j | V_{\text{int}} | \varphi_j \varphi_i \rangle \right) \\ & - \sum_{i,j=1}^N \Lambda_{ij} \langle \delta\varphi_i | \varphi_j \rangle + \text{complex-conjugate}. \end{aligned}$$

Now, if arbitrary infinitesimal values of $|\delta\varphi_i\rangle$ makes the expression above vanish, the the following equation should be satisfied for the i^{th} state:

$$(h + V_{\text{Coul}} + V_{\text{Exch}}) | \varphi_i \rangle = \sum_{j=1}^N \Lambda_{ij} | \varphi_j \rangle \quad , \quad (6)$$

where V_{Coul} and V_{Exch} are operators which are a little bit complicated. In the abstract case that we are using in here, we will define them by their matrix

elements. For arbitrary one-particle states $|\phi\rangle$ and $|\psi\rangle$,

$$\langle\phi|V_{\text{Coul}}|\psi\rangle = \sum_{j=1}^N \langle\phi\varphi_j|V_{\text{int}}|\psi\varphi_j\rangle \quad , \quad (7)$$

$$\langle\phi|V_{\text{Exch}}|\psi\rangle = - \sum_{j=1}^N \langle\phi\varphi_j|V_{\text{int}}|\varphi_j\psi\rangle \quad . \quad (8)$$

We are going to explain the nature of these new operators in the section below.

For now, we just need to note that both of these operators depends on the N one-particle states $\varphi_1, \dots, \varphi_N$ that the fermions populate, on an equal way. We should explain what that “equal way” means in some detail. Remember that the Slater determinant constructed from $\varphi_1, \dots, \varphi_N$ does not depend on the order of these states, nor does it depend on the particular linear combinations of the states. We have assumed at the beginning in Eq. (2) that these states are chosen as an orthonormal set. But, even with this restriction, there is a lot of freedom in choosing them. By a unitary transformation,

$$|\varphi'_i\rangle = \sum_{j=1}^N U_{ij} |\varphi_j\rangle \quad ,$$

where U_{ij} is a unitary matrix (i.e., $U^\dagger U = I$), we can obtain another orthonormal set that would construct the same Slater determinant. Show that, such a unitary transformation of the set $\varphi_1, \dots, \varphi_N$ does not change the definition of the operators V_{Coul} and V_{Exch} .

Second of all, you can easily verify that both of these operators are hermitian. As a result

$$h_{\text{eff}} = h + V_{\text{Coul}} + V_{\text{Exch}} \quad ,$$

is a hermitian operator which we call as the “effective Hamiltonian”. In terms of the effective Hamiltonian, the condition that the total energy of the N -particle system, $\langle\Psi|H|\Psi\rangle$, is a minimum can be expressed as

$$h_{\text{eff}} |\varphi_i\rangle = \sum_{j=1}^N \Lambda_{ij} |\varphi_j\rangle.$$

This is a non-linear equation if you remember that h_{eff} depends on the φ_i , which are the unknowns.

This equation can be simplified further. First note that,

$$\langle \varphi_j | h_{\text{eff}} | \varphi_i \rangle = \Lambda_{ij} \quad ,$$

which shows that Λ is a hermitian matrix (something we already knew). As a result, it can be diagonalized by a unitary transform. That is, there is a unitary $N \times N$ matrix U such that $U^\dagger \Lambda U = \epsilon$ where ϵ is a diagonal matrix. Or,

$$\sum_{k,l=1}^N U_{ki}^* \Lambda_{kl} U_{lj} = \epsilon_i \delta_{ij}, \quad .$$

We use that unitary matrix U for a transformation to a different one-particle state set $\varphi'_1, \dots, \varphi'_N$ with,

$$| \varphi'_i \rangle = \sum_{j=1}^N U_{ij} | \varphi_j \rangle \quad ,$$

which yields an eigenvalue equation:

$$h_{\text{eff}} | \varphi'_i \rangle = \epsilon_i | \varphi'_i \rangle \quad .$$

Therefore, the one-particle states can be chosen as the eigenstates of the effective Hamiltonian. There is a considerable simplification at this point. We see that, if one chooses to describe the interacting fermion system as a collection of independent particles, then the particles will occupy eigenstates of an effective one-particle Hamiltonian. Of course, the effective Hamiltonian depends on the states occupied by the particles, as a result, finding the effective Hamiltonian itself is a big problem.

4 Coulomb and Exchange operators

What is the nature of the effective Hamiltonian? A natural guess would be like this: Since particles are moving independently, each particle should feel the average of the interaction potential with the rest of $N - 1$ particles. (Each particle sees only the average locations of the particles). This is the Hartree approximation, the one you would get if you assumed that the particles are distinguishable. We will find out that the effective Hamiltonian for indistinguishable fermions is pretty close to that with some minor differences. However, before we go on further, we should simplify the problem.

From now on, we will concentrate on the problem of N electrons in an atom with proton number Z . We will also assume that the electrons do not have any spin (the perfectionist may assume that spins of all electrons are chosen parallel.)

Let us start with the operator related to the Coulomb integral (7). It can be easily seen that this operator is a potential operator,

$$(V_{\text{Coul}}\psi)(\mathbf{r}) = V_{\text{Coul}}(\mathbf{r})\psi(\mathbf{r}) \quad ,$$

where

$$V_{\text{Coul}}(\mathbf{r}) = \sum_{j=1}^N \int \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} |\varphi_j(\mathbf{r}')|^2 d^3\mathbf{r}' \quad .$$

The same expression can be written in terms of the average charge density of N electrons,

$$\rho(\mathbf{r}) = \sum_{j=1}^N (-e) |\varphi_j(\mathbf{r})|^2 \quad ,$$

in terms of which,

$$V_{\text{Coul}}(\mathbf{r}) = (-e) \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' \quad .$$

As a result, $V_{\text{Coul}}(\mathbf{r})$ is the average Coulomb potential energy that a particle with charge $-e$ will feel. To be precise, a particle other than the system's N electrons. We should stress on two points in here. First of all, this potential depends on the average positions of the electrons, and not the instantaneous ones. Second is that $V_{\text{Coul}}(\mathbf{r})$ depends on the the charges of all of the N electrons. Since an electron does not interact with itself, we would expect that the effective potential that an electron feels should be an average of other $N - 1$ electrons. However, this unphysical contribution in V_{Coul} is a result of the C_{ii} terms added to the total energy of the system. Since $C_{ii} = E_{ii}$, we expect that this unphysical part of V_{Coul} will be eliminated by a corresponding part of V_{Exch} .

Now, we turn to the operator V_{Exch} coming from the exchange integrals. The definition in Eq. (8) can be expressed as,

$$(V_{\text{Exch}}\psi)(\mathbf{r}) = - \sum_{j=1}^N \left(\int \varphi_j(\mathbf{r}')^* \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \psi(\mathbf{r}') d^3\mathbf{r}' \right) \varphi_j(\mathbf{r}) \quad .$$

This is a very strange operator, something that you have never seen before. First of all, it is called a non-local operator. When a non-local operator acts on a wavefunction, it produces a new wavefunction which depends on old wavefunction at different locations. The non-local operators can be expressed as

$$(K\psi)(\mathbf{r}) = \int K(\mathbf{r}; \mathbf{r}')\psi(\mathbf{r}')d^3\mathbf{r}' \quad ,$$

where the function $K(\mathbf{r}; \mathbf{r}')$ is non-zero for arguments $\mathbf{r} \neq \mathbf{r}'$. For the exchange operator that function can be expressed as

$$K(\mathbf{r}; \mathbf{r}') = - \sum_{j=1}^N \varphi_j(\mathbf{r}) \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \varphi_j^*(\mathbf{r}') \quad ,$$

which will certainly produce a non-local operator. There is nothing strange about non-local operators. In fact, almost all conceivable operators are non-local. The strange thing about V_{Exch} is that it appears in a Hamiltonian and we are somehow forced to interpret it as a “potential energy”.

If you would like to think of V_{Exch} in physical terms, this is a possible interpretation: A particle at a point feels a potential whose value depends on how the particle is doing at other points. Such a thing is possible in quantum mechanics where a particle can be at different points at the same time with appropriate phase and probability (expressed as the wavefunction), but classically it is meaningless. An ordinary potential energy is independent of the global wavefunction of the particle, but the exchange potential is not.

One should not forget that there is no physical reality of the exchange potential, it just came out of some approximation procedure. It is often the case that new concepts arise from different approximations to physical problems, and when these concepts are used over and over again, some people start to think that it has some physical reality. Although this is not totally wrong in all cases, (like the Lithium atom having two 1s and one 2s electrons,) it is good not to forget the real (unsolvable) picture. Obviously, the exchange potential is not real, it is just an annoying factor that we have to include to obtain the best picture.

Finally, let's solve the problem of an electron interacting with its average Coulomb and Exchange problems created by the inclusion of C_{ii} and E_{ii} into the energy expectation value in Eq. (4). Suppose that we are concentrating on the i^{th} orbital φ_i . The expression

$$h_{\text{eff}}\varphi_i = \epsilon_i\varphi_i \quad ,$$

can be written openly as follows:

$$\left\{ \frac{\mathbf{p}^2}{2m} - \frac{Ze^2}{r} + \sum_{j \neq i} \int \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} |\varphi_j(\mathbf{r}')|^2 d^3\mathbf{r}' \right\} \varphi_i(\mathbf{r}) - \sum_{j \neq i} \varphi_j(\mathbf{r}) \int \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \varphi_j^*(\mathbf{r}') \varphi_i(\mathbf{r}') d^3\mathbf{r}' = \epsilon_i \varphi_i(\mathbf{r}) \quad . \quad (9)$$

The terms of the effective Hamiltonian corresponding to orbital- i cancelled out. As a result, we have a linear problem for the orbital φ_i where the problem is expressed in terms of all the other remaining $N - 1$ orbitals. Although in this last form the equation is physically more meaningful, it has a disturbing feature that the Hamiltonian, the operator whose eigenfunctions are sought, changes from one orbital to the other. For this reason, it is useful to keep using h_{eff} instead of the form above.

5 Self Consistency

Since the effective Hamiltonian is used to calculate the orbitals φ_i , and the Hamiltonian itself is constructed from these operators, we have a intricate problem. If both of these conditions are not satisfied, then that means we are not using the power of the variational theory. We call any solution to the problem “self consistent” if the orbitals found constructs an effective Hamiltonian, where the orbitals are the eigenfunctions of the that operator. Therefore the question to be answered is “how can you achieve self consistency?”

There are no direct methods for solving such kind of equations, but the iteration methods are known to give good solutions. Iteration is the general name of algorithms where you start from an initial point (which is not the solution) and in each step you make some corrections to the point. If your corrections are good, then in each step you get closer to a correct solution. After carrying out the iteration a lot of times you stop at a place where you think that you are sufficiently close to a solution. Obviously, such algorithms are best suited for computers. (Although the first self-consistent Hartree-Fock calculation is done by human computers.)

For the Hartree-Fock problem, the “natural” algorithm is known to converge (although it converges slowly). In this natural algorithm you start

from some initial set of N orbitals, which we can denote as $\varphi_i^{(1)}$. From these orbitals we construct the effective Hamiltonian denoted as $h_{\text{eff}}^{(1)}$. At this point we need to find the eigenfunctions of this operator. Although such problems cannot be solved exactly, since $h_{\text{eff}}^{(1)}$ is a one-particle operator, good approximations can be found easily. For example a LCAO approximation with hundreds of wavefunctions will give excellent approximate solutions to such problems.

Obviously there will be an infinite number of eigenfunctions of the effective Hamiltonian. But we need to choose only N of them. Supposing that $\epsilon_i^{(2)}$ are the eigenvalues ordered in increasing order,

$$\epsilon_1^{(2)} \leq \epsilon_2^{(2)} \leq \dots \leq \epsilon_N^{(2)} \leq \epsilon_{N+1}^{(2)} \leq \dots$$

We choose the functions $\varphi_i^{(2)}$ as the eigenfunctions corresponding to the first N eigenvalues. We repeat the same calculation starting with this new set. The sequence of the orbitals $\varphi_i^{(n)}$ obtained after the step $n - 1$ will converge to a set of self-consistent functions. Obviously, since the convergence is slow, we have to stop the procedure at some point.

6 Excitation Energies

We have obtained an approximate value of the ground state energy and the ground state wavefunction of the whole N -particle system. How about the excited levels? Since h_{eff} has infinitely many eigenfunctions (we have used only the first N), can we use the remaining eigenfunctions of h_{eff} for obtaining approximations for the excited levels? In that case, since the orbital set is different for the excited states, the self-consistency is not satisfied. For example if the first excited state of the N particle system is to be found, we might want to choose the set $\varphi_1, \dots, \varphi_{N-1}, \varphi_{N+1}$ where the N^{th} orbital is emptied and $(N + 1)^{\text{th}}$ is filled in. However, we need to start over the iteration procedure again and achieve self-consistency.

The next question is: “What is the excitation energy?” Obviously the answer should be the difference of the expectation value of the Hamiltonian, H , of the system as expressed in Eqs. (3) and (4). Excitation energies should always be calculated like this. With some rearrangement, we can express the energy of the system in terms of the eigenvalues of the effective Hamiltonian.

Since,

$$\begin{aligned}\epsilon_i &= \langle \varphi_i | h_{\text{eff}} | \varphi_i \rangle \quad , \\ &= E_i + \sum_{j=1}^N (C_{ij} - E_{ij}) \quad ,\end{aligned}$$

the total energy can be expressed as

$$\begin{aligned}\langle H \rangle &= \sum_{i=1}^N \epsilon_i - \frac{1}{2} \sum_{i,j=1}^N (C_{ij} - E_{ij}) \quad , \\ &= \frac{1}{2} \sum_{i=1}^N (\epsilon_i + E_i) \quad .\end{aligned}$$

Therefore, the changes in the value of these expressions will give the excitation energies.

Note that the eigenvalues of the effective Hamiltonian, ϵ_i , cannot be interpreted in a straightforward way. However, if h_{eff} were the true one-particle Hamiltonian, the eigenvalues would have found an easy interpretation. So, if the orbital- i is emptied and the orbital- j is filled in, the excitation energy would be $\epsilon_j - \epsilon_i$. Since, this is not the case, we view ϵ_i as some numbers that arise in our approximation procedure.

However, when the number of the particles in the system is large, then it turns out that the differences in ϵ_i gives quite good values for the excitation energies. This result is known as Koopman's Theorem. You may try to understand it like this: Since a large number of orbitals are used, if we change only a few of these orbitals, the effective Hamiltonian does not change much. So, we can assume that h_{eff} is always the same. (We can talk about a single effective Hamiltonian independent of the state of the N particle system.) Apart from this, since there are a lot of particles, most of the particles are too far away from each other. As a result, most of the Coulomb and exchange integrals are small. Tied to this fact, the changes in the total Coulomb and exchange integrals turns out to be negligible. Especially for the case of electrons in a metal, we have $N \sim 10^{23}$ (say), and all electrons have extended wavefunctions. As a result, the change in one of the eigenfunctions would change neither the effective Hamiltonian nor the Coulomb and exchange integrals.