

Chapter 1

Hartree-Fock Theory

1.1 Formalism

For N electrons in an external potential $V_{ext}(r)$, the many-electron Hamiltonian can be written as follows:

$$H = \sum_{i=1}^N \left[\frac{p_i^2}{2m} + V_{ext}(r_i) \right] + \frac{1}{2} \sum_{i,j=1}^N v(r_i - r_j) = \sum_{i=1}^N h(r_i) + \frac{1}{2} \sum_{i,j=1}^N v_{ij} = H^{(1)} + H^{(2)} \quad (1.1)$$

If the second term is zero, this is called a "non-interacting" problem and the many electron wavefunction is written as a product of one-electron wavefunctions. The complication arises when one introduces the interaction (Coulomb) between the electrons. The wavefunction then acquires a very complicated form, and except for some specific problems in one dimension, this problem can not be solved exactly.

The Hamiltonian, being spin-independent, commutes with the spin operator. Therefore the eigenstates of H must also be eigenstates of all the spin operators. On the other hand, Pauli's principle implies that the total wavefunction must be antisymmetric under the exchange of two electrons.

In the HF approximation, one assumes the electronic wavefunction to be an antisymmetric product of one-electron wavefunctions. This is clearly not the exact ground state wavefunction (its most general form would be a linear combination of such products). The best approximation to it can be found by minimizing the expectation value of H in this state: $E_o \simeq \langle \Phi(\mathbf{r}) | H | \Phi(\mathbf{r}) \rangle$. This way, one finds the best N spin-orbitals that form $\Phi(\mathbf{r}) = \text{Det}(\psi_{\lambda\mathbf{s}})$. To represent each of these spin-orbitals $\psi_{\lambda\mathbf{s}}$, one can chose a basis set and

expand them on this fixed basis: $\psi_{\lambda\mathbf{s}} = \sum_i c_i^{\lambda\mathbf{s}} \phi_i(r)\chi(\mathbf{s})$ where the spin part of the wavefunction, χ is either up or down. The problem is then reduced to find the set of coefficients $c_i^{\lambda\mathbf{s}}$. Without loss of generality, one can assume that the set of spin-orbitals $\psi_{\lambda\mathbf{s}}$ is orthonormal[1].

The total energy of the N electron system is written as: $E = E^{(1)} + E^{(2)}$ where $E^{(1)}$ is the one-body contribution coming from the first two terms in H, and $E^{(2)}$ the two-body contribution coming from the last term, i.e. the electron-electron interaction term. After some algebra, one finds:

$$E^{(1)} = \sum_{\lambda,\mathbf{s}} \langle \psi_{\lambda\mathbf{s}} | h | \psi_{\lambda\mathbf{s}} \rangle ; \quad (1.2)$$

$$E^{(2)} = \frac{1}{2} \sum_{\lambda\mu,\mathbf{s}\mathbf{s}'} [\langle \psi_{\lambda\mathbf{s}}(r)\psi_{\mu\mathbf{s}'}(r') | v(r-r') | \psi_{\lambda\mathbf{s}}(r)\psi_{\mu\mathbf{s}'}(r') \rangle \quad (1.3)$$

$$- \delta_{\mathbf{s}\mathbf{s}'} \langle \psi_{\lambda\mathbf{s}}(r)\psi_{\mu\mathbf{s}'}(r') | v(r-r') | \psi_{\mu\mathbf{s}'}(r)\psi_{\lambda\mathbf{s}}(r') \rangle]$$

$$= \frac{1}{2} \sum_{\lambda\mu,\mathbf{s}\mathbf{s}'} [V(\lambda\mathbf{s}, \mu\mathbf{s}') - \delta_{\mathbf{s}\mathbf{s}'} J(\lambda\mathbf{s}, \mu\mathbf{s}')] \quad (1.4)$$

The second term in $E^{(2)}$ where the two orbitals λ and μ are exchanged is called the “exchange energy” and comes from the constraint of antisymmetry in Φ , whereas the first one is the Coulomb term which represents the electrostatic interaction between the electrons in the orbitals λ and μ considered. Note that the number of exchange terms is half that of the Coulomb terms because of the $\delta_{\mathbf{s}\mathbf{s}'}$ term. We also see that because of Pauli’s principle, the interaction between states of parallel spins is reduced by J compared to the Coulomb interaction between states of antiparallel spins. This less repulsive interaction between states of parallel spins favors ferromagnetism. This would be in competition with the kinetic energy which will increase if the system becomes magnetic. If the overlap between the states λ and μ is small, then the exchange interaction is small. The latter can usually become important in metals where such overlap is not always negligible. If the states λ and μ are localized, the corresponding exchange interaction $J(\lambda\mathbf{s}, \mu\mathbf{s})$ is usually short-ranged. At far distances, regardless of their spin, the interaction between two electrons is purely Coulombic, but as they become closer to each other, exchange-correlation effects become important, and affect their interaction.

To find the ground state, one must now minimize the total energy with respect to the orbitals $\psi_{\lambda,\mathbf{s}}$. The minimum condition, along with the constraint of orthonormality of the orbitals, introduced by using Lagrange multipliers

$\epsilon_{\lambda\mathbf{s},\mu\mathbf{s}'}$, leads straightforwardly to:

$$\begin{aligned} & \left[h(r) + \int \sum_{\mu\mathbf{s}'} |\psi_{\mu\mathbf{s}'}(r')|^2 v(r-r') dr' \right] \psi_{\lambda\mathbf{s}}(r) \\ & - \sum_{\mu} \left[\int \psi_{\mu\mathbf{s}}^*(r') \psi_{\lambda\mathbf{s}}(r') v(r-r') dr' + \epsilon_{\lambda\mathbf{s},\mu\mathbf{s}} \right] \psi_{\mu\mathbf{s}}(r) = 0 \end{aligned}$$

Again, the third term in the left hand side is the non-local exchange potential. For all practical purposes, the interaction v is the Coulomb interaction $v(r) = 1/r$, but the above holds for any Fermion system with arbitrary interaction. One can rewrite the above equation in a basis where the matrix ϵ is diagonal. It is possible to show that the form of the above equation is invariant after this unitary transformation[1, 2]. In the new basis, after relabeling the orbital indices, one ends up with an eigenvalue problem.

$$\begin{aligned} & \left[h(r) + \int \sum_{\mu\mathbf{s}'} |\psi_{\mu\mathbf{s}'}(r')|^2 v(r-r') dr' - \epsilon_{\lambda\mathbf{s}} \right] \psi_{\lambda\mathbf{s}}(r) \\ & - \int \sum_{\mu} \psi_{\mu\mathbf{s}}^*(r') \psi_{\lambda\mathbf{s}}(r') v(r-r') dr' \psi_{\mu\mathbf{s}}(r) = 0 \end{aligned} \quad (1.5)$$

Here, $\epsilon_{\lambda\mathbf{s}}$'s are only a set of Lagrange multipliers, and should not be taken as the electronic energy levels, though in practice, it is assumed so. The reason being **Koopman's theorem** stating that the energy difference between the N particle system and the $N - 1$ particle system in which one electron has been taken out from the level λ , is simply the eigenvalue ϵ_{λ} . Indeed, the difference can easily be computed from the above equation; we have:

$$E_N - E_{N-1}^{\lambda\mathbf{s}} = \langle \lambda\mathbf{s} | h | \lambda\mathbf{s} \rangle + \sum_{\mu\mathbf{s}'} [V(\lambda\mathbf{s}, \mu\mathbf{s}') - \delta_{\mathbf{s}\mathbf{s}'} J(\lambda\mathbf{s}, \mu\mathbf{s})] = \epsilon_{\lambda\mathbf{s}}$$

From the above, one should not conclude that the total energy is the sum of the eigenvalues, because the two-body interactions will be counted twice. If one sums up the above difference over all occupied states, the two-body term will come with a factor twice larger than in equation 1.4. Thus the total energy is also given by:

$$E_N = \sum_{\lambda\mathbf{s}} \epsilon_{\lambda\mathbf{s}} - \frac{1}{2} \sum_{\lambda\mu,\mathbf{s}\mathbf{s}'} [V(\lambda\mathbf{s}, \mu\mathbf{s}') - \delta_{\mathbf{s}\mathbf{s}'} J(\lambda\mathbf{s}, \mu\mathbf{s}')] \quad (1.6)$$

Notice the exact cancellation of $\lambda = \mu; \mathbf{s} = \mathbf{s}'$ term in the Coulomb and exchange terms of equations 1.5 and 1.6. Since representing the Coulomb interaction of the electron in spin-orbital $\lambda\mathbf{s}$ with itself, this term is called the **self-interaction** term and, unlike in DFT, is correctly and fully cancelled in HF. In practice, it is included in both sums, since the total electron density is needed.

1.1.1 Electron Affinity, Ionization Potential and Chemical Hardness

Previously, we defined the chemical potential or the Fermi energy as the energy of the highest occupied state at zero temperature. It was also obtained from the definition of the total electron number written as an integral over the energy of the DOS times the Fermi-Dirac function. Its thermodynamic definition is however given by: $\mu = \partial\mathcal{E}/\partial\mathcal{N}$ It is the energy required to add a particle to the system keeping everything else constant, namely the external potential. This definition is a bit similar to that of the ionization potential (I) and electron affinity (A), which can be calculated from Koopmans' theorem within the HF theory.

$$I = E(N - 1) - E(N); \quad A = E(N) - E(N + 1)$$

As their definition shows, I and A are the negative of the slopes of the curve $E(N)$ taken by finite difference from left and right respectively. I or the ionization potential is the energy necessary to take away one electron from the system. A or the electron affinity is the energy gained when one electron is added to the system.

An important concept in the stability of a compound or molecule is its chemical hardness η . It says how easy it is to add or remove an electron from the system. In other words, it is its chemical stiffness, and therefore can be defined as

$$\eta = \frac{1}{2} \left(\frac{\partial^2 \mathcal{E}}{\partial \mathcal{N}^2} \right)_{V_{\text{ext}}} = \frac{1}{2} \left(\frac{\partial \mu}{\partial \mathcal{N}} \right)_{V_{\text{ext}}}$$

Equivalently, the **softness** can be defined as $S = 1/2\eta = (\partial\mathcal{N}/\partial\mu)_{V_{\text{ext}}}$. Note that these definitions can be generalized to become a matrix in the case derivatives are taken with respect to occupation of specific orbitals. This is identical to the definition of the inverse capacitance matrix which is also the second derivative of the energy of charged conductors with respect to the

charge of each conductor. In the latter case, only electrostatic contributions to the total energy are included, whereas in the former, in general, other contributions such as exchange and correlations are also included.

If one uses the finite difference as an approximation to the derivatives, chemical hardness can be related to the electron affinity and ionization potential as:

$$\eta = (\mathcal{E}(\mathcal{N} + 1) - 2\mathcal{E}(\mathcal{N}) + \mathcal{E}(\mathcal{N} - 1))/2 = (I - A)/2$$

Similarly, the chemical potential can also be related to I and A by

$$\mu = -(I + A)/2 = -\chi$$

where χ is called the **electronegativity** of the molecule or atom under consideration.

Within the HF theory, we have :

$$I = -\epsilon_N; A = -\epsilon_{N+1}; \mu = (\epsilon_{N+1} + \epsilon_N)/2; \eta = (\epsilon_{N+1} - \epsilon_N)/2;$$

where N labels the highest occupied state, and $N+1$ is the lowest unoccupied state.

More local concepts can also be defined. For example the **Fukui function** defined as $f(r) = (\delta\mathcal{N}/\delta\rho(r))_{V_{\text{ext}}}$, tells us where an added or removed electron will be localized (wherever $f(r)$ is smallest). Knowing the space dependence of the Fukui function, one would have information about where it is hard and where it is easy to add or remove electrons.

1.1.2 Matrix form of the HF Hamiltonian, and density matrix formulation

As usual, after expanding the eigenfunctions on a basis:

$$\psi_{\lambda\mathbf{s}}(r) = \sum_i c_i^{\lambda\mathbf{s}} \phi_i(r) \chi(\mathbf{s})$$

the problem is reduced to find the set of coefficients $c_i^{\lambda\mathbf{s}}$. A generalized eigenvalue matrix problem results from equation 1.5. It can be solved by the standard eigenvalue packages once the matrix elements of the Hartree-Fock Hamiltonian have been calculated. The solution must be found self-consistently since the Hamiltonian itself depends of the eigenfunctions. This

formalism can be applied to both open-shell and closed-shell systems and is called the Unrestricted Hartree-Fock (UHF) method. After expansion on a basis set ϕ_i , one has the matrix eigenvalue equation which is much easier to solve than the above integro-differential equations. Let us introduce the density and magnetization matrices as:

$$\rho_{ij} = \sum_{\lambda, \mathbf{s}} f^{\lambda \mathbf{s}} c_i^{\lambda \mathbf{s}*} c_j^{\lambda \mathbf{s}}$$

$$\mathcal{M}_{ij} = \sum_{\lambda} f^{\lambda \uparrow} c_i^{\lambda \uparrow*} c_j^{\lambda \uparrow} - f^{\lambda \downarrow} c_i^{\lambda \downarrow*} c_j^{\lambda \downarrow},$$

where $f^{\lambda \mathbf{s}} = 1$ if the state $\lambda \mathbf{s}$ is occupied and 0 otherwise (at finite temperatures, it can be replaced by the Fermi-Dirac distribution function). Note that the diagonal elements of these matrices represent respectively the charge (ρ_{ii}) and the magnetization (\mathcal{M}_{ii}) on the orbital i .

We also define the Coulomb integral \mathcal{U} by:

$$\mathcal{U}_{ij,kl} = \int \frac{\phi_i^*(r) \phi_j(r) \phi_k^*(r') \phi_l(r')}{|r - r'|} dr dr',$$

and the overlap matrix by $S_{ij} = \langle \phi_i | \phi_j \rangle$. The generalized eigenvalue equation becomes for each i :

$$\sum_j \left(h_{ij} + \sum_{kl} [\mathcal{U}_{ij,kl} - \mathcal{U}_{ik,lj}/2] \rho_{kl} - p_{\mathbf{s}} \mathcal{M}_{lk} \mathcal{U}_{ik,lj}/2 - S_{ij} \epsilon_{\lambda \mathbf{s}} \right) c_j^{\lambda \mathbf{s}} = 0 \quad (1.7)$$

where $p_{\mathbf{s}} = +1$ for up spins and -1 for down spins. Here, in order to treat degenerate levels, we can introduce a fractional occupation $0 < f^{\lambda \mathbf{s}} < 1$, so that for a triply degenerate level such as the p states in an atom, the occupancy of the three levels for an electron would be $1/3$. This artifact must be interpreted with a statistical meaning.

The magnetization term appears clearly in this equation. This term contributes when the exchange integral $\mathcal{U}_{ik,lj}$ becomes large. This occurs if the overlap between states k and i and that between states j and l is important. The appearance of magnetization is not always trivial, since it depends on the **self-consistent solution** of the eigenvalue problem, the output of which are the density and spin matrices ρ and \mathcal{M} .

The total energy is given by:

$$E = \sum_{ij} \left(h_{ij} \rho_{ij} + \sum_{kl} \left[\frac{1}{2} \rho_{ij} (\mathcal{U}_{ij,kl} - \frac{1}{2} \mathcal{U}_{il,kj}) \rho_{kl} - \frac{1}{4} \mathcal{M}_{ij} \mathcal{U}_{il,kj} \mathcal{M}_{kl} \right] \right)$$

The energy functional in the HF theory is quadratic in the density and spin matrices, in this sense, it is a very simple functional. The quadratic form in the magnetization may justify the use of the Heisenberg Hamiltonian for some model calculations.

The total energy functional includes the exchange effect and the self-interaction correction exactly, but does not incorporate the correlations between the electrons. To include the latter, one must consider other Slater determinants which include unoccupied states as well, and use these determinants as many-body basis functions. The simplest treatment of correlations is to compute the effect of the extra part of the Coulomb interaction not included in HF by using many-body perturbation theory. A better, but more complicated treatment would be to diagonalize the Hamiltonian matrix in this many-body basis. This method is called the Configuration-Interaction (CI) method. These are mostly adopted by quantum chemists to describe molecules very accurately, but one is very limited in the number of electrons. The other approach is the many-body technique in which a set of diagrams (called the bubble diagrams) are summed to infinite order. This constitutes the Random-Phase-Approximation (RPA) and incorporates screening effects which are absent in the original HF treatment. The lack of screening leads to a zero density of states at the Fermi level in the case of the uniform electron gas. This result is in contradiction with RPA and more exact Quantum Monte Carlo calculations. The long-range Coulomb correlations that lead to screening are not included in HF; this theory is therefore inappropriate for treating metallic systems and bulk systems in general. It always overestimates the bandgap and usually underestimates the binding energy.

1.2 Application to the Jellium model

Exchange energy in the spectrum, and the total energy in 1,2 and 3D shortcomings (gap) screening

1.3 Another simple example: The H₂ molecule

Bibliography

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