Hartree-Fock Approximation

The expectation value of two-body part of Hamiltonian given by equation (**??**) is,

$$\left\langle \hat{H}_2 \right\rangle = \langle \psi_0 | \hat{V}_{ee} | \psi_0 \rangle = \frac{1}{2} \sum_{\nu\lambda\alpha\beta} \langle \nu\ \lambda | \frac{e^2}{r_1 - r_2} | \alpha\ \beta \rangle \left\langle a_\nu^\dagger a_\lambda^\dagger a_\beta a_\alpha \right\rangle \tag{1}$$

Using the relation $a_\alpha |n_\alpha\rangle = \sqrt{n_\alpha - 1}\,|n_\alpha - 1\rangle$, we have

$$\left\langle n_\alpha n_\beta \right| a_\nu^\dagger a_\lambda^\dagger a_\beta a_\alpha \left| n_\alpha n_\beta \right\rangle = \sqrt{n_\alpha n_\beta} \left\langle n_\alpha n_\beta \right| a_\nu^\dagger a_\lambda^\dagger \left| n_\alpha - 1, n_\beta - 1 \right\rangle \tag{2}$$

This quantity is nonvanishing only if $\nu = \beta$ and $\lambda = \alpha$, or $\nu = \alpha$ and $\lambda = \beta$. Because of the anticommutation relations of the α's, these two cases will give contributions differing by minus sign. We find then,

$$\left\langle n_\alpha n_\beta \right| a_\nu^\dagger a_\lambda^\dagger a_\beta a_\alpha \left| n_\alpha n_\beta \right\rangle = \left(\delta_{\nu\alpha}\delta_{\lambda\beta} - \delta_{\nu\beta}\delta_{\lambda\alpha} \right) n_\alpha n_\beta \tag{3}$$

or, for the ground state given in equation (**??**)

$$\left\langle a_\nu^\dagger a_\lambda^\dagger a_\beta a_\alpha \right\rangle = \left(\delta_{\nu\alpha}\delta_{\lambda\beta} - \delta_{\nu\beta}\delta_{\lambda\alpha} \right) \left\langle \hat{n}_\beta \right\rangle \langle \hat{n}_\alpha \rangle \tag{4}$$

We rewrite $\left\langle \hat{H}_2 \right\rangle$ as a sum of two integrals,

$$\left\langle \hat{H}_2 \right\rangle = \frac{1}{2} \sum_{\lambda,\nu} \langle \nu\lambda | \frac{e^2}{|r_1 - r_2|} | \nu\lambda \rangle\, n_\lambda n_\nu - \frac{1}{2} \sum_{\lambda,\nu} \langle \nu\lambda | \frac{e^2}{|r_1 - r_2|} | \lambda\nu \rangle\, n_\lambda n_\nu \tag{5}$$

$$= \frac{1}{2} \sum_{\lambda,\nu(occ.)} \left(U_{\nu\lambda} - \delta_{\sigma_\nu\sigma_\lambda} J_{\nu\lambda} \right) \tag{6}$$

The direct Coulomb interaction,

$$U_{\nu\lambda} = \int \left|\phi_\nu(r_1)\right|^2 \frac{e^2}{|r_1 - r_2|} \left|\phi_\lambda(r_2)\right|^2\ dr_1\ dr_2 \tag{7}$$

is a measure of the repulsion between two electrons at positions r_1 and r_2; the exchange interaction,

$$J_{\nu\lambda} = \int \phi_\nu^*(r_1)\phi_\lambda^*(r_2) \frac{e^2}{|r_1 - r_2|} \phi_\nu(r_2)\phi_\lambda(r_1)\ dr_1\ dr_2 \tag{8}$$

arises solely when electrons of like spin exchange spatial coordinates. The negative sign accompanying the exchange term leads to an effective attraction between electrons of like spin. This attraction is the basis of Heisenberg's explanation of ferromagnetism. The Pauli exclusion principle, which results from the Fermi-Dirac statistics obeyed by electrons, leads to a depletion of electrons of the same spin in neighborhood of an electron of given spin. The depletion is commonly called the *exchange hole*.

The total Hartree-Fock energy is,

$$E_{HF} = \left\langle \hat{H}_1 \right\rangle + \frac{1}{2} \sum_{\lambda,\nu(occ.)} \left(U_{\nu\lambda} - J_{\nu\lambda} \right) \tag{9}$$

To determine ϕ_ν and ϕ_λ we minimize the ground state energy E_{HF} with respect to ϕ, subject to condition that the ϕ's remain normalized. This can be imposed by introducing Lagrange multiplier, ϵ_ν in the minimization such that

$$\frac{\delta E_{HF}}{\delta \phi_\nu^*(r)} = \epsilon_\nu \frac{\delta}{\delta \phi_\nu^*(r)} \int \left|\phi_\nu(r')\right|^2 dr' \tag{10}$$

Then we can get the relation,

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + \hat{V}_{ion}(r) + \sum_\lambda \int n_\lambda(r')\frac{e^2}{|r-r'|}dr'\right]\phi_\nu(r) - \sum_\lambda \int \phi^*_\lambda(r')\phi_\nu(r')\frac{e^2}{|r-r'|}\phi_\lambda(r)dr' = \epsilon_\nu\phi_\nu(r) \tag{11}$$

This is called Hartree-Fock equation.

Multiplying equation (11) by $\phi^*_\nu(r)$ and integrating over r, we derive the result for the single-particle energy ϵ_ν,

$$\epsilon_\nu = \langle\nu|H_1|\nu\rangle + \sum_{\lambda(occ.)}(U_{\nu\lambda} - J_{\nu\lambda}) \tag{12}$$

Because these energies involve the interaction with electrons in all other occupied orbitals, ϵ_ν can not be interpreted simply as the energy of the electron in orbital ν. In fact, the total energy is not simply the sum of these single-particle energies, but, as follows from equation (9)

$$E_{HF} = \sum_{\nu(occ.)}\epsilon_\nu - \frac{1}{2}\sum_{\lambda,\nu(occ.)}(U_{\nu\lambda} - J_{\nu\lambda}) \tag{13}$$

The Hartree-Fock single particle energy, ϵ_ν, is the energy required to add a particle in the previously unoccupied orbital ν. Consider adding an extra electron to a set of filled orbitals in a previously unoccupied orbital ν. The change in the Hartree-Fock energy due to adding the particle is

$$\delta E_{HF} = E^{new}_{HF} - E_{HF} = \langle\nu|H_1|\nu\rangle + \sum_{\alpha\neq\nu}(U_{\nu\alpha} - J_{\nu\alpha}) = \epsilon_\nu \tag{14}$$

Likewise, had we removed an electron, the resultant Hartree-Fock energy would simply decrease by the energy of the orbital from which the electron was taken.

In general, in going from N to an $N-1$ particle system,

$$\delta E_{HF} = \epsilon_N = E^{HF}_N - E^H_{N-1}F$$

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Google-Exercise: *Show that* $\left\langle a_\nu^\dagger a_\lambda^\dagger \cdots a_l^\dagger a_\rho a_\alpha \cdots a_\gamma \right\rangle$ *is given by the sum of all contractions, with the sign of each term determined by the number of particle interchanges necessary to line up side-by-side the contracted operators. Note, when two operators are contracted, their indices become equal.*
Hint: Look for Wick's Theorem.