Hartree-Fock equation – very elementary introduction

One electron Schrodinger equation is:

$$\mathcal{H}\psi(\boldsymbol{r}) = \left(-\frac{\hbar^2}{2m}\nabla^2 + \mathrm{U}(\mathbf{r})\right)\psi(\boldsymbol{r}) = \varepsilon\psi(\boldsymbol{r})$$

How do we include electron-electron interaction in $U(\boldsymbol{r})$? Need to start with the wave function for all *N* electrons in the material $\psi(\boldsymbol{r}_1, \boldsymbol{r}_2 \dots\dots..\boldsymbol{r}_N)$

$$\sum_{i=1}^{N}\left(-\frac{\hbar^2}{2m}\nabla_i{}^2 - \frac{Ze^2}{4\pi\varepsilon_0}\sum_R \frac{1}{|\boldsymbol{R}-\boldsymbol{r}_i|^2}\right)\psi(\boldsymbol{r}) + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{4\pi\varepsilon_0}\frac{1}{\left|\boldsymbol{r}_i-\boldsymbol{r}_j\right|^2}\psi(\boldsymbol{r}) = \varepsilon\psi(\boldsymbol{r})$$

Impossible to solve for a realistic system with $\sim 10^{23}$ particles

Way out: Look for alternate forms of $U(\boldsymbol{r})$ that yields a solvable Hamiltoninan but is also as close to reality as possible.

Ionic part of $U(\boldsymbol{r})$: $U^{ion}(\boldsymbol{r}) = \frac{Ze^2}{4\pi\varepsilon_0}\sum_R \frac{1}{|\boldsymbol{R}-\boldsymbol{r}_i|^2}$

Electronic part of $U^{el}(\boldsymbol{r})$: Treat all electrons as forming a smooth charge distribution $\rho(\boldsymbol{r})$. The potential energy of a particular electron at $\boldsymbol{r}$ due to this potential is

$$U^{el}(\boldsymbol{r}) = -\frac{e}{4\pi\varepsilon_0}\int d\acute{\boldsymbol{r}}\,\rho(\acute{\boldsymbol{r}})\frac{1}{|\boldsymbol{r}-\acute{\boldsymbol{r}}|^2}$$

In the independent electron picture the contribution of an electron in level $\psi_i(\boldsymbol{r})$ to $\rho(\boldsymbol{r})$ is

$$\rho_i(\boldsymbol{r}) = -e\,|\psi_i(\boldsymbol{r})|^2$$

Hence, the total charge density at point $\boldsymbol{r}$ is

$$\rho(\boldsymbol{r}) = -e\sum_i |\psi_i(\boldsymbol{r})|^2$$

Using this the Hamiltonian for a particular electron in the system is:

$$\sum_{i=1}^{N}\left(-\frac{\hbar^2}{2m}\nabla_i{}^2 - \frac{Ze^2}{4\pi\varepsilon_0}\sum_R \frac{1}{|\boldsymbol{R}-\boldsymbol{r}_i|^2}\right)\psi_i(\boldsymbol{r}) + \frac{e^2}{4\pi\varepsilon_0}\sum_j\int d\acute{\boldsymbol{r}}\left|\psi_j(\acute{\boldsymbol{r}})\right|^2\frac{1}{|\boldsymbol{r}-\acute{\boldsymbol{r}}|^2}\psi_i(\boldsymbol{r})$$

There is one such equation for every electron in the system these are the **Hartree equations** – solved iteratively – select a trial wave function for $\psi_i(\boldsymbol{r})$ - calculate $U^{el}(\boldsymbol{r})$ based on this – solve the Hartree equation to get the $\psi_i(\boldsymbol{r})$ - continue till the results converge.

This method is also called the '**self consistent field approximation**'.

Inadequacy of the Hartree theory:

1. Deals with the average and not individual position of electrons in the system.
2. Does not contain 'exchange terms'.
3. Cannot give proper screening.

Hartree- Fock Equation

Variational form of the wave function: solution of $\mathcal{H}\psi = \varepsilon\psi$ is any function that makes the quantity

$$\langle \mathcal{H}\rangle_{\psi} = \frac{\langle \psi, \mathcal{H}\psi\rangle}{\langle \psi, \psi\rangle} = \frac{\int dr_1 dr_2 \dots .\, dr_N \psi^*(\boldsymbol{r}_1, \boldsymbol{r}_2 \dots\dots ..\boldsymbol{r}_N)\mathcal{H}\psi(\boldsymbol{r}_1, \boldsymbol{r}_2 \dots\dots ..\boldsymbol{r}_N)}{\int dr_1 dr_2 \dots .\, dr_N \psi^*(\boldsymbol{r}_1, \boldsymbol{r}_2 \dots\dots ..\boldsymbol{r}_N)\psi(\boldsymbol{r}_1, \boldsymbol{r}_2 \dots\dots ..\boldsymbol{r}_N)}$$

stationary. Using this procedure for the Hartree equations give:

$$\psi(\boldsymbol{r}_1 s_1, \boldsymbol{r}_2 s_2 \dots\dots ..\boldsymbol{r}_N s_N) = \psi_1(\boldsymbol{r}_1 s_1)\, \psi_2(\boldsymbol{r}_2 s_2) \dots \psi_N(\boldsymbol{r}_N s_N)$$

where $\psi(\boldsymbol{r}_i s_i)$ are the orthonormal single electron wave functions (orbitals).

For Pauli principle to be applicable, the above solution should be anti-symmetric upon the exchange of the co-ordinates two electrons *i.e.*

$$\psi\big(\boldsymbol{r}_1 s_1, \boldsymbol{r}_2 s_2 \dots \boldsymbol{r}_i s_i \boldsymbol{r}_j s_j \dots ..\boldsymbol{r}_N s_N\big) = -\,\psi\big(\boldsymbol{r}_1 s_1, \boldsymbol{r}_2 s_2 \dots \boldsymbol{r}_j s_j \boldsymbol{r}_i i \dots ..\boldsymbol{r}_N s_N\big)$$

This can be true only if the wavefunction is identically zero. Thus the variational solution to the Hartree equation does not satisfy Pauli principle as it should for a fermionic system.

Generalization of the Hartree solution – Slater determinant: This problem can be avoided if the wave function is expressed as a combination of all its permutations taking the Pauli principle into account (whenever an odd number of electron pairs interchange places the wave function picks up a negative sign). This can be conveniently described by the Slater determinant:

$$\psi = \begin{vmatrix} \psi_1(\boldsymbol{r}_1 s_1) & \psi_1(\boldsymbol{r}_2 s_2) & . & . & . & \psi_1(\boldsymbol{r}_N s_N) \\ \psi_2(\boldsymbol{r}_1 s_1) & \psi_2(\boldsymbol{r}_2 s_2) & . & . & . & \psi_2(\boldsymbol{r}_N s_N) \\ \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\ . & . & . & . & . & . \\ \psi_N(\boldsymbol{r}_1 s_1) & \psi_N(\boldsymbol{r}_2 s_2) & . & . & . & \psi_N(\boldsymbol{r}_N s_N) \end{vmatrix}$$

Evaluate the energy using this wavefunction:

$$\begin{aligned} \langle \mathcal{H}\rangle_{\psi} = {} & \sum_{i=1}^{N} \int d\boldsymbol{r}\, {\psi^*}_i(\boldsymbol{r}) \left(-\frac{\hbar^2}{2m} {\nabla_i}^2 + U^{ion}(\boldsymbol{r}) \right) \psi_i(\boldsymbol{r}) \\ & + \frac{1}{2} \sum_{i,j} \int d\boldsymbol{r} d\acute{\boldsymbol{r}}\ \frac{e^2}{4\pi\varepsilon_0} \frac{1}{|\boldsymbol{r} - \acute{\boldsymbol{r}}|^2}\, |\psi_i(\boldsymbol{r})|^2 \big|\psi_j(\acute{\boldsymbol{r}})\big|^2 \\ & - \frac{1}{2} \sum_{i,j} \int d\boldsymbol{r} d\acute{\boldsymbol{r}}\ \delta_{s_i s_j} \frac{e^2}{4\pi\varepsilon_0} \frac{1}{|\boldsymbol{r} - \acute{\boldsymbol{r}}|^2} {\psi_i}^*(\boldsymbol{r}) \psi_i(\acute{\boldsymbol{r}}) {\psi_j}^*(\acute{\boldsymbol{r}}) \psi_j(\boldsymbol{r}) \end{aligned}$$

Minimizing this with respect to ${\psi_i}^*(\boldsymbol{r})$ we get the Hartree-Fock Hamiltonian:

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + U^{ion}(\boldsymbol{r}) + U^{el}(\boldsymbol{r}) \right) \psi_i(\boldsymbol{r}) - \sum_j \int d\acute{\boldsymbol{r}}\ \frac{e^2}{4\pi\varepsilon_0} \frac{1}{|\boldsymbol{r} - \acute{\boldsymbol{r}}|^2} \psi_i(\acute{\boldsymbol{r}}) {\psi_j}^*(\acute{\boldsymbol{r}}) \psi_j(\boldsymbol{r}) \delta_{s_i s_j}$$

The last term is the *exchange term* – this one has no classical analogue and arises solely due to the Fermionic statistics of the electronic system.

Solution of Hartree-Fock (HF) equation for free electrons: Artificial problem. Wavefunction of free electron is

$$\psi_i(\boldsymbol{r}) = 1/\sqrt{V}\, e^{i\boldsymbol{k}.\boldsymbol{r}} \times \text{spin function}$$

Check if this function satisfies the HF equation. For this wavefunction $U^{el}(\boldsymbol{r})$ is uniform in space – for free electron case the ions are treated as a uniform distributed of positive charge with the same density as the electronic charge; hence $U^{el}(\boldsymbol{r}){+}U^{ion}(\boldsymbol{r}) = 0$

Evaluating the exchange term:

$$\frac{1}{|\boldsymbol{r}-\acute{\boldsymbol{r}}|^2} = 4\pi \int \frac{d\boldsymbol{q}}{(2\pi)^3}\frac{1}{q^2}e^{i\boldsymbol{q}.(\boldsymbol{r}-\acute{\boldsymbol{r}})}$$

Put this in the HF equation to get

$$\mathcal{H}\psi_i(\boldsymbol{r}) = \varepsilon(\boldsymbol{k}_i)\psi_i(\boldsymbol{r})$$

with

$$\varepsilon(\boldsymbol{k}) = \frac{\hbar^2 k^2}{2m} - \int \frac{d\acute{\boldsymbol{k}}}{(2\pi)^3}\frac{e^2}{4\pi\varepsilon_0}\frac{4\pi}{\left|\boldsymbol{k}-\acute{\boldsymbol{k}}\right|^2} = \frac{\hbar^2 k^2}{2m} - \frac{e^2}{2\pi^2\varepsilon_0}k_F \times F\left(\frac{k}{k_F}\right)$$

where $F(x) = \frac{1}{2} + \frac{1-x^2}{4x}\ln\left|\frac{1+x}{1-x}\right|$

This shows that the plane wave solution satisfies the HF equation – energy is no longer $\frac{\hbar^2 k^2}{2m}$- there is a second term (comparable to the first) arising due to e-e interactions.