

The following note is based on the 2nd edition of **Computational Materials Science: An Introduction** by June Gunn Lee

▼ Chapter 4: First-principles methods

Energy for a many-body system:

For a many-body system with $N \in \mathbb{N}$ nuclei and $n \in \mathbb{N}$ electron, where $I \in N, i \in n$, the total energy involved is given as:

$$\hat{H} = E_I^k + E_i^k + U_{Ii} + U_{ij} + U_{IJ}.$$

Here, E^k -terms are kinetic energy terms and U terms are potential energy terms due to Coulomb interaction between nucleus-electron, electron-electron, and nucleus-nucleus.

Because of *Born-Oppenheimer approximation*, i.e., the nucleus is much heavier than the electrons and hence they can be treated as fixed, we can discard the terms coming from nuclei interaction (but not U of electron due to nuclei). So,

$$\hat{H} = E_i^k + U_{Ii} + U_{ij}.$$

In atomic units ($\hbar = e = m_e = a_0 = 1$):

$$\hat{H} = -\frac{1}{2} \sum_i^n \nabla_i^2 - \sum_I^N \sum_i^n \frac{Z_I}{|r_{Ij}|} + \frac{1}{2} \sum_{i \neq j}^n \frac{1}{|r_{ij}|}$$

Hartree approximation:

Hartree method assumes that the effect is not coming from each individual electron but rather from a mean field due to all of the electron. So, for a single electron:

$$\hat{H} = -\frac{1}{2} \nabla^2 + U_{ext} + U_H$$

where, U_{ext} is the potential due to Coulomb interaction between nuclei and electrons, and U_H is the *Hartree Potential* due to interaction between the electron and the mean field.

The total energy is just the sum of all the electron energy, i.e.,

$$E_{tot} = \sum_i^n E_i$$

However, this method doesn't take account of Pauli's exclusion principle, and exchange and correlation energies.

Hartree-Fock (HF) approximation: HF method takes account of the exclusion principle, namely it preserves the antisymmetry of the wavefunction (for fermions - here electron). For example, for a 2-electron system, $\psi(r_1, r_2) = -\psi(r_2, r_1)$

In general, the wavefunction of an n -electron system is given by the respective Slater determinant:

$$\psi(r_1, r_2, \dots, r_n) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \psi_1(r_1) & \psi_2(r_1) & \dots & \psi_n(r_1) \\ \psi_1(r_2) & \psi_2(r_2) & \dots & \psi_n(r_2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(r_n) & \psi_2(r_n) & \dots & \psi_n(r_n) \end{vmatrix}$$

Considering the wavefunction in the Slater determinant form, the total energy becomes:

$$E_{tot} = E^k + E_{ext} + E_H + E_x$$

where the new term E_x denotes the exchange energy coming due to the antisymmetric nature of the Slater determinant. The Hartree energy is given as:

$$E_H = \frac{1}{2} \int \int \frac{\rho(r)\rho(r')}{|r - r'|} dr dr'$$

HF approximation is better than Hartree approximation in the sense that it gives closer result to the actual energy by adding the exchange energy term. E_x is negative, so while Hartree approximation gives us an overestimate, it gets corrected in HF approximation. More about E_x will be discussed later.

Variational approach:

One thing that is ubiquitous in *ab initio* methods is the *variational approach*. It says if we minimize the system energy with respect to the wavefunction, then the least energy possible is the ground state energy.

Lastly, HF approximation is better than Hartree approximation that it takes account the effect that same-spin electron must stay away from each other. But HF approximation doesn't consider electron correlation energy which is due to the fact that even different spin electrons have a *tendency* to stay away from each other.