Simulation Methods II

SS 2019

Lecture 2

2.1 The Hartree (H) approximation

Electrons are modelled as non-interacting particles with a total wavefunction:

$$\Psi^H(\{\vec{r}_i\}) = \phi_1(\vec{r}_1)\,\phi_2(\vec{r}_2)\cdots\phi_N(\vec{r}_N)$$

$\phi_i(\vec{r}_i)$: single-particle normalized state

Total Energy: $E^H = \langle \Psi^H | \mathcal{H} | \Psi^H \rangle$

$$= \sum_i \langle \phi_i \left| -\frac{\hbar^2 \nabla^2_{\vec{r}}}{2m} + V_{ion}(\vec{r}) \right| \phi_i \rangle$$

$$+ \frac{e^2}{2} \sum_{\substack{i,j \\ (i \neq j)}} \langle \phi_i \phi_j \left| \frac{1}{|\vec{r} - \vec{r}'|} \right| \phi_i \phi_j \rangle$$

Variational calculation of ϕ_i with Ψ^H a stationary state (any variation in Ψ^H leads to a zero variation in E^H)

+ Lagrange multipliers

$$\rightarrow \delta \left[E^H - \sum_i \varepsilon_i \left(\langle \phi_i | \phi_i \rangle - 1 \right) \right] = 0$$

$\Rightarrow$ ... $\Rightarrow$

$$\left[-\frac{\hbar^2}{2m}\nabla^2_{\vec{r}} + V_{ion}(\vec{r}) + e^2 \underbrace{\sum_{i\neq j} \langle \phi_j | \frac{1}{|\vec{r}-\vec{r}_1|} | \phi_i \rangle}_{V^H(\vec{r})}\right] \phi_i(\vec{r}) = \varepsilon \phi_i(\vec{r})$$

$V^H(\vec{r})$ the Hartree potential

- The equation above is the Hartree single-particle equation including only correlations from the Coulomb interactions (no exchange).
- $V^H(\vec{r})$ is different for each particle and includes the Coulomb interactions in a mean-field way.

2.2. The Hartree-Fock (HF) method

- Next level of sophistication, at which exchange interactions are included through one Slater determinant for N electrons
- HF is a properly antisymmetrized version of the Hartree approach.