MANY-ELECTRON ATOMS REVIEW

many-electron atom review

THE iNOTES

Atomic Units

$m_e = e = \hbar = 4\pi\varepsilon_0 = 1$, $E_H = -0{,}5$ Hartree

Helium Atom

$$\hat{H} = \underbrace{-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2}_{\text{Kinetic energies both electrons}} \underbrace{- \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}}_{\text{Interactions}}$$

Antisymmetry

$\psi(1,2) \neq -\psi(2,1)$ → Pauli

$\uparrow\downarrow$ $\cancel{\uparrow\uparrow}$

To satisfy Pauli

Slater Determinant

$$\psi(1,2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_1(1) & \psi_2(1) \\ \psi_1(2) & \psi_2(2) \end{vmatrix}$$

→ **How to Estimate Energy of Atoms and Electrons?**

⇒ **Hartree - Foch Theory**

- $\psi_i = \sum_{m=i}^{k} c_{mi}\,\phi_m$

  $\{\phi_m\}$ → Basis set

  $\{\psi_i\}$ → Orbitals

  ψ → Slater Determinant

- $E = \sum_{i=1}^{N} h_i + \underbrace{\frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}(J_{ij} - K_{ij})}_{\text{Mean Field}}$

  $J_{ij} = [ii|jj]$

  $K_{ij} = [ij|ji]$ "Pauli"

  $h_i = \langle i | -\frac{1}{2}\nabla^2 - Z/r | i \rangle$

Mean Field

Basically how electrons interact with each other

$\hat{F}\psi_i = \varepsilon_i \psi_i$

↳ Foch Operator acting on orbitals

$\underline{F}\,\underline{c} = \varepsilon\,\underline{\underline{S}}\,\underline{c}$

↳ Hartree - Foch Equation