

MANY-ELECTRON



ATOMS REVIEW



THE iNOTES

ATOMIC UNITS

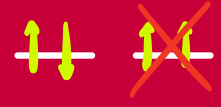
$$m_e = e = \hbar = 4\pi\epsilon_0 = 1, E_H = -0,5 \text{ HARTREE}$$

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

$$\psi(1,2) \neq -\psi(2,1) \rightarrow \text{PAULI}$$



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

- $\psi_i = \sum_{m=1}^k c_{mi} \phi_m$ $\{\phi_m\} \rightarrow$ BASIS SET
- $\{\psi_i\} \rightarrow$ ORBITALS
- $\psi \rightarrow$ SLATER DETERMINANT

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

$J_{ij} = [ii|jj]$
 $K_{ij} = [ij|ji]$ "PAULI"

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

MEAN FIELD
BASICALLY HOW ELECTRONS INTERACT WITH EACH OTHER

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

↳ FOCHE OPERATOR ACTING ON ORBITALS

$$\underline{F} \underline{c} = \underline{\epsilon} \underline{S} \underline{c}$$

↳ HARTREE-FOCH EQUATION