

Lecture 29

Hour exam Friday

How to calculate any molecular property:

$$1) \hat{H} = \sum_{i=1}^N \left\{ \frac{\hat{p}_i^2}{2m_e} - \sum_n \frac{e^2 Z_n}{4\pi\epsilon_0 r_{in}} \right\} + \sum_{i=1}^N \sum_{j>i}^N \frac{e^2}{4\pi\epsilon_0 r_{ij}} + \sum_n \sum_{m \neq n} \frac{e^2 Z_n Z_m}{4\pi\epsilon_0 r_{nm}}$$

$$= \underbrace{\sum_i \hat{h}_i}_{\text{each kinetic E \& nuclear attraction}} + \underbrace{\sum_{i,j \geq 1} V_{ij}}_{\text{e-e repulsion}} + \underbrace{\sum_{n,m} E_{nm}}_{\text{nuclear repulsion}}$$

$$2) \phi_i(\vec{r}_i) = \sum_{m=1}^M C_m \psi_m(\vec{r}_i) \cdot \alpha \beta$$

↑
one e⁻ orbital

Each MO or VB (hybrid) one-electron wave function = orbital ϕ is a sum over atomic orbitals ψ_m

$$3) \Psi_0(\vec{r}_1, \dots, \vec{r}_N, S) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\vec{r}_1) & \dots & \phi_N(\vec{r}_1) \\ \vdots & & \vdots \\ \phi_1(\vec{r}_N) & \dots & \phi_N(\vec{r}_N) \end{vmatrix}$$

↑
total ground state wavef. product over all orbitals

The determinant or Hartree-Fock wavefunction, a single e⁻ configuration

4) Variational principle: vary $c_m \Rightarrow E_0 \leq \langle \Psi_0 | \hat{H} | \Psi_0 \rangle = E_{HF}$
 ↳ get the best energy possible with the basis set $\{\psi_m(\vec{r}_i)\}$

5) $\hat{F}\hat{A}$ is the operator for any property, $A = \langle \Psi_0 | \hat{A} | \Psi_0 \rangle$

6) Usually $\Psi_0 \neq E_{HF}$ is good enough, otherwise diagonalize matrix

$$\hat{H} = \begin{pmatrix} H_{00} & 0 & H_{02} & \dots \\ 0 & H_{11} & H_{12} & \dots \\ H_{20} & H_{21} & H_{22} & \dots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \begin{matrix} e \\ e_2 \\ e_1 \end{matrix} \begin{matrix} \psi_0 \\ \psi_2 \\ \psi_1 \end{matrix}$$

Calculate Ψ or E or any property of a molecule

The formula for E_{HF} : for $2e^-$

$$\begin{aligned}
 E_{HF} &= \langle \psi_0 | \hat{H} | \psi_0 \rangle \geq E_0 \\
 &= \frac{1}{2} \sum \langle \phi_1(1) | \langle \phi_2(2) | - \langle \phi_2(1) | \langle \phi_1(2) | \} (\hat{h}_1 + \hat{h}_2 + U_2 + E_{nuc}) \cdot \frac{1}{2} \{ \} \\
 &= \frac{1}{2} \{ \langle 12 | - \langle 21 | \} (\hat{h}_1 + \hat{h}_2 + \hat{U}_{12}) \{ |12\rangle - |21\rangle \} + E_{nuc} \\
 &= \frac{1}{2} \{ \langle 12 | \hat{h}_1 | 12 \rangle - \langle 12 | \hat{h}_1 | 21 \rangle + \dots - \langle 12 | \hat{U}_{12} | 12 \rangle - \langle 12 | \hat{U}_{12} | 21 \rangle + \dots \} \\
 &= \frac{1}{2} \{ \langle 1 | \hat{h}_1 | 1 \rangle \cdot \underbrace{\langle 2 | 2 \rangle}_1 - \langle 1 | \hat{h}_1 | 2 \rangle \underbrace{\langle 2 | 1 \rangle}_0 + \dots - \dots + \dots \} \\
 &= \frac{1}{2} \{ h_{1,0} \quad \quad \quad - \quad \quad \quad 0 \quad + \dots \quad \underbrace{J_{12}}_{\text{Coulomb operator}} - \underbrace{k_{12}}_{\text{Coulomb repulsion term, but has a "-" sign}} + \dots \}
 \end{aligned}$$

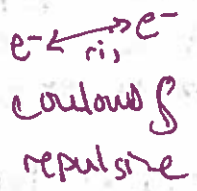
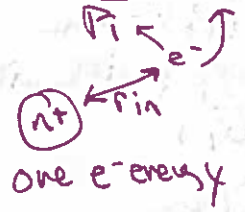
$\Rightarrow E_{HF} = h_1 + h_2 + J_{12} - k_{12} + E_{nuc}$

- exchange integral

For N electrons,

$$E_{HF} = \sum_{i=1}^N h_i + \sum_{i,j>i}^N J_{ij} - \sum_{i,j>i}^N k_{ij}$$

antisymmetry, Pauli principle



exchange only in QM attractive

Chemical bonding only exists bc e^- 's can be in 2 places at once, overcoming e^- repulsion energy

QM allows bonding bc

- 1) e^- 's can tunnel into the forbidden region b/w nuclei
- 2) $k_{ij} < 0$ overcomes the J_{ij} e^- repulsion

Next lecture: HF-SCF: how to improve QM to get the

lowest $E_{HF} \geq E_0$