Lecture 30

kinetic and attraction nuc

$$E_0 \le E_{HF} = \sum_{i=1}^{N} h_i + \frac{1}{2}\underbrace{\sum_{i,j\neq i}^{N} J_{ij}}_{\text{Coulomb repulsion}} - \overbrace{\frac{1}{2}\sum_{i,j=1}^{N} K_{ij}}^{\text{exchange term}}$$

$$= \sum_i \langle i|\hat{h}_i|i\rangle + \frac{1}{2}\sum_{i,j=1}\langle ij|\frac{1}{r_{ij}}|ij\rangle - \frac{1}{2}\sum_{i,j=1}\langle ij|\frac{1}{r_{ij}}|ji\rangle$$

$$\phi_i(\vec{r}_i) = \sum c_m \varphi_n(\vec{r}_n) \cdot \alpha_n \text{ or } \beta_n$$

6-31G** — include d-orbitals in the calc.

6 — #6 for core e⁻

31 — 2 basis fn for valence e⁻'s, 3G + 1G

G — gaussian

Gaussian Basis

$$\Psi_0(\vec{r}_1, \vec{r}_2 \ldots \vec{r}_n) = \frac{1}{\sqrt{N}}\begin{vmatrix} \phi_1(1) & \cdots & \phi_N(1) \\ \phi_N(1) & \cdots & \phi_N(N)\end{vmatrix}$$

How to systematically get the best c_m that gives the lowest E_{HF}?

A: SCF turns one N-e⁻ S.eq. into N 1e⁻ S eq.

Write E_{HF} as

$$E_{HF} = \sum_i \langle i|\{\hat{h}_i|i\rangle + \frac{1}{2}\sum_{j\neq i}\langle j|\frac{1}{r_{ij}}|j\rangle|i\rangle - \frac{1}{2}\sum_{j\neq i}\langle j|\frac{1}{r_{ij}}|i\rangle|j\rangle\}$$

$$= \sum_i \langle i|\{\hat{h}_i - \frac{1}{2}\sum_{j\neq i} J_j - K_j\}|i\rangle = \sum_{i=1}^{N}\langle i|\hat{H}_i|i\rangle = \sum_{i=1}^{N} e_i$$

$$\hat{J}_j|i\rangle = \langle j|\frac{1}{r_{ij}}|j\rangle|i\rangle$$

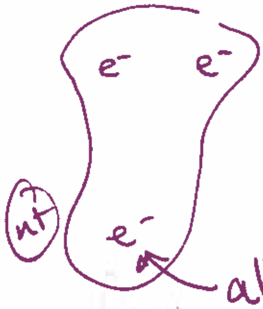
$$K_j|i\rangle = \langle j|\frac{1}{r_{ij}}|i\rangle|j\rangle$$

$$J_j(\vec{r}_i)\varphi_i(r_i) = \varphi_i(r_i)\int d\vec{r}_j \frac{\varphi_j^*(\vec{r}_j)\varphi(r_j)}{r_{ij}}$$

K switches = exchanges the $|i\rangle$ and $|j\rangle$ functions

Now remove the $\sum_i \langle i|$ and solve the resulting N equations separately, each with its own $1e^-$ orbital energy e_i

$$\Rightarrow \Big(\hat h_i + \frac{1}{2}\sum_{j\neq i} \underbrace{\hat J_j(\vec r_i) - K_j(\vec r_i)}_{\substack{\text{has averaged over all other } e^-\text{'s "j"} \neq \text{"i"} \\ \text{but depends only on } \vec r_i.}}\Big)|i\rangle = e_i|i\rangle \text{ or } \hat H_i|i\rangle = e_i|i\rangle$$



e^- ← electron "i"

all other e^- "j" cause sheilding = repulsion

Proof: See N30b

1) Guess $|j\rangle = \phi_j = \sum c_m \varphi_m(\vec r_j)|\pm\frac{1}{2}\rangle$

2) Calc. $\hat J_j$ & $\hat K_j$ by doing integrals

such as $J_2(\vec r_1) = \int d\vec r_2 \dfrac{\phi_2^*(\vec r_2)\phi_2(\vec r_2)e^2}{4\pi\varepsilon_0 r_{12}}$

$$K_2(\vec r_1) = \int d\vec r_2 \frac{\phi_2^*(\vec r_2)\phi_1(\vec r_2)e^2}{4\pi\varepsilon_0 r_{12}}$$

3) Solve $H_i|i\rangle = \varepsilon_i|i\rangle$ to get new $|i\rangle$'s $\equiv \phi_i$
N times

Upon convergence, you get the best possible determinant wavefn by letting

$$\psi_0 = \frac{1}{\sqrt{N!}}\begin{vmatrix} \phi_1(1) & \cdots & \phi_N(1) \\ \phi_1(N) & \cdots & \phi_N(N) \end{vmatrix}$$

If not good enough, try diff e^- configurations $\psi_{n\neq 0}$

ground state $\bar\psi$ ψ doubly excited state ψ_2

$$\Rightarrow \underset{\approx}{H} = \begin{pmatrix} H_{00} & H_{02} & \cdots \\ H_{20} & H_{22} & \cdots \\ \vdots & \vdots & \end{pmatrix}$$

$H_{01} = 0!$