

Hartree-Fock

$$\Psi \approx |\psi_i \psi_j \psi_k \psi_l \dots|$$

Need "best" ψ_i available \rightarrow Minimize E

$$E_{Det} = \sum_{i=1}^N h_{ii} + \frac{1}{2} \sum_{ij} \langle ij | ij \rangle - \langle ij | ji \rangle$$

$$h_{ii} = \langle \phi_i | \hat{h} | \phi_i \rangle = \sum_{\lambda\sigma} c_{\lambda i}^* c_{\lambda i} \langle x_\lambda | \hat{h} | x_\lambda \rangle c_{\lambda i}$$

$$\langle ij | ij \rangle - \langle ij | ji \rangle = \sum_{\lambda\sigma\lambda'\sigma'} c_{\lambda i}^* c_{\lambda j}^* c_{\lambda i} c_{\sigma j} (\langle \mu\nu | \lambda\sigma \rangle - \langle \mu\nu | \sigma\lambda \rangle)$$

$$E_{Det} = \sum_{\mu\nu} h_{\mu\nu} \sum_i c_{\mu i}^* c_{\nu i} + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} (\langle \mu\nu | \lambda\sigma \rangle - \langle \mu\nu | \sigma\lambda \rangle) \sum_{ij} c_{\mu i}^* c_{\lambda i} c_{\nu j}^* c_{\sigma j}$$

$$E_{Det}[\underline{\underline{P}}] = \sum_{\mu\nu} h_{\mu\nu} P_{\mu\nu} + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} (\quad \quad \quad) P_{\mu\lambda} P_{\nu\sigma}$$

Minimization in Terms of Density Matrix \rightarrow Min $E[\underline{\underline{P}}]$

Recall that \mathbf{P} is idempotent:

$$\mathbf{P}\mathbf{P} = \mathbf{P} \quad \text{or} \quad \sum_{\lambda} P_{\mu\lambda} P_{\lambda\nu} = P_{\mu\nu}$$

$$\begin{aligned} \underline{\underline{L}}[\underline{\underline{P}}, \underline{\underline{X}}] &\equiv E_{Det}[\underline{\underline{P}}] + \underbrace{\left(\sum_{\lambda\sigma} P_{\mu\lambda} P_{\lambda\nu} - P_{\mu\nu} \right)}_{\text{Tr } (\underline{\underline{X}} (\underline{\underline{P}} \underline{\underline{P}} - \underline{\underline{P}}))} X_{\mu\nu} \\ &= \text{Tr} (\underline{\underline{P}} \underline{\underline{X}} \underline{\underline{P}} - \underline{\underline{X}} \underline{\underline{P}}) \end{aligned}$$

$$\frac{\partial \text{Tr}(\underline{\underline{P}})}{\partial P_{\mu\nu}} = \underline{\underline{X}} \underline{\underline{P}} + \underline{\underline{P}} \underline{\underline{X}} - \underline{\underline{X}}$$

$$\frac{\partial E_{Det}}{\partial P_{\mu\nu}} = h_{\mu\nu} + \sum_{\lambda\sigma} P_{\lambda\sigma} (\langle \mu\lambda | \nu\sigma \rangle - \langle \mu\lambda | \sigma\nu \rangle) \equiv F_{\mu\nu}$$

F ≡ Fock Matrix

one electron part + avg. potential

$$\sum_{\lambda\sigma}^M P_{\lambda\sigma} \langle \mu\lambda | v\sigma \rangle = \int \sum_{\lambda\sigma}^M P_{\lambda\sigma} \frac{\chi_\mu^*(\mathbf{r}_1) \chi_\lambda^*(\mathbf{r}_2) \chi_\nu(\mathbf{r}_1) \chi_\sigma(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2$$

$$= \int \frac{\chi_\mu^*(\mathbf{r}_1) \chi_\nu(\mathbf{r}_1) \rho(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2$$

$$= \int \chi_\mu^*(\mathbf{r}_1) \chi_\nu(\mathbf{r}_1) V_{\text{Coulomb}}(\mathbf{r}_1) d\mathbf{r}_1$$

Second Interaction Term:

$$-\sum_{\lambda\sigma}^M P_{\lambda\sigma} \langle \mu\lambda | \sigma\nu \rangle$$

Not Classical ; Attractive ; Antisymmetry

Exchange

In any case, assembling the full derivative of L

$$\frac{dL}{dP} = F + XP + PX - X = 0$$

How to Simplify? Define $Q=1-P$ $\underline{\underline{Q}} \underline{\underline{P}} = \underline{\underline{P}} - \underline{\underline{P}}^2 = \underline{\underline{Q}} = \underline{\underline{P}} \underline{\underline{Q}}$

$$\underline{\underline{P}} (\underline{\underline{F}} + \underline{\underline{X}} \underline{\underline{P}} + \underline{\underline{P}} \underline{\underline{X}} - \underline{\underline{X}}) \underline{\underline{P}} = \underline{\underline{P}} \underline{\underline{F}} \underline{\underline{P}} + \underline{\underline{P}} \underline{\underline{X}} \underline{\underline{P}} + \cancel{\underline{\underline{P}} \underline{\underline{X}} \underline{\underline{P}} - \underline{\underline{P}} \underline{\underline{X}} \underline{\underline{P}}} = 0$$

$$\underline{\underline{P}} (\underline{\underline{F}} + \underline{\underline{X}} \underline{\underline{P}} + \cancel{\underline{\underline{P}} \underline{\underline{X}} - \underline{\underline{X}}}) \underline{\underline{Q}} = \underline{\underline{P}} \underline{\underline{F}} \underline{\underline{Q}} + \cancel{\underline{\underline{P}} \underline{\underline{X}} \underline{\underline{P}} \underline{\underline{Q}}} + \cancel{\underline{\underline{P}} \underline{\underline{X}} \underline{\underline{Q}} - \underline{\underline{P}} \underline{\underline{X}} \underline{\underline{Q}}} = 0$$

....

$$\underline{\underline{Q}} \underline{\underline{F}} \underline{\underline{P}} = 0$$

$$\underline{\underline{Q}} (\underline{\underline{F}} + \cancel{\underline{\underline{X}} \underline{\underline{P}} + \underline{\underline{P}} \underline{\underline{X}} - \underline{\underline{X}}}) \underline{\underline{Q}} = \dots \underline{\underline{Q}} \underline{\underline{F}} \underline{\underline{Q}} + \cancel{\underline{\underline{Q}} \underline{\underline{X}} \underline{\underline{Q}}} = 0$$

$$F = \frac{(\underline{\underline{P}} + \underline{\underline{Q}}) \underline{\underline{F}}}{(\underline{\underline{P}} + \underline{\underline{Q}})}$$

$$[\underline{\underline{F}}, \underline{\underline{P}}] = [\underline{\underline{P}} \underline{\underline{F}} \underline{\underline{P}} + \underline{\underline{Q}} \underline{\underline{F}} \underline{\underline{Q}}, \underline{\underline{P}}] = \cancel{\underline{\underline{P}} \underline{\underline{F}} \underline{\underline{P}}} + \cancel{\underline{\underline{P}} \underline{\underline{F}} \underline{\underline{Q}} \underline{\underline{P}}} - \cancel{\underline{\underline{P}} \underline{\underline{F}} \underline{\underline{Q}}} - \cancel{- \underline{\underline{P}} \underline{\underline{Q}} \underline{\underline{F}} \underline{\underline{Q}}}$$

$$= 0$$

Note: $F[\underline{\underline{P}}]$

Self Consistent Field (SCF) Iterations

- 1) First, guess an approximate Fock matrix (e.g. $F_{\mu\nu} = h_{\mu\nu}$).
- 2) Diagonalize F to obtain c .
- 3) Use c to build P and $F' = F[P]$.
- 4) If $[F', P] \neq 0$, return to step 2) with $F=F'$. *
- 5) If $F'=F$, then the HF equations are solved.

Information we can get from Φ_{HF} :

- 1) The Total Energy

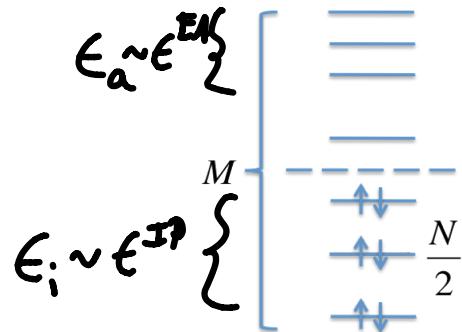
$H_2O: E_{HF} \approx -76.068 \text{ a.u.} = -2069.9 \text{ eV}$

- 2) Molecular Orbital Energies –

$$\mathbf{F}\mathbf{c}_i = \varepsilon_i \mathbf{c}_i \quad \varepsilon_i = h_{ii} + \sum_{j=1}^N \langle ij | ij \rangle - \langle ij | ji \rangle$$

M basis fns.

$N/2$ occupied ..



Koopman's "Theorem"

The HF eigenvalue of every occupied MO is a first order approximation to the ionization energy required to remove an electron from that orbital – $E_{IP}^i \approx \varepsilon_i^{HF}$. The HF eigenvalue of every virtual MO is a first order approximation to the electron affinity of the associated orbital – $E_{EA}^a \approx \varepsilon_a^{HF}$.

- 3) Molecular Orbitals
- 4) Partial Charges and Bond Orders

charge on atom $q_A = Z_A - \sum_{\mu \in A} \sum_{i=1}^N c_{\mu i} c_{\mu i}$

Bond Order Btw. A & B $O_{AB} = \sum_{\mu \in A} \sum_{\nu \in B}^N c_{\mu i} c_{\nu i}$

$$E_{HF} > E_{exact} \Rightarrow E_{corr} = E_{exact} - E_{HF}$$

Perturbation Theory

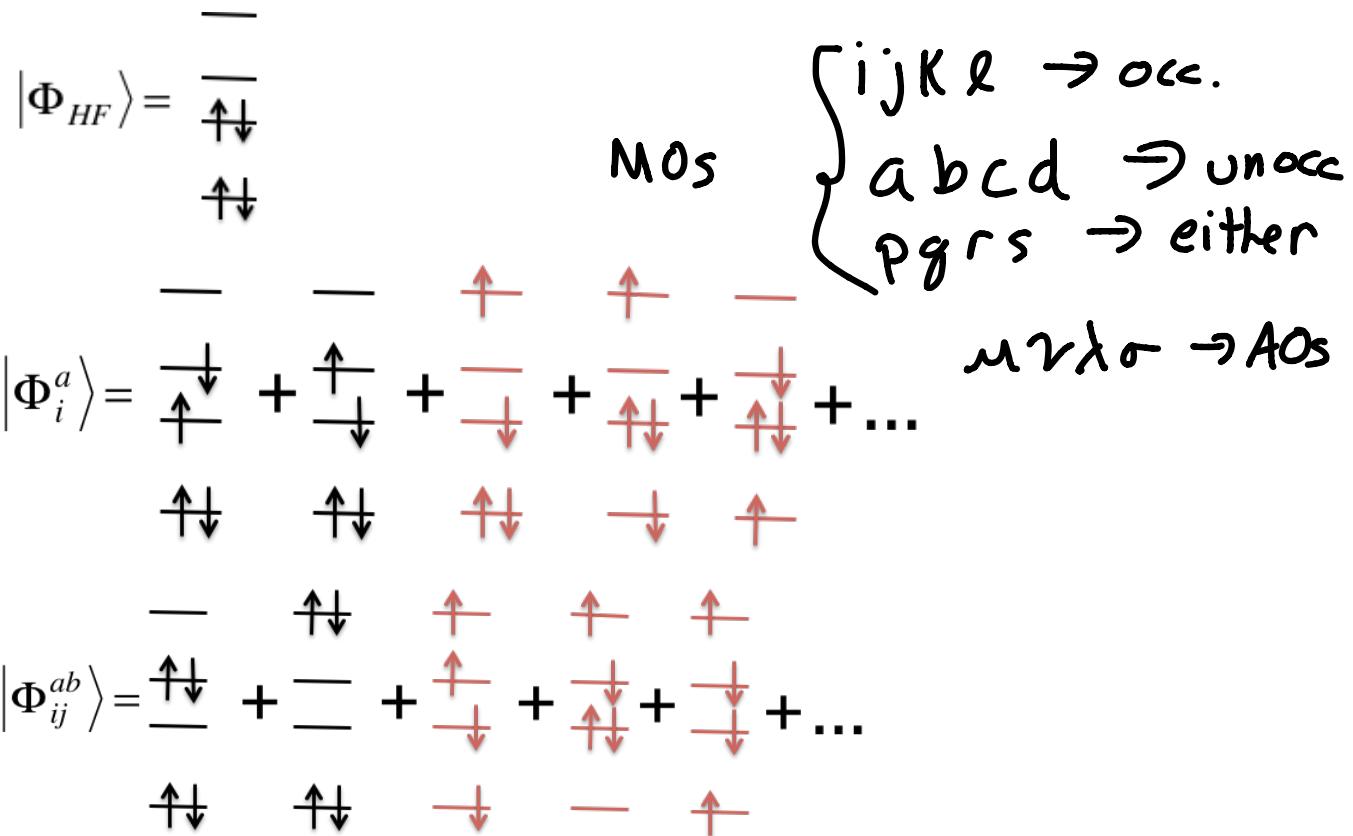
$$\hat{F}|\Phi_{HF}\rangle = E_{HF}|\Phi_{HF}\rangle \quad \hat{H}|\Psi\rangle = E_{Exact}|\Psi\rangle$$

$$\hat{H} = \hat{F} + (\hat{H} - \hat{F})$$

$$\hat{H}^{(0)} \quad \hat{H}^{(1)}$$

$$E_0^{(1)} = 0$$

$$E_0^{(2)} = \sum_i \frac{|\langle \Phi_0 | \hat{H}^{(1)} | \Phi_i \rangle|^2}{E_0 - E_i}$$



$$\begin{aligned}
 E_0^{(2)} &= \sum_x \frac{\left| \langle \Phi_0 | \hat{H}^{(1)} | \Phi_x \rangle \right|^2}{E_0 - E_x} \\
 &= \sum_{ia} \frac{\left| \langle \Phi_0 | \hat{H}^{(1)} | \Phi_i^a \rangle \right|^2}{E_0 - E_i^a} + \sum_{ijab} \frac{\left| \langle \Phi_0 | \hat{H}^{(1)} | \Phi_{ij}^{ab} \rangle \right|^2}{E_0 - E_{ij}^{ab}} + \sum_{ijkabc} \frac{\left| \langle \Phi_0 | \hat{H}^{(1)} | \Phi_{ijk}^{abc} \rangle \right|^2}{E_0 - E_{ijk}^{abc}} + \dots
 \end{aligned}$$

O for HF

$\text{ASA} \rightarrow E_0^{(2)} = \sum_{ijab} \frac{|\langle ij || ab \rangle|^2}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j}$ MP2

MP3 = MP2 + $E_0^{(3)}$ MP4, MP5 ...

When with Perturbation Theory Work?

$$\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j \gtrsim -2 (\epsilon_{\text{HOMO}} - \epsilon_{\text{LUMO}})$$

