

# Approximation Methods Review - Chem 347

Problem: We have neglected part of real multi-electron Hamiltonian to obtain "nice" result. Now must account for the balance.

Perturbation theory: — expansion approach, only useful if "perturbation" —  $\mathcal{H}_1$  is small

$$E_i = E_i^0 + E_i^{(1)} + E_i^{(2)} + \dots$$

$$\Psi_i = \Psi_i^0 + \Psi_i^{(1)} + \Psi_i^{(2)} + \dots$$

where:  $\Psi_i^0, E_i^0$  sol'n to  $\mathcal{H}^0$   
rest ( $\Psi^{(1)}, E^{(1)}, \dots$ ) are correction terms to get "exact" values

1st order:  $E_i^{(1)} = \int \Psi_i^{0*} \mathcal{H}_1 \Psi_i^0 d\tau$

2nd order:  $E_i^{(2)} = - \sum_{k \neq i} \frac{(\int \Psi_i^{0*} \mathcal{H}_1 \Psi_k^0 d\tau)(\int \Psi_k^{0*} \mathcal{H}_1 \Psi_i^0 d\tau)}{E_k^0 - E_i^0}$

1st order:  $\Psi_i^{(1)} = - \sum_{k \neq i} \frac{\int \Psi_k^{0*} \mathcal{H}_1 \Psi_j^0 d\tau}{E_k^0 - E_j^0} \Psi_k^0$

The general result is that the 2nd order energies come from calculation with 1st order wave functions, etc.

Effects:  $E$  - (1) shift, (2) split;  $\Psi$  - (1) mix  $\Psi^0$ 's

Derivation: Hanna George, Flygare (89)

"exact" solution:

represent  $\mathcal{H}_1$  as:

$$\begin{pmatrix} \mathcal{H}_{11} & \mathcal{H}_{12} & \dots & \mathcal{H}_{1n} \\ \mathcal{H}_{21} & \mathcal{H}_{22} & & \vdots \\ \vdots & & & \vdots \\ \mathcal{H}_{n1} & \dots & \dots & \mathcal{H}_{nn} \end{pmatrix}$$

where:

$$\mathcal{H}_{ij} = \int \phi_i^* \mathcal{H}_1 \phi_j$$

now - exact sol'n an eigen function of

$$\mathcal{H}_1 : \mathcal{H}_1 \Psi = \lambda \Psi$$

if  $\Psi = \sum_{i=1}^n a_i \phi_i^0$ , then represent as a column vector  $\begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ a_n \end{pmatrix}$ ; operate matrix

of  $\mathcal{H}_1$  on it and you will get  $\lambda$ .

To determine the values of  $a_i$ , you must solve:  $(\mathcal{H}_1 - \lambda) \Psi = 0$ . To do this we wish to diagonalize  $\mathcal{H}_1$ , which means solving the determinant  $|\mathcal{H}_1 - \lambda| = 0$

The eigen values,  $\lambda_j$ , are then substituted back in to determine the coef:  $a_i$  on the eigen vectors

ex: let:  $\mathcal{H}_{11} = \mathcal{H}_{22} = a$      $\mathcal{H}_{12} = \mathcal{H}_{21} = b$      $\det \begin{pmatrix} a-\lambda & b \\ b & a-\lambda \end{pmatrix} = 0$

eigen values:

$$(a-\lambda)^2 - b^2 = 0$$

$$\lambda^2 - 2a\lambda + a^2 - b^2 = 0$$

$$[(a-\lambda)-b][(a-\lambda)+b] = 0$$

$$\Rightarrow \lambda = a-b, a+b$$

eigen fct:  $(a-\lambda)a_1 + ba_2 = 0$

$\lambda_1 = a-b : ba_1 + ba_2 = 0$

$a_1 = -a_2 = \frac{1}{\sqrt{2}}$

$\lambda_2 = a+b : -ba_1 + ba_2 = 0$

$a_1 = a_2 = \frac{1}{\sqrt{2}}$

note - values  $\frac{1}{\sqrt{2}}$  for normalization

Variation Method: improved wave functions  
used most generally in molecular problems

Theorem:  $E_{\text{grd}} \leq \langle \mathcal{H} \rangle = \frac{\int \Psi_{\text{ap}}^* \mathcal{H} \Psi_{\text{ap}} d\tau}{\int \Psi_{\text{ap}}^* \Psi_{\text{ap}} d\tau}$

$\mathcal{H}$  - exact Hamiltonian

$\Psi_{\text{ap}}$  - "trial" approximate w/f

Proof: use  $\Psi_{\text{ap}} = \sum_i c_i \phi_i$   $\phi_i$ 's eigenfct  $\mathcal{H}$

$$\begin{aligned} \text{Left: } \int \Psi_{\text{ap}}^* \mathcal{H} \Psi_{\text{ap}} d\tau &= \int \left( \sum_i c_i \phi_i \right)^* \mathcal{H} \left( \sum_j c_j \phi_j \right) \\ &= \int \left( \sum_i c_i \phi_i \right)^* \left( \sum_j c_j E_j \phi_j \right) \\ &= \sum_{i,j} c_i^* c_j E_j \underbrace{\int \phi_i^* \phi_j d\tau}_{\delta_{ij}} \\ &= \sum_i c_i^* c_i E_i \end{aligned}$$

$$\begin{aligned} \text{Right: } E_{\text{grd}} \int \Psi_{\text{ap}}^* \Psi_{\text{ap}} d\tau &= E_{\text{grd}} \int \left( \sum_i c_i \phi_i \right)^* \left( \sum_j c_j \phi_j \right) d\tau \\ &= E_{\text{grd}} \sum_i c_i^* c_i \quad (\text{as above}) \end{aligned}$$

$$\text{Left} - \text{Right} = \sum_i c_i^* c_i (E_i - E_{\text{grd}}) \geq 0 \quad \text{i.e. } E_{\text{grd}} \leq E$$

$$\therefore \int \Psi_{\text{ap}}^* \mathcal{H} \Psi_{\text{ap}} d\tau \geq E_{\text{grd}} \int \Psi_{\text{ap}}^* \Psi_{\text{ap}} d\tau$$

Use: pick trial function with an adjustable parameter ( $p$ )  
minimize energy, i.e. set  $\frac{\partial \langle \mathcal{H} \rangle}{\partial p} = 0$   
solve for  $p$  - - the lower the energy, the better  $\Psi$

Hartree-Fock Self Consistent field

yields most exact energies, atoms or molecules

Approximate potential (i.e. "field") of each electron:

$$V_i = -\frac{Ze^2}{r_i} + \underbrace{\sum_{j \neq i} \int \psi_j^* \frac{e^2}{r_{ij}} \psi_j d\tau}_{\text{average repulsion}}$$

hence:

$$\mathcal{H} = \sum_{i=1}^n h_i ; \quad h_i = -\frac{\hbar^2}{2m} \nabla_i^2 + V_i$$

Problem:  $\psi$ 's determined by  $V$  which depends on  $\psi$

Hartree solution: iterate from trial function

- Calculate  $V_i$  from trial fct
- Solve for  $\psi_i, E_i$
- Use new  $\psi_j$ 's to generate  $V_i$ 's, resolve
- Continue cycle until  $V_i$  constant - SCF

Fock: correct  $V_i$  for spin - add exchange term

$$\text{Note: } E_{HF} = \sum_{i=1}^n E_i, \quad \Psi_{HF} = \prod_{i=1}^n \psi_i$$

Correlation of motion of electrons ignored:  $E_{cor} = E - E_{HF}$

This method is the core of many modern quantum chemical calculations. For large molecules,  $\Psi$  is approximated as a linear combination of AO's. Often certain integrals in  $V_i$  are neglected to speed calculations.