THE VARIATIONAL METHOD

CHEM 2430

The Variational Method

$$\int \phi^* \hat{H} \phi d\tau \geq E_1$$ (where ϕ is a normalized trial function and E_1 is the ground state energy)

To prove this, write $\phi = \sum a_i \psi_i$,

where $\{\psi_i\}$ are eigenfunctions of $\hat{H}$

$$\langle E \rangle = \int \sum_k a_k^* \psi_k^* \hat{H} \int \sum_j a_j \psi_j d\tau = \int \sum_{k,j} a_k^* a_j \langle \psi_k | H | \psi_j \rangle$$

$$= \sum_{k,j} a_k^* a_j E_j \langle \psi_k | \psi_j \rangle = \sum_k |a_k|^2 E_k \geq E_1 \sum_k |a_k|^2$$

If ϕ is not normalized, then we need to use

$$\frac{\int \phi^* \hat{H} \phi d\tau}{\int \phi^* \phi d\tau} \geq E_1$$

Example: e^{-cx^2} trial function for the H.O. problem (i.e., c is a variational parameter)

$$\frac{\langle \phi | \hat{H} | \phi \rangle}{\langle \phi | \phi \rangle} = \frac{\int_{-\infty}^{\infty} e^{-cx^2} \left(-\frac{1}{2} \frac{d^2}{dx^2} + \frac{1}{2} kx^2 \right) e^{-cx^2} dx}{\int_{-\infty}^{\infty} e^{-2cx^2} dx}$$

(in a.u.)

$$= \frac{1}{2} c + \frac{\pi^2 \upsilon^2}{2c}$$

Note that because we are varying c, we cannot assume that the function is normalize, i.e., it is necessary to include the denominator

$$\frac{d\langle E \rangle}{dc} = \frac{1}{2} - \frac{\pi^2 \upsilon^2}{2c^2} = 0$$

$$c^2 = \pi^2 \upsilon^2$$

$c = \pi\upsilon$ is the physical solution

$$< E >= \frac{1}{2} \pi\upsilon + \frac{\pi^2 \upsilon^2}{2(\pi\upsilon)} = \frac{1}{2} \pi\upsilon + \frac{1}{2} \pi\upsilon$$

Undo the atomic units.

$$< E >= \frac{h\upsilon}{2} = \frac{\hbar\omega}{2}$$

We get the exact answer because we chose the correct functional form

Extending the method to the first excited state

Suppose ϕ_2 is $\perp$ to ψ_1 then $\langle \phi_2 | \psi_1 \rangle = 0$

$$\langle \phi_2 | H | \phi_2 \rangle = \sum_{i=1} b_i \langle \phi_2 | \psi_i \rangle E_i$$

Here, we expanded ϕ_2 in terms of the eigenstates

but $\langle \phi_2 | \psi_1 \rangle = 0$, so the sum starts at 2

$$\langle \phi_2 | H | \phi_2 \rangle = \sum_{i=2} |b_i|^2 E_i \geq E_2$$

In general one actually has $\phi_1 \perp \phi_2$, where ϕ_1 gives an approximation to ψ_1. This is trickier, but there are cases where spin or symmetry makes it easy to optimize excited states. E.g., if the ground state is odd and the first excited state is even.

Linear variational method

$$\phi = c_1 f_1 + c_2 f_2 + \ldots + c_n f_n$$

Simplify to two basis functions f_1, f_2 , and assume $\langle f_1 | f_2 \rangle = 0,$ and c_1, c_2 real

$$E = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{c_1{}^2 H_{11} + 2c_1 c_2 H_{12} + c_2{}^2 H_{22}}{c_1{}^2 + c_2{}^2}$$

we have assumed $H_{12} = H_{21}$

$$\frac{\partial E}{\partial c_1} = \frac{2c_1 H_{11} + 2c_2 H_{12}}{c_1{}^2 + c_2{}^2} - 2c_1 \frac{c_1{}^2 H_{11} + 2c_1 c_2 H_{12} + c_2{}^2 H_{22}}{\left(c_1{}^2 + c_2{}^2\right)^2} = 0$$

$$\frac{\partial E}{\partial c_2} = \frac{2c_1 H_{12} + 2c_2 H_{22}}{c_1{}^2 + c_2{}^2} - 2c_2 \frac{c_1{}^2 H_{11} + 2c_1 c_2 H_{12} + c_2{}^2 H_{22}}{\left(c_1{}^2 + c_2{}^2\right)^2} = 0$$

$$H_{11} c_1 + H_{12} c_2 - E c_1 = 0$$

$$H_{21} c_1 + H_{22} c_2 - E c_2 = 0$$

Cast in form of matrix/vector equation

$$\begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = E\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$ or

$$\begin{pmatrix} H_{11}-E & H_{12} \\ H_{21} & H_{22}-E \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

Nontrivial solution found from solving the determinant equation

$$\begin{vmatrix} H_{11}-E & H_{12} \\ H_{21} & H_{22}-E \end{vmatrix} = 0$$

$$(H_{11}-E)(H_{22}-E) - H_{12}{}^2 = 0$$

$$E^2 - E(H_{11}+H_{22}) + H_{11}H_{22} - H_{12}{}^2 = 0$$

$$E_{\pm} = \frac{H_{11} + H_{22}}{2} \pm \frac{1}{2}\sqrt{\left(H_{11} + H_{22}\right)^2 - 4\left(H_{11}H_{22} - H_{12}{}^2\right)}$$

$$E_{\pm} = \frac{H_{11} + H_{22}}{2} \pm 1/2\sqrt{\left(H_{11} - H_{22}\right)^2 + 4H_{12}{}^2}$$

Now how do we find the eigenvectors?

Plug E_+ and $E\_$ back into the system of liner equations:

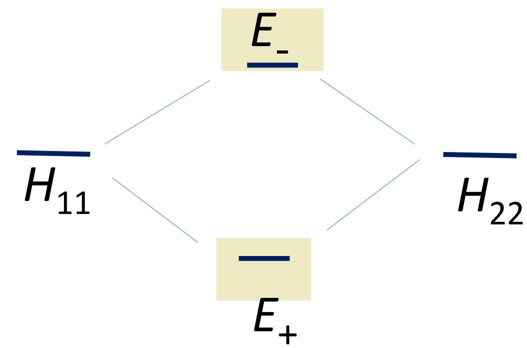
$$\left(H_{11} - E\right)c_1 + H_{12}c_2 = 0$$

$$H_{21}c_1 + \left(H_{22} - E\right)c_2 = 0$$

Plug in each of the energies. For $E\_$

$$\left(H_{11} - E_-\right)c_1 + H_{12}c_2 = 0$$

so $c_1 = -\frac{H_{12}}{H_{11} - E_-}c_2$



Assumes H_{12} is negative

So the vector is $\begin{pmatrix} \frac{-H_{12}}{H_{11} - E_-} c_2 \\ c_2 \end{pmatrix}$

Normalize: $\frac{H_{12}^{\ 2}}{\left(H_{11} - E_-\right)^2} c_2^{\ 2} + c_2^{\ 2} = 1$

$$c_2 = 1 / \sqrt{1 + \frac{H_{12}^{\ 2}}{\left(H_{11} - E_-\right)^2}}$$

If $H_{11} = H_{22}$ (as for the interacting 1s orbital of two H atoms) , then

$$E_1 = H_{11} + H_{12}$$

$$E_2 = H_{11} - H_{12}$$

and $c_1 = \pm c_2$ depending on which eigenvalue is considered

We made an important assumption in the above treatment:

Namely, we assumed $\langle \phi_1 | \phi_2 \rangle = 0$

Earlier we used f_1 and f_2 for the two basis functions. Here I have switched to ϕ_1 and ϕ_2.

Certainly not true for two interacting H atoms with the basis $\phi_1 = 1s_A, \quad \phi_2 = 1s_B,$

Then our equations become

$$\begin{pmatrix} H_{11} - E & H_{12} - S_{12}E \\ H_{21} - S_{21}E & H_{22} - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0$$

The determinant gives

$$E^2 - E(H_{11} + H_{22}) + H_{11}H_{22} - H_{12}^{\ 2} + 2H_{12}S_{12}E - S_{12}^{\ 2}E^2 = 0$$

If $H_{11} = H_{22}$

$$E_1 = \frac{H_{11} + H_{12}}{1 + S_{12}} \qquad E_2 = \frac{H_{11} - H_{12}}{1 - S_{12}}$$

Splitting become asymmetric

H_{12} is negative for our H_2 example