Chemical Physics Cumulative Sept 21, 2011

Key

1. Given a Hamiltonian $\hat{\mathcal{H}}$ & a function χ which satisfies the boundary conditions on the exact eigenvalues of $\hat{\mathcal{H}}$, then the number $E = \dfrac{\langle \chi | \hat{\mathcal{H}} | \chi \rangle}{\langle \chi | \chi \rangle}$ is $\geq$ the exact lowest eigenvalue of $\hat{\mathcal{H}}$.

2. Suppose $\hat{\mathcal{H}} \phi_i = E_i \phi_i$ & χ is the function described above, then $\chi = \sum_{i=0}^{\infty} c_i \phi_i$ &

$$E = \frac{\langle \sum_{i=0}^{\infty} c_i \phi_i | \hat{\mathcal{H}} | \sum_{j=0}^{\infty} c_j \phi_j \rangle}{\sum_{ij} \langle c_i \phi_i | c_j \phi_j \rangle} = \frac{\sum_{i=0}^{\infty} |c_i|^2 E_i}{\sum_{i=0}^{\infty} |c_i|^2}$$

$$E = \frac{\sum_{i=0}^{\infty} |c_i|^2 E_i}{\sum_{i=0}^{\infty} |c_i|^2} - E_0 \frac{\sum_{i=0}^{\infty} |c_i|^2}{\sum_{i=0}^{\infty} |c_i|^2} = \frac{\sum_{i=0}^{\infty} |c_i|^2 (E_i - E_0)}{\sum_{i=0} |c_i|^2}$$

Since $E_0 < E_i$ when $i \neq 0$ & $|c_i|^2$ is > 0 the number E is $> E_0$

3. Define the Hamiltonian

$$\hat{\mathcal{H}}(\lambda) = \hat{\mathcal{H}}^0 + \lambda V$$

& consider the eigenvalue problem

$$\hat{\mathcal{H}}(\lambda)\phi_\mu(\lambda) = E_\mu(\lambda)\,\phi_\mu(\lambda)$$

a. Then $\displaystyle \phi_\mu(\lambda) = \sum_{N=0}^{\infty} \left(\frac{d^N\phi_\mu(\lambda)}{d\lambda^N}\right)_0 \lambda^N/N! = \sum_{N=0}^{\infty} \phi_\mu^{(N)}\lambda^N$

where $\displaystyle \phi_\mu^{(N)} = \frac{1}{N!}\left(\frac{d^N\phi_\mu(\lambda)}{d\lambda^N}\right)_0$

Likewise $\displaystyle E_\mu(\lambda) = \sum_{N=0}^{\infty} E_\mu^{(N)}\lambda^N$

So we have

$$(\hat{\mathcal{H}}^\circ + \lambda\hat{V})(\phi_\mu^\circ + \lambda\phi_\mu^{(1)} + \cdots) = (E_\mu^\circ + \lambda E_\mu^{(1)} + \cdots)(\phi_\mu^\circ + \lambda\phi_\mu^{(1)} + \cdots)$$

equating powers of λ & keeping terms through first order

$$\hat{\mathcal{H}}^\circ\phi_\mu^\circ = E_\mu^\circ\phi_\mu^\circ$$

& $\hat{\mathcal{H}}^\circ\phi_\mu^{(1)} + \hat{V}\phi_\mu^\circ = E_\mu^\circ\phi_\mu^{(1)} + E_\mu^{(1)}\phi_\mu^\circ$

So $(\hat{\mathcal{H}}^\circ - E_\mu^\circ)\phi_\mu^{(1)} = -(\hat{V} - E_\mu^{(1)})\phi_\mu^\circ$ QED.

b. Multiply through by $(\phi_\mu^\circ)^*$ & integrate

$$\langle\phi_\mu^\circ|\hat{\mathcal{H}}^\circ - E_\mu^\circ|\phi_\mu^{(1)}\rangle = -\langle\phi_\mu^\circ|\hat{V} - E_\mu^{(1)}|\phi_\mu^\circ\rangle = 0$$

($\hat{\mathcal{H}}^\circ$ is Hermetian)

$$\therefore \quad E_\mu^{(1)} = \langle\phi_\mu^\circ|\hat{V}|\phi_\mu^\circ\rangle$$

c. To solve for $\phi_\mu^{(1)}$ let

$$\phi_\mu^{(1)} = \sum_{\nu=0}^{\infty}\phi_\nu^\circ C_{\nu\mu}$$

Then $(\hat{\mathcal{H}}^{\circ} - E_{\mu}^{\circ}) \sum_{\nu=0}^{\infty} \phi_{\nu}^{\circ} C_{\nu\mu} = -(\hat{V} - E_{\mu}^{(1)})\phi_{\mu}^{\circ}$

$\Rightarrow \sum_{\nu=0}^{\infty} \phi_{\nu}^{\circ}(E_{\nu}^{\circ} - E_{\mu}^{\circ}) C_{\nu\mu} = -(\hat{V} - E_{\mu}^{(1)})\phi_{\mu}^{\circ}$

$\langle \phi_{\sigma}^{\circ} | \Rightarrow$

$$\sum_{\nu=0}^{\infty} \delta_{\nu\sigma}(E_{\nu}^{\circ} - E_{\mu}^{\circ}) C_{\nu\mu} = -\langle \phi_{\sigma}^{\circ} | \hat{V} | \phi_{\mu}^{\circ} \rangle + E_{\mu}^{(1)} \delta_{\sigma\mu}$$

$$\Rightarrow \quad C_{\sigma\mu}(E_{\sigma}^{\circ} - E_{\mu}^{\circ}) = -V_{\sigma\mu} + E_{\mu}^{(1)} \delta_{\sigma\mu}$$

when $\sigma = \mu$ $\quad E_{\mu}^{(1)} = V_{\mu\mu}$ as required.

for $\sigma \neq \mu$ $\quad C_{\sigma\mu} = \dfrac{-V_{\sigma\mu}}{E_{\sigma}^{\circ} - E_{\mu}^{\circ}} = \dfrac{V_{\sigma\mu}}{E_{\mu}^{\circ} - E_{\sigma}^{\circ}}$

we then require $\langle \phi_{\mu}^{(1)} | \phi_{\mu}^{\circ} \rangle = 0$

$$\therefore \quad \phi_{\mu}^{(1)} = \sum_{\nu \neq \mu} \frac{V_{\nu\mu}}{E_{\mu}^{\circ} - E_{\nu}^{\circ}} \phi_{\nu}^{\circ} \qquad QED.$$

<u>Part 2</u> $\quad \hat{\mathcal{H}} = -\dfrac{\hbar^2}{2m}\dfrac{d^2}{dx^2} - qFX = \hat{\mathcal{H}}^{\circ} + V$

where $\hat{\mathcal{H}}^{\circ} = -\dfrac{\hbar^2}{2m}\dfrac{d^2}{dx^2}$ & $V = -qFX$

a. Let the trial function be a linear combination of the eigenfunctions of $\hat{\mathcal{H}}^{\circ}$.

$\hat{\mathcal{H}}^{\circ}\psi_i = E_i \psi_i \quad ; \quad \psi_i = \sqrt{\frac{2}{a}} \sin\left(\frac{i\pi x}{a}\right) \quad i = 1, 2, \ldots$

$$\chi = \sum_{i=0}^{\infty} c_i \psi_i(x)$$

$$E = \frac{\langle \chi | \hat{H} | \chi \rangle}{\langle \chi | \chi \rangle} = \frac{\sum_{i,j} c_i c_j H_{ij}}{\sum_{ij} c_i c_j \delta_{ij}} = \frac{N}{D}$$

$$\frac{\partial E}{\partial c_k} = \frac{D \frac{\partial N}{\partial c_k} - N \frac{\partial D}{\partial c_k}}{D^2} = 0 \Rightarrow \frac{\partial N}{\partial c_k} = E \frac{\partial D}{\partial c_k}$$

$$\frac{\partial N}{\partial c_k} = \sum_{ij} H_{ij} (c_i \delta_{jk} + c_j \delta_{ik}) = 2 \sum_{i=1}^{\infty} H_{ik} c_i$$

$$\frac{\partial D}{\partial c_k} = \frac{\partial}{\partial c_k} \sum c_i^2 = 2 c_k$$

So $$\sum_{i=1}^{\infty} (H_{ik} - E\delta_{ik}) c_i = 0$$

Truncate the sum so H is a finite matrix & diagonalize

Note $H_{ik} = \langle \psi_i | \hat{H}^\circ - qFx | \psi_k \rangle = E_i^\circ - qF \langle i | x | k \rangle$

b. For perturbation theory

$$E_1^{(1)} = \langle \psi_1^\circ | -qFx | \psi_1^\circ \rangle = -qFa/2$$

$$E = -\frac{\hbar^2}{2M}\left(\frac{\pi}{a}\right)^2 - qFa/2$$