Chemical Physics Key Oct 22, 2001

1. $$\hat{H} = \hat{H}^\circ - q\varepsilon x = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2 - q\varepsilon x$$

Lets complete the square on the potential energy

$$\frac{1}{2}kx^2 - q\varepsilon x = \frac{1}{2}k\left(x^2 - \frac{2q\varepsilon}{k}x\right)$$

$$= \frac{1}{2}k\left[\left(x^2 - \frac{q2\varepsilon}{k}x + \left(\frac{q\varepsilon}{k}\right)^2 - \left(\frac{q\varepsilon}{k}\right)^2\right)\right]$$

$$= \frac{1}{2}k\left(x - \frac{q\varepsilon}{k}\right)^2 - \frac{k}{2}\left(\frac{q\varepsilon}{k}\right)^2$$

Let $x - \frac{q\varepsilon}{k} = \xi$

Then

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{d\xi^2} + \frac{1}{2}k\xi^2 - \frac{k}{2}\left(\frac{q\varepsilon}{k}\right)^2$$

& so

$$\hat{H} = \hat{H}^\circ - (q\varepsilon)^2/2k$$

so $$\hat{H}\psi(\xi) = E\psi(\xi)$$

$$\hat{H}^\circ\psi(\xi) = \left(E + (q\varepsilon)^2/2k\right)\psi(\xi)$$

$\therefore$ $$\psi(\xi) = \psi_N(\xi)$$

$$E_N = E + (q\varepsilon)^2/2k = \hbar\omega(N + 1/2)$$

$$E = \hbar\omega(N + 1/2) - (q\varepsilon)^2/2k$$

since $\omega = \sqrt{\frac{k}{M}}$; $k = \omega^2 M$

$$E_N = \hbar\omega\,(N + \tfrac{1}{2}) - \frac{q^2 \varepsilon^2}{2M\omega^2}$$

2.

a. $$E_N^{(2)} = \sum_{\substack{K=0 \\ K \neq N}}^{\infty} \frac{|\langle N|\hat{V}|K\rangle|^2}{E_N^\circ - E_K^\circ}$$

$$\langle N|\hat{V}|K\rangle = \langle N| -q\varepsilon x |K\rangle = -q\varepsilon \langle N|x|K\rangle$$

$$\langle N|x|K\rangle = \delta_{K,N+1}\sqrt{\frac{N+1}{2\alpha}} + \delta_{K,N-1}\sqrt{\frac{N}{2\alpha}}$$

$$\therefore\ E_N^{(2)} = \frac{|\langle N|\hat{V}|N+1\rangle|^2}{E_N^\circ - E_{N+1}^\circ} + \frac{|\langle N|\hat{V}|N-1\rangle|^2}{E_N^\circ - E_{N-1}^\circ}$$

$$E_N^\circ - E_{N+1}^\circ = \hbar\omega\,(N + \tfrac{1}{2} - N - 1 - \tfrac{1}{2}) = -\hbar\omega$$

$$E_N^\circ - E_{N-1}^\circ = \hbar\omega\,(N + \tfrac{1}{2} - (N - 1 + \tfrac{1}{2})) = +\hbar\omega$$

$$\frac{E_N^{(2)}\hbar\omega}{(q\varepsilon)^2} = -\left(\sqrt{\frac{N+1}{2\alpha}}\right)^2 + \left(\sqrt{\frac{N}{2\alpha}}\right)^2$$

$$= -\left(\frac{N+1}{2\alpha}\right) + \left(\frac{N}{2\alpha}\right) = -\frac{1}{2\alpha}$$

$$\therefore\ E_N^{(2)} = -\frac{\hbar\omega}{2\alpha}(q\varepsilon)^2$$

$$\alpha = M\omega/\hbar$$

$$E_N^{(2)} = -\frac{\hbar\omega^2}{2M\omega}(q\varepsilon)^2 =$$

$$E_N^{(2)} = \frac{(q\mathcal{E})^2}{\hbar\omega}\left(-\frac{1}{2\alpha}\right)$$

$$\alpha = m\omega/\hbar$$

$$E_N^{(2)} = \frac{(q\mathcal{E})^2}{\hbar\omega}\left(-\frac{1}{2}\right)\left(\frac{\hbar}{m\omega}\right) = -\frac{q^2\mathcal{E}^2}{2m\omega^2}$$

b. Now for the correction to ψ_N°

$$\psi_N^{(1)} = \sum_K{}' \frac{\psi_K^\circ \langle K|\hat{V}|N\rangle}{E_N^\circ - E_K^\circ}$$

$$\langle N|\hat{V}|K\rangle = \langle K|\hat{V}|N\rangle = -q\mathcal{E}\langle N|x|K\rangle$$

$$= -q\mathcal{E}\left\{\delta_{K,N+1}\sqrt{\frac{N+1}{2\alpha}} + \delta_{K,N-1}\sqrt{\frac{N}{2\alpha}}\right\}$$

$$\psi_N^{(1)} = \frac{\psi_{N+1}^\circ \langle N+1|\hat{V}|N\rangle}{-\hbar\omega} + \frac{\psi_{N-1}^\circ \langle N-1|\hat{V}|N\rangle}{\hbar\omega}$$

$$\psi_N^{(1)} = -\frac{q\mathcal{E}}{\hbar\omega}\left\{-\psi_{N+1}^\circ\sqrt{\frac{N+1}{2\alpha}} + \psi_{N-1}^\circ\sqrt{\frac{N}{2\alpha}}\right\}$$

3.

$$E_{P,K} = \hbar\omega(P+K+1) \; ; \quad P, K = 0, 1, 2, 3, \dots$$

$E_{0,0} = \hbar\omega$ non degenerate

$E_{10} = E_{01} = 2\hbar\omega$ doubly degenerate

$E_{11} = E_{02} = E_{20} = 3\hbar\omega$ triply degenerate wavefunctions for E_{10} & E_{01} are

$\psi_1^\circ(x)\,\psi_0^\circ(y)$ & $\psi_0^\circ(x)\,\psi_1^\circ(y)$ respectively

Matrix of Perturbation :

$$\mathbb{V} = \begin{pmatrix} V_{10,10} & V_{10,01} \\ V_{01,10} & V_{01,01} \end{pmatrix}$$

$$V_{10,10} = \langle 10|\hat{V}|10\rangle = a\,\langle 1|x|1\rangle\langle 0|y|0\rangle \equiv 0$$

$$V_{10,01} = \langle 10|\hat{V}|01\rangle = a\,\langle 1|x|0\rangle\langle 0|y|1\rangle$$

now $\langle 1|x|0\rangle = \dfrac{1}{\sqrt{2\alpha}}$ & $\langle 0|y|1\rangle = \dfrac{1}{\sqrt{2\alpha}}$

$$V_{01,01} \equiv 0$$

$$\therefore \quad \mathbb{V} = \begin{pmatrix} 0 & a/2\alpha \\ a/2\alpha & 0 \end{pmatrix} = a/2\alpha \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$\therefore$ ~~$E^{(1)}$~~ Eigenvalues of $\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$ must sum to 0

& have a product $= -1$ $\therefore$ ± 1

$$\therefore \quad E^{(1)} = \pm\, a/2\alpha$$

Eigenfunctions are eigenvectors of $\mathbb{V}$ (dont worry about $a/2\alpha$ as it will vanish as we normalize vectors)

$$\therefore \quad \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \pm \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$

$$\Rightarrow \quad c_2 = \pm c_1 \qquad \#.$$

The "proper" linear combination of zero order function are

$$\frac{1}{\sqrt{2}} \left(\psi_1^0(x)\psi_0^0(y) \pm \psi_0^0(x)\psi_1^0(y) \right) \text{ corresponding to}$$

$$E_\pm = 2\hbar\omega \pm a/2\alpha$$

4.

$$\langle 0 | x^3 | 1 \rangle = \langle 0 | x^2 | \sum |N\rangle\langle N | x | 1 \rangle$$

$$= \sum_N \langle 0 | x^2 | N \rangle \langle N | x | 1 \rangle$$

better yet

$$\langle 0 | x^3 | 1 \rangle = \sum_N \langle 0 | x | N \rangle \langle N | x^2 | 1 \rangle$$

$$\langle 0 | x | N \rangle = \langle N | x | 0 \rangle = \delta_{0,N-1} \sqrt{\frac{N}{2\alpha}}$$

$$\langle 0 | x^3 | 1 \rangle = \frac{1}{\sqrt{2\alpha}} \langle 1 | x^2 | 1 \rangle$$

$$\langle 1 | x^2 | 1 \rangle = \sum_N \langle 1 | x | N \rangle \langle N | x | 1 \rangle$$

now $\langle N | x | 1 \rangle = \delta_{1,N+1} \sqrt{\frac{N+1}{2\alpha}} + \delta_{1,N-1} \sqrt{\frac{N}{2\alpha}}$

So $\langle 1 | x^2 | 1 \rangle = |\langle 1 | x | 0 \rangle|^2 + |\langle 1 | x | 2 \rangle|^2 = \left(\frac{1}{\sqrt{2\alpha}}\right)^2 + \left(\frac{1}{\alpha}\right) = \frac{3}{2\alpha}$

$$\therefore \quad \langle 0 | x^3 | 1 \rangle = \frac{3}{2\sqrt{2}\,\alpha^{3/2}} = \frac{3}{(2\alpha)^{3/2}}$$