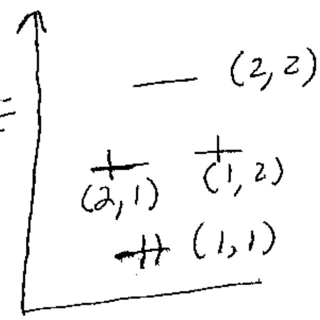
HW #3 Chem 1410.

1. Estimate the excitation energy of cyclobutadiene using the 2-dimensional particle-in-the-box ~~pro~~ model.

$$E = \frac{h^2}{8mR^2}\left(n_x^2 + n_y^2\right)$$



- two electrons in the (1,1) level
- two electrons in the degenerate pair of orbitals (2,1) and (1,2)

The lowest excitation involves promoting an electron from (2,1) to (2,2)

$$\Delta E = \frac{h^2}{8mR^2}\left\{(4+4) - (4+1)\right\} = \frac{3h^2}{8mR^2}$$

the CC bond length is ≈ 1.4 Å. We need to make the box bigger to allow for the size of the atoms. Take $R = 2$ Å

$$\Delta E = \frac{3(6.63\times10^{-34})^2}{8(9.11\times10^{-31})(2\times10^{-10})^2} = 4.5\times10^{-18}\ \mathrm{J}$$

$$\Delta E = 28\ \mathrm{eV}.$$

2. For the 1-dimensional particle-in-the-box problem, what is the probability of finding the particle between $a/3$ and $2a/3$?

$$\text{Prob} = \frac{2}{a}\int_{a/3}^{2a/3} \sin^2\left(\frac{n\pi x}{a}\right)dx = \frac{2}{a}\frac{a}{n\pi}\int_{n\pi/3}^{2n\pi/3} \sin^2 z\, dz$$

$$= \frac{2}{n\pi}\left(\frac{z}{2} - \frac{\sin 2z}{4}\right)\Bigg|_{n\pi/3}^{2n\pi/3}$$

$$= \frac{2}{n\pi}\left(\frac{n\pi}{6}\right) - \frac{2}{4n\pi}\left\{\sin\left(\frac{4n\pi}{3}\right) - \sin\left(\frac{2n\pi}{3}\right)\right\}$$

$$= \frac{1}{3} - \frac{1}{2\pi}\left(\sin\frac{4\pi}{3} - \sin\frac{2\pi}{3}\right) \leftarrow$$ specializing on the $n=1$ level

$$= 0.609$$

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3. Problem 4-6 from text.

Consider the trial wavefunction for the particle-in-the-box problem: $\psi = \sqrt{\frac{630}{a^9}}\, x^2(a-x)^2$

$$\langle E\rangle = \left(\frac{630}{a^9}\right)\int_0^a x^2(a-x)^2\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\right)x^2(a-x)^2 dx$$

$$= \left(-\frac{\hbar^2}{2m}\right)\left(\frac{630}{a^9}\right)\int_0^a (x^4 - 2ax^3 + a^2x^2)(12x^2 - 12ax + 2a^2)\,dx$$

$$= \left(-\frac{\hbar^2}{2m}\right)\left(\frac{630}{a^9}\right)\left(\frac{-2a^7}{105}\right) = \frac{6\hbar^2}{ma^2}$$

$$\langle E^2 \rangle = \left(\frac{630}{a^9}\right)\left(\frac{\hbar^4}{4m^2}\right)\int_0^a (x^4 - 2ax^2 + a^2x^2)\ (24)\ dx$$

the result of taking four derivatives

$$= \frac{126\,\hbar^4}{m^2 a^4}$$

$$\langle E^2 \rangle - \langle E \rangle^2 = \frac{90\,\hbar^4}{m^2 a^4}.$$

This is not zero because ψ is not an eigenfunction of $\hat{H}$. As a result ψ must be a linear combination of eigenfunctions which causes a spread in E.

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4. If the vibrational frequency of H_2 is 4401 cm^{-1}, what is the frequency of HD? of D_2?

$$\tilde{\nu} \propto \sqrt{\frac{k}{\mu}} \qquad \frac{\nu(HD)}{\nu(H_2)} = \sqrt{\frac{\mu_{H_2}}{\mu_{HD}}} \approx \sqrt{\frac{\frac{1\cdot 1}{1+1}}{\frac{2\cdot 1}{1+2}}}$$

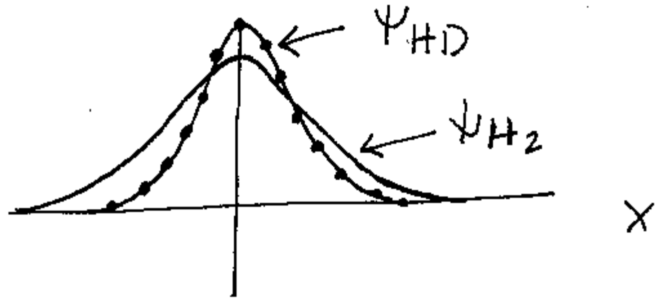
$$\frac{\nu(HD)}{\nu(H_2)} \approx \sqrt{\frac{1/2}{2/3}} = \sqrt{\frac{3}{4}} = 0.866$$

$$\nu(HD) \approx (4401)(.866) = 3811\ cm^{-1}.$$

$$\frac{\nu(D_2)}{\nu(H_2)} = \sqrt{\frac{1/2}{1}} = .707$$

$$\nu(D_2) = 4401\ (.707) = 3112\ cm^{-1}$$

4. Continued



#5. 5-26 from text.

Show that $\langle x^2 \rangle = \frac{1}{\alpha}\left(v+\frac{1}{2}\right)$

$\langle x^4 \rangle = \frac{3}{4\alpha^2}\left(2v^2+2v+1\right)$

$$\int_{-\infty}^{\infty} \psi_v \, x^2 \, \psi_v \, dx = N_v^2 \int_{-\infty}^{\infty} (x\,\psi_v)^2 dx$$

From the text: $\xi H_v = \dfrac{H_{v+1} - 2v H_{v-1}}{2}$

$$x H_v = \frac{H_{v+1} - 2v H_{v-1}}{2\sqrt{\alpha}}$$

$$\int_{-\infty}^{\infty} \psi_v x^2 \psi_v dx = \frac{N_v^2}{4\alpha}\int_{-\infty}^{\infty} \left(H_{v+1} - 2v H_{v-1}\right)^2 e^{-\alpha x^2} dx$$

$$= \frac{N_v^2}{4\alpha}\left\{\int_{-\infty}^{\infty} (H_{v+1})^2 e^{-\alpha x^2} dx + 4v^2\int_{-\infty}^{\infty} (H_{v-1})^2 e^{-\alpha x^2} dx\right\}$$

$$= \frac{N_v^2}{4\alpha}\left\{\frac{1}{N_{v+1}^2} + \frac{4v^2}{N_{v-1}^2}\right\} = \frac{1}{4\alpha}\frac{\left(\alpha/\pi\right)^{1/2}}{2^v v!}\left\{\frac{2^{v+1}(v+1)!}{(\alpha/\pi)^{1/2}} + \frac{4v^2 2^{v-1}(v-1)!}{(\alpha/\pi)^{1/2}}\right\}$$

$$= \frac{1}{4\alpha}\left\{\frac{2^{v+1}(v+1)!}{2^v v!} + \frac{4v^2 2^{v-1}(v-1)!}{2^v v!}\right\}$$

$$= \frac{1}{4\alpha}\left\{2(v+1) + \frac{4v^2}{2v}\right\} = \frac{1}{4\alpha}\left\{2(v+1) + 2v\right\}$$

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

$$\int_{-\infty}^{\infty} x^4 \psi_v^2 \, dx = \int_{-\infty}^{\infty} x^2 (x\psi_v)^2 \, dx$$

$$= \frac{N_v^2}{4\alpha}\int_{-\infty}^{\infty} x^2 \left(H_{v+1} - 2vH_{v-1}\right)^2 e^{-\alpha x^2} \, dx$$

$$= \frac{N_v^2}{4\alpha}\int x^2\left(H_{v+1}^2 - 4vH_{v+1}H_{v-1} + 4v^2 H_{v-1}^2\right) e^{-\alpha x^2} \, dx$$

$$xH_{v+1} = \frac{H_{v+2} - 2(v+1)H_v}{2\sqrt{\alpha}}, \quad xH_{v-1} = \frac{H_v - 2(v-1)H_{v-2}}{2\sqrt{\alpha}}$$

$$\frac{N_v^2}{4\alpha}\left\{\int_{-\infty}^{\infty}\frac{\left(H_{v+2}-2(v+1)H_v\right)^2}{4\alpha} e^{-\alpha x^2} \, dx + \frac{4v(2)(v+1)}{4\alpha}\int_{-\infty}^{\infty} H_v^2 e^{-\alpha x^2} \, dx \right.$$

$$\left. + \int_{-\infty}^{\infty}\frac{\left(H_v^2 + 4(v-1)^2 H_{v-2}^2\right)e^{-\alpha x^2} \, dx}{4\alpha}\cdot 4v^2\right\}$$

$$= \frac{N_v^2}{16\alpha^2}\left\{\frac{1}{N_{v+2}^2} + \frac{4(v+1)^2}{N_v^2} + \frac{8v(v+1)}{N_v^2} + \frac{4v^2}{N_v^2} + \frac{16v^2(v-1)^2}{N_{v-2}^2}\right\}$$

$$= \frac{1}{16\alpha^2}\left\{\frac{N_v^2}{N_{v+2}^2} + 4(v+1)^2 + 8v(v+1) + 4v^2 + \frac{16v^2(v-1)^2 N_v^2}{N_{v-2}^2}\right\}$$

$$= \frac{1}{16\alpha^2}\left\{\frac{2^{v+2}(v+2)!}{2^v v!} + 4(v+1)^2 + 8v(v+1) + 4v^2 + \frac{16v^2(v-1)^2 2^{v-2}(v-2)!}{2^v v!}\right\}$$

$$= \frac{1}{16\alpha^2}\left\{4(v+2)(v+1) + 4(v+1)^2 + 8v(v+1) + 4v^2 + \frac{16}{4}v(v-1)\right\}$$

$$= \frac{1}{4\alpha^2}\left(6v^2 + 6v + 3\right) = \frac{3}{4\alpha^2}\left(2v^2 + 2v + 1\right)$$

(6) $\hat{L}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}\right)\right]$

$\hat{L}^2 1 = 0\, 1 \longrightarrow$ eigenvalue $= 0$

$$\hat{L}^2\cos\theta = -\frac{\hbar^2}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\cos\theta$$

$$= -\frac{\hbar^2}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta(-\sin\theta) = \frac{\hbar^2}{\sin\theta}2\sin\theta\cos\theta$$

$$= 2\hbar^2\cos\theta \Rightarrow \text{eigenvalue} = 2\hbar^2$$

$$\hat{L}^2\sin\theta\, e^{i\phi} = -\hbar^2\left\{\frac{e^{i\phi}}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\sin\theta + \frac{\sin\theta}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}e^{i\phi}\right\}$$

$$= -\hbar^2\left\{\frac{e^{i\phi}}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\cos\theta) + \frac{e^{i\phi}}{\sin\theta}(i)^2\right\}$$

$$= -\hbar^2\left\{\frac{e^{i\phi}}{\sin\theta}\left(\cos^2\theta - \sin^2\theta\right) - \frac{e^{i\phi}}{\sin\theta}\right\}$$

$$= -\hbar^2 e^{i\phi}\left\{\frac{\cos^2\theta - \sin^2\theta - 1}{\sin\theta}\right\} = -\hbar^2 e^{i\phi}\frac{(-2\sin^2\theta)}{\sin\theta}$$

$$= 2\hbar^2\sin\theta\, e^{i\phi} \Rightarrow \text{eigenvalue} = 2\hbar^2$$