Chem 344 Sample QM Problems

"Old QM" – pre-Schroedinger observations

black body – importance is restrict energy / relate to freq.
photo electric effect – light is quantized: $E = h\nu - \phi$

(1) determine binding energy of an e^- to Na metal if light of 300 nm = λ causes electrons to be emitted from surface with an energy of 2eV

$$E = h\nu - \phi \rightarrow \phi = h\nu - E = (6.6\times10^{-34}\,J\cdot s)\left(\frac{3\times10^{8}\,m/s}{300\times10^{-9}\,m}\right) - (2eV)(1.6\times10^{-19}\,J/eV)$$

or in eV: ~~h~~ 0.5 eV $\quad = (6.6 - 3.2)\times10^{-19}\,J = 3.4\times10^{-19}\,J$

(2) Wave–particle duality – deBroglie $p = h/\lambda$ {momentum ~ frequency

determine the momentum of a 300 nm photon

$$p = h/300\,nm = 6.6\times10^{-34}\,J\text{-}s / 300\times10^{-9}\,m = 2.2\times10^{-27}\,\frac{Kg\,m}{s}$$

(3) How many watts (light power) of 300 nm light would be required from a laser to suspend (counteract gravity) for a 1 mm^2 disk (reflecting) weighing 1 mg ?

idea: must have force of light balance force of gravity

$$F_g = mg = (10^{-6}\,Kg)\cdot(9.8\,m/s^2) = 9.8\times10^{-6}\,N$$

each photon reverse direction on reflection

$$F_{ph} = dp/dt = 2(h/\lambda) = 2(2.2\times10^{-27}\,N\cdot s) = 4.4\times10^{-27}\,N\cdot s$$

instantaneous "force" per photon

to balance need # photon / sec to generate force equivalent to F_g

$$F_g = F_{ph}\cdot\left(\frac{\#\,phot}{sec}\right)$$

$$\#\,photon/sec = F_g/F_{ph} = \frac{9.8\times10^{-6}\,N}{4.4\times10^{-27}\,N\cdot s} = 2.2\times10^{+21}\,s^{-1}$$

Schroedinger Equation: Energy eigenvalue eqn: $\underline{H\Psi = E\Psi}$

$$H = T + V = \left[\left(\frac{-\hbar^2}{2m}\right)\nabla^2 + V(r)\right]$$

wave function – contains all information / interpret as Probability

(4) what is probability of a particle in a box being in the first 1/5 of the box for ψ_3?

$$\int_0^{L/5} \psi_3^* \psi_3 \, dx = N^2 \int_0^{L/5} \sin^2(3\pi x/L)\, dx \qquad N = \left(\frac{2}{L}\right)^{1/2}$$

indefinite $\int \sin^2 ax \, dx = \frac{1}{2}x - \frac{1}{4a}\sin 2ax + C$,

$$= \frac{2}{L}\left[\left(\frac{L}{10} - \frac{1}{4\left(\frac{3\pi}{L}\right)}\sin\left(\frac{6\pi}{L}\cdot\frac{L}{5}\right)\right) - \left(0 - \frac{1}{4a}\cdot 0\right)\right]$$

$$= \frac{1}{5} - \left(\frac{2}{12\pi}\right)\underset{(-)}{\sin}\left(\frac{6\pi}{5}\right) = 0.2 + 0.03 = \underline{0.23}$$

Particle in box is a favorite example because of ease of derivation and ability to illustrate principles of QM

(5) eg. orthogonality: show $\int_0^L \psi_1^* \psi_3 \, dx = 0$

$$\frac{2}{L}\int_0^L \sin\left(\frac{\pi x}{L}\right)\sin\left(\frac{3\pi x}{L}\right)dx$$

can use $\sin 3x = 3\sin x - 4\sin^3 x$

or $\sin x \sin y = \frac{1}{2}[\cos(x-y) - \cos(x+y)]$

$$\frac{1}{L}\int_0^L \left[\cos\left(\frac{2\pi x}{L}\right) - \cos\left(\frac{4\pi x}{L}\right)\right]dx$$

$$= \frac{+L}{2\pi}\left[\sin\left(\frac{2\pi}{L}x\right) - \frac{1}{2}\sin\left(\frac{4\pi}{L}x\right)\right]_0^L = 0 \quad \text{(each term is zero)}$$

Transition energies also can be modeled, with idea

$\Delta E = E_n - E_m$ for transition from state $m \to n$

(6) normally ask to model polyenes – $2e^-$/per level

transition from highest filled to lowest empty

hexatriene $n = 3$

$$\Delta E = E_{n+1} - E_n = \frac{h^2}{8mL^2}\left[(n+1)^2 - n^2\right] = \frac{h^2}{8mL^2}(2n+1)$$

if $L = 8(0.15\ \text{nm/bond}) = 1.2\ \text{nm}$ — count the terminal C-H

$$= \frac{(6.6\times10^{-34}\,\text{Js})^2(2\cdot3+1)}{8(9.1\times10^{-31}\,\text{kg})(1.2\times10^{-9}\,\text{m})^2}$$

<u>The uncertainty principle also makes good model problems</u>

$\Delta p \, \Delta x \geq \hbar/2$ usual / book mentions $\Delta E \, \Delta t \geq \hbar$

7 So we can ask if we just know particle is in box $0 \to L$
what is uncertainty in its momentum?
$\Delta p \geq (\hbar/2) / (L)$

8 But also ask if the excited state for the hexatriene has a lifetime of 1 ns, what is the uncertainty (or bandwidth in $\Delta\nu$) of its transition frequency for emission of light on going from $E_{n+1} \to E_n$

$\Delta E \geq \hbar/\Delta t = 1.05 \times 10^{-34}\,\text{J-s} / 10^{-9}\,\text{s} = 1.05 \times 10^{-25}\,\text{J}$

now to be useful express: $\Delta\nu = \Delta E/h = 1/2\pi \cdot 10^{-9}\,\text{s} = \underline{1.6 \times 10^{8}\,\text{s}^{-1}}$

<u>Note</u>: uncertainty in λ depends on λ because $E \sim 1/\lambda$

<u>Tunneling</u> is important and can be the topic of model problems as summarized in homework and text

Harmonic Oscillator provides a simple model with a potential

$$H\psi = \left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \tfrac{1}{2}kx^2\right]\psi = E\psi$$

9 obvious kinds of problems are
transition frequencies $v=2 \to v=3$ $\Delta E = \tfrac{7}{2}h\nu - \tfrac{5}{2}h\nu = h\nu$

$\nu = \frac{1}{2\pi}\sqrt{k/\mu}$ and $\mu = \frac{m_1 + m_2}{m_1 m_2}$

if transition frequency for $C{\equiv}O$ is $2000\,\text{cm}^{-1}$
what is the force constant?

$\mu = \frac{12 \times 16}{12+16} = (6.86\,\text{amu})(1.66 \times 10^{-27}\,\frac{\text{Kg}}{\text{amu}}) = 1.14 \times 10^{-26}\,\text{Kg}$

recall $\tilde{\nu} = \nu/c = 1/\lambda$

$* [E = h\nu = hc\tilde{\nu} = (6.6 \times 10^{-34}\,\text{J-s})(3 \times 10^{8}\,\text{m/s})(3000\,\text{cm}^{-1}) \cdot (100\,\text{cm/m}) = 5.9 \times 10^{-20}\,\text{J}$

$k = (2\pi\nu)^2 \cdot \mu = (2\pi \cdot 3000\,\text{cm}^{-1} \cdot 100\,\frac{\text{cm}}{\text{m}} \cdot 3 \times 10^{8}\,\frac{\text{m}}{\text{s}})^2 \cdot (1.14 \times 10^{-26}\,\text{Kg})$

$= 3.6 \times 10^{3}\,\text{Nt/m}$ (seems too high by ~50% ?)

Expectation values are the average of what we would observe in a series of measurements for a system that is not in an eigenfunction of the operator

$$\langle \alpha \rangle = \frac{\int \psi^* \alpha \psi \, dx}{\int \psi^* \psi \, dx}$$ if normalized ψ ($\int \psi^* \psi dx = 1$): $\langle \alpha \rangle = \int \psi^* \hat{\alpha} \psi \, dx$

(10) What is expectation value for position $\langle x \rangle$ for harmonic oscillator $v = 1$

recall: $x \psi_1 = x\psi_1 \neq \text{const}\, \psi_1$ so need $\langle x \rangle$

$$\psi_1 = \left(\frac{4\alpha^3}{\pi}\right)^{1/4} x e^{-\frac{1}{2}\alpha x^2} \qquad \alpha = \sqrt{k\mu/\hbar^2} \quad \left[\frac{(N m^{-1})(kg)}{(J \cdot s)^2}\right]^{1/2}$$

$$m^{-2} = \left[\frac{kg^2/s^2}{(kg\, m^2/s)^2}\right]^{1/2}$$

$$\langle x \rangle = \int_{-\infty}^{\infty} \left(\frac{4\alpha^3}{\pi}\right)^{1/2} x e^{-\frac{1}{2}\alpha x^2} x \cdot x e^{-\frac{1}{2}\alpha x^2} dx$$

$$= \left(\frac{4\alpha^3}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} x^3 e^{-\alpha x^2} dx = \underline{0}$$

Note: x^3 - odd, $e^{-\alpha x^2}$ - even; $\int_{-\infty}^{\infty} x^3 e^{-\alpha x^2} = 0$

Avg. position is in the middle → x is a vector (has sign)

(11) What about rms (root mean square): $\langle x^2 \rangle^{1/2}$?

$$\langle x^2 \rangle = \left(\frac{4\alpha^3}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} x^4 e^{-\alpha x^2} dx$$

use: $\int_0^{\infty} x^{2n} e^{-\alpha x^2} dx = \frac{1 \cdot 3 \cdot 5 \cdots (2n-1)}{2^{n+1} \alpha^n} \sqrt{\frac{\pi}{\alpha}}$

here $n = 2$

$$= \left(\frac{4\alpha^3}{\pi}\right)^{1/2} \left(\frac{3}{2^3 \alpha^2}\right) \left(\sqrt{\frac{\pi}{\alpha}}\right) \cdot 2 = \frac{3}{2\alpha}$$

$$\text{rms} = \langle x^2 \rangle^{1/2} = \sqrt{3/2\alpha}$$

~~(as written appears to have units prob.)~~

see - stronger force (k), heavier mass (μ)

avg. displacement is reduced, (x^2 not vector)

Units problem for H atom we used $V = -Ze^2/r$ esu form

book uses SI units → $V = -Ze^2/4\pi\varepsilon_0 r$

for r — meter, e — Coulomb $\}$ $\varepsilon_0 = 8.85 \times 10^{-12}\, C^2 J^{-1} m^{-1}$ so $V \sim$ Joule

correlary is: $a_0 = 4\pi\varepsilon_0 \hbar^2 / me^2 = 5.29 \times 10^{-11}$ m

$$E_n = -\frac{me^4}{8\varepsilon_0^2 h^2 n^2} \quad - n = 0, 1, 2 \cdots \text{ in J}$$

for esu $E = \frac{2\pi^2 m e^4}{n^2 h^2}$ which for $m = g$, $h = \text{erg} \cdot s$, $e = \text{esu}$ ⇒ erg $\frac{g \cdot cm^2}{s^2}$