Chem 332: Second Exam (80 pts. possible) Friday, March 8, 2013

Please budget your time carefully and show all work for partial credit. Read each problem carefully!

$h = 6.62608 \times 10^{-34}$ J s	1 Å = 1 x 10^{-10} m = 0.1 nm	$\int_0^\infty x^n e^{-ax}\,dx = \frac{n!}{a^{n+1}}$
$N_A = 6.02214 \times 10^{23}$ mol^{-1}	1 amu = 1.66054 x 10^{-27} kg	
$c = 2.99792 \times 10^8$ m/s	$m_e = 9.10939 \times 10^{-31}$ kg	
$k_B = 1.38065 \times 10^{-23}$ J K^{-1}	$e^{\pm i\theta} = \cos\theta \pm i\sin\theta$	$\int_0^\infty x^2 e^{-ax^2}\,dx = \frac{1}{4a}\left(\frac{\pi}{a}\right)^{1/2}$
$p_x = -i\hbar\frac{\partial}{\partial x}$	$[\ell_x, \ell_y] = i\hbar\ell_z$	$\frac{\hbar^2}{2\mu r^2}J(J+1)$
$B = \frac{h}{8\pi^2\mu r^2}$	$\frac{h}{2\pi}\sqrt{\frac{k}{m}}\left(n+\frac{1}{2}\right)$	$\frac{n^2h^2}{8mL^2}$
$\psi_n(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} H_n e^{-\alpha x^2/2}$	$\psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi}{L}x\right)$	$\psi_k(\phi) = \frac{1}{\sqrt{2\pi}}e^{ik\phi}$
$\ell^2 Y_{l,m_l} = l(l+1)\hbar^2 Y_{l,m_l}$ $\ell_z Y_{l,m_l} = m_l\hbar Y_{l,m_l}$	$-\frac{\hbar^2}{2m}\nabla^2 + \frac{1}{2}kx^2$	$\ell_x = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$

(1) (10 pts) Show that the spherical harmonic $Y_{2,1}$ is an eigenfunction of the operator $\ell_x^2 + \ell_y^2$ by finding its eigenvalue. (Hint: remember that $\ell^2 = \ell_x^2 + \ell_y^2 + \ell_z^2$)

$$\ell_x^2 + \ell_y^2 = \ell^2 - \ell_z^2$$

$$(\ell^2 - \ell_z^2)Y_{2,1} = \ell^2 Y_{2,1} - \ell_z^2 Y_{2,1}$$

$$= \hbar^2(2)(2+1)Y_{2,1} - [(\hbar)(1)]^2 Y_{2,1}$$

$$= 5\hbar^2 Y_{2,1}$$

(2) (15 pts) Short answers (very short)

(a) For the particle of mass m undergoing free rotation in 2-dimensions, what was the key boundary condition on the wavefunction that led to quantization?

ψ must be single-valued, $\psi(\phi+2\pi)=\psi(\phi)$

(b) Briefly discuss the role of mass in regards to the Bohr Correspondence Principle for the particle in an infinitely deep 1-dimensional box.

$E_n = \frac{n^2 h^2}{8mL^2}$ as $m \to \infty$, $\Delta E \to 0$

approaches the continuous energy distribution of the classical case

(c) Using the vector model of quantized angular momentum, what is the length of the angular momentum vector for the case with $\ell = 5$? What are the possible projections on the z-axis that this vector can have?

$l^2 Y_{\ell m_\ell} = \hbar^2 \ell(\ell+1) Y_{\ell, m_\ell}$

$|\vec{\ell}| = \hbar\sqrt{\ell(\ell+1)} = \hbar\sqrt{5(5+1)} = \hbar\sqrt{30}$

$\langle \ell_z \rangle = -5\hbar, -4\hbar, -3\hbar, -2\hbar, -1\hbar, 0, 1\hbar, 2\hbar, 3\hbar, 4\hbar, 5\hbar$

(d) In terms of the rotational constant B, how does an allowed pure rotational absorption frequency depend on the final quantum state J′ ?

$\nu = 2BJ'$

(e) How many nodes are in a harmonic oscillator wavefunction when n=6 ? Is this wavefunction symmetric or anti-symmetric (or neither) with respect to x=0 ?

For the harmonic oscillator, #nodes $= n$

so $n=6$ has 6 nodes

it will be symmetric wrt $x=0$

(3) (15 pts) In the microwave spectrum of carbon monoxide, the $J = 0 \rightarrow 1$ transition was measured at 115,217.204 MHz. Calculate the rotational constant B (in MHz), moment of inertia I (in amu Å^2), and the bond length r (in Å) of CO. (use $m_O = 15.994915$ amu, $m_C = 12.000$ amu)

$$\nu = 115{,}217.204 \text{ MHz}$$

$$= 2BJ' = 2B$$

$$\therefore \quad B = \frac{\nu}{2} = 57{,}608.602 \text{ MHz}$$

$$B = \frac{h}{8\pi^2 I}, \quad \text{so} \quad I = \frac{h}{8\pi^2 B} = \frac{6.62608 \times 10^{-34}}{(8)(\pi)^2 (\cancel{115{,}217.204}\ 57{,}608.602 \times 10^6)}$$

$$= 1.4567 \times 10^{-46}\ \text{kg} \cdot \text{m}^2$$

$$\times \frac{1 \text{ amu}}{1.66054 \times 10^{-27} \text{ kg}} \times \left(\frac{1 \text{ Å}}{10^{-10} \text{ m}}\right)^2$$

$$I = 8.773 \text{ amu Å}^2$$

$$I = \mu r^2, \quad r = \sqrt{\frac{I}{\mu}}$$

$$\mu = \frac{(15.994915)(12)}{15.994915 + 12}$$

$$= 6.85621 \text{ amu}$$

$$r = \sqrt{\frac{8.773}{6.85621}}$$

$$= 1.1312 \text{ Å}$$

(4) (10 pts) The energy levels of a particular 3-dimensional particle in a box (non-cubical) are given by

$E_{n_x,n_y,n_z} = \frac{h^2}{8mL}\left(4n_x^2 + 4n_y^2 + n_z^2\right)$, where L is the height of the box in the z direction. What are the energies and degeneracies of the 4 lowest energy levels? Label each state by its quantum numbers.

quantum number	E	degeneracy
1,1,1	$9h^2/8mL^2$	1
1,1,2	$12h^2/8mL^2$	1
1,1,3	$17h^2/8mL^2$	1
1,2,1 2,1,1	$21h^2/8mL^2$	2

(5) (10 pts) For a quantum harmonic oscillator of mass m, show that the function $f(x) = xe^{-\alpha x^2/2}$ is an eigenfunction of the Hamiltonian for this system. Give the eigenvalue. Note that $\alpha = \sqrt{\frac{mk}{\hbar^2}}$.

$$H = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2$$

$$Hf = \frac{-\hbar^2}{2m}\frac{d}{dx}\left[x(-\alpha x)e^{-\alpha x^2/2} + e^{-\alpha x^2/2}\right] + \frac{1}{2}kx^2\left(xe^{-\alpha x^2/2}\right)$$

$$= \frac{-\hbar^2}{2m}\left[-\alpha x^2(-\alpha x)e^{-\alpha x^2/2} - 2\alpha x e^{-\alpha x^2/2} - \alpha x e^{-\alpha x^2/2}\right] + \frac{1}{2}kx^3 e^{-\alpha x^2/2}$$

$$= xe^{-\alpha x^2/2}\left[\frac{-\hbar^2}{2m}\alpha^2 x^2 + \frac{3\alpha\hbar}{2m} + \frac{1}{2}kx^2\right] \quad \text{but } k = \frac{\alpha^2\hbar^2}{m}$$

$$= xe^{-\alpha x^2/2}\left[\frac{3\alpha\hbar^2}{2m}\right] = xe^{-\alpha x^2/2}\left[\frac{3}{2}\frac{\hbar^2}{m}\sqrt{\frac{mk}{\hbar^2}}\right]$$

$$= \boxed{\frac{3}{2}\hbar\omega}\, f$$

(6) (10 pts) For a particle in a 1-dimensional infinitely deep box of length L, the normalized wave function for the 1st excited state can be written as $\Psi_2(x) = \frac{1}{i\sqrt{2L}}\left(e^{ibx} - e^{-ibx}\right)$, where $b = \frac{2\pi}{L}$.

Give the full expression that you would need to solve to determine the probability of finding the particle in the 1st third of the box. Simplify as much as possible but do not solve any integrals.

$$\text{prob} = \int_0^{\frac{1}{3}L} \psi^* \psi \, dx = \int_0^{\frac{1}{3}L} \left[\frac{-1}{i\sqrt{2L}}\left(e^{-ibx} - e^{ibx}\right)\right]\left[\frac{1}{i\sqrt{2L}}\left(e^{ibx} - e^{-ibx}\right)\right] dx$$

$$= \frac{1}{2L}\int_0^{\frac{1}{3}L} \left(e^{-ibx} - e^{ibx}\right)\left(e^{ibx} - e^{-ibx}\right) dx = \frac{1}{2L}\int_0^{\frac{1}{3}L} \left(2 - e^{-2ibx} - e^{2ibx}\right) dx$$

$$\left[= \frac{1}{L}\int_0^{1/3L} \left(1 - \cos(2bx)\right) dx \right]$$

(7) (10 pts) Consider the 1-dimensional time dependent Schrödinger equation,

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \Psi}{\partial x^2} + V(x)\Psi$$

where Ψ is a function of both x and t (as shown above, V is a function only of x). Use the separation of variables technique to recover the time independent Schrödinger equation. Show all work and justify your steps where appropriate.

(1) for $V(x)$ only, assume $\Psi = \psi(x) f(t)$

substitute: $i\hbar \frac{\partial}{\partial t}\psi f = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi f + V\psi f$

(2) $i\hbar \psi \frac{\partial f}{\partial t} = -\frac{\hbar^2}{2m} f \frac{\partial^2 \psi}{\partial x^2} + V\psi f$

divide by ψf:

(3) $\underbrace{i\hbar \frac{1}{f}\frac{\partial f}{\partial t}}_{t \text{ only}} = \underbrace{-\frac{\hbar^2}{2m}\frac{1}{\psi}\frac{\partial^2 \psi}{\partial x^2} + V}_{x \text{ only}}$ both must equal a constant

(4) $\therefore -\frac{\hbar^2}{2m}\frac{1}{\psi}\frac{\partial^2 \psi}{\partial x^2} + V = E$ or $\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V\right]\psi = E\psi$ ✓