Name:

Chem 3322 test #2 solutions, out of 40 marks

I want complete, detailed answers to the questions. Show all your work to get full credit.

$$\int_{-\infty}^{\infty} e^{-cx^2} = \frac{\sqrt{\pi}}{\sqrt{c}} \tag{1}$$

$$\int_{-\infty}^{\infty} x^2 e^{-cx^2} = \frac{\sqrt{\pi}}{2c^{3/2}} \tag{2}$$

$$\int r^2 e^{-cr}\, dr = -\frac{e^{-cr}(2 + 2cr + c^2r^2)}{c^3} \tag{3}$$

The Schrödinger time dependent equation is, for $\psi(x,t)$

$$i\hbar\frac{\partial\psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\psi(x,t)}{\partial x^2} + V(x)\psi(x,t) \tag{4}$$

The Schrödinger time independent equation is, for $\psi(x)$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \tag{5}$$

A wavefunction $\psi(x,y,z,t)$ is normalized if $\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \psi^*\psi dx\, dy\, dz = 1$

The particle in a one dimensional box energy levels are

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} \qquad \text{n} = 1, 2, 3, ... \tag{6}$$

energy levels of the particle on a ring:

$$E_n = \frac{n^2\hbar^2}{2mR^2} \qquad \text{n} = 0, 1, 2, ... \tag{7}$$

energy levels of the harmonic oscillator: $E_n = (n + 1/2)\hbar\omega$, n = 0, 1, 2, ...

ground state wavefunction of the harmonic oscillator:

$$\psi(x) = \left(\frac{2\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2} \tag{8}$$

with

$$\alpha = \frac{m\omega}{2\hbar} \qquad \text{and} \qquad \omega = (k/m)^{1/2} \tag{9}$$

where k is the force constant and m is the mass.

Speed of light = c = 3.0×10^8 m/s

electron mass = 9.11×10^{-31} kg

Avogadro's constant = $N_A = 6.022 \times 10^{23}$ mol^{-1}

Planck constants: h = 6.6262×10^{-34} Js and $\hbar = 1.05459 \times 10^{-34}$ Js

Boltzmann's constant k_B=1.38066×10^{-23}J K^{-1}

$\pi = 3.14159$

mass conversion from amu to kg: 1.66×10^{-27} kg/amu

Relationship between the wavelength of a photon and its energy

$$\lambda = \frac{hc}{E} \tag{10}$$

Volume of a sphere is $4\pi r^3/3$ and the surface area is $4\pi r^2$

Problem 1 – 10 marks

In the early stages of this course, we looked at the monochromatic waves

$$e^{i(kx-\omega t)} \qquad \sin(kx-\omega t) \qquad \cos(kx-\omega t) \tag{11}$$

a) – 5 marks Which of these are eigenfunctions of the p_x operator, and, for those that are, give the corresponding eigenvalue. Eq. (19) is useful.

Solution:

Only $e^{i(kx-\omega t)}$ is an eigenfunction, with eigenvalue $\hbar k$. This is because the derivative of sin is cos, and the derivative of cos is $-\sin$.

b) – 5 marks Repeat part a) for the p_x^2 operator.

Solution:

All three are eigenfunctions, all with eigenvalue $\hbar^2 k^2$.

Problem 2 – 10 marks

a) – 2 marks State the textbook's version of the correspondence principle to relate the behavior of quantum and classical mechanics (hint: something about large quantum numbers).

Solution:

Quantum mechanical behavior resembles the corresponding classical mechanics behavior in the limit of large quantum number values.

b) – 3 marks Illustrate and explain your answer to (a) using either the harmonic oscillator or the particle in a box model.

Solution:

The textbook's discussion of this, including graphs, of the particle in a box model is on page 85 and of the harmonic oscillator model is on page 186.

c) – 2 marks State the version of the correspondence principle we used in class to relate the behavior of quantum and classical mechanics in order to derive the form of the momentum operator.

Solution:

Quantum mechanics corresponds to classical mechanics at the level of expectation values, so that we can take the expectation value of a classical mechanics expression to obtain a quantum mechanical expression.

d) – 3 marks Illustrate and explain your answer to (c) using either the harmonic oscillator or the particle in a box model.

Solution:

There are several ways to answer this; one way is to draw the square of the wavefunction for either the particle in a box or the harmonic oscillator model and compare this probability density to the classical mechanics probabilty distribution in terms of the average value.

Problem 3 – 10 marks

a) – 5 marks Why did we change variables to spherical polar coordinates in our treatment of the hydrogen atom?

Solution:

Putting the proton at the origin and the electron at cartesian coordinates (x, y, z) results in the Coulomb attraction being

$$-\frac{1}{\sqrt{x^2 + y^2 + z^2}} \tag{12}$$

from which we will not be able to separate variables to solve the TISE because the three variables are inside the square root. Instead, by moving to spherical polar coordinates, with the proton at the origin and the electron at coordinates (r, θ, ϕ), the Coulomb attraction is $-1/r$ which does not contain the angular variables, which after some effort allows us to successfully separate variables in the TISE to obtain three separate ordinary differential equations (coupled through some constants).

b) – 5 marks

$$\psi_{2p_x}(r,\theta,\phi) = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{5/2} r\,e^{-Zr/2a_0}\sin\theta\cos\phi \tag{13}$$

$$\psi_{2p_y}(r,\theta,\phi) = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{5/2} r\,e^{-Zr/2a_0}\sin\theta\sin\phi \tag{14}$$

$$\psi_{2p_z}(r,\theta,\phi) = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{5/2} r\,e^{-Zr/2a_0}\cos\theta \tag{15}$$

where Z is the nuclear charge, and $a_0 = (4\pi\epsilon_0\hbar^2)/(m_e e^2)$ is the Bohr radius (where m_e is the electron mass and e is the electron charge).

Show that the total probability density of the $2p$ orbitals of a hydrogenic atom (given above) is spherically symmetric by evaluating

$$\psi^*_{2p_x}\psi_{2p_x} + \psi^*_{2p_y}\psi_{2p_y} + \psi^*_{2p_z}\psi_{2p_z} \tag{16}$$

(Hint: you will need the trigonometic identity $\sin^2 t + \cos^2 t = 1$ for any value of t.)

Solution:

The probability density is

$$\frac{1}{32\pi}(Z/a_0)^5 r^2\,e^{-Zr/a_0}B \tag{17}$$

where

$$\begin{aligned} B &= \sin^2\theta\cos^2\phi + \sin^2\theta\sin^2\phi + \cos^2\theta \\ &= \sin^2\theta(\cos^2\phi + \sin^2\phi) + \cos^2\theta = \sin^2\theta + \cos^2\theta = 1 \end{aligned} \tag{18}$$

Therefore the probability density has no dependence on the angular variables which means it is spherically symmetric.

Problem 4 – **10 marks**

Recall that the operator corresponding to the x-component of momentum is

$$\hat{p}_x = -i\hbar \frac{\partial}{\partial x} \tag{19}$$

a) – 2 marks For the ground state of the harmonic oscillator, show that the expectation value of momentum, $\langle p_x \rangle$, is zero.

Solution:

$$\begin{aligned} \langle p_x \rangle &= \int_{-\infty}^{\infty} \psi^*(-i\hbar)\frac{d}{dx}\psi\, dx & (20) \\ &= (-i\hbar)\sqrt{2\alpha/\pi}\int_{-\infty}^{\infty} e^{-2\alpha x^2}(-2\alpha x)dx & (21) \end{aligned}$$

which is zero by symmetry (odd function, even domain of integration). You can also easily find the antiderivative and directly evaluate this integral, which gives zero.

b) – 4 marks Since $p_x = mv_x$, the result from part (a) establishes that, on average, the particle has a velocity of zero. There are two ways this could occur: on the one hand, the particle could have a speed of zero (and hence not be moving at all), while on the other hand, the particle could be moving to the left as often as it is moving to the right, and hence have no *net* motion. You are to establish which of these two situations we have by computing the variance of the momentum,

$$\text{Var } p_x = \sqrt{\langle p_x^2 \rangle - \langle p_x \rangle^2} \tag{22}$$

Make sure you explain how the value you get for the variance helps you answer the question.

Solution:

$$\begin{aligned} \langle p_x^2 \rangle &= \frac{\sqrt{2\alpha}}{\sqrt{\pi}}\int_{-\infty}^{\infty} e^{-\alpha x^2}(-\hbar^2)\frac{d}{dx}(-2\alpha x e^{-\alpha x^2})dx & (23) \\ &= \frac{\sqrt{2\alpha}}{\sqrt{\pi}}\hbar^2\int_{-\infty}^{\infty} e^{-\alpha x^2}(2\alpha e^{-\alpha x^2} - 4\alpha^2 x^2 e^{-\alpha x^2})dx & (24) \\ &= \frac{\sqrt{2\alpha}}{\sqrt{\pi}}2\alpha\hbar^2\int_{-\infty}^{\infty} e^{-2\alpha x^2}(1-2\alpha x^2) & (25) \\ &= \frac{\sqrt{2\alpha}}{\sqrt{\pi}}2\alpha\hbar^2\left(\frac{\sqrt{\pi}}{\sqrt{2\alpha}} - 2\alpha\frac{\sqrt{\pi}}{2(2\alpha)^{3/2}}\right) = \alpha\hbar^2 & (26) \end{aligned}$$

Hence the variance is $\hbar\sqrt{\alpha}$ which is nonzero, hence the particle is moving.

c) − 4 marks There is another way to answer part (b): a general result in quantum mechanics says that a property Q has a precise, well-defined value (with zero variance) only if the wavefunction of the particle is an eigenfunction of the operator $\hat{Q}$. You are to establish which of the two situations we have as described in part (b) by using this eigenfunction approach.

Solution:

Is $\hat{p}_x\psi = q\psi$ for q a constant element of the complex numbers? No, because

$$\hat{p}_x\psi = -i\hbar\left(\frac{2\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2}(-2\alpha x) = 2i\hbar\alpha x\psi \tag{27}$$

Hence the particle does not have a precisely defined value for its momentum, but rather a distribution of values, hence it is moving.