CHM102A Model Questions and Solutions

Set-1

1. Calculate the minimum uncertainty in the speed of a ball of mass 500 g that is known to be within 1.0 μm of a certain point on a bat.

$$\Delta v = \frac{\hbar}{2m\Delta x} = \frac{1.05\times10^{-34}\,\mathrm{m^2kgs^{-1}}}{2\times0.5\,\mathrm{kg}\times1.0\times10^{-6}\,\mathrm{m}} = 1.05\times10^{-28}\,\mathrm{m\,s^{-1}}$$

2. What is the minimum uncertainty in the position of a bullet of mass 5.0 g that is known to have a speed somewhere between 350.00001 m s^{-1} and 350.00000 m s^{-1}.

$$\Delta x = \frac{\hbar}{2m\Delta v} = \frac{1.05\times10^{-34}\,\mathrm{m^2kgs^{-1}}}{2\times5.0\times10^{-3}\,\mathrm{kg}\times1.0\times10^{-5}\,\mathrm{m}} = 1.05\times10^{-27}\,\mathrm{m\,s^{-1}}$$

3. Calculate the de Broglie wavelength of a Helium atom travelling at 1000 m s^{-1} and compare it with that of a mass of 1.0 g travelling at the same speed.

$$\lambda_{\mathrm{He}} = \frac{h}{p} = \frac{6.626\times10^{-34}\,\mathrm{m^2kg/s}}{6.64\times10^{-27}\,\mathrm{kg}\times1000\,\mathrm{m\,s^{-1}}}$$

$$\lambda_{\mathrm{wt}} = \frac{h}{p} = \frac{6.626\times10^{-34}\,\mathrm{m^2kg/s}}{1.0\times10^{-3}\,\mathrm{kg}\times1000\,\mathrm{m\,s^{-1}}}$$

4. Write down the Schrödinger for the following systems: (a) a particle of mass m in a cubical box of side a; (b) a particle of mass m in a spherical box of radius a; (c) a particle of mass m moving on the x-axis subjected to a force directed towards the origin, of magnitude proportional to the distance from the origin; (d) an electron moving in the presence of a nuclear charge $+Ze$; (e) two electrons moving in the presence of a fixed nucleus of charge $+Ze$.

$$-\frac{\hbar^2}{2m}\nabla^2\psi(x,y,z) = E\psi(x,y,z)$$

$$-\frac{\hbar^2}{2m}\nabla^2\psi(r,\theta,\phi) = E\psi(r,\theta,\phi)$$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + \frac{1}{2}kx^2\psi(x) = E\psi(x)$$

$$\left(-\frac{\hbar^2}{2m_N}\nabla_N^2 - \frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{Ze^2}{4\pi\epsilon_0 r}\right)\psi(r_n,\theta_N,\phi_N,r_e,\theta_e,\phi_e) = E\psi(r_n,\theta_N,\phi_N,r_e,\theta_e,\phi_e)$$

$$\left(-\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{Ze^2}{4\pi\epsilon_0 r_1} - \frac{Ze^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}}\right)\psi(r_1,\theta_1,\phi_1,r_2,\theta_2,\phi_2) = E\psi(r_1,\theta_1,\phi_1,r_2,\theta_2,\phi_2)$$

5. Which of the following functions cannot be solutions of the Schrödinger equation for all values of x? Why not? (a) $A\sec(x)$; (b) $A\tan(x)$; (c) $A\exp(x^2)$; (d) $A\exp(-x^2)$.

(a) No; infinite at $\pi/2$; (b) No; infinite at $\pi/2$; (c) No; infinite at $\pm\infty$; (d) Yes.

6. Determine $\psi^*\psi$ for the following wave functions: (a) $\cos\theta + i\sin\theta$ and (b) $\exp(-x^2)$.

$$\psi^*\psi = (\cos\theta - i\sin\theta)(\cos\theta + i\sin\theta)$$

$$\psi^*\psi = \exp(-2x^2)$$

7. The possible values obtained from a measurement of a discrete variable, x, are 1, 2, 3, and 4. (a) If the respective probabilities are 1/4, 1/4, 1/4, and 1/4, calculate the expectation values of x and x^2. (b) If the respective probabilities are 1/12, 5/12, 5/12, and 1/12, calculate the expectation values of x and x^2.

(a)$< x >= \frac{1}{4}(1+2+3+4) = 2.5$; $< x^2 >= \frac{1}{4}(1^2+2^2+3^2+4^2)$
(b)$< x >= \frac{1}{12}\times1 + \frac{5}{12}\times2 + \frac{5}{12}\times3 + \frac{1}{12}\times4)$; $< x^2 >= \frac{1}{12}\times1 + \frac{5}{12}\times2^2 + \frac{5}{12}\times3^2 + \frac{1}{12}\times4^2$

8. Determine the probability density of a particle as a function of its position if its wave function is $A\exp(ikx)$. What is the value of its momentum?

$$\psi^*\psi = A^2$$

Momentum is $\hbar k$ because

$$-i\hbar\frac{\partial A\exp(ikx)}{\partial x} = \hbar kA\exp(ikx)$$

9. A particle is in a state described by the wave function $\psi = (\cos\chi)\exp(ikx) + (\sin\chi)\exp(-ikx)$ where χ is a parameter. What is the probability that the particle will be found with a linear momentum (a) $+k\hbar$, (b) $-k\hbar$? What form would the waveunction have if it were 90% certain that the particle had linear momentum $+k\hbar$?

   A momentum of $\hbar k$ arises from the contribution of the function $\exp(ikx)$ while the contribution from $\exp(-ikx)$ would be $-\hbar k$. Probability, if the wave function is normalized, is the square of coefficient. Hence the probabilities are (a) $\cos^2\chi$ and (b) $\sin^2\chi$. A function with 90% probability of having momentum $\hbar k$ would imply that $\cos^2\chi = 0.9$.

10. Normalize the following wave functions to unity: (a) $\sin(n\pi x/L)$ for the range $0 < x < L$, (b) c, a constant in the range $-L < x < L$, (c) $\exp(-r/a_0)$ in three dimensions, (d) $x\exp(-r/2a_0)$ in three dimensions.

    (a) $N = \frac{1}{\sqrt{\int_0^L \sin^2(n\pi x/L)dx}}$; (b) $N = \frac{1}{\sqrt{\int_{-L}^{L} c^2 dx}}$; (c) $N = \frac{1}{\sqrt{\int_0^\infty \exp(-2r/a_0)r^2 dr}}$;

    (d) $N = \frac{1}{\sqrt{\int_0^\infty r^2\exp(-r/a_0)r^2 dr \int_0^\pi \sin^2\theta\sin\theta d\theta \int_0^{2\pi}\cos^2\phi d\phi}}$;

11. (a) Calculate the energy levels for $n = 1$, 2, and 3 for an electron in an infinite potential well of width 0.25 nm. (b) If an electron makes a transition from $n = 2$ to $n = 1$ what will be the wavelength of the emitted radiation?

    (a) The energies for a particle in a box are given by $E_n = \frac{n^2h^2}{8mL^2}$. Here $L = 0.25 \times 10^{-9}$ m.
    (b) The wavelength of the emitted radiation is obtained from the relation $\frac{hc}{\lambda} = E_2 - E_1$ or $\lambda = \frac{hc}{E_2 - E_1}$.

12. (a) Evaluate the probability of locating a particle in the middle third of 1-D box. (b) Find the probability that a particle in a box L wide can be found between $x = 0$ and $x = L/n$ when it is in the nth state.

    (a)

$$P = \frac{2}{L}\int_0^{L/3} \sin\left(\frac{n\pi x}{L}\right)\sin\left(\frac{n\pi x}{L}\right)dx$$
$$P = \frac{1}{L}\left(\int_0^{L/3} dx - \int_0^{L/3} \cos\left(\frac{2n\pi x}{L}\right)dx\right)$$
$$P = \frac{1}{3} - \frac{1}{2n\pi}\sin\left(\frac{2n\pi}{3}\right)$$

    (b)

$$P = \frac{2}{L}\int_0^{L/n} \sin\left(\frac{n\pi x}{L}\right)\sin\left(\frac{n\pi x}{L}\right)dx$$
$$P = \frac{1}{L}\left(\int_0^{L/n} dx - \int_0^{L/n} \cos\left(\frac{2n\pi x}{L}\right)dx\right)$$
$$P = \frac{1}{n}$$

13. Consider two wave functions which describe any two different states of a particle in a box. Show that these satisfy the relation $\int_0^L \psi_i^*\psi_j dx = \delta_{ij}$, where $\delta_{ij} = 1$ if $i = j$ and $\delta_{ij} = 0$ if $i \neq j$.
    This is what is called the orthonormality condition.

14. Verify the uncertainty principle for the particle in a box.

    We need to show that $\Delta x\Delta p \geq \hbar/2$. The uncertainty in x is obtained from $\Delta x = \sqrt{< x^2 > - < x >^2}$ and similarly for p. The expectation value of any operator is $< Op >= \int \psi^*\hat{Op}\psi dx$. Here, $\hat{Op}$ are x, x^2, $\hat{p} = -i\hbar\frac{d}{dx}$, and $\hat{p^2} = -\hbar^2\frac{d^2}{dx^2}$. By symmetry arguments, $< x >= \frac{L}{2}$, and $< p >= 0$. Moreover, $< p^2 >= 2mE_n = 2m\frac{n^2h^2}{8mL^2}$
    Thus one only needs to evaluate x^2, which is

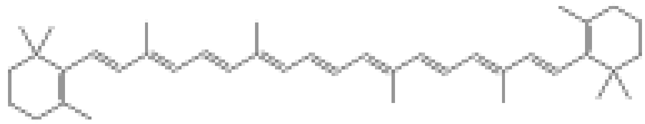
$$< x^2 >= \frac{2}{L}\int_0^L \sin\left(\frac{n\pi x}{L}\right)x^2\sin\left(\frac{n\pi x}{L}\right)dx$$
$$< x^2 >= \frac{2}{L}\left(\frac{L}{n\pi}\right)^3\left(\int_0^\pi y^2\sin^2 y dy\right),$$

    where $y = n\pi x/L$. This gives

$$< x^2 >= \left(\frac{2}{L}\right)\left(\frac{L}{n\pi}\right)^3\left(\frac{(n\pi)^3}{6} - \frac{n\pi}{4}\right) = L^2\left(\frac{1}{3} - \frac{1}{2n^2\pi^2}\right)$$
$$\Delta x = \sqrt{< x^2 > - < x >^2} = \sqrt{L^2\left(\frac{1}{3} - \frac{1}{2n^2\pi^2}\right) - \left(\frac{L}{2}\right)^2} = \frac{L}{2n\pi}\sqrt{\left(\frac{n^2\pi^2}{3} - 2\right)}$$
$$\Delta p = \sqrt{< p^2 >} = \hbar\left(\frac{n\pi}{L}\right)$$
$$\Delta x\Delta p = 1.136\left(\frac{\hbar}{2}\right) \geq \left(\frac{\hbar}{2}\right)$$

15. Describe the color of carrots using the particle in a box model. (Hint: Consider the π electrons to be confined to a box whose length is the length of the molecule. Use 1.54 Å as a C−C and 1.35 Å as a C=C bond length.)

The molecule that is present in carrots is β-carotene, a conjugated polyene, with the structure



Each carbon in this conjugated alkene has one π electron. Because of resonance the 22 π-electrons are free to move over the part of the molecule that is conjugated. The length of the σ framework that makes up the conjugated portion is $L = 10 \times 1.54 + 11 \times 1.35 = 30.25 =$Å. That is, the 22 electrons move in a box of length $L = 30.25$Å. According to the Pauli principle, each energy state can take two electrons. As a result, the lowest 11 states $(E_1, E_2, \cdots E_{11})$ contain two electrons each - the highest occupied state is E_{11} and the lowest unoccupied state is E_{12}. When light falls on the molecule, the lowest energy transition would excite an electron from E_{11} to E_{12}. The wavelength of the radiation corresponding to this transition is

$$\lambda = \frac{E_{12} - E_{11}}{hc} = \frac{h}{8m_e L^2 c}(144 - 121).$$

The color of carrots is complementary to the wavelength that is absorbed by β-carotene.

16. A particle is confined to a two dimensional square box of length L. What are the allowed energy levels?

The Schrödinger equation for a particle confined to a two-dimensional box of length L is

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)\psi(x,y) = E\psi(x,y)$$

The solutions can be shown to be

$$\psi(x,y) = \psi(x)\psi(y) = \sqrt{\frac{2}{L}}\sin\left(\frac{n_x \pi x}{L}\right)\sqrt{\frac{2}{L}}\sin\left(\frac{n_y \pi y}{L}\right),$$

with $n_x = 1, 2, \cdots$ and $n_y = 1, 2, \cdots$. The allowed values of the energy are

$$E = E_x + E_y = \frac{h^2}{8mL^2}\left(n_x^2 + n_y^2\right).$$

17. Below are some general statements about wave functions for stationary states of unique energy for a particle bound in a one-dimensional potential well $V(x)$. Decide whether each statement is true or false. Name one or more counterexamples for false statements. Be careful: except where noted, these are meant to be general statements, true, for example, even if there is a classically forbidden region *inside* the well. The phrase "outside the well" for any given energy E means a continuous classically forbidden region ($E < V(x)$) extending to infinity.

   (a) There are no nodes in the wave function outside the well.
   Almost true, but not always. For example, consider a finite well (V_0) and a state with energy $E > 0$ - a state that is not "bound." The wave function in this instance does have nodes.

   (b) There are no nodes in classically forbidden regions.
   True.

   (c) If the potential has only one relative minimum, the ground state probability function $|\psi|^2$ has only one maximum.
   True.

   (d) The ground state probability function has no nodes.
   True.

   (e) The ground state probability function has only one maximum. Not true. If the potential has two minima (for example, umbrella inversion in ammonia), the wave function and hence the probability would have two maxima.

   (f) The probability function for any state is greater at positions of higher potential than at positions of lower potential.
   False. Classically you expect this to be true because the kinetic energy is low (and the particle spends more time in regions of low KE) when the potential energy is high. This is true for states where the quantum-classical correspondence is good (states with high energy) but not true for low-lying states. The harmonic oscillator in the ground state has its highest probability where the potential energy is lowest!

(g) The probability function in a classically forbidden region is greater at positions of higher potential than at positions of lower potential.
False. It is the reverse. The probability function in a classically forbidden region is GREATER at positions of LOWER potential than at positions of higher potential.

(h) For a given region outside the well, the probability function is smaller as one goes farther from the well.
True. As you move away from the well, the probability drops off exponentially.