Problem Set 2
CHM102A

1. Considering nonrelativistic conditions (which is what this course is confined to), if a free electron has wave function $\psi(x,t) = sin(kx - \omega t)$, determine its de Broglie wavelength, momentum, kinetic energy and speed when k = 50 nm^{-1}.

   The equations relating the speed v, momentum p, de Broglie wavelength λ, wave number k, and kinetic energy E, for a nonrelativistic particle of mass m are:

$$p = mv = \frac{h}{\lambda} = \hbar k$$
$$E = \frac{1}{2}mv^2 = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} = \hbar\omega$$

   So, when k = 50 nm^{-1},
   λ = 126 × 10^{-12} m = 126 pm; p = 5.25 × 10^{-24} kgms^{-1}

   and, for an electron (m = 9.1 × 10^{-31} kg), E = 1.52 × 10^{-17} J = 95.2 eV; v = 5.77 × 10^{6} ms^{-1}

2. A particle is in the nth Energy state $\psi_n(x)$ of an infinite square well potential with width a. Determine the probability $P_n\left(\frac{1}{a}\right)$ that the particle is confined to the first $\left(\frac{1}{a}\right)$ of the width of the well. Comment on the n-dependence of $P_n\left(\frac{1}{a}\right)$.

   The wave function $\psi_n(x)$ for a particle in the nth energy state in an infinite square box with walls at x = 0 and x = a is

   $\psi_n(x) = \sqrt{\frac{2}{a}} sin\left(\frac{n\pi x}{a}\right)$

   The probability $P_n\left(\frac{1}{a}\right) = \int_0^{a/2} |\psi_n(x)|^2 dx = \frac{2}{a}\int_0^{a/2} sin^2\left(\frac{n\pi x}{a}\right) dx = \frac{1}{a} - \frac{sin\left(2n\pi/_a\right)}{2n\pi}$

   $P_n\left(\frac{1}{a}\right)$ is the probability that the particle in the state $\psi_n(x)$ is confined to the first $1/_a$ of the width of the well. The sinusoidal n-dependence term decreases as n increases and vanishes in the limit of large n:

$$P_n\left(\frac{1}{a}\right) \to \frac{1}{a} \text{ as } n \to \infty.$$

   $P_n\left(\frac{1}{a}\right) = \frac{1}{a}$ is the classical result. This analysis is consistent with the "correspondence principle", which may be stated as quantum mechanics → classical mechanics as $n \to \infty$.

3. A particle is in a state described by a wavefunction:

$$\psi(x) = \cos\theta\, e^{ikx} + \sin\theta\, e^{-ikx}$$

with θ being a constant. What is the probability that the particle will be found with linear momentum $+k\hbar$? If it is only 25 percent certain that the particle has linear momentum $+k\hbar$, then what is the value of θ?

We are given that a particle is in state:

$\psi(x) = \cos\theta . e^{ikx} + \sin\theta . e^{-ikx}$; θ is a constant.

Use the eigenvalue eigenfunction equation $\hat{p}_x \psi = (p_x)\psi, where\ \hat{p}_x = -i\hbar \frac{d}{dx}\ and\quad i = \sqrt{-1}$

So, $\hat{p}_x e^{ikx} = (+\hbar k)e^{ikx} \Rightarrow$ momentum eigenstate; value $+\hbar k$

$\hat{p}_x e^{-ikx} = (-\hbar k)e^{-ikx} \Rightarrow$ momentum eigenstate; value $-\hbar k$

$\therefore$ Probability of being found with linear momentum $+\hbar k = \cos^2\theta$

If 25% certain that particle has momentum $+\hbar k$

$\Rightarrow \quad \cos^2\theta = 0.25 \qquad \therefore\ \theta = \frac{\pi}{3}$

4. An electron in a one-dimensional box undergoes a transition from the n=3 level to the n=6 level by absorbing a photon of wavelength 500 nm. What is the width (L) of the box? Will the solution to the problem change if the electron is confined between $-\frac{L}{2}$ and $\frac{L}{2}$ instead of it being confined between 0 and L?

Energy of the absorbed photon of wavelength 500 nm is :

$$E = \frac{hc}{\lambda} = \frac{(6.626\times10^{-34}\,Js)(2.9979\times10^{8}\,ms^{-1})}{500\times10^{-9}\,m} = 3.973\times10^{-19}\,J$$

Now, for the energy states of a particle in a 1D box, we can write:

$$E_6 - E_3 = \Delta E = \frac{h^2}{8m_eL^2}(6^2-3^2) = \frac{27h^2}{8m_eL^2} = 3.973\times10^{-19}\,J$$

$\therefore$ The length of the box is:

$$L = \sqrt{\frac{27h^2}{8m_e\Delta E}} = \sqrt{\frac{27(6.626\times10^{-34}\,Js)^2}{8(9.109\times10^{-31}\,kg)(3.973\times10^{-19}\,J)}} = 2.02\times10^{-9}\,m = 2.02\,nm$$

No, the solution to this problem will not change if the electron is confined between $-\frac{L}{2}$ and $\frac{L}{2}$ instead of it being confined between 0 and L. This is because the energy is only related to the length of the box and not the exact location. However, the wavefunctions associated would undergo a phase shift.

5. Simplify the operator: $\hat{O} = \left(\frac{d}{dx} - x\right)\left(\frac{d}{dx} + x\right) - \left(\frac{d}{dx} + x\right)\left(\frac{d}{dx} - x\right)$.

The first term is:

$$\left(\frac{d}{dx} - x\right)\left(\frac{d}{dx} + x\right) f(x) = \frac{d^2y}{dx^2} + \frac{d}{dx}xf - x\frac{df}{dx} - x^2 f \qquad \text{(A)}$$

Similarly, the second term is:

$$\left(\frac{d}{dx} + x\right)\left(\frac{d}{dx} - x\right) f(x) = \frac{d^2y}{dx^2} - \frac{d}{dx}xf + x\frac{df}{dx} - x^2 f \qquad \text{(B)}$$

Thus, the operator can be arrived as (A) – (B), which is:

$$\hat{O}f(x) = 2\left(\frac{d}{dx}xf + x\frac{df}{dx}\right) = 2\left(f + x\frac{df}{dx} - x\frac{df}{dx}\right) = 2f(x)$$

Thus, the operator is 2 (i.e. multiplication by 2).