CHM 3411 – Problem Set 3

Due date: Wednesday, January 30th

Do all of the following problems. Show your work.

1) Two of the normalized solutions to the particle in a box problem discussed in class are

$$\psi_2(x) = (2/L)^{1/2} \sin(2\pi x/L) \tag{1.1}$$

$$\psi_3(x) = (2/L)^{1/2} \sin(3\pi x/L) \tag{1.2}$$

inside the box, and zero outside the box ($x < 0$ or $x > L$).

a) Show that $\psi_2(x)$ is normalized.

b) Show that $\psi_3(x)$ is orthogonal to $\psi_2(x)$.

c) Find the value for the probability of being between 040 L and 0.60 L for a particle in the n = 2 state of a particle in a box.

d) Find the value for $\langle p \rangle$ and $\langle p^2 \rangle$ for a particle in the n = 2 state of a particle in a box.

e) Using the expression for uncertainty

$$\Delta p = [\ \langle p^2 \rangle - \langle p \rangle^2\ ]^{1/2} \tag{1.3}$$

and your answers in d find the value for Δp for a particle in the n = 2 state of the particle in a box.

2) Consider the function

$$f(x) = \exp(ikx) \quad 0 < x < L \tag{2.1}$$

$$f(x) = 0 \quad x < 0 \text{ or } x > L \tag{2.2}$$

as a possible solution to the particle in a box system discussed in class.

a) Is f(x) an eigenfunction of the Hamiltonian operator for the particle in a box? If your answer is yes, what is the corresponding eigenvalue?

b) Is f(x) an acceptable wavefunction for the particle in a box? Why or why not?

3) Let ψ_1 and ψ_2 be solutions to a particular TISE

$$\hat{H}\ \psi_1 = E_1\ \psi_1 \tag{3.1}$$

$$\hat{H}\ \psi_2 = E\ \psi_2 \tag{3.2}$$

a) Show that the function

$$\phi = a\ \psi_1 + b\ \psi_2 \tag{3.3}$$

where a and b are constants is also a solution to the same TISE <u>if and only if</u> $E_1 = E_2$.

b) Assume that ψ_1 and ψ_2 are normalized functions. What is the requirement for the constants a and b that will make ϕ a normalized function?

4) The fundamental vibrational frequency for the cyanide radical CN is $\omega = 2068.7\ cm^{-1}$. Based on this, find the value for k, the force constant for the bond in the CN radical (note that a large value for k implies a strong chemical bond). The masses for the atoms involved are $m(^{12}C) = 12.0000$ amu and $m(^{14}N) = 14.0031$ amu.

Solutions.

1) a) The normalization integral is

$\int_0^L \psi_2(x)\, \psi_2(x)\, dx = \int_0^L [(2/L)^{1/2} \sin(2\pi x/L)]\, [(2/L)^{1/2} \sin(2\pi x/L)]\, dx$

$= (2/L) \int_0^L [\sin(2\pi x/L)]^2\, dx$

The general form for this integral is

$\int [\sin(ax)]^2\, dx = x/2 - (1/4a) \sin(2ax)$

So, if we set $a = 2\pi/L$, we get

$= (2/L) \{ (x/2) – (L/8\pi) \sin(4\pi x/L) \}_0^L$

$= (2/L) \{ [(L/2) – (L/8\pi) \sin(4\pi)] – [0 – (L/8\pi) \sin(0)] \}$

Since $\sin(4\pi) = \sin(0) = 0$, this gives

$= (2/L) (L/2) = 1$

So the n = 2 solution is normalized.

b) To test whether the n = 2 and n = 3 solutions are orthogonal, we need to carry out the following integral

$\int_0^L \psi_2(x)\, \psi_3(x)\, dx = \int_0^L [(2/L)^{1/2} \sin(2\pi x/L)]\, [(2/L)^{1/2} \sin(3\pi x/L)]\, dx$

$= (2/L) \int_0^L [\sin(2\pi x/L) \sin(3\pi x/L)]\, dx$

We need the following general integral

$$\int \sin(mx) \sin(nx)\, dx = \frac{\sin(m-n)x}{2(m-n)} - \frac{\sin(m+n)x}{2(m+n)} \qquad m^2 \neq n^2$$

Let $m = 2\pi/L$ and $n = 3\pi/L$, then

$$= (2/L) \left\{ \frac{\sin(-\pi x/L)}{(-2\pi/L)} - \frac{\sin(5\pi x/L)}{(10\pi/L)} \right\}_0^L$$

$= 0$, (since $\sin(-\pi) = \sin(5\pi) = \sin(0) = 0$)

c) To find the probability of being between two values of x, we need to do the following integral

$P (0.4\, L < x < 0.6\, L) = \int_{0.4L}^{0.6L} \psi_2(x)\, \psi_2(x)\, dx = \int_{0.4L}^{0.6L} [(2/L)^{1/2} \sin(2\pi x/L)]\, [(2/L)^{1/2} \sin(2\pi x/L)]\, dx$

$= (2/L) \int_{0.4L}^{0.6L} [\sin(2\pi x/L)]^2\, dx$

This is the same general integral used in part a of this problem. So

$\int [\sin(ax)]^2\, dx = x/2 - (1/4a) \sin(2ax)$

So, if we set $a = 2\pi/L$, we get

$$= (2/L) \{ (x/2) - (L/8\pi) \sin(4\pi x/L) \}_{0.4L}^{0.6L}$$

$$= (2/L) \{ [(0.6L/2) - (L/8\pi) \sin(2.4\pi)] - [(0.4L/2) - (L/8\pi) \sin(1.6\pi)] \}$$

$$= 2 \{ 0.2622 - 0.2378 \} = 0.0488$$

This is smaller than one would expect classically (P = 0.20), because the region being looked at is near the central node of the wavefunction.

d) $\langle p \rangle = \int_0^L \psi_2(x)\, (- i\hbar\, d/dx)\, \psi_2(x)\, dx = \int_0^L [(2/L)^{1/2} \sin(2\pi x/L)]\, (- i\hbar\, d/dx)\, [(2/L)^{1/2} \sin(2\pi x/L)]\, dx$

$$= (- i\hbar)\, (2/L)\, (2\pi/L) \int_0^L \sin(2\pi x/L) \cos(2\pi x/L)]\, dx$$

The general form for this integral is

$$\int \sin(ax) \cos(ax)\, dx = (1/2a)\, (\sin(ax))^2$$

So if we set $a = 2\pi/L$, we get

$$= (- i\hbar)\, (2/L)\, (2\pi/L)\, \{ (L/4\pi)\, ((\sin(2\pi x/L)^2 \}_0^L = 0 \quad (\text{since } \sin(2\pi) = \sin(0) = 0\ )$$

So $\langle p \rangle = 0$

$$\langle p^2 \rangle = \int_0^L \psi_2(x)\, (- \hbar^2\, d^2/dx^2)\, \psi_2(x)\, dx = \int_0^L [(2/L)^{1/2} \sin(2\pi x/L)]\, (- \hbar^2\, d^2/dx^2)\, [(2/L)^{1/2} \sin(2\pi x/L)]\, dx$$

$$= (- \hbar^2)\, (2/L)\, (2\pi/L)^2\, (-1) \int_0^L [\sin(2\pi x/L)]^2\, dx$$

But we know from part a of this problem that $(2/L) \int_0^L [\sin(2\pi x/L)]^2\, dx$. Therefore

$$\langle p^2 \rangle = \frac{4\pi^2\hbar^2}{L^2} = \frac{h^2}{L^2} \quad (\text{since } \hbar = h/2\pi)$$

e) $\Delta p = [\langle p^2 \rangle - \langle p \rangle^2]^{1/2} = [(h^2/L^2) - (0)2]^{1/2} = h/L$

2) a) To test if a function is an eigenfunction of an operator, we see if the function satisfies the eigenvalue equation

$\hat{O}\, f(x) = c\, f(x)$, where c is a constant

The Hamiltonian operator for the particle in a box, inside the box, is $\hat{H} = (- \hbar^2/2m\, d^2/dx^2)$

So $\hat{H}\, f(x) = (- \hbar^2/2m\, d^2/dx^2)\, \exp(ikx) = (- \hbar^2/2m)\, (ik)^2 \exp(ikx)$

And so $f(x) = \exp(ikx)$ is an eigenfunction, with eigenvalue $(- \hbar^2/2m)\, (ik)^2 = \hbar^2 k^2/2m$

b) No, this is not an acceptable wavefunction for the particle in a box, because it is not continuous at x = 0 and x = L. For example, at x = 0, f(x) = exp(0) = 1, but outside the box f(x) = 0, so there is a discontinuity at x = 0.

3) a) To test whether a function is an eigenfunction of $\hat{H}$ we substitute into the eigenvalue equation (see problem 2). So

$$\hat{H}\,\phi = \hat{H}\,(a\,\psi_1 + b\,\psi_2) = a\,\hat{H}\,\psi_1 + b\,\hat{H}\,\psi_2$$

Since $\hat{H}\,\psi_1 = E_1\,\psi_1$ and $\hat{H}\,\psi_2 = E_2\,\psi_2$ then

$$= a\,E_1\,\psi_1 + b\,E_2\,\psi_2 = E_1\,(a\,\psi_1 + b\,\psi_2) + (E_2 - E_1)\,b\,\psi_2$$

This would satisfy the eigenvalue equation if the second term above dropped out, which will only happen if $E_1 = E_2$. We have therefore showed that ϕ is an eigenfunction of $\hat{H}$ if and only if $E_1 = E_2$.

b) Normalization means

$$1 = \int_{-\infty}^{\infty} \phi^*\,\phi\,dx = \int_{-\infty}^{\infty} (a\,\psi_1 + b\,\psi_2)^*\,(a\,\psi_1 + b\,\psi_2)\,dx$$

$$= a^2 \int_{-\infty}^{\infty} \psi_1^*\psi_1\,dx + ab \int_{-\infty}^{\infty} \psi_1^*\psi_2\,dx + ab \int_{-\infty}^{\infty} \psi_2^*\psi_1\,dx + b^2 \int_{-\infty}^{\infty} \psi_2^*\psi_2\,dx$$

Since ψ_1 and ψ_2 are orthonormal functions, the above is

$$1 = a^2 + 0 + 0 + b^2 = a^2 + b^2$$

4) Since $\omega = (1/2\pi c)\,(k/\mu)^{1/2}$, then

$$\omega^2 = (1/2\pi c)^2\,(k/\mu)$$

or $\quad k = 4\pi^2 c^2 \omega^2 \mu$

It is usually a good idea to enter values into equations in MKS units.

$c = 2.998 \times 10^8$ m/s $\qquad \omega = 2068.7\ \text{cm}^{-1}\ (100\ \text{cm/m}) = 2.0687 \times 10^5\ \text{m}^{-1}$

$$\mu = \frac{m_C m_N}{(m_C + m_N)} = \frac{(12.0000\ \text{amu})\ (14.0031\ \text{amu})}{(12.0000 + 14.0031)\ \text{amu}} = 6.4622\ \text{amu}\ \ \frac{1\ \text{kg}}{6.022 \times 10^{26}\ \text{amu}} = 1.073 \times 10^{-26}\ \text{kg}$$

And so $\quad k = 4\pi^2(2.998 \times 10^8\ \text{m/s})^2(2.0687 \times 10^5\ \text{m}^{-1})^2(1.073 \times 10^{-26}\ \text{kg})$

$$= 1629.\ \text{kg/s}^2 = 1629.\ \text{N/m}\ \ (\text{since } 1\ \text{N} = 1\ \text{kg}\cdot\text{m/s}^2)$$

While both sets of units are correct, I prefer N/m as that corresponds to how I think about a force constant.