Chemistry 1410; HW # 3
Q4.6, Q4.7, P4.5, P4.10, P4.25, P5.4, P5.5 and one additional problem:

What is the probability of a particle in a 1D box of length *a*, to be found between $x = 0$ and $a/3$ in the case of (a) the ground state and (b) the first excited state?

Q4.6

The nodes in traveling waves move with time. This is incompatible with the boundary conditions for the particle in the box.

Q4.7

The zero point energy $E = n^2h^2/8ma^2$ (Eqn. 4.17) varies inversely with the mass, and the mass of a He atom is much greater than the mass of an electron.

P4.5

a) $A\cos\dfrac{n\pi x}{a}$ is not an acceptable wave function because it does not satisfy the boundary condition that $\psi(0) = 0$.

b) $B\left(x + x^2\right)$ is not an acceptable wave function because it does not satisfy the boundary condition that $\psi(a) = 0$.

c) $C\,x^3\left(x - a\right)$ is an acceptable wave function. It satisfies both boundary conditions and can be normalized.

d) $\dfrac{D}{\sin\dfrac{n\pi x}{a}}$ is notan acceptable wave function. It goes to infinity at $x = 0$ and cannot be normalized in the desired interval.

P4.10

For $n = 3$,

$$\langle p\rangle = \int_0^a \psi^*(x)\left(-i\hbar\frac{d}{dx}\right)\psi(x)\,dx = \frac{-2i\hbar}{a}\frac{3\pi}{a}\int_0^a \sin\left(\frac{3\pi x}{a}\right)\cos\left(\frac{3\pi x}{a}\right)dx$$

Using the standard integral $\int \sin(bx)\cos(bx)\,dx = \frac{\cos^2(bx)}{2b}$

$$\langle p\rangle = \frac{-2i\hbar}{a}\frac{3\pi}{a}\left[\frac{\cos^2(3\pi)}{2b} - \frac{\cos^2(0)}{2b}\right] = \frac{-2i\hbar}{a}\frac{3\pi}{a}\left[\frac{1}{2b} - \frac{1}{2b}\right] = 0$$

For $n = 5$,

$$\langle p\rangle = \int_0^a \psi^*(x)\left(-i\hbar\frac{d}{dx}\right)\psi(x)\,dx = \frac{-2i\hbar}{a}\frac{5\pi}{a}\int_0^a \sin\left(\frac{5\pi x}{a}\right)\cos\left(\frac{3\pi x}{a}\right)dx$$

Using the standard integral $\int \sin(bx)\cos(bx)\,dx = \frac{\cos^2(bx)}{2b}$

$$\langle p\rangle = \frac{-2i\hbar}{a}\frac{5\pi}{a}\left[\frac{\cos^2(5\pi)}{2b} - \frac{\cos^2(0)}{2b}\right] = \frac{-2i\hbar}{a}\frac{5\pi}{a}\left[\frac{1}{2b} - \frac{1}{2b}\right] = 0$$

This is the same result that would be obtained using classical physics. The classical particle is equally likely to be moving in the positive and negative x directions. Therefore the average of a large number of measurements of the momentum is zero for the classical particle moving in a constant potential.

P4.25

a) We first determine if the wave function is normalized.

$$\int \psi^*(x)\psi(x)\,dx = \frac{1}{4}\int \phi_1^*(x)\phi_1(x)\,dx + \frac{1}{16}\int \phi_2^*(x)\phi_2(x)\,dx + \left(\frac{3-\sqrt{2}\,i}{4}\right)\left(\frac{3+\sqrt{2}\,i}{4}\right)\int \phi_3^*(x)\phi_3(x)\,dx$$

$$+\frac{1}{4}\int \phi_1^*(x)\phi_2(x)\,dx + \frac{3+\sqrt{2}\,i}{16}\int \phi_1^*(x)\phi_3(x)\,dx + \frac{3-\sqrt{2}\,i}{16}\int \phi_3^*(x)\phi_1(x)\,dx\frac{1}{2}\phi_1(x)$$

$$+\frac{3+\sqrt{2}\,i}{8}\int \phi_2^*(x)\phi_3(x)\,dx + \frac{3-\sqrt{2}\,i}{8}\int \phi_3^*(x)\phi_2(x)\,dx$$

All but the first three integrals are zero because the functions $\phi_1(x), \phi_2(x)$, and $\phi_3(x)$ are orthogonal. The first three integrals have the value one, because the functions are normalized. Therefore,

$$\int \psi^*(x)\psi(x)\,dx = \frac{1}{4} + \frac{1}{16} + \left(\frac{3-\sqrt{2}\,i}{4}\right)\left(\frac{3+\sqrt{2}\,i}{4}\right) = \frac{1}{4} + \frac{1}{16} + \frac{11}{16} = 1$$

b) The only possible values of the observable kinetic energy that you will measure are those corresponding to the finite number of terms in the superposition wave function. In this case, the only values that you will measure are E_1, $3E_1$, and $7E_1$.

c) For a normalized superposition wave function, the probability of observing a particular eigenvalue is equal to the square of the magnitude of the coefficient of that kinetic energy eigenfunction in the superposition wave function. These coefficients have been calculated above. The probabilities of observing E_1, $3E_1$, and $7E_1$ are ¼, 1/16, and 11/16, respectively.

d) The average value of the kinetic energy is given by

$$\langle E \rangle = \sum P_i E_i = \frac{1}{4}E_1 + \frac{1}{16}3E_1 + \frac{11}{16}7E_1 = 5.25E_1$$

P5.4

The length of the box is $a = 4\times135\,\text{pm} + 3\times154\,\text{pm} = 1002\,\text{pm}$. The energy levels are given by

$E_n = \dfrac{n^2h^2}{8ma^2}$ and the transition is between $n = 4$ and $n = 5$.

$$\lambda = \frac{c}{\nu} = \frac{c}{E/h} = \frac{8ma^2c}{h\left(n_2^2 - n_1^2\right)} = \frac{8\times9.11\times10^{-31}\text{kg}\times\left(10.02\times10^{-10}\text{m}\right)^2\times2.998\times10^{8}\text{ms}^{-1}}{6.626\times10^{-34}\text{J s}\times\left(5^2-4^2\right)}$$

$$= 368\,\text{nm}$$

P5.5

For silicon, we obtain

$$T_{Si} = \frac{-\Delta E}{k \ln\left[\left(\frac{g_{valence}}{g_{conduction}}\right)\left(\frac{n_{conduction}}{n_{valence}}\right)\right]} = \frac{-1.12\text{eV}\times 1.602\times 10^{-19}\text{J/eV}}{1.381\times 10^{-23}\text{J K}^{-1}\times \ln\left(5.5\times 10^{-7}\right)} = 901\text{K}$$

For diamond, we obtain

$$T_{C} = \frac{-\Delta E}{k \ln\left[\left(\frac{g_{valence}}{g_{conduction}}\right)\left(\frac{n_{conduction}}{n_{valence}}\right)\right]} = \frac{-5.5\,\text{eV}\times 1.602\times 10^{-19}\text{J/eV}}{1.381\times 10^{-23}\text{J K}^{-1}\ln\left(5.5\times 10^{-7}\right)} = 4427\,\text{K}$$

We predict that diamond would not become conductive before it decomposes.

Additional

In a 1D system the probability *P* that a particle is between the points *b* and *c* is given by:

$$P = \int_b^c \left|\Psi\right|^2 dx$$

The normalized wave function for the PIB is given in Eqn. 4.15. For the ground state *n* = 1. Thus, for part (a), we do:

$$P = \int_0^{a/3} \left|\sqrt{\frac{2}{a}}\sin\left(\frac{\pi x}{a}\right)\right|^2 dx = \frac{2}{a}\int_0^{a/3} \sin^2\left(\frac{\pi x}{a}\right) dx$$

For the first excited state *n* = 2. Thus, for part (b), we do:

$$P = \int_0^{a/3} \left|\sqrt{\frac{2}{a}}\sin\left(\frac{2\pi x}{a}\right)\right|^2 dx = \frac{2}{a}\int_0^{a/3} \sin^2\left(\frac{2\pi x}{a}\right) dx$$

From integral tables, we can easily evaluate the above *analytically without yet another computer program that does the thinking for you*. The necessary integral is:

$$P = \int \sin^2 mx\, dx = \frac{x}{2} - \frac{\sin 2mx}{4m} + C$$

(Of course, even integral tables are cheating for the purist mathematician. Do you know how to obtain the indefinite integral cited above?) For part (a) you should get 0.1955. For part (b) you should get 0.4022. There are a few key points. Note that for part *a* the answer is ***not*** $\frac{1}{3}$. That is the classical value. The answer is *less than* $\frac{1}{3}$. When comparing the answers for part (a) and (b), note that the answer for (b) is larger than $\frac{1}{3}$ *and* larger than the answer for (a). This is the expected result if you carefully examine Figure 4.3.