Chem. 1410: Solutions for Hand-In Problems.

a) The normalization constraint is:

$$1=\int_{-\infty}^{\infty} dx\psi^*(x)\psi(x)=\frac{1}{\left[2\pi\sigma^2\right]^{1/2}}\int_{-\infty}^{\infty} dx\exp(\frac{-x^2}{2\sigma^2})$$

The integral identity given in part a)-ii) confirms that $\psi(x)$ in Eq. [1] is properly normalized.

b) [Again …] When a quantum mechanical system is prepared in a state described by wavefunction $\psi(x)$, then the expectation (average) value of an observable A is given formally by:

$$<A>=\int_{-\infty}^{\infty} dx\psi^*(x)\hat{A}\psi(x),$$

where $\hat{A}$ is the quantum mechanical operator corresponding to A. Thus, $<x>=\int_{-\infty}^{\infty} dx\psi^*(x)x\psi(x)$. Using the specific form of $\psi(x)$ in Eq. [1]:

$$<x>=\frac{1}{\left[2\pi\sigma^2\right]^{1/2}}\int_{-\infty}^{\infty} dx\exp(\frac{-x^2}{2\sigma^2})x=0 \quad ,$$

because the overall integrand is odd [why?].

Next, $<p>=\int_{-\infty}^{\infty} dx\psi^*(x)\left[\frac{\hbar}{i}\frac{\partial}{\partial x}\right]\psi(x)$. Using the specific form of $\psi(x)$ in Eq. [1], then $\partial\psi(x)/\partial x\propto x\exp(-x^2/4\sigma^2)$ [to within a constant factor]. Hence $<p>=0$, since the overall integrand is odd [why?].

c) $<x^2>=\int_{-\infty}^{\infty} dx\psi^*(x)x^2\psi(x)$. Using the specific form of $\psi(x)$ in Eq. [1], then

$$<x^2>=\frac{1}{\left[2\pi\sigma^2\right]^{1/2}}\int_{-\infty}^{\infty} dx\exp(\frac{-x^2}{2\sigma^2})x^2=\sigma^2 \quad ,$$

where the explicit evaluation of the integral is given in the statement of the problem.

d) For this $\psi(x)$:

$$< p^2 >= \frac{1}{\sqrt{2\pi\sigma^2}} \int_{-\infty}^{\infty} dx e^{-x^2/4\sigma^2} \left[-\hbar^2 \frac{\partial^2}{\partial x^2} \right] e^{-x^2/4\sigma^2}$$

Note:

$$\frac{\partial^2 e^{-ax^2}}{\partial x^2} = \left[(2ax)^2 - 2a \right] e^{-ax^2}$$

Thus:

$$< p^2 >= \frac{\hbar^2}{\sqrt{2\pi\sigma^2}} \int_{-\infty}^{\infty} dx e^{-x^2/2\sigma^2} \left[2\left(\frac{1}{4\sigma^2}\right) - 4\left(\frac{1}{4\sigma^2}\right)^2 x^2 \right] = \frac{\hbar^2}{4\sigma^2} \qquad \textbf{(A1)}$$

Hence, $\alpha = 1/4$.

Note: the final equality on the r.h.s.of Eq. (A1) is achieved by appealing to the generic integrals provided in parts a) and c) above.

e) Since $< x >= 0$, then $\delta x = \sqrt{< x^2 >}$, and analogously for δp. Using the results from parts c) and d), we thus obtain:

$$\delta x \delta p = \sqrt{\alpha}\hbar = \hbar/2$$

f) The result obtained in e) is consistent with the general constraints of the Heisenberg Uncertainty Principle. In particular, any Gaussian wavefunction of the type given in Eq. [1] represents a “minimum uncertainty state”, in the sense that it is impossible to device a physically acceptable wavefunction which has a position-momentum uncertainty product less than $\hbar/2$.

2) Given that a particle is prepared in energy eigenstate *n* of a 1D box spanning the interval *[0,L]*. First, calculate the probability $P_n(l)$ to find the particle in the interval $[0,l]$, with *0<l<L*:

$$P_n(l) = \frac{2}{L}\int_0^l \sin^2(n\pi x/L)dx = \frac{l}{L} - \frac{1}{2\pi n}\sin(\frac{2\pi nl}{L})$$

[The integral above may be reduced to elementary forms using the trigonometric identity $\sin^2(z) = [1 - \cos(2z)]/2$.]

Since the probability density for a particle prepared in any energy eigenstate *n* of a 1D infinite-walled box is symmetric about the midpoint of the box (why?), then:

P_n^{MT} = Probability to find the particle in the interval *[L/3,2L/3]* (the middle third of the box) =

$$1 - 2P_n(L/3) = 1 - 2\left[\frac{1}{3} - \frac{1}{2n\pi}\sin(2n\pi/3)\right] = \frac{1}{3} + \frac{1}{n\pi}\sin(2n\pi/3)$$

for a particle prepared in energy eigenstate *n*.

Specifically, $P_1^{MT} = 0.61$, $P_3^{MT} = \frac{1}{3}$ [why?], and $P_\infty^{MT} = \frac{1}{3}$, as expected [why?].

P4.5) Explain why each of the following unnormalized functions is or is not an acceptable wave function based on criteria such as being consistent with the boundary conditions, and with the association of $\psi^*(x)\psi(x)dx$ with probability.

a) $A\cos\frac{n\pi x}{a}$ b) $B(x+x^2)$ c) $Cx^3(x-a)$ d) $\frac{D}{\sin\frac{n\pi x}{a}}$

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

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

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

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

P4.10) Are the eigenfunctions of $\hat{H}$ for the particle in the one-dimensional box also eigenfunctions of the momentum operator $\hat{p}_x$? Calculate the average value of p_x for the case $n=3$. Repeat your calculation for $n=5$ and, from these two results, suggest an expression valid for all values of n. How does your result compare with the prediction based on classical physics?

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.

P4.15)

[redacted]) What is the solution of the time-dependent Schrödinger equation $\Psi(x,t)$ for the total energy eigenfunction $\psi_4(x)=\sqrt{\frac{2}{a}}\sin\left(\frac{4\pi x}{a}\right)$ in the particle in the box model? Write $\omega=\frac{E}{\hbar}$ explicitly in terms of the parameters of the problem.

$$\psi(x,t)=\psi(x)e^{-i\omega t}=\psi(x)e^{-i\frac{Et}{\hbar}}$$

Because $E=\frac{n^2h^2}{8ma^2}=\frac{16h^2}{8ma^2}$,

$$\psi(x,t)=\sqrt{\frac{2}{a}}\sin\left(\frac{4\pi x}{a}\right)e^{-i\frac{4\pi ht}{ma^2}}$$

P4.17)

[redacted]) Normalize the total energy eigenfunction for the rectangular two-dimensional box,

$$\psi_{n_x,n_y}(x,y)=N\sin\left(\frac{n_x\pi x}{a}\right)\sin\left(\frac{n_y\pi y}{b}\right)$$

in the interval $0\le x\le a$, $0\le y\le b$.

$$1=\int_0^a\int_0^b\psi^*(x,y)\psi(x,y)\,dx\,dy=N^2\int_0^a\sin^2\left(\frac{n_x\pi x}{a}\right)dx\int_0^b\sin^2\left(\frac{n_y\pi y}{b}\right)dy$$

Using the standard integral $\int\sin^2\alpha x\,dx=\frac{x}{2}-\frac{\sin(2\alpha x)}{4\alpha}$

$$N^2\int_0^a\sin^2\left(\frac{n_x\pi x}{a}\right)dx\int_0^b\sin^2\left(\frac{n_y\pi y}{b}\right)dy$$

$$=N^2\left[\frac{a}{2}-\frac{a}{4n_x\pi}(\sin n_x\pi-\sin 0)\right]\times\left[\frac{b}{2}-\frac{a}{4n_y\pi}(\sin n_y\pi-\sin 0)\right]=N^2\frac{ab}{4}$$

$$N=\sqrt{\frac{4}{ab}}\text{ and }\psi(x,y)=\sqrt{\frac{4}{ab}}\sin\left(\frac{n_x\pi x}{a}\right)\sin\left(\frac{n_y\pi y}{b}\right)$$

P4.23)

[redacted]) Generally, the quantization of translational motion is not significant for atoms because of their mass. However, this conclusion depends on the dimensions of the space to which they are confined. Zeolites are structures with small pores that we describe by a cube with edge length 1 nm. Calculate the energy of a H_2 molecule with $n_x=n_y=n_z=10$. Compare this energy to kT at $T=300$ K. Is a classical or a quantum description appropriate?

$$E_{n_x,n_y,n_z}=\frac{h^2}{8ma^2}\left(n_x^2+n_y^2+n_z^2\right)$$

$$=\frac{\left(6.626\times10^{-34}\text{J s}\right)^2\left(10^2+10^2+10^2\right)}{8\times2.016\,\text{amu}\times1.661\times10^{-27}\text{kg(amu)}^{-1}\times\left(10^{-9}\text{m}\right)^2}=4.92\times10^{-21}\text{J}$$

Using the results of P15.22, the ratio of the energy spacing between levels and kT determines if a classical or quantum description is appropriate.

$$E_{\alpha+1} - E_\alpha = \frac{h^2}{8ma^2}\left([\alpha+1]^2 - \alpha^2\right) = \frac{h^2(2\alpha+1)}{8ma^2} \text{ where } \alpha = \sqrt{\left(n_x^2 + n_y^2 + n_z^2\right)}$$

$$= \frac{\left(6.626\times10^{-34}\text{Js}\right)^2\left(\sqrt{300}+1\right)}{8\times2.016\,\text{amu}\times1.661\times10^{-27}\text{kg(amu)}^{-1}\times\left(10^{-9}\text{ m}\right)^2} = 3.00\times10^{-22}\text{J}$$

$$\frac{E_{\alpha+1} - E_\alpha}{kT} = \frac{3.00\times10^{-22}\text{J}}{1.361\times10^{-23}\text{J K}^{-1}\times298\text{ K}} = 0.073$$

Because this ratio is not much smaller than one, a quantum description is appropriate.

(3) Engel, P4.25)

Suppose that the wave function for a system can be written as $\psi(x) = \frac{1}{2}\phi_1(x) + \frac{1}{4}\phi_2(x) + \frac{3+\sqrt{2}i}{4}\phi_3(x)$ and that $\phi_1(x), \phi_2(x)$ and $\phi_3(x)$ are normalized eigenfunctions of the operator $\hat{E}_{kinetic}$ with eigenvalues E_1, $3E_1$, and $7E_1$, respectively.

a) Verify that $\psi(x)$ is normalized.

b) What are the possible values that you could obtain in measuring the kinetic energy on identically prepared systems?

c) What is the probability of measuring each of these eigenvalues?

d) What is the average value of $E_{kinetic}$ that you would obtain from a large number of measurements?

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

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