Problem Set 3

P15.1) This problem explores under what conditions the classical limit is reached for a macroscopic cubic box of edge length *a*. An argon atom of average translational energy 3/2 *kT* is confined in a cubic box of volume $V = 0.500\ \text{m}^3$ at 298 K. Use the result from Equation (15.25) for the dependence of the energy levels on *a* and on the quantum numbers n_x, n_y, and n_z.

a. What is the value of the "reduced quantum number" $\alpha = \sqrt{n_x^2 + n_y^2 + n_z^2}$ for $T = 298$ K?

b. What is the energy separation between the levels α and $\alpha + 1$? (*Hint*: Subtract $E_{\alpha+1}$ from E_α *before* plugging in numbers.)

c. Calculate the ratio $(E_{\alpha+1} - E_\alpha)/kT$ and use your result to conclude whether a classical or quantum mechanical description is appropriate for the particle.

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

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

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

$$\alpha = \sqrt{\frac{8 \times 39.95\ \text{amu} \times 1.661\text{x}10^{-27}\ \text{kg (amu)}^{-1} \times \left(0.500\ \text{m}^3\right)^{2/3} \times 1.5 \times 1.381 \times 10^{-23}\ \text{J K}^{-1} \times 298\ \text{K}}{\left(6.626 \times 10^{-34}\ \text{J s}\right)^2}}$$

$$\alpha = 6.86 \times 10^{10}$$

b) What is the energy separation between the levels α and $\alpha + 1$? (Hint: Subtract $E_{\alpha+1}$ from E_α *before* plugging in numbers.

$$E_{\alpha+1} - E_\alpha = \frac{h^2}{8ma^2}\left([\alpha+1]^2 - \alpha^2\right) = \frac{h^2(2\alpha+1)}{8ma^2}$$

$$= \frac{\left(6.626\times10^{-34}\text{ J s}\right)^2\left(2\times6.86\times10^{10}+1\right)}{8\times39.95\text{amu}\times1.661\times10^{-27}\text{kg (amu)}^{-1}\times\left(0.500\text{m}^3\right)^{2/3}} = 1.80\times10^{-31}\text{ J}$$

c) Calculate the ratio $\frac{E_{\alpha+1} - E_\alpha}{kT}$ and use your result to conclude whether a classical or quantum mechanical description is appropriate for the particle.

$$\frac{E_{\alpha+1} - E_\alpha}{kT} = \frac{1.80\times10^{-31}\text{ J}}{1.361\times10^{-23}\text{ J K}^{-1}\times298\text{ K}} = 4.44\times10^{-11}$$

Because $\Delta E << kT$, a classical description is appropriate.

P15.5) 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 $7E_1$ are1/4, 1/16, and 11/16, respectively.

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

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

P15.9) The function $\psi(x) = A(x/a)^2[1-(x/a)]$ is an acceptable wave function for the particle in the one-dimensional infinite depth box of length a. Calculate the normalization constant A and the expectation values $\langle x\rangle$ and $\langle x^2\rangle$.

$$1 = A^2\int_0^a\left[\left(\frac{x}{a}\right)^2\left(1-\frac{x}{a}\right)\right]^2 dx = \frac{A^2}{a^4}\int_0^a\left[\frac{x^6}{a^2}-2\frac{x^5}{a}+x^4\right]dx$$

$$1 = \frac{A^2}{a^4}\left[\frac{x^7}{7a^2}-\frac{x^6}{3a}+\frac{x^5}{5}\right]_0^a = \frac{A^2}{a^4}\left[\frac{a^5}{7}-\frac{a^5}{3}+\frac{a^5}{5}\right]_0^a = \frac{A^2}{a^4}\frac{a^5}{105}$$

$$A = \sqrt{\frac{105}{a}}$$

$$\langle x\rangle = \int_0^a \psi^*(x)x\psi(x)dx = \frac{105}{a}\int_0^a x\left[\left(\frac{x}{a}\right)^2\left(1-\frac{x}{a}\right)\right]^2 dx = \frac{105}{a^5}\int_0^a\left[\frac{x^7}{a^2}-2\frac{x^6}{a}+x^5\right]dx$$

$$= \frac{105}{a^5}\left[\frac{x^8}{8a^2}-\frac{2}{7}\frac{x^7}{a}+\frac{x^6}{6}\right]_0^a = \frac{105}{a^5}\left[\frac{a^6}{8}-\frac{2a^6}{7}+\frac{a^6}{6}\right] = \frac{105}{a^5}\frac{a^6}{168} = \frac{5a}{8}$$

$$\langle x^2\rangle = \int_0^a \psi^*(x)x^2\psi(x)dx = \frac{105}{a^5}\int_0^a\left[\frac{x^8}{a^2}-2\frac{x^7}{a}+x^6\right]dx$$

$$= \frac{105}{a^5}\left[\frac{x^9}{9a^2}-\frac{x^8}{4a}+\frac{x^7}{7}\right]_0^a = \frac{105}{a^5}\left[\frac{a^7}{9}-\frac{a^7}{4}+\frac{a^7}{7}\right] = \frac{105}{a^5}\frac{a^7}{252} = \frac{5a^2}{12}$$

P15.11) Derive an equation for the probability that a particle characterized by the quantum number n is in the first quarter $(0 \le x \le a/4)$ of an infinite depth box. Show that this probability approaches the classical limit as $n \to \infty$.

Using the standard integral $\int \sin^2(by)\,dy = \frac{y}{2} - \frac{1}{4b}\sin(2by)$

$$P = \frac{2}{a}\int_0^{0.25a}\sin^2\left(\frac{n\pi x}{a}\right)dx = \frac{2}{a}\left[\frac{x}{2}-\frac{a}{4n\pi}\sin\left(\frac{2n\pi x}{a}\right)\right]_0^{0.25a}$$

$$= \frac{2}{a}\left[0.125\,a - \frac{a}{4n\pi}\sin\left(\frac{n\pi}{2}\right)-\frac{0}{2}+\frac{a}{4n\pi}\sin(0)\right] = 0.25 - \frac{1}{2n\pi}\sin\left(\frac{n\pi}{2}\right)$$

As $n \to \infty$, the second term goes to zero, and the probability approaches 0.25.

This is the classical value, because the particle is equally likely to be found anywhere in the box.

P15.12) It is useful to consider the result for the energy eigenvalues for the one-dimensional box $E_n = h^2n^2/8ma^2$, $n = 1,2,3,\ldots$ as a function of n, m, and a.

a. By what factor do you need to change the box length to decrease the zero point energy by a factor of 275 for a fixed value of m?

b. By what factor would you have to change n for fixed values of a and m to increase the energy by a factor of 600?

c. By what factor would you have to change a at constant n to have the zero point energies of a He atom be equal to the zero point energy of a proton in the box?

a) $\frac{E_n}{E_{n'}} = \frac{(a')^2}{a^2} = 275; \quad \frac{a'}{a} = 16.6$

b) $\frac{E_n}{E_{n'}} = \frac{n^2}{(n')^2} = 600.; \quad \frac{n}{n'} = 24.5$

c)

$$\frac{1}{m_{He}\,a_{He}^2} = \frac{1}{m_p\,a_p^2}$$

$$\frac{a_{He}}{a_p} = \sqrt{\frac{m_p}{m_{He}}} = \sqrt{\frac{1.673\times10^{-27}\text{ kg}}{4.003\times1.661\times10^{-27}\text{ kg}}} = 0.502$$

P15.14)

a. Show by substitution into Equation (15.19) that the eigenfunctions of $\hat{H}$ for a box with lengths along the *x*, *y*, and *z* directions of *a*, *b*, and *c*, respectively, are

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

b. Obtain an expression for E_{n_x,n_y,n_z} in terms of n_x, n_y, n_z, and *a*, *b*, and *c*.

$$-\frac{\hbar^2 N}{2m}\left(\begin{array}{l}\sin\left(\frac{n_y\pi y}{b}\right)\sin\left(\frac{n_z\pi z}{c}\right)\frac{\partial^2}{\partial x^2}\sin\left(\frac{n_x\pi x}{a}\right)+\sin\left(\frac{n_x\pi x}{a}\right)\sin\left(\frac{n_z\pi z}{c}\right)\frac{\partial^2}{\partial y^2}\sin\left(\frac{n_y\pi y}{b}\right)\\ +\sin\left(\frac{n_x\pi x}{a}\right)\sin\left(\frac{n_y\pi y}{b}\right)\frac{\partial^2}{\partial z^2}\sin\left(\frac{n_z\pi z}{c}\right)\end{array}\right)$$

$$=\frac{\hbar^2 N\pi^2}{2m}\left(\frac{n_x^2}{a^2}+\frac{n_y^2}{b^2}+\frac{n_z^2}{c^2}\right)\sin\left(\frac{n_x\pi x}{a}\right)\sin\left(\frac{n_y\pi y}{b}\right)\sin\left(\frac{n_z\pi z}{c}\right)$$

$$=E\left(n_x,n_y,n_z\right)N\sin\left(\frac{n_x\pi x}{a}\right)\sin\left(\frac{n_y\pi y}{b}\right)\sin\left(\frac{n_z\pi z}{c}\right) \text{ where}$$

$$E\left(n_x,n_y,n_z\right)=\frac{h^2}{8m}\left(\frac{n_x^2}{a^2}+\frac{n_y^2}{b^2}+\frac{n_z^2}{c^2}\right)$$

P15.18) 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.

P15.22) 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 P15.1, the ratio of the energy spacing between levels and kT determines if a classical or quantum description is appropriate.

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

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

$$\frac{E_{\alpha+1}-E_\alpha}{kT} = \frac{3.00\times10^{-22}\text{ J}}{1.361\times10^{-23}\text{ J K}^{-1}\times300.\text{ K}} = 0.073$$

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

P15.32) Consider a particle in a one-dimensional box defined by $V(x)=0,\ a > x > 0$ and $V(x)=\infty,\ x \ge a,\ x \le 0$. 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. $\frac{D}{\sin(n\pi x/a)}$

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) $B\left(x+x^2\right)$ 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 not an acceptable wave function. It goes to infinity at $x = 0$ and cannot be normalized in the desired interval.