Solution to Problem Set 3

1. L = 5 nm ;

A. $E_{n_x n_y n_z} = \frac{h^2}{8mL^2}\left[n_x^2 + n_y^2 + n_z^2\right]$

i. $\frac{h^2}{8mL^2} = \frac{(6.626*10^{-34})^2}{8*9.1*10^{-31}*(5*10^{-9})^2} = 2.4123*10^{-21}$

$E_{111} = 2.4123*10^{-21}*3 = 7.24*10^{-21}\,J$

Degenearcy = 1

ii. $E_{211} = E_{121} = E_{112} = 2.4123*10^{-21}*6 = 1.45*10^{-20}\,J$

Degeneracy = 3

iii. $E_{122} = E_{212} = E_{221} = 2.4123*10^{-21}*9 = 2.17*10^{-20}\,J$

Degenearcy = 3

iv. $E_{113} = E_{131} = E_{311} = 2.4123*10^{-21}*11 = 2.65*10^{-20}\,J$

Degeneracy = 3

B. $\frac{hc}{\lambda} = E_2 - E_1 \Rightarrow \lambda = \frac{hc}{E_2 - E_1}$

i. $\lambda_1 = \frac{6.626*10^{-34}*3*10^8}{1.45*10^{-20} - 7.24*10^{-21}} = 27380.2nm$

ii. $\lambda_2 = \frac{6.626*10^{-34}*3*10^8}{2.17*10^{-20} - 7.24*10^{-21}} = 13746.9nm$

iii. $\lambda_3 = \frac{6.626*10^{-34}*3*10^8}{2.65*10^{-20} - 7.24*10^{-21}} = 10320.9nm$

2. A. L = 1 cm ;

kT = $1.381*10^{-23}$ JK^{-1} * 300 K = $4.143*10^{-21}$ J = $\frac{4.143*10^{-21}}{hc*100} = 208.42cm^{-1}$;

m = $32*1.66*10^{-27} = 5.313*10^{-26}$ kg ;

$E_1 = \frac{h^2}{8mL^2} = 1.033*10^{-38}\,J = 5.2*10^{-16}\,cm^{-1}$;

No. of states with energy < kT = $\frac{\pi}{6}\left(\frac{kT}{E_1}\right)^{\frac{3}{2}} = \frac{\pi}{6}\left(\frac{208.42}{5.2*10^{-16}}\right)^{\frac{3}{2}} = 1.33*10^{26}$

B. Density of states at E = kT = $\frac{\pi}{4}\left(\frac{kT^{\frac{1}{2}}}{E_1^{\frac{3}{2}}}\right) = \frac{\pi}{4}\left(\frac{(208.42)^{\frac{1}{2}}}{(5.2*10^{-16})^{\frac{3}{2}}}\right)$

= $9.57*10^{23}$ states per cm^{-1}

C. A. L = 50 μm ;

kT = $1.381*10^{-23}$ JK^{-1} * 10^{-7} K

= $1.381*10^{-30}$ J = $\frac{1.381*10\text{-}30}{hc*100} = 6.947*10^{-8}\,cm^{-1}$;

m = $87*1.66*10^{-27}$ = $1.44*10^{-25}$ kg ;

$E_1 = \frac{h^2}{8mL^2} = 1.52*10^{-34}\,J = 7.67*10^{-12}\,cm^{-1}$;

No. of states with energy < kT = $\frac{\pi}{6}\left(\frac{kT}{E_1}\right)^{\frac{3}{2}} = \frac{\pi}{6}\left(\frac{6.947*10^{-8}}{7.67*10^{-12}}\right)^{\frac{3}{2}} = 4.53*10^5$

B. Density of states at E = kT = $\frac{\pi}{4}\left(\frac{kT^{\frac{1}{2}}}{E_1^{\frac{3}{2}}}\right) = \frac{\pi}{4}\left(\frac{(6.947*10^{-8})^{\frac{1}{2}}}{(7.67*10^{-12})^{\frac{3}{2}}}\right)$

= $9.75*10^{12}$ states per cm^{-1}

Problems from Levine :

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

Probability in the left quarter of the box = $\int_0^{\frac{l}{4}} \psi_n^2(x)dx$

=

$$\frac{2}{l}\int_0^{\frac{l}{4}} \sin^2\left(\frac{n\pi x}{l}\right)dx = \frac{2}{l}\left[\frac{x}{2} - \frac{l}{4n\pi}\sin\left(\frac{2n\pi x}{l}\right)\right]_0^{\frac{l}{4}} = \frac{2}{l}\left[\frac{l}{8} - \frac{l}{4n\pi}\sin\left(\frac{n\pi}{2}\right)\right]$$

$$= \frac{1}{4} - \frac{l}{2n\pi}\sin\left(\frac{n\pi}{2}\right)$$

b. This probability is maximum for $\sin\left(\frac{n\pi}{2}\right)$ = -1 and $\frac{l}{2n\pi}$ is maximum(or n is minimum). i.e. when n = 3

c. For n → ∞, the probability = $\frac{1}{4} - \frac{l}{\infty} = \frac{1}{4}$

d. Part c. illustrates the Bohr correspondence principle.

2.6 L = 2 A^o ; n = 1 ;

a. The no. of times the electron will be found between 0.6A^o and 0.601A^o

$$= N \cdot \psi^2(x)dx = 10^6 \cdot \frac{2}{2}\sin^2\left(\frac{\pi x}{2}\right)dx = 10^6 * \sin^2\left(\frac{\pi * 0.6}{2}\right) * (0.601 - 0.6) = 654.5$$

b. n = 1 ;

$$126 = \sin^2\left(\frac{\pi * 0.7}{2}\right) * (0.701 - 0.7) * N \Rightarrow N = \frac{126}{0.7939 * 10^{-3}} = 158711.64$$

$$N_1^{1.001} = N * \sin^2\left(\frac{\pi * 1}{2}\right) * (1.001 - 1) = 158.71$$

2.7 a. L = 1 A^o ;

Separation between 2 lowest energy levels = $E_2 - E_1$

$$= \frac{h^2}{8mL^2}\left(n_2^2 - n_1^2\right) = \frac{(6.626 * 10^{-34})^2}{8 * 9.1 * 10^{-31} * (1 * 10^{-10})^2} * (2^2 - 1^2) = 1.81 * 10^{-17} J = 113.1 eV$$

b. $$\lambda = \frac{hc}{E_2 - E_1} = \frac{6.626 * 10^{-34} * 3 * 10^8}{1.81 * 10^{-17}} = 10.98 nm$$

c. This wavelength is in the ultraviolet region of the electromagnetic spectrum.

2.12. Origin at the center of the box :

ψ = A sin(kx) + Bcos(kx)

$$\psi(-\frac{l}{2}) = 0$$

$$\Rightarrow -A\sin\left(\frac{kl}{2}\right) + B\cos\left(\frac{kl}{2}\right) = 0 \qquad (1)$$

$$\psi(\frac{l}{2}) = 0$$

$$\Rightarrow A\sin\left(\frac{kl}{2}\right) + B\cos\left(\frac{kl}{2}\right) = 0 \qquad (2)$$

From (1) and (2), we get :

i) $$2A\sin\left(\frac{kl}{2}\right) = 0$$

Therefore, if A = 0 $\Rightarrow \psi = B\cos(kx)$

Also, $B\cos\left(\frac{kl}{2}\right) = 0 \Rightarrow \frac{kl}{2} = \frac{(2n-1)\pi}{2}$

So, $k = \frac{n\pi}{l}$ and $\psi = B\cos\left(\frac{n\pi x}{l}\right)$ for odd n

Normalizing the wavefunction, we get

$$B^2 \int_{-\frac{l}{2}}^{\frac{l}{2}} \cos^2\left(\frac{n\pi x}{l}\right) = 1$$

Or, B = $(2/l)^{1/2}$

Therefore, $\psi_n = \sqrt{\frac{2}{l}} \cos\left(\frac{n\pi x}{l}\right)$ **odd n**

ii) $2B\cos\left(\frac{kl}{2}\right) = 0$

Therefore, if B = 0 $\Rightarrow \psi = A\sin(kx)$

Also, $A\sin\left(\frac{kl}{2}\right) = 0 \Rightarrow \frac{kl}{2} = n\pi$

So, $k = \frac{n\pi}{l}$ and $\psi = A\sin\left(\frac{n\pi x}{l}\right)$ for even n

Normalizing the wavefunction, we get

$$A^2 \int_{-\frac{l}{2}}^{\frac{l}{2}} \sin^2\left(\frac{n\pi x}{l}\right) = 1$$

Or, A = $(2/l)^{1/2}$

Therefore, $\psi_n = \sqrt{\frac{2}{l}} \sin\left(\frac{n\pi x}{l}\right)$ **even n**

$$E_n = \frac{k^2\hbar^2}{2m} = \frac{n^2h^2}{8ml^2}$$

$\psi_1 = \sqrt{\frac{2}{l}} \cos\left(\frac{\pi x}{l}\right)$; $\psi_2 = \sqrt{\frac{2}{l}} \sin\left(\frac{2\pi x}{l}\right)$; $\psi_3 = \sqrt{\frac{2}{l}} \cos\left(\frac{3\pi x}{l}\right)$;

$\psi_4 = \sqrt{\frac{2}{l}} \sin\left(\frac{4\pi x}{l}\right)$; $\psi_5 = \sqrt{\frac{2}{l}} \cos\left(\frac{5\pi x}{l}\right)$; $\psi_6 = \sqrt{\frac{2}{l}} \sin\left(\frac{6\pi x}{l}\right)$;

3.31. a = 1 nm ; b = 2 nm ; c = 5 nm ;

a. Probability = $\frac{8}{abc} \int_0^{0.4} \sin^2\left(\frac{n_x\pi x}{a}\right)dx \int_{1.5}^{2} \sin^2\left(\frac{n_y\pi y}{b}\right)dy \int_2^3 \sin^2\left(\frac{n_z\pi z}{c}\right)dz$

=

$$0.8 * \left[\frac{x}{2} - \frac{a}{4\pi}\sin(\frac{2\pi x}{a})\right]_0^{0.4} * \left[\frac{y}{2} - \frac{b}{4\pi}\sin(\frac{2\pi y}{b})\right]_{1.5}^{2} * \left[\frac{z}{2} - \frac{c}{4\pi}\sin(\frac{2\pi y}{c})\right]_2^3$$

$0.8 * 0.153226 * 0.0908451 * 0.967745$

= 0.01078

b. Probability = $\frac{8}{abc}\int_0^{0.4}\sin^2\left(\frac{n_x\pi x}{a}\right)dx\int_0^{2}\sin^2\left(\frac{n_y\pi y}{b}\right)dy\int_0^{5}\sin^2\left(\frac{n_z\pi z}{c}\right)dz$

= 0.306451

c. Assuming $0 \le y \le 2$ and $0 \le z \le 5$, probability in the x coordinate between 0 and 0.4 nm = **0.306451** .