Problem Set 3
CHM102A

1. Assuming particle in a 1-D box model, calculate the energy separation between the lowest two levels for a particle confined in a box of length 3 nm (consider the particle to be the H_2 molecule). In this model, at what quantum number, *n*, does the energy of the molecule equal k_BT when T=300K. Compare the results to the case of nitrogen molecule whose mass is 14-times higher.

For a particle in a 1-D box: $E_n = n^2 \frac{\pi^2\hbar^2}{2mL^2}$ where, $n = 1, 2, 3, \ldots$

Energy seperation can be written as:

$$\Delta E = E_{n+1} - E_n = [(n+1)^2 - n^2]\frac{\pi^2\hbar^2}{2mL^2} = (2n+1)\frac{\pi^2\hbar^2}{2mL^2}$$

For the gap between the lowest two levels, $n = 1$. So, $\Delta E = \frac{3\pi^2\hbar^2}{2mL^2}$

Considering H_2 molecule, m = 2 amu = $2 \times 1.67 \times 10^{-27}$ kg. Also given is the Box Length, L = 3 nm = 3×10^{-9} m

$$\text{Thus, } \Delta E = \frac{3\pi^2\hbar^2}{2mL^2} = \frac{3\times(3.14)^2\times(1.06\times10^{-34})^2}{2\times2\times1.67\times10^{-27}\times(3\times10^{-9})} = 5.53\times10^{-24} J$$

Now, Energy in a particle in a 1-D box is: $E_n = n^2\frac{\pi^2\hbar^2}{2mL^2}$. For this energy to be equal to the energy k_BT when T = 300K, we can equate: $n^2\frac{\pi^2\hbar^2}{2mL^2} = k_BT$ to find the value of n.

$$\frac{n^2\times(3.14)^2\times(1.06\times10^{-34})^2}{2\times2\times1.67\times10^{-27}\times(3\times10^{-9})^2} = 1.38\times10^{-23}\times300$$

$$n^2 \approx 2246$$

$$\Rightarrow n \approx 47.4$$

$$n_{H_2} = 48$$

$$E_n = n^2\frac{\pi^2\hbar^2}{2mL^2} \quad \Rightarrow n^2 = E_n\frac{2mL^2}{\pi^2\hbar^2} \quad \Rightarrow n^2 \propto m \quad \Rightarrow n \propto \sqrt{m}$$

$$\frac{n_{N_2}}{n_{H_2}} = \sqrt{\frac{m_{N_2}}{m_{H_2}}} = \sqrt{14} \quad \Rightarrow n_{N_2} = \sqrt{14}\, n_{H_2} \approx 177.35 \quad \Rightarrow n_{N_2} = 178$$

2. Consider a system of two non-interacting particles of mass m_1 and m_2 confined along the x-axis such that:

$$V(x_1, x_2) = \begin{cases} 0 & if\ 0 < x_1 < L, and\ 0 < x_2 < L \\ \infty & otherwise \end{cases}$$

where x_1 and x_2 are coordinates of particles 1 and 2.

- Solve the Schrodinger equation for this problem.
- How many quantum numbers are required to specify a state of this system?
- Can degenerate states appear for this problem as special case? Explain.
- Sketch the ground state wave function.
- For the ground state, sketch the probability density for finding both particle 1 and particle 2 simultaneously at the same point for $0 < x < L$?

Solution: Schrodinger equation for the problem:

$$\begin{aligned} \psi &\equiv \psi(x_1, x_2) \\ \hat{H} &= -\frac{\hbar^2}{2m_1}\frac{\partial^2}{\partial x_1^2} - \frac{\hbar^2}{2m_2}\frac{\partial^2}{\partial x_2^2} \end{aligned}$$

Thus

$$\begin{aligned} \hat{H}\psi(x_1, x_2) &= E\psi(x_1, x_2) \\ -\frac{\hbar^2}{2m_1}\frac{\partial^2\psi}{\partial x_1^2} - \frac{\hbar^2}{2m_2}\frac{\partial^2\psi}{\partial x_2^2} &= E\psi(x_1, x_2) \end{aligned}$$

Separation of variables:

$$\psi(x_1, x_2) = X_1(x_1)X_2(x_2)$$

Thus we get two differential equations:

$$-\frac{\hbar^2}{2m_1}\frac{d^2X_1}{dx_1^2} = E_1X_1(x_1)$$

and

$$-\frac{\hbar^2}{2m_2}\frac{d^2X_2}{dx_2^2} = E_2X_2(x_2)$$

Boundary conditions:

$$\psi(0, x_2) = \psi(L, x_2) = \psi(x_1, 0) = \psi(x_1, L) = 0$$

Then we obtain

$$X_1(0) = X_1(L) = X_2(0) = X_2(L) = 0$$

Thus, following the steps for PIB-2D problem, we can find that

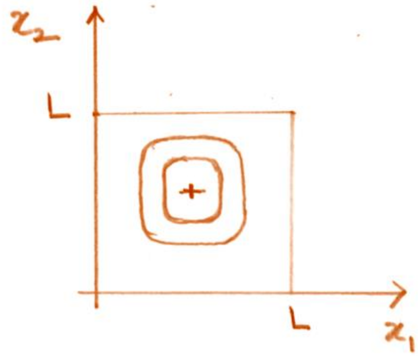
$$\psi_{n_1,n_2}(x_1, x_2) = \sqrt{\frac{2}{L}}\sin(n_1\pi x_1/L) \times \sqrt{\frac{2}{L}}\sin(n_2\pi x_2/L)$$

with $n_1 = 1, 2, \cdots$ and $n_2 = 1, 2, \cdots$. Also,

$$E_{n_1,n_2} = \frac{n_1^2h^2}{8m_1L^2} + \frac{n_2^2h^2}{8m_2L^2}$$

Quantum numbers required are 2.

Yes, degenerate states can appear and it depends on the ratio of ${}^{m_1}/_{m_2}$. One example is the case of ${}^{m_1}/_{m_2} = 1$.

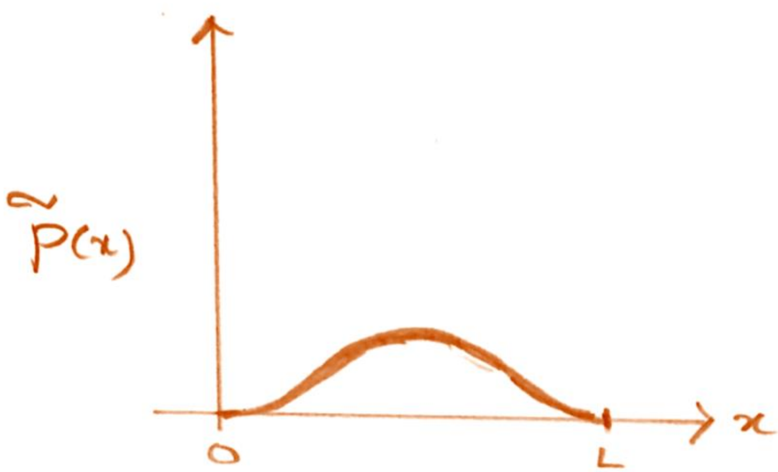


The probability density for finding both particle 1 and particle 2 simultaneously at the same point for 0 < x < L is:

$$P(x_1, x_2) = |\psi_{1,1}(x_1, x_2)|^2$$

For the special case when $x_1 = x_2 = x$,

$$P(x, x) \equiv \tilde{P}(x) = |\psi_{1,1}(x, x)|^2 \propto \sin^4(\pi x/L)$$



3. For the ground state of a quantum mechanical 1-D simple harmonic oscillator, compute the expectation value of Kinetic Energy $\langle T \rangle$.

Solution:

$$\psi_0(x) = Ce^{-\alpha^2 x^2/2}, \quad \text{where } C = \sqrt{\frac{\alpha}{\pi^{-1/2}}}$$

$$\frac{d\psi_0}{dx} = -C\alpha^2 x e^{-\alpha^2 x^2/2}$$

$$\frac{d^2\psi_0}{dx^2} = \frac{d}{dx}\left(-C\alpha^2 x e^{-\alpha^2 x^2/2}\right) = -c\alpha^2\left[1-\alpha^2 x^2\right] e^{-\alpha^2 x^2/2}$$

Now,

$$\begin{aligned}\langle T \rangle &= \int_{-\infty}^{\infty} \psi_0^*(x)\left(\frac{-\hbar^2}{2m}\right)\frac{d^2\psi_0}{dx^2}\ dx \\ &= \frac{C^2\alpha^2\hbar^2}{2m}\int_{-\infty}^{\infty}\left[1-\alpha^2x^2\right]e^{-\alpha^2x^2/2}\ dx \\ &= \frac{C^2\alpha^2\hbar^2}{2m}\left[\sqrt{\frac{\pi}{\alpha^2}} - \alpha^2\frac{1}{2}\sqrt{\frac{\pi}{\alpha^6}}\right] \\ &= \frac{1}{4}\hbar\omega = \frac{1}{2}E_0\end{aligned}$$

4. Assuming a particle in a 1-D box model, calculate the separation between the lowest two energy levels for a $^{14}N_2$ molecule in a box of length 3 nm. In this model, at what quantum number, n, does the energy of the molecule equal k_BT when T = 300K.

Answer: Particle in 1D box, Energy gap is given by:

$$\Delta E = E_{n+1} - E_n = \left(\frac{\pi^2\hbar^2}{2mL^2}\right)(2n+1)$$

Lowest gap when n = 1, which gives:

$$\Delta E = \left(\frac{3\pi^2\hbar^2}{2mL^2}\right) = 3.95\times10^{-25}\,J$$

At 300K; $k_BT = 414\times10^{-23}$ J

$$For\ \left(\frac{n^2\pi^2\hbar^2}{2mL^2}\right) = k_BT \Rightarrow n^2 = 31454$$

$$\Rightarrow n = \quad 177.3$$

n has to be an integer; $\therefore\ n = 177$

5. Consider the wavefunction $\psi = A\cos\left(\frac{n\pi x}{a}\right)$, where n is a nonzero positive integer and 'a' is the length of the box as a possible solution for a particle in a 1D box with infinite potential. Under what condition, if any, will ψ be an allowed wavefunction for this 'particle in a 1D box'.

Answer: For this 'particle in a 1D box', if we consider the box to exist from 0→*a*, ψ cannot be an allowed wavefunction though ψ is an eigenfunction of the Hamiltonian for the problem! However, if the box range is $-a/2$ to $a/2$ and has quantum number $n = 2m+1$, then ψ can be an allowed wavefunction.

6. For a 3D rigid rotor with quantum number $l = 1$, what are the possible angles (θ) the angular momentum vector with the z-axis?

Answer: The angle between the z-axis and the angular momentum can be written using:

$$\cos\theta = \frac{L_z}{|L|}$$

$$\text{Now, } L = \sqrt{l(l+1)} = \sqrt{2}, \text{ since } l = 1$$

$$\text{So, } \cos\theta = 0, \pm\frac{1}{\sqrt{2}}$$

$\therefore$ $\theta = 45$; $\theta = 90$; & $\theta = 135$