Problem Set 1

Physical Chemistry 2, Summer 2021

Lecturer : Jiho Son, PS for Lecture 01, 02, 03, 04

1. **Derivation of Rayleigh-Jeans law.**

   (a) Consider a cube of edge length L in which radiation is begin reflected inside. For non-destructive interference, light waves should form standing wave inside. For this problem, define wavenumber as
   $$k = \frac{2\pi}{\lambda}$$
   Then show that standing wave condition yields $k_i = n\pi/L$ $(i = x, y, z)$ where n is an non-negative integer.

   (b) Let n_x, n_y, n_z denotes the integer for x, y, z direction. Then
   $$k^2 = \pi^2 \left[\left(\frac{n_x}{L}\right)^2 + \left(\frac{n_y}{L}\right)^2 + \left(\frac{n_z}{L}\right)^2 \right]$$
   Show that this reduces into
   $$n_x^2 + n_y^2 + n_z^2 = \frac{4L^2\nu^2}{c^2}$$

   (c) We want to calculate the number of possible combination of (n_x, n_y, n_z) that satisfies
   $$n_x^2 + n_y^2 + n_z^2 \leq \frac{4L^2\nu^2}{c^2}$$
   Find the number of points inside the shell $R \sim R + dR$, dN. Show that
   $$\frac{dN}{d\nu} = \frac{4\pi L^3}{c^3}\nu^2$$

   (d) Calculate the average radiation energy per unit frequency,
   $$\frac{dE}{d\nu} = k_{\mathrm{B}}T\frac{dN}{d\nu}$$

   (e) Show that energy density is given by
   $$\rho_\nu(T) = \frac{8\pi\nu^2}{c^3}k_{\mathrm{B}}T$$
   Note that radiation has two polarization; don't forget to multiply factor 2.

2. **Derivation of Planck distribution.**

   (a) Assume that oscillators inside the blackbody has energy of $E = nh\nu$ $(n = 0, 1, 2, \ldots)$. Boltzmann distribution is given by
   $$p(E_n) = \frac{e^{-\beta E_n}}{\sum_{n=0}^{\infty} e^{-\beta E_n}} \text{ where } \beta = \frac{1}{k_{\mathrm{B}}T}$$
   Show that
   $$\langle E_n \rangle = \sum_{n=0}^{\infty} E_n p(E_n) = \frac{h\nu}{e^{h\nu/k_{\mathrm{B}}T} - 1}$$

   (b) By multiplying number of modes, yield Planck distribution.

3. **Atkins, P7A.3.** Demonstrate that the Planck distribution reduces to the Rayleigh-Jeans law at long wavelengths.

4. **Atkins, P7A.4.** Prove Wien's law.

5. **Atkins, P7A.7.** Prove Stefan-Boltzmann law.

6. Suppose that we normalized wavefunction at $t = 0$. How do we know that the wavefunction will stay normalized as time evolves? Prove that wavefunction stays normalized under time revolution, for the one-dimensional case. Apply appropriate boundary conditions.

7. **Griffiths, 1.5.** Consider the wavefunction

$$\Psi(x,t) = Ae^{-\lambda|x|}e^{-i\omega t}$$

where A, λ and ω are positive real constants.

(a) Normalize Ψ.

(b) Determine the expectation value of x and x^2.

(c) Find the standard deviation of x. Sketch the graph of $|\Psi|^2$ as a function of x.

8. Let's justify the form of momentum operator, in classical mechanics analogy. Show that

$$m\frac{d\langle x\rangle}{dt} = \int \Psi^* \left(-i\hbar\frac{\partial}{\partial x}\right)\Psi\, dx$$

9. **Atkins, P7B.1. Particle on a ring.** Imagine a particle confined to move on a circumference of a circle with radius r.

(a) Find the Schrödinger equation of this case. Use the fact that $x = r\phi$ in polar coordinates.

(b) Show that $\psi(\phi) = e^{im\phi}$ $(m \in \mathbb{Z})$ satisfies the Schrödinger equation.

(c) Normalize the solution.

10. **McQuarrie 4-17.** Show that

$$[\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z, \quad [\hat{L}_y, \hat{L}_z] = i\hbar\hat{L}_x, \quad [\hat{L}_z, \hat{L}_x] = i\hbar\hat{L}_y$$

We usually call this relation a *cyclic commutation relation*, $[L_i, L_j] = i\hbar\epsilon_{ijk}L_k$ where ϵ_{ijk} is Levi-civita tensor.

11. If you are familiar with linear algebra, then *basis* is not an awkward concept. It is well-known that eigenfunctions of particle-in-a-box problem are *complete*, in the sense that any other function can be expressed as a linear combination of $\psi_n(x)$.

$$f(x) = \sum_{n=0}^{\infty} c_n\psi_n(x) = \sqrt{\frac{2}{a}}\sum_{n=0}^{\infty} c_n \sin\frac{n\pi x}{L}$$

Consider a particle in the infinite square well with length a has the initial wavefunction

$$\Psi(x,0) = Ax(a-x)\ (0 \le x \le a)$$

Find $\Psi(x,t)$.

12. In this problem, you should re-solve the particle-in-a-box problem, with shifted box region. Consider the infinite potential well, located in $-a/2 \le x \le a/2$. Obtain the wavefunction (you don't need to normalize it) with appropriate boundary condition. What can you observe from that wavefunction, and what is different from the original wavefunction we calculated in class?