Problem Set 2

Physical Chemistry 2, Summer 2021

Lecturer : Jiho Son, PS for Lecture 05, 06, 07, 08

1. **Energy-time uncertainty.** There is another well-known uncertainty principle for energy and time.

$$\Delta E \Delta t \geq \frac{\hbar}{2}$$

Strictly speaking, time is **not** a quantum-mechanical observable: we regard that time can always be clearly measured. Our goal is to derive it first.

(a) Compute the time derivative of the expectation value of some observable, $Q(x, p, t)$. Show that

$$\frac{d}{dt}\langle Q\rangle = \frac{i}{\hbar}\left\langle\left[\hat{H}, \hat{Q}\right]\right\rangle + \left\langle\frac{\partial \hat{Q}}{\partial t}\right\rangle$$

(b) In typical case, the operator does not depend explicitly on time. Argue that expectation value is time-independent if the operator commutes with Hamiltonian.

(c) Plug $\hat{H}$ and $\hat{Q}$ into the generalized uncertainty principle. Show that

$$\sigma_H \sigma_Q \geq \frac{\hbar}{2}\left|\frac{d\langle Q\rangle}{dt}\right|$$

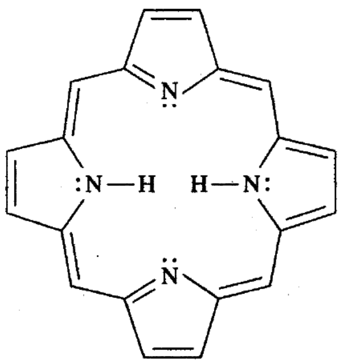
COMMENT. If we define $\Delta E \equiv \sigma_H$ and

$$\Delta t \equiv \frac{\sigma_Q}{|d\langle Q\rangle/dt|}$$

Then we yield $\Delta E \Delta t \geq \hbar/2$.

(d) What is the physical meaning of energy-time uncertainty? This is quite hard question to answer.

2. **McQuarrie, 3-27.** Many proteins contain metal porphyrin molecules. The general structure of the porphyrin molecule is



This molecule is planar and so we can approximate the π electrons as being confined inside a square. What are the energy levels and degeneracies of a particle in a square of side a? The porphyrin molecule has 26 π electrons. If we approximate the length of the molecule by 1000 pm, then what is the predicted lowest energy absorption of the porphyrin molecule? (The experimental value is about 17000 cm^{-1}.)

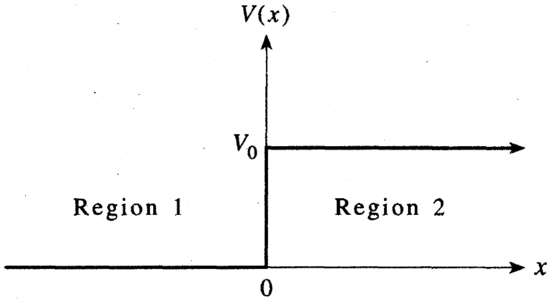
3. **Free particle.** In advance to complicated one-dimensional problems, we should understand the free particle situation clearly. Consider a free, *free* particle without any potential ($V = 0$ everywhere!).

   (a) Write down the Schrödinger equation for this case.

   (b) Write down the general solution of this Schrödinger equation, with *exponential form.*

   (c) Is this wavefunction normalizable? From this result, argue the physical meaning of free particle in quantum mechanics.

4. **Scattering on step function.** Consider a particle of energy E moving in the potential energy



$$V(x) = 0 \ (x < 0), \quad V_0 \ (x > 0)$$

   (a) First, consider the case $E > V_0$ (Assume that $V_0 > 0$). Construct the wavefunctions for region 1 and 2, respectively. Write down the boundary conditions at $x = 0$.

   (b) Obtain the reflection and transmission coefficient, defined as below:

$$R \equiv \frac{v_1|B|^2N_0}{v_1|A|^2N_0} = \frac{\hbar k_1|B|^2N_0/m}{\hbar k_1|A|^2N_0/m} = \left|\frac{B}{A}\right|^2, \ T \equiv \frac{v_2|C|^2N_0}{v_1|A|^2N_0} = \frac{\hbar k_2|C|^2N_0/m}{\hbar k_1|A|^2N_0/m} = \frac{k_2}{k_1}\left|\frac{C}{A}\right|^2$$

   What is the physical meaning of R and T? Also show that $R + T = 1$.

   (c) What are the values of R and T, for $E \to V_0$ and $E \to \infty$ limit?

   (d) Next, consider the case $0 < E < V_0$. Construct wavefunctions for region 1 and 2, and write down the boundary conditions at $x = 0$.

   (e) Calculate R and T, respectively.

   (f) Draw the reflection coefficients as a funtion of E/V_0 for positive E.

5. **Electron tunneling.** Consider the scattering problem for the potential given by

$$V(x) = +V_0 \ (|x| \leq a), \quad 0 \ (|x| > a)$$

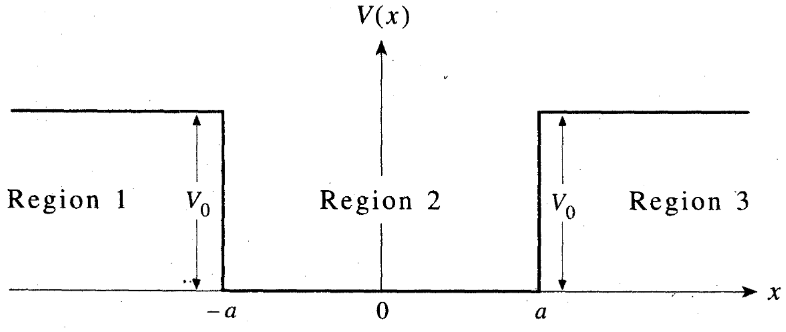
   where $V_0 > 0$.

   (a) For $0 \leq E < V_0$, show that the transmission constant T is given by

$$T^{-1} = 1 + \frac{V_0^2}{4E(V_0 - E)} \sinh^2 2\kappa a \quad \text{where} \quad \hbar^2\kappa^2 = 2m(V_0 - E)$$

   (b) Determine the transmission coefficient for $E = V_0$ and $E > V_0$.

   (c) For $R^2 \equiv 2ma^2V_0/\hbar^2 = 16$, draw T as a function of $E/V_0 \geq 0$. You will observe **Ramsauer-Townsend effect**.



6. **Finite potential well.** Consider a particle in following potential

$$V(x) = 0\ (|x| < a), \quad +V_0\ (|x| \geq a)$$

From the wavefunctions and appropriate boundary conditions, find out *allowed energies* of the particle confined inside the well. Specifically, show that there are only two bound state for

$$\frac{2ma^2V_0}{\hbar^2} = 4$$

7. **Ladder operator techniques for expectation values: Griffiths 2.12** Find $\langle x \rangle, \langle p \rangle, \langle x^2 \rangle, \langle p^2 \rangle$, and $\langle T \rangle$, for the n-th stationary state of the harmonic oscillator. *Hint: express $\hat{x}$ and $\hat{p}$ with $\hat{a}$ and $\hat{a}^\dagger$.*

8. **Analytic method for HO.** We will solve following equation with power series method.

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \frac{1}{2}m\omega^2x^2\psi = E\psi$$

(a) First, introduce dimensionless variable. Show that

$$\xi \equiv \sqrt{\frac{m\omega}{\hbar}}x,\ K \equiv \frac{2E}{\hbar\omega} \implies \frac{d^2\psi}{d\xi^2} = (\xi^2 - K)\psi$$

(b) Investigate the $\xi \to \infty$ limit. Which term becomes dominant in RHS? Obtain the *asymptotic form* in such limit. *Answer:*

$$\psi(\xi) \sim e^{-\xi^2/2} \text{ at large } \xi$$

(c) Result of (b) suggests us to *peel off* the exponential part.

$$\psi(\xi) = h(\xi)e^{-\xi^2/2}$$

I propose to look for $h(\xi)$, in the form of *power series.*

$$h(\xi) = a_0 + a_1\xi + a_2\xi^2 + \cdots = \sum_{j=0}^{\infty} a_j$$

Show that $h(\xi)$ satisfies

$$\frac{d^2h}{d\xi^2} - 2\xi\frac{dh}{d\xi} + (K-1)h = 0$$

Then by substituting power series, obtain the relation

$$(j+1)(j+2)a_{j+2} - 2ja_j + (K-1)a_j = 0$$

which yields *recursion formula*, $a_{j+2} = \dfrac{2j+1-K}{(j+1)(j+2)}a_j$.

(d) Starting from $j = 0$ and $j = 1$ yields even and odd coefficients, respectively. Therefore, we can write the complete solution as

$$h(\xi) = h_{\text{even}}(\xi) + h_{\text{odd}}(\xi)$$

Following coefficients belongs to the initial value, a_0 and a_1, indeed. However, not all the solutions so obtained are normalizable. Show that for at large j,

$$a_{j+2} \sim \frac{2}{j} a_j, \quad a_j \sim \frac{C}{(j/2)!}$$

By using this asymptotic expression, show that power series diverges at large ξ. *Therefore, for normalizable solutions, power series should terminate at some point.*

(e) From now on, call j as n. Show that for physically acceptable solutions, K should satisfy

$$K = 2n + 1$$

From this equation, obtain the quantized energy of harmonic oscillator we derived in class.

(f) Obtain ψ_0, ψ_1 and ψ_2 from the recursion. For odd n, choose $a_0 = 1$ and $a_1 = 0$. For even n, choose $a_0 = 1$ and $a_1 = 0$ respectively.

9. **Griffiths, 2.41.** Find the allowed energies of the *half* harmonic oscillator,

$$V(x) = \frac{1}{2} m\omega^2 x^2 \ (x > 0), \quad 0 \ (x < 0)$$

This represents stretchable, but not compressible spring.

10. **Minimum uncertainty wavepacket.** Remember the fact that uncertainty principle was derived from Cauchy-Schwarz inequality.

(a) For following Cauchy-Schwarz inequality,

$$\langle f \,|\, f \rangle \langle g \,|\, g \rangle \geq |\, \langle f \,|\, g \rangle \,|^2$$

find the condition when the equality holds.

(b) Recall that

$$f = (\hat{A} - \langle A \rangle)\Psi, \ g = (\hat{B} - \langle B \rangle)\Psi$$

By substituting $\hat{A} = \hat{x}$ and $\hat{B} = \hat{p}$, show that

$$\left(-i\hbar \frac{d}{dx} - \langle p \rangle \right) \Psi = ia(x - \langle x \rangle)\Psi$$

(c) Show that *gaussian* wave packet satisfies the minimum-uncertainty.

$$\Psi(x) = Ae^{-a(x - \langle x \rangle)^2/2\hbar} e^{i\langle p \rangle x/\hbar}$$

11. **Griffiths, 3.40.** The most general wave function of a particle in the simple HO potential is

$$\Psi(x,t) = \sum_n c_n \psi_n(x) e^{-iE_n t/\hbar}$$

Show that the expectation value of position is

$$\langle x \rangle = C \cos(\omega t - \phi)$$

where

$$Ce^{-i\phi} = \sqrt{\frac{2\hbar}{m\omega}} \sum_{n=0}^{\infty} \sqrt{n+1} c_{n+1}^* c_n$$

12. **Coherent states of HO: Griffiths, 3.42.** Among the stationary states of the HO, $|n\rangle$, only $n = 0$ has the uncertainty limit ($\sigma_x \sigma_p = \hbar/2$). In general, $\sigma_x \sigma_p = (2n+1)\hbar/2$. But certain linear combinations known as *coherent states*, also minimize the uncertainty product. They are eigenfunctions of the annihilation operator.

$$\hat{a}\,|\alpha\rangle = \alpha\,|\alpha\rangle$$

where the eigenvalues α can be complex.

(a) Calculate $\langle x\rangle, \langle p\rangle, \langle x^2\rangle, \langle p^2\rangle$ in the state $|\alpha\rangle$.

(b) Show that $\sigma_x \sigma_p = \hbar/2$.

(c) Like any other wavefunction, a coherent state can be expanded in terms of energy eigenstates:

$$|\alpha\rangle = \sum_{n=0}^{\infty} c_n\,|n\rangle$$

Show that $c_n = \dfrac{\alpha^n}{\sqrt{n!}} c_0$.

(d) From the normalization, show that $c_0 = e^{-|\alpha|^2/2}$.

(e) Now put the time dependence $|n\rangle \to e^{-iE_n t/\hbar}\,|n\rangle$. Show that $|\alpha(t)\rangle$ remains an eigenstates of $\hat{a}$, but the eigenvalue evolves in time as

$$\alpha(t) = e^{-i\omega t}\alpha$$

(f) Show that $\langle \alpha\,|\,\hat{a}^{\dagger m}\hat{a}^n\,|\,\alpha\rangle = \alpha^{*m}\alpha^n$.

(g) For $\alpha \neq \alpha'$, obtain $\langle \alpha\,|\,\alpha'\rangle$ and discuss about orthogonality of the states.

(h) Obtain the completeness relation.

13. **Particle in a spherical well.**

(a) Start from the radial equation.

$$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}[V(r) - E]R = l(l+1)R$$

By changing variables into $u(r) \equiv rR(r)$, show that

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[V + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right]u = Eu$$

Note that we have **effective potential** now.

$$V_{\text{eff}} = V + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}$$

(b) Consider the infinite spherical well, such that

$$V(r) = 0\ (r \le a), \quad \infty\ (r > a)$$

Find the wavefunctions and the allowed energies. *Hint: search your obtained differential equation in wolframalpha. Which kind of special function is the solution of this equation?*

14. **Three-dimensional HO: Griffiths 4.46.**

$$V(r) = \frac{1}{2}m\omega^2 r^2$$

Show that

$$E_n = (n + \frac{3}{2})\hbar\omega$$

What is the degeneracy of the quantized energy?

15. Some spectroscopic exercises.

    (a) **McQuarrie 5-13.** In the infrared spectrum of $H^{79}Br$, there is an intense line at $2559\,\mathrm{cm^{-1}}$. Calculate the force constant and the period of vibration of this molecule.

    (b) **McQuarrie 5-14.** The force constant of $^{79}Br^{79}Br$ is $240\,\mathrm{N \cdot m^{-1}}$. Calculate the fundamental vibrational frequency and the zero-point energy of this molecule.

    (c) **McQuarrie 5-34.** In the far infrared spectrum of $H^{79}Br$, there is a series of lines separated by $16.72\,\mathrm{cm^{-1}}$. Calculate the values of the moment of inertia and the internuclear separation in $H^{79}Br$.

    (d) **McQuarrie 5-35.** The $J = 0$ to $J = 1$ transition for carbon monoxide ($^{12}C^{16}O$) occurs at 1.153×10^5 MHz. Calculate the value of the bond length in carbon monoxide.