**PHYS3021 Quantum Mechanics I Problem Set 4**
**Due: 15 November 2017 (Wednesday) "T+2" = 17 November 2017 (Friday)**
All problem sets should be handed in not later than 5pm on the due date. Drop your assignments into the PHYS3021 box outside Rm.213.
*Please work out the steps of the calculations in detail. Discussions among students are highly encouraged, yet it is expected that we do your homework independently.*

4.0 **Reading Assignment.** (Don't need to hand in everything for this item.) Chapter VI uses the standard problems to further illustrate the key features of solutions to TISE in 1D problems. The symmetry of $U(x)$ in finite well and harmonic oscillator classifies the energy eigenstates into even (symmetric) and odd (antisymmetric) functions. We see again that the main theme of physics requirements (well-behaving) on the wavefunction that selects the proper discrete energy eigenvalues. The oscillator problem is important in that it permeates different areas in physics. The answer is useful in understanding vibrational spectrum of molecules (why $CO_2$ is a greenhouse gas). We introduce the method of Series Solution in solving the oscillator problem. It is a method that can be applied to spherically symmetric $U(r)$ problems in 2D and 3D, and the hydrogen atom problem (Chapters VII, VIII, IX). Chapters VII/VIII/IX form a set on high dimensional QM problems. Chapter VII points out that separation of variables method is useful (but need to inspect the form of $U$ first) and there are often degenerate states (different states corresponding to the same energy) in high dimensional QM problems. Chapter VIII focuses on 3D spherically symmetric $U(r)$ (function of $r$ only). It turns out that the angular part does not depend on the explicit form of $U(r)$ and the solutions are called spherical harmonics $Y_{\ell m_\ell}(\theta,\phi)$. The energy is in general $E_{n\ell}$, the magnitude squared of orbital angular momentum is $L^2 = \ell(\ell+1)\hbar^2$, and the $z$-component $L_z = m_\ell\hbar$. Near the end of Chapter VIII, we diverted to a discussion on orbital angular momentum and introduced a picture called the vector model. A by-product of the discussion is that we can solve the 3D rigid rotor problem without any effort. The answer is important for understanding rotational spectrum of molecules. Chapter IX applies Ch.VIII to the hydrogen atom problem, with results that you have seen in previous courses but now explicitly obtained by solving TISE.

Chapters in Rae's *Quantum Mechanics*, Griffiths' *An introduction to quantum mechanics*, McQuarrie's *Quantum Chemistry*, and Engels' *Quantum Chemistry and Spectroscopy* are good places to look up more discussion. The chemistry books are better illustrations of the hydrogen atomic orbitals.

4.1 **Oscillator's Hermite Polynomials**

We solved TISE for a harmonic oscillator using the series solution method. The solutions $\psi_n$ are related to the Hermite Polynomials $H_n(y)$ of $H_n(\sqrt{\alpha}x)$ through

$$\psi_n(x) = A_n H_n(\sqrt{\alpha}x) e^{-(1/2)\alpha x^2} \tag{1}$$

where $\alpha = (m\omega_0)/\hbar$ and

$$A_n = \frac{1}{\sqrt{2^n n!}} \left(\frac{\alpha}{\pi}\right)^{1/4} \tag{2}$$

is a normalization constant. The first few energy eigenfunctions are

$$\begin{aligned}
\psi_0(x) &= \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-(1/2)\alpha x^2} \\
\psi_1(x) &= \left(\frac{4\alpha^3}{\pi}\right)^{1/4} x\, e^{-(1/2)\alpha x^2} \\
\psi_2(x) &= \left(\frac{\alpha}{4\pi}\right)^{1/4} \left(2\alpha x^2 - 1\right) e^{-(1/2)\alpha x^2} \\
\psi_3(x) &= \left(\frac{\alpha^3}{9\pi}\right)^{1/4} \left(2\alpha x^3 - 3x\right) e^{-(1/2)\alpha x^2}
\end{aligned} \tag{3}$$

(a) **Make a table** that lists the separate factors $A_n$ and $H_n(\sqrt{\alpha}x)$ for the given oscillator eigenstates.

(b) Take the $H_n$ in the lowest three eigenstates, **show that** they satisfy the relationship

$$\alpha^{1/2} x H_n(\sqrt{\alpha}x) = n H_{n-1}(\sqrt{\alpha}x) + \frac{1}{2} H_{n+1}(\sqrt{\alpha}x) \tag{4}$$

(c) Eq. (4) is called the recursive relation of Hermite Polynomials. One application is that - if we know $H_{n-1}$ and $H_n$, then $H_{n+1}$ follows, and so on. Therefore, once we know $H_0$ and $H_1$, Eq. (4) can be used to generate the other $H_n$ iteratively.

Hence, **show** that using $H_1$ and $H_2$ and Eq. (4), $H_3$ follows (as given in $\psi_3$).

### 4.2 An important integral between Hermite Polynomials

[Here is an important application of Eq. (4).]

An important application of oscillator physics is to understand the effects of vibrational motions in molecules (on spectrum). Spectroscopy is meant to study the transitions between one state to another under the influence of light. We will learn the (perturbation) theory to handle it next term. Without going into the details (and thinking like a physicist), there is an initial state $\psi_n(x)$ (oscillator in $n$-th state) and there is a final state $\psi_m(x)$ (oscillator in $m$-th state). It is the light that causes the transition. For light polarized in the $x$-direction, the influence is related to the operator $\hat{x} = x$. The relevant integral determining whether a transition could happen or not is

$$\begin{aligned} x_{mn} &\equiv \int_{-\infty}^{\infty} \psi_m^*(x)\, x\, \psi_n(x) dx \\ &= \int_{-\infty}^{\infty} \psi_m(x)\, x\, \psi_n(x) dx \ \text{ (because } \psi_n\text{'s are real)} \\ &= A_m A_n \int_{-\infty}^{\infty} \left(e^{-(1/2)\alpha x^2} H_m(\sqrt{\alpha}x)\right)\, x\, \left(e^{-(1/2)\alpha x^2} H_n(\sqrt{\alpha}x)\right) dx \ \text{ (using Eq. (1))} \\ &= A_m A_n \int_{-\infty}^{\infty} H_m(\sqrt{\alpha}x)\, x\, H_n(\sqrt{\alpha}x) e^{-\alpha x^2} dx \end{aligned} \tag{5}$$

This integral is the "electric dipole matrix element" (it has two indices so it looks like the $mn$-element of a matrix). The name doesn't bother us. If $x_{mn}$ is big, transition happens readily (allowed). If $x_{mn}$ is small but finite, transition can happen but rarely. If $x_{mn}$ is zero, the electric dipole transition does not occur (forbidden). To evaluate $x_{mn}$, there are two methods. One way is to use the operator method (see notes posted but untaught). Another way is to make use of the recursive relation Eq. (4).

Using Eq. (4) to express the part $xH_n$ and recalling that $\psi_n's$ are orthogonal to each other, **show that** $x_{mn} \neq 0$ only when $m = n + 1$ or $m = n - 1$. Hence, **evaluate** the integral for these two cases.

[Remarks: The same method can be used to evaluate $(x^2)_{mn}$, where $x^2$ appears in the integrand instead of $x$. For those interested in mathematical or theoretical physics, try it (no bonus points, sorry). The same integral can also be done by the operator method. Next, there are integrals with $\hat{p}_x$ in between the oscillator eigenstates, have fun! Practically, they are also useful for studying transitions.]

### 4.3 Mathematical sense versus mathematical techniques - A standard PhD exam problem that undergraduates can answer without effort

In solving QM problems, a mathematical sense is as important as mathematical technique. TISE is a differential equation to be solved with appropriate boundary conditions governing the behavior of acceptable wavefunction.

**Here is the key math sense:** If TWO different problems share the SAME TISE and the SAME boundary conditions in the SAME range in space, they have the SAME solutions.

First **read and digest** the above statement. Now consider the following classic example. There is a 1D half-space oscillator problem described by the potential energy function

$$U(x) = \begin{cases} \frac{1}{2} m\omega_0^2 x^2 & \text{for } x > 0 \\ \infty & \text{for } x \leq 0 \end{cases} \tag{6}$$

Note that there is a hard wall at $x = 0$ and it will impose a boundary condition at $x = 0$.

**Sketch** $U(x)$, **write down** the time-independent Schrödinger equation to be solved for in the range $x > 0$, **state the boundary conditions** for acceptance solutions (now the hard wall kicks in), **relate** the problem to the standard 1D harmonic oscillator problem and **find all the energy eigenfunctions and eigenvalues** of this half-space oscillator problem without doing any mathematics.

4.4 **2D circularly symmetric problems** (See SQ24)

In Chapter VIII, we studied spherically symmetric potential in 3D with the property that $U(r,\theta,\phi) = U(r)$ only. It turns out that much physics can be done without even invoking the explicit form of $U(r)$. Here, it is your turn to explore similar problems in 2D. You saw a case in the mid-term exam about 2D isotropic oscillator.

In 2D, in general we have $U(x,y)$ or $U(r,\phi)$, where $(r,\phi)$ are the plane polar coordinates. In SQ24, TA worked out the transformation of the Laplacian to plane polar coordinates. The result is (if TA got it right)

$$\nabla^2_{2D} = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} = \left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \phi^2}\right) \tag{7}$$

Consider a 2D problem in which $U(r,\phi) = U(r)$ only, i.e. $U$ is circularly symmetrical. For whatever direction $\phi$, the potential energy function is the same as long as it is at a distance $r$ from the origin. [Read Chapter VII for how to handle the 3D case.] Using the method of separation of variables, i.e.,

$$\psi(r,\phi) = R(r)\Phi(\phi) \tag{8}$$

**find** the equations satisfied by radial function $R(r)$ and the angular (or azimuthal) function $\Phi(\phi)$. Next, **solve** the angular equation for physically acceptance wavefunctions.

[Remark: You just rewrite Chapter VIII for 2D circularly symmetrical potential energy functions.]

4.5 **2D rigid rotor - buy one get one free for Problem 4.4**

Near the end of Ch.VIII, we solved the 3D rigid rotor problem without any effort (because $Y_{\ell,m_\ell}$ are solutions). The problem is important for understanding rotational spectrum of molecules (how microwave oven works). Here, you will get this free gift in 2D.

This problem is also important. The problem is a mass $m$ freely moving on the circumference of a circle, i.e., the radial distance is kept constant at $R$. By freely moving, it means $U = 0$. **Write down** the TISE for this problem. [Hint: It is important to observe that the problem becomes effectively 1D (only one variable $\phi$ is involved).] Hence, **make use** of your answer in Problem 4.4 to **obtain** the energy eigenvalues and the normalized eigenstates of a 2D rigid rotor without doing more mathematics.

4.6 **Orbital Angular Momentum - Spherical Coordinates** (See SQ25)

In Ch.VII, we discussed orbital angular momentum and showed that $Y_{\ell,m_\ell}$ are simultaneous eigenstates of $\hat{L}^2$ and $\hat{L}_z$. In Problem 3.1, you did $[\hat{L}_y, \hat{L}_z]$ in Cartesian Coordinates.

Here, you will explore more on orbital angular momentum using spherical coordinates.

From class notes, copy out $\hat{L}_x$, $\hat{L}_y$ and $\hat{L}_z$, $\hat{L}^2$ in spherical coordinates. [SQ25 showed the steps in getting $\hat{L}_y$.] Let's start.

(a) Using the operators in spherical coordinates, **show that** $[\hat{L}^2, L_x] = 0$ and $[\hat{L}_z, \hat{L}_x] = i\hbar\hat{L}_y$.
[Remark: You saw these results in general form. The operators are now "represented" in spherical coordinates. Of course, the commutators will not be changed by the way we represent the operators.]

(b) **(Read parts (c) and (d) with SQ25)** The spherical harmonics $Y_{1,-1}(\theta,\phi)$ has definite $L_z = -\hbar$ and $L^2 = 2\hbar^2$. Since $[\hat{L}_z, \hat{L}_x] = i\hbar\hat{L}_y \neq 0$, $\hat{L}_z$ and $\hat{L}_x$ do not have simultaneous eigenstates. To show this, **operate** $\hat{L}_x$ on $Y_{1,-1}$ (look up $Y_{1,-1}$) and **show that** $Y_{1,-1}$ is NOT an eigenstate of $\hat{L}_x$. Further **show that** the result is proportional to $Y_{1,0}$.

(c) Hence, **show that** the expectation value $\langle L_x\rangle$ for the state $Y_{1,-1}$ vanishes.
[**Important Remarks:** Part (b) shows that a state with definite $L_z$ (namely $-\hbar$) has uncertain values of $L_x$. In class, we discussed that the $z$-direction is nothing special. Given that there are 3 possible values of the $z$-component ($\ell = 1$), there are also 3 possible components in any direction (including $x$-direction or $y$-direction or any direction). $Y_{1,-1}$ has definite $L_z = -\hbar$. If we take the state and measure $L_x$, we will obtain different values (sometimes $\hbar$, sometimes 0, sometimes $-\hbar$) when the measurements are carried out on identical copies of the state $Y_{1,-1}$. The mean value of the result, i.e. the expectation value, $\langle L_y\rangle = 0$ as shown in (c).]

4.7 **(MUST TRY) Orbital Angular Momentum ($\ell = 1$ case) - Matrix representation**

Angular momentum is a perfect place to get a sense on why matrices are useful in QM problems. Let's consider orbital angular momentum in the $\ell = 1$ case. We KNOW that commutators between any two among $\hat{L}_x$, $\hat{L}_y$, $\hat{L}_z$, and $\hat{L}^2$. For $\ell = 1$, we know that $\hat{L}_z$ (and in fact any other component) has eigenvalues $+\hbar$, 0, $-\hbar$, and $L^2 = 2\hbar^2$.

With the known information, we can also represent the operators by $3 \times 3$ matrices. Immediately, we know

$$[L_z] = \hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{9}$$

This is obviously correct as the eigenvalues are indeed $+\hbar$, 0, and $-\hbar$, as required.

How about the matrices for $L_x$ and $L_y$? [You did part of it in Problem 4.6 and TA did part of it in SQ25.] Let's consider

$$[L_x] = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \tag{10}$$

and

$$[L_y] = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix} \tag{11}$$

These matrices are good representations of the $\ell = 1$ orbital angular momentum components.

(a) **Show** that these matrices indeed satisfy the cyclic commutators, i.e. do $[\hat{L}_x, \hat{L}_y]$ and the other combinations by multiplying matrices.

(b) **Construct** the matrix representing $\hat{L}^2$. **What** are the eigenvalues? Are the results as expected?

(c) The nice thing of using matrices in studying orbital angular momentum is that the matrices are small in size ($3 \times 3$ here) and thus easy to handle. **Find the eigenvalues and eigenvectors** of $[L_x]$, $[L_y]$, and $[L_z]$.

[Remark: Pay attention to the eigenvalues. You will see they all come out to be the same. This is the point about the $z$-direction is NOTHING special. Of course, the eigenvectors are different for different operators.]

(d) This part echoes Problem 4.6(b). Take the eigenvector of $[L_z]$ for eigenvalue $-\hbar$, which is obviously a column matrix with elements (0,0,1) [it is a column and plays the role of $Y_{1,-1}$ in spherical coordinates representation]. **Show** that this is NOT an eigenvector of $[L_x]$.

(e) This part echoes Problem 4.6(c). Now **expand** this eigenvector in terms of the three eigenvectors of $[L_x]$. Hence, **give the probabilities** of getting $L_x$ being $+\hbar$, 0, and $-\hbar$ in measurements done over identical copies of the column $(0, 0, 1)^T$ (transpose will give a column). [Use what you learned in Ch.II and Ch.III.] Then, **find** the expectation value $\langle L_x \rangle$ given the state $(0, 0, 1)^T$ by (i) averaging over the probabilities, and (ii) by plugging the formula $(0, 0, 1)[L_x](0, 0, 1)^T$, which is the analogy to $\int \psi^* \hat{A} \psi dx$.

[Remarks: You may take any eigenvector of one component and expand it in terms of those in another component and ask questions.]

(f) This echoes SQ25. Take the eigenvector of $[L_z]$ for the eigenvalue $+\hbar$. **Expand** it in terms of the three eigenvectors of $[L_y]$, **give the probabilities** of getting $L_y$ being $+\hbar$, 0, and $-\hbar$ in measurements done over identical copies of the state. Hence, **find** the expectation value $\langle L_y \rangle$ for the given state.

(g) **The essence of QM measurement theory.** Here is a final check on your QM concepts. I start with the column $(1, 0, 0)^T$. Let's measure $L_z$. **What will you get**? Then take the resulting state after measurement (no need to consider time), measure $L_x$, **what can you say about the outcome?** Now you do the measurement on $L_x$, the outcome is $+\hbar$. **What is the state right after the measurement?** Now, I use the state and measure $L_z$, **what can you say about the outcome?** [And we can go on and one..., that's QM.]