PHYS3022 Applied Quantum Mechanics Problem Set 1
Due: 21 January 2020 (Tuesday); "T+2" = 23 January 2020 (Thursday) (20% discount)

All problem sets should be handed in not later than 5pm on the due date. Drop your assignments in the box labelled PHYS3022 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.

1.0 **Reading Assignment.** It is a guide to supplementary reading. No need to hand in anything. This year, PHYS3022 started off with topics left out from PHYS 3021 last term. We discussed the orbital angular momentum based on the operators $\hat{L}^2$, $\hat{L}_x$, $\hat{L}_y$, $\hat{L}_z$ written in spherical coordinates and the special functions $Y_{\ell,m_\ell}(\theta,\phi)$ that we obtained in PHYS 3021. We discussed the special features of orbital angular momentum in QM that $\vec{L}$ cannot be pointing at a fixed direction, and the best we can know is the magnitude squared and one component (usually taken to be $\hat{L}_z$). The vector model is a way to visualize these quantum results. We then discuss the solutions to the TISE of the hydrogen atom. The problem was first solved by Schrödinger in 1926. We looked at the mathematical solutions and the pictures representing the atomic states (atomic orbitals). You should have seen some of these pictures before, but now they are backed up by quantum mechanics. We will then move on to discuss Hermitian operators and the generalized uncertainty relation. Details on solving the radial functions $R_{n\ell}(r)$ of the hydrogen atom problem is given in an optional appendix. For further reading, Rae's *Quantum Mechanics* is a good place. A softer (less math) discussion with nice pictures can be found in *Modern Physics for Scientists and Engineers* by Taylor, Zafiratos, and Dubson, and *Quantum Chemistry and Spectroscopy* by Engel. A rather rigorous and clear discussion can be found in *Quantum Chemistry* by McQuarrie.

In Sample Questions, we introduced spectroscopic data, center-of-mass and relative motions, and relativistic correction to the kinetic energy term in Week 1 and Week 2.

1.1 **(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 Quantum Mechanics. [Heisenberg formulated his QM using matrices.] Let's consider the orbital angular momentum with the $\ell = 1$ case. We know that ℓ can take on many more values, i.e., $\ell = 0, 1, 2, \ldots$. If we want to represent $\hat{L}^2$ by a matrix for which the eigenvalues give all the possible values, then the size must be $\infty \times \infty$. That's not encouraging!

However, if we restrict ourselves to one possible value, e.g. $\ell = 1$, then we know that the corresponding eigenvalues of $\hat{L}_z$ can only be $+\hbar$, 0, $-\hbar$, or $m_\ell\hbar$ with $m_\ell = 1, 0, -1$, and $L^2 = 2\hbar^2$. So within the sub-structure of one ℓ value, the matrices involved should be of small sizes.

Let's consider $\ell = 1$. We know that commutators between any two components among $\hat{L}_x$, $\hat{L}_y$, $\hat{L}_z$, and the commutators of $\hat{L}^2$ and any component. Since $\hat{L}_z$ has only 3 eigenvalues, it hints us to use 3×3 matrices to represent the operators. Immediately, we know

$$[L_z] = \hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \qquad (1)$$

This is obviously correct as the eigenvalues are indeed $+\hbar$, 0, and $-\hbar$, as required. [More rigorously, with $Y_{1,m}$ being the spherical harmonics of $\ell = 1$, the matrix elements are those given by $\int Y^*_{1,m}(\theta,\phi)\,\hat{L}_z\,Y_{1m'}(\theta,\phi)\,d\Omega$, with m and m' running over $1, 0, -1$ (thus given 9 elements) and the integration is over all solid angles.]

How about the matrices for L_x and L_y? Let's consider

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

and

$$[L_y] = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix} \tag{3}$$

These matrices can be constructed by the same method with $\hat{L}_x$ and $\hat{L_y}$ replacing $\hat{L}_z$ in the integral above. These matrices are good representations of the $\ell = 1$ orbital angular momentum components. Let's see they work fine.

(a) **Show** that these matrices indeed satisfy the cyclic commutators, i.e. **evaluate** $[\hat{L}_x, \hat{L}_y]$ and **show** that it gives $i\hbar\hat{L}_z$. Check over the other combinations by multiplying matrices. [I hope you know how to multiply 3×3 matrices together.]

(b) **Construct** the matrix representing $\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$ by multiplying matrices together and adding up the results. **Illustrate** that the eigenvalues of $[L^2]$ are those you expected for $\ell = 1$.

(c) Small (3×3 here) matrices are easy to handle. To warm up, **write down** (by inspection is OK) the **eigenvectors** of $[L_z]$.

(d) **(Important idea of angular momentum in QM.) Find the eigenvalues and normalized eigenvectors** of $[L_x]$ and $[L_y]$.

[Important Remark: Pay attention to the eigenvalues of $[L_x]$, $[L_y]$ and $[L_z]$. You will see they all come out to be the same. This is the point about the z-direction is NOTHING special. In the differential equation method (solving for $Y_{\ell,m_{ell}}(\theta,\phi)$), we chose $\hat{L}_z$ because the operator is the simplest. We could have chosen any direction to be the "z"-direction. Here, you see explicitly that three different matrices $[L_x]$, $[L_y]$, and $[L_z]$ have the same eigenvalues. However, once you picked a certain direction to take on a simpler form ($[L_z]$ here), then the the eigenvectors in the other two directions are more complicated.]

(e) Let's learn something new. Let $[M]$ be a $n \times n$ matrix. If the matrix elements obey M_{ij} and M_{ji}^*, the matrix is called a Hermitian Matrix. **Identify** whether the matrices $[L_x]$, $[L_y]$, $[L_z]$, and $[L^2]$ are Hermitian Matrices.

[Learning something from a special case: Hermitian matrices have real eigenvalues.]

(f) You did a simpler problem in Problem Set 5 in PHYS 3021 last term (in differential form). Take the eigenvector of $[L_z]$ for eigenvalue $+\hbar$, which is obviously a column matrix with elements (1,0,0) [it is a column and plays the role of $Y_{1,1}$ in spherical coordinates representation]. **Show** that this is NOT an eigenvector of $[L_x]$.

(g) You also did this last term. Now **expand** this eigenvector in terms of the three normalized 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 $(1,0,0)^T$ (transpose will give a column). [Recall: Measurement theory.] Then, **find** the expectation value $\langle L_x \rangle$ given the state $(1,0,0)^T$ by (i) averaging over the probabilities, and (ii) by plugging the following formula $(1,0,0)[L_x](1,0,0)^T$, which is the analogy to $\int \psi^* \hat{A} \psi dx$ in finding the expectation value. Finally, **find** the variance $(\Delta L_x)^2$ and the uncertainty ΔL_x.

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

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

(i) **The essence of QM measurement theory.** Here is a check on your QM concepts. Let's start with the column $(1,0,0)^T$ and 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?** [This appeared in the Take-Home Final Exam Part II. And we can go on and on..., that's QM.]

1.2 Hydrogen atom and hydrogen-like stuffs

We solved the TISE of the hydrogen atom. You may look up the solutions from class notes in working out the following questions.

(a) **Write down the full Hamiltonian operator** $\hat{H}$ for the hydrogen atom. **Look up** the explicit form of the full wavefunction (radial times angular parts) $\psi_{2p_z}(r,\theta,\phi)$ from class notes or books or the web. By directly operating $\hat{H}$ on $\psi_{2p_z}(r,\theta,\phi)$, **show that** it is really an energy eigenstate and **find** the corresponding energy. [Educational value: Something straight forward often needs patience.]

(b) Beyond the hydrogen atom, there are other systems with a nucleus plus an electron. They are called hydrogen-like ions. Based on the H-atom result in part (a), **find the energy** of the $2p$ states for a He$^+$ ion.

(c) **Construct** the radial probability density $P(r)$ for the hydrogen $2p$ states. **Make a sketch** and **find** the most probable distance of an electron to be found in $2p$.

(d) Another hydrogen-like stuff is called muonic hydrogen. Muon is a particle just like an electron, but with a bigger mass. It is one of the 12 particles in the standard model of particle physics. Muonic hydrogen is a proton plus a muon (playing the role of the electron). Without solving TISE again, **find the ground state energy** and the **modified Bohr radius** of a muonic hydrogen. [Remark: This is real stuff, being made in accelerators.]

1.3 Integrals useful for evaluating hydrogen atom properties and in statistical physics

Background: The H-atom wavefunctions are of the form $R_{n\ell}(r)Y_{\ell m_\ell}(\theta,\phi)$. The spherical harmonics $Y_{\ell m_\ell}(\theta,\phi)$ have nice properties that help us handle the angular integrations when calculating quantities from the wavefunction (e.g. expectation value). For the radial part, $R(r)$ is a product of the Laguerre polynomial and an exponentially decaying function $\exp(-\beta r)$. [Often, you will see $\exp(-r/a_0)$, so there is a decaying term.] In particular, the polynomial part has the highest term of the form r^n. In integrating over all space (3D spherical coordinates), there is also a factor $r^2 dr$. All in all, we often encounter the following form of integrals in H-atom calculations. We call it I_n:

$$I_n(\beta) = \int_0^\infty r^n e^{-\beta r}\, dr \tag{4}$$

The same form of integrals also appear in statistical physics, in which the $e^{-\beta r}$ term appears as $e^{-\beta E} = e^{-E/kT}$ representing the Boltzmann factor, and the integral in Eq. (4) will be over E. Many of you are taking a thermodynamics and statistical physics course. So it worths the effort in studying how to evaluate I_n. It is simpler than you thought.

(a) **Evaluate** $I_0(\beta)$ by doing the integral.

(b) **Explore** how I_1 can be related to a derivative of I_0. Use the relation to **evaluate** $I_1(\beta)$.

(c) **Explore** how I_2 can be related to the second derivative of I_0. Use the relation to **evaluate** $I_2(\beta)$.

(d) **Generalize** the results in parts (b) and (c) to obtain $I_n(\beta)$.

[Remark: What we do here is also related to the Gamma Function, which will show up in statistical physics calculations.]

1.4 **Reduced Mass μ, transformation, and separation of variables (Related to SQ2 and SQ6)**

Background: In SQ6, TA showed that the two equations of motion for two balls connected by a spring can be manipulated into a center-of-mass (CM) equation and a relative motion equation. The reduced mass μ emerges in the process. Since the spring connects the two balls (a model of diatomic molecules) provides only an internal force and no external forces are exerted on the system, the CM moves freely. There are many similar situations in physics (including QM). Hydrogen atom is another example. It has a proton and electron. We often fix the proton at the origin and then solve the one-body electron problem. In SQ2, we saw that a correction by replacing the bare electron mass m by the reduced mass μ gives a better agreement between theoretical result and spectroscopic data in the hydrogen atom.

Here, you will consider a similar problem as in SQ6. There are two masses both living in 1D (on the x-axis): a heavier mass m_1 and a lighter mass m_2 and they interact through a potential energy function $U(x_2 - x_1)$, where x_1 and x_2 are the positions of mass m_1 and m_2, respectively. An example is that of two particles connected by a spring (as in a diatomic molecule). The time-independent Schrödinger equation (TISE) of the two-body problem is

$$\underbrace{\left\{\left[-\frac{\hbar^2}{2m_1}\frac{\partial^2}{\partial x_1^2} - \frac{\hbar^2}{2m_2}\frac{\partial^2}{\partial x_2^2}\right] + U(x_1 - x_2)\right\}}_{\hat{H}} \psi(x_1, x_2) = E\,\psi(x_1, x_2)\ , \tag{5}$$

where the Hamiltonian $\hat{H}$ is marked.

(a) We want to do a transformation from the variables x_1 and x_2 to two new variables X and x, where X is the center-of-mass (CM) coordinate and x is the relative coordinate. **Write down** (see classical mechanics book if necessary) X and x in terms of m_1, m_2, x_1 and x_2. **Carry out the transformation** of the second derivatives and **show that** the Hamiltonian $\hat{H}$ becomes

$$\hat{H} = -\frac{\hbar^2}{2M}\frac{\partial^2}{\partial X^2} - \frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial x^2} + U(x)\ , \tag{6}$$

and **identify** what M and μ are in terms of m_1 and m_2. [Hint: The transformation involves carrying out several partial derivatives. See Math Skill books in book list if necessary.]

(b) Hence, writing $\psi = \Phi(X) \cdot \phi(x)$, apply the **method of separation of variables** to TISE to **obtain** two equations, one for $\Phi(X)$ and another for $\phi(x)$. **Check** whether $\Phi(X)$ has the form $\exp(iKX)$, indicating the center-of-mass motion is free with an energy $\hbar^2 K^2/2M$.

[Remarks: Important concept here. For a N_2 molecule in a gas, its energy has several contributions. You saw the freely moving CM motion, which is the translational part. There are vibrational and rotational energies. The translational part gives the picture of point particles moving around in a gas as discussed in secondary school physics. In statistical mechanics, each part has a corresponding partition function.]