PHYS3021 Quantum Mechanics I   Problem Set 5
Due: 22 November 2017 (Wednesday)   "T+2" = 24 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.

5.0 **Reading Assignment.** (Don't need to hand in everything for this item.) Chapter IX discusses the most important 3D spherically symmetric problem in QM, namely the hydrogen atom. The main point is that for each $U(r)$, the radial equation is different and thus $R_{n\ell}(r)$ will be different, the angular part $Y_{\ell,m_\ell}(\theta,\phi)$ is the same for all $U(r)$ problem. For H-atom, the radial equation can be solved by the same Series Solution method. The results are very special due to the Coulomb $U(r) \sim -\frac{1}{r}$ form. The allowed energies $E_{n\ell}$ depends only on n (the principal quantum number) and thus E_n, giving raise to a higher degeneracy expected only of general spherically symmetric $U(r)$. In addition, for given n, the orbital quantum number runs from 0 to $n-1$. The mathematical details are given in an appendix. The more important point is to get a good sense of what the atomic orbitals are about mathematically and pictorially. For example, what you learned in the past as p_x and p_y orbitals are linear combinations of $Y_{1,1}$ and $Y_{1,-1}$. The shape of the s, p, d orbitals are important in understanding atoms, molecules, and solids. For example, d orbitals are necessary for understanding magnetism in materials. Chapter IX ends with a comparison of the QM H-atom treatment and Bohr's model.

With the experience in solving 1D, 2D, 3D standard problems, Chapter X goes back to some formal QM. It is about Hermitian operators, which carry real expectation values $\langle\hat{A}\rangle$ for any state, real eigenvalues, orthogonal eigenstates, non-negative $\langle\hat{A}^2\rangle$ for any state, and many more useful properties. Obviously, the properties are perfect for physical quantities in QM. Thus, all physical quantities in QM are represented by Hermitian operators. This statement is a postulate of QM. Chapter X explores the properties that are most relevant to QM, including simultaneous eigenstates of two commuting operators. A **general uncertain relation** concerning two operators will be derived. Operator method can also give us general results for **general QM angular momentum eigenvalue problems**. The results cover the orbital angular momentum already discussed and also the spin angular momentum to be covered in the next chapter.

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.

5.1 Hydrogen atom's energy eigenstates

While solving the radial equation requires some math maturity, testing whether a given wavefunction is an energy eigenstate requires only math patience on doing derivatives. Here is a simple case for you to test your math patience.

(a) **Write down** the full Hamiltonian operator $\hat{H}$ for H-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.

(b) Using the result in part (a), **give the energy** of the $2p$ states for He^+ ion and for Li^{2+} ion.

5.2 Probability of finding electron in hydrogen atomic orbitals

Consider the simplest case of a hydrogen atom in the $1s$ state. **Calculate** the radius of the sphere centered at the nucleus that encloses a probability of 50% of finding the electron.

5.3 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 many 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 $\exp(-\beta r)$. In particular, the polynomial part has the highest term of the form r^n. This leads to the following form of integrals that often appear in H-atom calculations.

$$I_n(\beta) = \int_0^\infty r^n e^{-\beta r}\, dr \tag{1}$$

It happens that the same form of integrals also appear in statistical physics. In that context, the $e^{-\beta r}$ term appears as $e^{-\beta E} = e^{-E/kT}$, which is the Boltzmann factor, and the integral in Eq. (1) will be over E. Thus, it worths the effort in studying how to evaluate I_n.

(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.]

5.4 **Hermitian Operators** (See SQ28)

(a) If $\hat{A}$ is a Hermitian operator, **test** whether $i\hat{A}$ is a Hermitian operator or not.

(b) **Test** whether $x\frac{d}{dx}$ is a Hermitian operator or not.

(c) After solving a QM Schrödinger equation problem in which a particle only lives in the range of $0 \leq \phi \leq 2\pi$ with eigenstates given by

$$\psi(\phi) = \frac{1}{\sqrt{2\pi}}\, e^{im\phi}\ , \quad m = 0,\, \pm 1,\, \pm 2,\, \ldots \tag{2}$$

Show that the eigenstates are orthogonal.
[Remark: If you have done Problem Set 4, you would recognize what these eigenstates are about.]

(d) **Simplest example of Schmidt orthonormalization procedure.** The point is: Two degenerate states can always be made orthogonal. Here is the procedure. Assume two normalized and degenerate eigenstates ψ_1 and ψ_2 of a QM operator $\hat{A}$, i.e.,

$$\hat{A}\psi_1 = a_1\psi_1\ , \quad \hat{A}\psi_2 = a_1\psi_2 \tag{3}$$

with the **same eigenvalue**. However, ψ_1 and ψ_2 may not be orthogonal. We want to **construct two orthogonal eigenstates** out of ψ_1 and ψ_2.

(i) **Show** that a linear combination $\phi = c_1\psi_1 + c_2\psi_2$ is also an eigenstate of $\hat{A}$ with the same eigenvalue a_1.

(ii) Thus, we can find suitable combinations ϕ_1 and ϕ_2 such that they are orthogonal, i.e., we hope that

$$\int \phi_1^* \phi_2 d\tau = 0 \tag{4}$$

by suitable choosing the coefficients in the combinations.
Without loss of generality, we can choose $\phi_1 = \psi_1$, which is normalized. For ϕ_2, we write

$$\phi_2 = \psi_2 + c\phi_1 \tag{5}$$

where c is to be adjusted so that the orthogonality requirement is satisfied. **Find** c so that Eq. (4) is satisfied.
[Remarks: (1) You may want to extend the procedure to three degenerate states or more. (2) A similar procedure is useful in forming the so-called hybridized states from atomic orbitals of one atom, e.g. you must have heard of sp^3 hybridization with four states pointing at different directions (they are orthogonal) coming from linear combining one s-orbital and three p-orbitals.]

5.5 **An alternative definition of Hermitian operators**

We defined the Hermitian operator as one that satisfies

$$\int f^* \hat{A} g \, d\tau = \int (\hat{A} f)^* g \, d\tau = \int g \hat{A}^* f^* \, d\tau \tag{6}$$

in which the definition invokes **any** two well-behaved functions f and g.

In some books, Hermitian operators are motivated by requiring real expectation values. Thus, **an alternative definition** invoking only **one** (must be any) well-behaved function f is

$$\int f^* \hat{A} f \, d\tau = \int (\hat{A} f)^* f \, d\tau = \int f \hat{A}^* f^* \, d\tau \ , \tag{7}$$

which obviously is a statement about real expectation values.

Writing $\psi = c_1 f + c_2 g$, where c_1 and c_2 are arbitrary complex constants, f and g are two well-behaved functions, **show** that the definition in Eq. (7) as applied to ψ gives the definition Eq. (6).

5.6 **Ehrenfest's theorem**

We gave a general equation for the time variation of expectation value $d\langle \hat{A} \rangle / dt$ in previous chapter and proved it in Chapter X.

The time-dependent Schrödinger equation (TDSE) is

$$\hat{H} \Psi = i\hbar \frac{\partial}{\partial t} \Psi \tag{8}$$

(a) Starting with the definition of expectation value of the position

$$\langle x \rangle = \int \Psi^*(x,t) \, x \, \Psi(x,t) \, dx \tag{9}$$

and using TDSE and its complex conjugated form, **show** that

$$m \frac{d\langle x \rangle}{dt} = \langle \hat{p}_x \rangle \tag{10}$$

[Remark: This has a close cousin in classical mechanics.]

(b) Similarly, **show** that

$$\frac{d\langle \hat{p}_x \rangle}{dt} = \left\langle -\frac{dU}{dx} \right\rangle \tag{11}$$

[Remark: This also has a close cousin in classical mechanics. More formally, the equation is written as

$$\frac{d\langle \hat{p}_x \rangle}{dt} = \left\langle -\frac{d\hat{U}}{dx} \right\rangle \tag{12}$$

where $\hat{U}$ is a function of the position operator $\hat{x}$. For the meaning of a function of an operator, **see SQ29**.]

Eq. (10) and Eq. (12) have close analogy with equations in classical mechanics. They are worth remembering as they are one of the closest gaps between QM and classical mechanics. However, pay attention to Eq. (10) and Eq. (12) – they are talking about expectation values!