PHYS3022 Applied Quantum Mechanics Problem Set 3
Due Date: 20 February 2019 (Wednesday) "T+2" = 22 February 2019 (Friday)

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

3.0 Reading Assignment.

In Part 1 of the module on the physics of atoms, we introduced various effects in atoms using the strategy of a hydrogen atom PLUS some effects. We covered spin-orbit interaction (and so reviewed orbital and spin angular momenta and introduced the total angular momentum), relativistic correction (SQ and class notes), the fine structure, Zeeman effect, and hyperfine structure, and atomic polarizability (problem set). There are two levels of understanding. Level 1 is the big picture (key ideas). They are covered in standard textbooks on *Modern Physics* (e.g. by Taylor, Zafiratos, Dubson; and by Harris) or *Quantum Physics* (e.g. by Eisberg and Resnick). These books **describes** the key ideas very clearly. For applying QM's mathematical and approximation methods to these topics, see standard QM books such as Griffiths and Rae's books. Quantum Chemistry books (e.g. by McQuarrie and by Engel) are also good. But QM treatments should be seasoned by the physics discussions in the Modern Physics books. In Part 2, we will discuss the physics of atoms beyond hydrogen. The strategy is to do a high-level popular physics treatment, i.e., making use of QM but not working out the details. For more serious discussion on Atomic Physics, see C.J. Foot, *Atomic Physics*; Mark Fox, *A student's guide to Atomic Physics*; and Bransden and Joachain, *Physics of Atoms and Molecules.*

3.1 Counting f-states ($\ell = 3$) in two ways (Closely related to SQ11)

Consider the hydrogen atom described by

$$\hat{H}_0 = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} \tag{1}$$

We solved the TISE analytically. The energy eigenstates are $\psi_{n\ell m_{ell},m_s}$, where the last quantum number m_s takes on $\pm 1/2$ for spin-up and spin-down states. To be very explicit, the set of quantum numbers $(n, \ell, m_\ell; s = 1/2, m_s)$ label the energy eigenstates. Since the single and only electron hydrogen has $s = 1/2$ always, s is usually suppressed. In SQ11, TA did this problem for the $2p$ states. Now it is your turn to work on the same problem for the $4f$ states.

(a) Consider $4f$ states, i.e., $n = 4$ and $\ell = 3$. **List out all the states** using the notations $|4, 3, m_\ell\,; s = 1/2, m_s\rangle$. **What** is the energy for each of these states?

(b) We could linearly combine the states $|4, 3, m_\ell; s = 1/2, m_s\rangle$ to form an equal number of states labelled by $|n = 4, \ell = 3, s = 1/2; j, m_j\rangle$. Using the rule of obtaining the allowed values of j and m_j, **list out all the possible states** using the notations $|4, 3, 1/2; j, m_j\rangle$. **Illustrate** that (using one example) a state $|4, 3, 1/2; j, m_j\rangle$ is an energy eigenstate of $\hat{H}_0$ given by Eq. (1) and **find** its energy.

(c) Now consider the spin-orbit interaction represented by an additional term

$$\hat{H}'_{so} = f(r)\vec{S}\cdot\vec{L} \tag{2}$$

where $\vec{S}$ is the spin angular momentum, $\vec{L}$ is the orbital angular momentum, and $f(r)$ is a function depending only on the variable r. Using the states (many of them) $|4, 3, 1/2; j, m_j\rangle$

to **form a matrix** for $\hat{H}_0 + \hat{H}'_{so}$. **Illustrate** that the $j = \ell + 1/2$ states and the $j = \ell - 1/2$ states take on different energies in the presence of $\hat{H}'_{so}$. **Given** the Term Symbol for these two groups of states. [You will go back to $4f$ states in Problem 3.3.]

3.2 Spin-orbit interaction term $\hat{H}'_{so} = f(r)\vec{S} \cdot \vec{L}$

Background: In QMI, we know that the condition for two operators to share a common set of eigenstates is that the two operators commute. This idea is the reason why we invoke the total angular momentum **J** when we need to handle spin-orbit interaction. This question (reminds you of) takes you through the argument.

We showed that the spin-orbit interaction leads to an addition term

$$\hat{H}'_{so} = f(r)\vec{S} \cdot \vec{L} \, . \tag{3}$$

This term is to be added to $\hat{H}_{atom}$ that includes the Coulomb potential energy term due to the nucleus. An example is $\hat{H}_0$ in Eq. (1) for a hydrogen atom. With $\hat{H}_{atom}$ alone, the electron's states can be labelled by $(n, \ell, m_\ell, s, m_s)$, where $s = 1/2$ (always) is the spin quantum number of an electron. The form $\hat{H}'_{so}$ is typical of two coupled angular momenta. At this point, recall the standard commutation relations that define an angular momentum in quantum mechanics.

(a) **Show or Argue** that $\hat{H}'_{so}$ does **not commute** with $\hat{L}_z$ and $\hat{S}_z$.

(b) **Show or Argue** that $\hat{H}'_{so}$ **commutes** with $\hat{L}^2$ and $\hat{S}^2$.

(c) **Show** also that $\hat{H}'_{so}$ commutes with $\hat{J}^2$ and $\hat{J}_z$, where $\vec{J} = \vec{L} + \vec{S}$ is the total angular momentum.

[**Remark on Physics (Read me):** Part (a) says quantum numbers m_ℓ and m_s are no good when $\hat{H}'_{so}$ is present. Part (b) says quantum numbers ℓ and s remain good. Part (c) says quantum numbers j and m_j are good when $\hat{H}'_{so}$ is present. Putting these together, the description (ℓ, s, j, m_j) of electron states is useful in the presence of spin-orbit interaction, while the description (ℓ, m_ℓ, s, m_s) is not. This is what you already showed by yourself in Problem 3.1.]

3.3 Weak-field Zeeman splitting for f states

The aim here is (i) to lead you to review class notes on weak-field Zeeman effect, and (b) to apply the results. You don't need to repeat the derivation. Just jump to the result and apply it. [Hint: We did the case of p states in class notes. Follow the discussion there and work out the case of f states here.]

"Weak-field" means that the spin-orbit interaction term $f(r)\mathbf{L} \cdot \mathbf{S}$ is more important than the Zeeman term due to the external field. As shown in SQ12, the internal magnetic field related to the spin-orbit interaction is not small and it is bigger in heavier atoms. Thus, the "weak-field Zeeman effect" is rather common. Before turning on the external field, the $4f$ states split into two groups according to the value of j, as you should have done in Problem 3.1.

Now, an external field **B** in turned on. For each value of j, **find** the corresponding Landé g-factor. Hence, **sketch** a figure that **illustrates the cases** of (i) no spin-orbit interaction and $\mathbf{B} = 0$, (ii) with spin-orbit interaction and $\mathbf{B} = 0$, and (iii) with spin-orbit interaction and a weak field $\mathbf{B} \neq 0$.

3.4 Strong-field Zeeman splitting plus spin-orbit interaction for f states

This problem accompanies Problem 3.3, but the external field **B** is strong so that the Zeeman splitting due to m_ℓ and m_s in the interaction term $(-\mu_L \cdot \mathbf{B} - \mu_S \cdot \mathbf{B})$ should be handled first and then the spin-orbit interaction is treated within perturbation theory. We did the case of p-states in class notes. You will work out the case of f-states.

Review class notes, take the results and **illustrate** how the degenerate f states are affected by both the Zeeman term and spin-orbit interaction in the strong field case. **Sketch** a figure similar to that of the p-states discussed in class notes.]

3.5 Adding an angular momentum of quantum number of quantum number $L = 2$ to another angular momentum of quantum number $S = 1$

Background: In hydrogen atom, there is only one electron and its spin quantum number is always $s = 1/2$. However, there are several electrons in other atoms and the electrons' spins will sum up to a total spin angular momentum characterized by a quantum number S. Similarly, the orbital angular momenta of electrons can be summed up to a total orbital angular momentum characterized by a quantum number L. Here, we follow the convention of using capital letters in situations beyond the hydrogen atom.

(a) Now for the value of $L = 2$, there are values of M_L behind it. Similarly, for the value of $S = 1$, there are values of M_S behind it. **Give the total number** of states characterized by (M_L, M_S).

(b) Two angular momenta can be added up to form a total angular momentum $\mathbf{J}$, which is characterized by possible values of its quantum number J. **What are the possible values of** J for $L = 2$ and $S = 1$? Hence, **show explicitly** that the total number of states characterized by (J, M_J) are the same as that in part (a), i.e., no more and no less.

3.6 Rewriting Hamiltonian of Helium Atom in Atomic Units (See SQ13)

Read class notes (an appendix in AP II) on the atomic units. The system measures physical quantities in units of what are set by the hydrogen atom problems, i.e., typical in atomic/molecular physics. The helium atom has its Hamiltonian in SI units as

$$\hat{H}_{helium} = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{2e^2}{4\pi\epsilon_0 r_1} - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{2e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}} \; , \tag{4}$$

where $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ and the last term is the electron-electron interaction term that makes the problem unsolvable. Starting from Eq. (4), **rewrite the Helium atom Hamiltonian** step-by-step in atomic units.

3.7 Explain a phenomenon in atomic physics

Background: In AP II, we discuss multi-electron atoms. The TISE problems cannot be solve analytically (nobody can). So our strategy is to try to **turn the many-electron problem** into **single-electron** problem. In this approach, the focus is on one electron in the atom and then regard the other electrons as providing an additional potential energy term in the single-electron Hamiltonian from which single-electron states are solved. (Do you understand the sentence? If not, read it again!) In this way, the **notion of single-electron states** or **atomic orbitals** is saved. We can then talk about $3s$ states or $3d$ states of a sodium atom, say.

Phenomenon: Take sodiium atom as an example, you probably know that the energies of $3s$, $3p$ and $3d$ are different, with $E_{3s} < E_{3p} < E_{3d}$. Rather interestingly, E_{3d} is quite close to the hydrogen $n = 3$ energy. Similarly, $E_{4s} < E_{4p} < E_{4d} < E_{4f}$ in sodium, and E_{4f} happens to be quite close to the hydrogen $n = 4$ energy.

Give an explanation (physical picture)of this phenomenon based on quantum mechanics.