PHYS3022 Applied Quantum Mechanics Problem Set 3
Due Date: 4 March 2021 (Thursday) "T+2" = 6 March 2021 (Saturday)

You should submit your work in **ONE PDF file via Blackboard** to the appropriate submission folder no later than 23:59 on the due date. Follow Blackboard → Course Contents → Problem Sets → **Problem Set Submission Folder**.

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 Physics of Atoms module, we introduced various effects in atoms using the strategy of a hydrogen atom PLUS some effects. We covered the spin-orbit interaction (and in doing so discussed general angular momentum in QM, reviewed orbital and spin angular momenta and introduced the total angular momentum), relativistic correction (SQ), the fine structure, Zeeman effect, and hyperfine structure. 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 are very good in **describing** the key ideas. 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 mathematical treatments should be seasoned by the physics discussions in the Modern Physics books. In Part 2 of the module, 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 discussions on Atomic Physics, see C.J. Foot, *Atomic Physics*; and Mark Fox, *A student's guide to Atomic Physics*. For a detailed QM treatment, see Bransden and Joachain, *Physics of Atoms and Molecules* and *Quantum Mechanics*.

3.1 (18 points) **Counting f-states ($\ell = 3$) in two ways (Related to SQ9)**

Consider the hydrogen atom described by

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

The TISE can be solved 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 in hydrogen always has $s = 1/2$, s is usually suppressed. In class notes, we illustrated that the p-states can be labelled in this way, i.e., using (m_ℓ, m_s) to account for the six p-states. Alternatively, one can use (j, m_j) to re-label the six p-states. The later labelling is needed when there is spin-orbit interaction, where the coupling asks for treatment through the total angular momentum $\vec{J}$.

Now it is your turn to work on the same problem for the $4f$ states.

(a) Consider the $4f$ 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 of each of these states after solving the TISE with $\hat{H}_0$?

(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 $|4,3,1/2;j,m_j\rangle$. **Argue** that (using one example) a state $|4,3,1/2;j,m_j\rangle$ is also an energy eigenstate of $\hat{H}_0$ and **find** its energy.

[Remark: As to what the exact linear combinations are, it will be discussed in a topic "Addition of Angular Momenta" in advanced quantum mechanics. The coefficients in the linear combination are related to the Clebsch-Gordan coefficients. We don't need them in our course.]

(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. Use the states (many of them) $|4,3,1/2;j,m_j\rangle$ to **form a matrix** for $\hat{H}_0 + \hat{H}'_{so}$ and **illustrate** that the $j=\ell+1/2$ states and the $j=\ell-1/2$ states take on different energies in the presence of $\hat{H}'_{so}$. **Give** the Term Symbol for these two groups of states. [You will go back to the $4f$ states in Problem 3.3.]

3.2 (10 points) **Spin-orbit interaction term $\hat{H}'_{so} = f(r)\vec{S}\cdot\vec{L}$**

Background: The condition for two operators to share a common set of eigenstates (simultaneous eigenstates) is that the two operators commute. This idea is the reason why we need to give up the description using (m_ℓ, m_s) and invoke the total angular momentum $\mathbf{J}$ and its z-component when there is spin-orbit interaction.

The spin-orbit interaction is given by

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

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,ℓ,m_ℓ,s,m_s), where $s=1/2$ (always) is the spin quantum number of an electron.

(a) **Show or Argue** that $\hat{H}'_{so}$ does **not commute** with $\hat{L}_z$ and $\hat{S}_z$. [Hint: Use the standard commutation relations that define an angular momentum in quantum mechanics.]

(b) **Show or Argue** that $\hat{H}'_{so}$ **commutes** with $\hat{L}^2$ and $\hat{S}^2$. [Remark: This is why we keep the $(\ell, s=1/2)$ when we invoke (j,m_j).

3.3 (16 points) **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 $f(r)\vec{L}\cdot\vec{S}$ is more important than the Zeeman term due to the external field. In SQ12, it was shown that the internal magnetic field related to the spin-orbit interaction is not small. 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 see in Problem 3.1.

Now, an external field $\mathbf{B}$ in turned on. For each value of j, **find the corresponding Landé g-factor**. Hence, **sketch** a figure for the $4f$ states 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 (18 points) **Strong-field Zeeman splitting plus spin-orbit interaction for f states**

This problem accompanies Problem 3.3, but the external field $\vec{B}$ is strong so that the Zeeman splitting due to m_ℓ and m_s in the interaction term $\hat{H}'_Z = -\vec{\mu}_L \cdot \vec{B} - \vec{\mu}_S \cdot \vec{B}$ should be handled first, and then followed by the spin-orbit interaction 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 **work out** how the degenerate f states are affected by both the Zeeman term and spin-orbit interaction in the strong field case. **Sketch a figure** illustrating how the f states are affected by the Zeeman term only **and** by the Zeeman term plus the spin-orbit interaction. [Hint: Refer to a similar figure for the p-states discussed in class notes.]

3.5 (20 points) **Very strong-field Zeeman effect: from $4f$ to $3d$**

Here, let's assume that the external magnetic field $\vec{B}$ is very strong. We need to include the effect of the Zeeman term $\hat{H}'_Z = -\vec{\mu}_L \cdot \vec{B} - \vec{\mu}_S \cdot \vec{B}$, but we **ignore the spin-orbit interaction**.

Let's consider the transition from $4f$ to $3d$ and the corresponding spectral lines. If we ignore spin-orbit interaction and there is no external field, we only expect one spectral line at the energy $(E_{4f} - E_{3d})$. For the hydrogen atom, it is the energy $13.6(\frac{1}{9} - \frac{1}{16})$ eV.

Now a strong magnetic field B is turned on. For the $4f$ states, you may take the result from Problem 3.4. Make a similar consideration for the $3d$ states. For optical transitions (light is involved (emitting light)), the allowed transitions are those with $\Delta m_s = 0$ (meaning spin is not involved in the transition mechanism) and $\Delta m_\ell = 0, \pm 1$. **Construct a figure to illustrate all the possible transitions** from $4f$ to $3d$ states. Hence, **find** the energies involved in the transitions and **demonstrate** that the result is a splitting from one line to three lines.

3.6 (18 points) **Rewriting Hamiltonian of Helium Atom in Atomic Units (Related to SQ13)**

SQ13 introduced the atomic units (see also an appendix in class notes). The system measures physical quantities in units of what are set by the hydrogen atom problems, i.e., typical in atomic/molecular physics.

(a) The helium atom has its Hamiltonian in SI units given by

$$\hat{H}_{helium} = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{2e^2}{4\pi\epsilon_0 r_1} - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{2e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}} , \tag{3}$$

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. (3), **rewrite the Helium atom Hamiltonian step-by-step in atomic units**.

(b) The Hamiltonian of a hydrogen-like atom/ion is given by

$$-\frac{1}{2}\nabla^2 - \frac{Z}{r} , \tag{4}$$

where the nucleus has Z charges (meaning Ze in SI units). **Show that**

$$\psi(\vec{r}) = A\, e^{-Zr} \tag{5}$$

is an eigenstate and **find** the corresponding eigenvalue. Hence, **give** the eigenvalue in SI units. **Find** the prefactor A by the normalization condition.