PHYS3022 Applied Quantum Mechanics Problem Set 4

Due Date: 1 March 2019 (Friday) "T+2" = 4 March 2019

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.

4.0 Reading Assignment.

After introducing the concepts of orbital and spin angular momenta, spin-orbit interaction, total angular momentum, relativistic correction, fine structure, Zeeman effect in strong and weak magnetic fields, hyperfine structure and radio astronomy within the context of the hydrogen atom, Part II of the Physics of Atoms module discussed atoms beyond the hydrogen atom. Without the electron-electron Coulomb interaction, the hydrogen atom problem is solvable. Quantum mechanics is perfect alright and essential for the understanding of the physics of multi-electron atoms, only that the Schrödinger equation cannot be solved analytically. There are two levels of understanding atoms. Level 1 is the big picture (key ideas). They are covered in standard texts such as *Modern Physics* (e.g. by Taylor, Zafiratos, Dubson; and by Harris) or *Quantum Physics* (e.g. by Eisberg and Resnick). These books **describes** the ideas clearly. For those who want to know more about the theory behind the independent particle approximation using the self-consistent field (Hartree and Hartree-Fock) approximation (Level 2), see *Physical Chemistry* and/or *Quantum Chemistry* by Donald McQuarrie. For those interested in exploring numerical calculations on atoms (molecules and solids), you may start with the free numerical package called **Quantum Espresso** available on the web. Many experimental and quantum chemistry research groups purchased a commercial software called **Guassian** for QM calculations. The next question is about filling electrons into the atomic orbitals. The key regulation is that a many-electron wavefunction must be anti-symmetric with respect to interexchanging the coordinates of two particles. This is due to the indistinguishability of the particles.

Please note

4.0.1 **Mid-Term Examination** – Please be reminded that the Mid-term Examination will be held on 16 March 2019 (Saturday) morning at 10am - 12noon in SC L1. Please pay attention to email about the exam coverage.

4.1 Writing down the ground state wavefunction of Beryllium atom formally

Many-electron wavefunctions must be anti-symmetric with respect to interchanging two electrons. This requirement can be readily implemented within the independent-particle approximation. There are single-electron states (atomic orbitals), which can be obtained by different ways. Electrons are filled into the atomic orbitals. For two-electron systems, we illustrated in class (see other problems in this Problem Set) that the wavefunction can be expressed into a product of a spatial part and a spin part. This factorization, however, may not be possible for other many-electron systems.

Beryllium is the 4th element in the periodic table. It has 4 electrons. In the ground state, the four electrons occupy the "1s-up", "1s-down", "2s-up", and "2s-down" states. We use $\phi_{1s\uparrow}$, $\phi_{1s\downarrow}$, $\phi_{2s\uparrow}$, and $\phi_{2s\downarrow}$ to represent these four normalized states. The key point is that (i) we can't tell which electron is in which state as they are indistinguishable, and thus (ii) the four-electron ground state wavefunction must change a sign when two particles are interchanged. We use 1, 2, 3, 4 for the coordinates of the four electrons.

(a) The situation is that we have four electrons in four different states. **Write down** a Slater Determinant that represents a properly normalized ground state wavefunction of Beryllium.

(b) **Argue or illustrate** that your answer in (a) is really anti-symmetric.

(c) If you were to put two electrons into 1s-down and leave 1s-up empty, **what would happen** to the corresponding 4-electron wavefunction?

(d) There are two up-spin states. For the two electrons in these up-spin states, we have one electron in 1s and another in 2s. **Discuss** what will happen to the wavefunction when we force these two electrons to be at the same place in space.

(e) A 4×4 determinant looks scary, does it? Look up how to write the determinant (4×4) into many terms with each term being a product of the four states.

4.2 **Forming two-particle states from single-particle states**

This is an important problem that Every CUHK student must do. The results will be useful in Statistical Mechanics, Astrophysics, and cold atom physics. It is related to the simplest QM problem – 1D particle-in-a-box. **Do it yourself! If not, the loss will be yours!**

(a) Consider a particle of mass m confined in a 1D infinite well of size L, e.g. $0 < x < L$. [No derivation needed – you did it the previous course.] **Write down** the normalized energy eigenstates $\psi_n(x)$ and the corresponding energy eigenvalues E_n. These are the single-particle states in this problem.

(b) **Forming two-particle states - distinguishable particles.** Consider **two distinguishable particles** of the same mass in a 1D well. The particles are non-interacting (e.g., they are chargeless). Given that particle 1 (labelled "1" or carrying a color red) is in the state ψ_m and particle 2 (labelled "2" or carrying another color blue) is in the state ψ_n, **write down** a two-particle wavefunction $\psi_{dist}(x_1, x_2)$. What is the corresponding energy eigenvalue? **Find the probability** that both particles are in the left hand side of the well, i.e., the probability that a measurement shows $0 < x_1 < L/2$ *and* $0 < x_2 < L/2$?

(c) **Forming two-particle states - symmetric spatial wavefunction.** Similar to (b), but now the **two particles are indistinguishable (identical). Don't worry about the spin part of the total wavefunction for the moment and focus on the spatial part. Write down** a two-particle wavefunction $\psi_{sym}(x_1, x_2)$ that is **symmetric** with respect to interchanging the coordinates x_1 and x_2 of the two particles. Hence, **find the probability** that both particles are in the left hand side of the well, i.e., the probability that a measurement shows $0 < x_1 < L/2$ *and* $0 < x_2 < L/2$? **Compare** your result with that in (b) and **comment**?

(d) **Forming two-particle states - antisymmetric spatial wavefunction.** Similar to (b), but now the two particles are indistinguishable (identical). Again, don't worry about the spin part of the total wavefunction for the moment and **focus on the spatial part. Write down** a two-particle wavefunction $\psi_{anti}(x_1, x_2)$ that is **anti-symmetric** with respect to interchanging the coordinates x_1 and x_2 of the two particles. Hence, **find the probability** that both particles are in the left hand side of the well, i.e., the probability that a measurement shows $0 < x_1 < L/2$ *and* $0 < x_2 < L/2$? **Compare** your results with those in (b) and (c) and **comment**?

(e) Make an observation – **Which symmetry** has an enhanced probability (relative to the case of distinguishable particles) of finding the two (non-interacting) particles in the same side? **Which symmetry** has a reduced probability of finding the two particles on the same side?

[**Read me:** Let's take a break. Recall that the system we are considering is that of two non-interacting particles in a 1D well. Although the particles are **non-interacting**, and yet the symmetry of the spatial wavefunction has an effect that seems to pull the particles closer

OR to push the particles farther apart. It looks as if the "exchange symmetry requirement" leads to a "effective force" between the particles (either attraction or repulsion). This is called the exchange force and it plays a fundamental role in many phenomena, e.g., the origin of magnetism when we include spin wavefunction into consideration.]

(f) **MUST TRY! A picture is worth a thousand words** Let's say one particle is in the single-particle ground state $m = 1$ (thus ψ_1) and another in the 1st excited state $n = 2$ (thus ψ_2). Here you need to (find a way to) do some 3D plots. Use your favorite graphic software and **plot** $\psi_{dist}(x_1, x_2)$, $\psi_{sym}(x_1, x_2)$, and $\psi_{anti}(x_1, x_2)$ as a function of x_1 and x_2 for the range $0 < x_1 < L$ and $0 < x_2 < L$. Note that these are 3D plots, as one axis being x_1, another being x_2 and the third axis is the quantity you want to plot.

(g) Also **plot** $|\psi_{dist}(x_1, x_2)|^2$, $|\psi_{sym}(x_1, x_2)|^2$, and $|\psi_{anti}(x_1, x_2)|^2$ as a function of x_1 and x_2 for the range $0 < x_1 < L$ and $0 < x_2 < L$.

Important: At this point, look at the plots carefully and **comment on** the difference between $|\psi_{sym}(x_1, x_2)|^2$ and $|\psi_{anti}(x_1, x_2)|^2$. In particular, **comment** on the difference between the two cases when the two particles are at the same place, i.e, when $x_1 = x_2$.

(h) **Identical Bosons.** Let's consider the ground state of the two identical non-interacting bosons in a 1D well. (These bosons have zero spin (quantum number $s = 0$), say, and they don't obey the Pauli exclusion principle.) **Construct** the ground state wavefunction.

(i) **Identical Fermions - Ground State. Construct** the ground state (total) wavefunction for two non-interacting identical spin-1/2 particles (thus fermions) in a 1D well (include the spin part of the wavefunction in your answer). For example, you may use α and β to denote the spin-up ($\hbar/2$) and spin-down ($-\hbar/2$) states, respectively.

[Hint: It will be useful to review how two spin-half can be added up into $S = 0$ (singlet) and $S = 1$ (triplet) states, and the mathematical forms of these states. This was discussed in adding two angular momenta.]

(j) **Identical Fermions - Excited States.** An excited state of the system in (h) is that one particle is in ψ_1 and the other in ψ_2. **Construct** all the possible total wavefunctions that satisfy the antisymmetric requirement. **Identify** the spin singlet $S = 0$ state and the spin triplet $S = 1$ states.

Finally, let's say there is actually a repulsive (e.g. Coulomb) interaction between the two fermions, would the $S = 0$ state or $S = 1$ states have a lower energy? **Don't try to do any calculation, but explain your answer.**

4.3 *Helium Atom - Excited States (1st order perturbation theory)*

This is another **must try/do** problem as it carries much physics. In class notes and SQ14, we applied 1st order perturbation theory to find the ground state energy. We also discussed the excited states in class notes for which you will explore the details here, based on the 1st order perturbation theory. The aim here is to "force you" to go over the steps in slow motion so that you can see by yourself how different terms emerge.

The helium atom Hamiltonian is given by

$$\hat{H}_{helium} = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{2e^2}{4\pi\epsilon_0 r_1} - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{2e^2}{4\pi\epsilon_0 r_2} \underbrace{+\frac{e^2}{4\pi\epsilon_0 r_{12}}}_{troublesome\ term} , \tag{1}$$

where $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$. The first four terms form the unperturbed Hamiltonian $\hat{H}_0$. The last electron-electron interaction term is the perturbation term $\hat{H}'$. Here, you will "work out" the excited states energies (**without doing the integrals explicitly**).

Consider the unperturbed Hamiltonian $\hat{H}_0$ (first four terms in Eq. (1)). It is two hydrogen-like problems. Thus, $\hat{H}_0$ can be solved analytically. We now explore the lowest excited states of two electrons. For $\hat{H}_0$, it is a separable problem. Low-energy excited states can be visualized as having one electron in 1s with wavefunction ϕ_{1s} and another electron in 2s with wavefunction ϕ_{2s}. [You don't need the explicit forms of ϕ_{1s} and ϕ_{2s} here, although they are known.] But the two electrons are **indistinguishable**. Let α and β denote the states of spin-up ($m_s = 1/2$) and spin-down ($m_s = -1/2$) of an electron, respectively.

(a) For the excited states, **write down** the possible normalized two-electron states and **classify** them into those corresponding to $S = 1$ (triplet states) and $S = 0$ (singlet state). [Hint: You did this in Problem 4.2. See also class notes]

(b) For the unperturbed Hamiltonian $\hat{H}_0$. **What** is the unperturbed energy $E^{(0)}$ of each of the excited states that you wrote down in part (a)?

(c) Let's take the last term in Eq. (1) as the perturbation, i.e.,

$$\hat{H}' = \frac{e^2}{4\pi\epsilon_0 r_{12}} \tag{2}$$

Note that $\hat{H}'$ does not depend on spin explicitly. When we consider the expectation value of $\hat{H}'$, we can simply focus on the spatial part of the triplet and singlet states. By applying the 1st order perturbation theory with the unperturbed states as those in part (a), **show that** the 1st order perturbation theory gives two different estimates

$$\begin{aligned} E_{singlet} &\approx E^{(0)} + J + K & (3) \\ E_{triple} &\approx E^{(0)} + J - K & (4) \end{aligned}$$

Here, J is an integral called the **Coulomb integral** that can be interpreted (using classical EM) as adding up the Coulomb energy of a bit charge $-e|\psi_{1s}(\mathbf{r}_1)|^2 d^3r_1$ of one electron interacting with a bit of charge $-e|\psi_{1s}(\mathbf{r}_2)|^2 d^3r_2$ of another electron. From your derivation, **write down** explicitly the expression for the integral J.

The is another integral K. **Write down** explicitly the expression for the integral K from your derivation. This integral is called the **exchange integral**. Textbooks say that "the exchange integral is a quantum effect". **Explain what this phrase really means** by thinking through where this term comes from.

(d) One can evaluate the integral K (at least numerically). The magnitude and the sign of K are both important. For helium, it turns out that $K > 0$. Given that, **which state** ($S = 0$ or $S = 1$) has the lower energy and thus become the first excited state? **Find the energy difference** between the triplet and the singlet states? Hence, **comment** on the spin alignment of the two electrons in the first excited state of helium.

(e) The following statements are often made about the origin of ferromagnetism (FM)/antiferromagnetism (AFM) (having atom's magnetic moments aligned/anti-aligned) at low temperature. (i) AF/AFM has their origin in Coulomb interaction between electrons (instead of coming from some magnetic dipole-dipole interaction as discussed in EM books), (b) it is the exchange integral that matters. **Write a few sentences** to illustrate your understanding of these two statements based on the calculations carried out in this Problem.

(f) Some students learned perturbation theory so well in the first module of PHYS3022. They saw that the singlet and triplet excited states have the same unperturbed energy. Thus, they want to start with the degenerate perturbation theory as there are 4 degenerate states. Therefore, we must have done something wrong in parts (c). Did we? We look up how to do degenerate perturbation theory. That's easy. **Set up** the 4×4 determinant for solving the eigenvalues using the singlet and triplet states in the presence of $\hat{H}'$. [Hint: The spin parts (three for $S = 1$ and one for $S = 0$) are constructed in a way that they are orthogonal to each other.] Hence, **find** the eigenvalues and **show** that the results are the same as in part (c). This justifies what we did is alright!

Read me – Important remarks: (a) Here you see an example of how the symmetry requirement of many-electron wavefunctions works to prefer spin-alignment (or for some cases spin-antialignment). (b) Note that that we don't need an external magnetic field to align them. (c) From Eqs. (3) and (4), the sign of the exchange integral K is important. It will determine alignment (ferromagnetic type preference) or anti-alignment (anti-ferromagnetic type preference) of spins. That's fine. We do have ferromagnetic and anti-ferromagnetic materials in reality. (d) A bit of statistical physics: Let's understand more about **ferromagnetism**. Think about the magnets that you play with, e.g. in motors or in souvenirs. Ferromagnets are materials that have the magnetic dipole moments (come from spins) of their atoms aligned without an applied magnetic field. Usually the temperature cannot be too high. Using the helium atom as an example, we see that quantum physics could lead to a preferred alignment of neighboring spins (thus neighboring spin magnetic moments). In a solid, atoms are arranged in a lattice. Each atom has a few nearest neighbors. Could the preference of neighboring alignment propagate to give an overall alignment of spins in the solid? What is the condition for this to occur? The answer to these questions is yes when the temperature is not too high. It is because a higher temperature (higher thermal energy kT) tends to randomize the directions of the magnetic moments and works against the alignment tendency of the exchange energy. The exchange energy competes with thermal energy in determining the extent of alignments.