PHYS3022 Applied Quantum Mechanics Problem Set 5
Due Date: 20 April 2020 (Monday) "T+2" = 22 April 2020
To submit your homework, **email your work** *to* **cuhkphys3022@gmail.com by 23:00 on the due date**. *TA will send you a reply confirming receipt of your work.*
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.**

Multi-electron atoms are examples of QM problems that cannot be solved analytically. Without the electron-electron Coulomb interaction as in the hydrogen atom, the Schrödinger Equation can be solved analytically. For multi-electron atoms, we know the Hamiltonian and the Schrödinger Equation, only that the equation cannot be solved by paper and pencil. But quantum mechanics is perfect alright and essential for the understanding of the physics of multi-electron atoms. There are two levels in 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 concept 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. The anti-symmetric wavefunction is also the key to understanding the origin of magnetism. This ends of module of Physics of Atoms.

5.1 **Writing down the ground state wavefunction of Beryllium atom**

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 (self-consistent method say). Electrons are filled into the atomic orbitals. For two-electron systems, we illustrated in class that the wavefunction can be expressed as a product of a spatial part and a spin part. This factorization, however, may not be possible for other many-electron systems (more than 2 electrons).

Beryllium is the 4th element in the periodic table. It has 4 electrons. In the ground state, the standard description is that 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 we interchange two particles. We use 1, 2, 3, 4 for the coordinates of the four electrons.

(a) **Write down** a Slater Determinant that represents a properly normalized ground state wavefunction of Beryllium.

(b) **Argue or demonstrate** 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) A 4×4 determinant looks scary, does it? The determinant can be written into a linear combination of many terms. Look up how to write the determinant ($4{\times}4$) and **write the four-electron ground state wavefunction** in part (a) into many terms with each term being a product of the four states with each electron residing in a state.

5.2 Forming two-particle states from single-particle states and looking at their behavior

This is an important problem that every CUHK student MUST do. The results will be useful in statistical mechanics, astrophysics, cold atom physics, and solid state physics. The aim is to get a good sense of how the spatial part of a two-particle symmetric (anti-symmetric) wavefunction looks like. This will help you understand a lot of stuff later in your studies. Technically, you did similar plots in the mid-term exam.

(a) Let's warm up by considering a particle of mass m confined in a 1D infinite well of size L, e.g. $0 < x < L$. [No derivation needed.] **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., taking them to be 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 right hand side of the well, i.e., the probability that a measurement shows $L/2 < x_1 < L$ *and* $L/2 < x_2 < L$?

(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 right hand side of the well, i.e., the probability that a measurement shows $L/2 < x_1 < L$ *and* $L/2 < x_2 < L$?

(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 right hand side of the well, i.e., the probability that a measurement shows $L/2 < x_1 < L$ *and* $L/2 < x_2 < L$?

(e) Looking at your results – **Compare your results in parts (b), (c), and (d) and comment? 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 **do NOT interact with each other**, yet the **symmetry of the spatial wavefunction alone 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 an "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. It is also the reason why bosons and fermions behave so differently.]

5.3 **Pictorial version of Problem 5.2**

The context is the same as that in Problem 5.2. Here, you need to use a tool to make 3D plots.

(a) **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). **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 ($\psi_{dist}(x_1, x_2)$ here).

(b) **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: 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 $x_1 = x_2$ (which is a diagonal line in the x_1-x_2 plane).

(c) **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.

(d) **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.

(e) **Identical Fermions - Excited States.** An excited state of the system in (d) 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 using the plots you did in the earlier parts.**

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

This is another **must try/do** problem as it carries much physics. The class notes outlined the physics. You will explore the details here. The aim here is to take you to go over the steps 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 can be taken as the unperturbed Hamiltonian $\hat{H}_0$. The last electron-electron interaction term can be treated as the perturbation term $\hat{H}'$. Here, you will "work out" the excited states energies (**without doing the integrals explicitly**).

For the unperturbed Hamiltonian $\hat{H}_0$ (first four terms in Eq. (1)), it is **two** hydrogen-like problems. The point is that the coordinates $\vec{r}_1$ and $\vec{r}_2$ are separable. Thus, $\hat{H}_0$ can be solved analytically. We now explore the lowest excited states of two electrons. 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 5.3 for two particles in a box.]

(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. [Students: See part (f) for what this implies in terms of a more serious treatment of evaluating all H_{ij} of the full Hamiltonian using the unperturbed states.] 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 (singlet and triplet states) as those in part (a), **show that** the 1st order perturbation theory gives two different estimates

$$E_{singlet} \approx E^{(0)} + J + K \tag{3}$$

$$E_{triple} \approx E^{(0)} + J - K \tag{4}$$

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 of charge $-e|\psi_{1s}(\mathbf{r}_1)|^2 d^3r_1$ of one electron interacting with a bit of charge $-e|\psi_{2s}(\mathbf{r}_2)|^2 d^3r_2$ of another electron. From your derivation, **write down explicitly the expression for the integral** J. [Remark: Formally the integral can be labelled by $J_{1s,2s}$.

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. [Remark: Formally the integral can be labelled by $K_{1s,2s}$.]

(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) You just did something profound. The **key concept** is that the **Coulomb interaction (see Eq. (2))** is responsible for the difference in energy between the triplet and the singlet spin states. In other words, it is the Coulomb interaction (between charges) that select the preferences of two spins being aligned or anti-aligned. This point must be firmly taken when you get into other courses (magnetic properties of solids in solid state physics).

It is tempting to think that classical electromagnetism can be used to explain the preference of alignment of magnetic dipole moments. Let's say there are two magnetic dipole moment, each with magnitude of the Bohr magneton μ_B and they are separated by standard atomic separation, say, 2 to 3 Å. For the dipole-dipole interaction, a rough estimation of the interacting energy is $E \sim \frac{\mu_0}{4\pi}\frac{\mu_B^2}{r^3}$, where the $1/r^3$ represents the short-range nature of dipole-dipole interaction. **Plug in numbers** to obtain the interaction energy in eV. Hence, **turn the energy** into a **temperature**.

Using the fact that Iron, Cobalt, and Nickel are magnetic at temperatures up to 1043 K, 1404 K, and 631 K, respectively, **discuss the validity** of using the dipole-dipole interaction as the mechanism for magnetism in solids.

(f) Some students learned perturbation theory well in 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? Let's do degenerate perturbation theory. **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! [Hint: The comment in part (c) about $\hat{H}'$ is spin-independent becomes important here.]

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) Here, we only worked on two spins. In a solid, atoms are arranged in a lattice. Each atom has a few nearest neighbors. There are many electrons and many spins. 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.