PHYS3022 Applied Quantum Mechanics Problem Set 4
Due Date: 18 March 2021 (Thursday) "T+2" = 20 March 2021

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.

4.0.0 **Mid-Term Examination (Must Read)** – Please be reminded that the Mid-term Examination will be held on 20 March 2021 (Saturday) morning at 10am - 12noon in SC L1 and L2. Details about seating and time of arrival will be announced via emails. **Those registered with me for online version because they are away from Hong Kong will be informed of the arrangements in due course. No more registration will be entertained after 11 March 2021.**

Coverage (has been announced in a earlier email): Module on approximation methods and Module on Physics of Atoms, including materials in class notes, lectures, sample questions, and problem sets.

4.0 **Reading Assignment.**

After discussing how the picture of atomic orbitals (single-electron states) can be retained even in many-electron atoms in second part of the module on the Physics of Atoms, we continued the discussion on the anti-symmetric requirement on many-electron wavefunctions. The anti-symmetric wavefunction requirement leads to the Pauli Exclusion Rule (which refers to filling of electrons into single-electron states and therefore is less general). Through the discussion on the Helium Atom ground state, we see that it must be a spin singlet ($S = 0$) state. For the Helium Atom excited states, we have the possibility of having a symmetric spatial part to go with the spin singlet ($S = 0$) and an anti-symmetric spatial part to go with the spin triplet ($S = 1$). We see that the indirect Coulomb integral or exchange integral enters. It has no classical physics interpretation, but it is crucial in determining such possibility has a lower energy. It is the origin of magnetism. We also discussed some features of the elements organized into the periodic table. For reading on the physical picture, see 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 are very good in **describing** the ideas. 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, 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.

This Problem Set covers the discussions on Multi-electron Atoms

4.1 (15 points) **Writing down the ground state wavefunction of Lithium atom** (See SQ16)

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). Electrons are filled into the atomic orbitals. For two-electron systems, we illustrated in class (helium atom ground and excited states) that the wavefunction can be factorized into a spatial part and a spin part. This factorization, however, may not be possible for other many-electron systems.

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

(a) **Write down** a properly normalized ground state wavefunction in the form of a Slater Determinant.

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

(c) If you were to put two electrons into 1s-up and leave 1s-down empty, **what would happen** to the corresponding 3-electron wavefunction?

(d) What will be the value of the wavefunction when two electrons happen to have the same coordinates, e.g. "1" = "2"?

(e) Although we are sure that there are electrons in "1s-up" and "1s-down", whether the "third electron" is in "2s-up" or "2s-down" is not sure. To take into account of our ignorance (don't know whether it is up or down), **what would you write down** as the wavefunction of the lithium atom ground state.

4.2 (30 points) **Forming two-particle states from single-particle states**

Every CUHK student must do this important problem. 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!**

(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 in 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) is in ψ_m and particle 2 (labelled "2" or carrying another color) is in ψ_n, **write down** a two-particle wavefunction $\psi_{dist}(x_1, x_2)$. **What** is the corresponding **energy eigenvalue**? **Find the probability** that the particles are both 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) Similar to (b), but now consider **two indistinguishable (identical) particles**. **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 the particles are both 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) Similar to (b), but now consider two indistinguishable (identical) particles. 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 the particles are both 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) Now compare the results in (b), (c) and (d), **which symmetry** has an enhanced probability (relative to the case of distinguishable particles) of finding the two particles on the same side? **Which symmetry** has a reduced probability of finding the two particles on the same side?

(f) Now if the two particles are spin-1/2 fermions and the two states are different ($m \neq n$). **Write down the two-fermion wavefunctions including spins** that invoke (i) the symmetric spatial wavefunction in part (c) and (ii) the antisymmetric spatial wavefunction in part (d). **What is the wavefunction** when the two states are the same, i.e. $m = n$? [You may use the symbols α and β for the spin-up and spin-down states, respectively.

[**Read me**: The two particles are **non-interacting**. Yet, the symmetry of the 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 an "effective force" between the particles (either attraction or repulsion), even there is no actual interaction between them. 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, and the pressure in ideal Fermi gas.]

(g) Up to here, we assumed that the particles are non-interacting. If we are to include a repulsive interaction modelled by $V(|x_1 - x_2|)$, **comment on** whether the symmetric wavefunction or the antisymmetric wavefunction would have a lower energy.

4.3 (30 points) **Plotting two-particle wavefunctions - A picture is worth a thousand words** (See SQ17)

(a) **MUST TRY!** This problem continues on with the context in Problem 4.2.

Let's say one particle is in the single-particle ground state 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** (i) $\psi_{dist}(x_1, x_2)$, $\psi_{sym}(x_1, x_2)$, and $\psi_{anti}(x_1, x_2)$ as a function of x_1 and x_2 for the range $0 < x_1 < L$ and $0 < x_2 < L$. (ii) **Plot** also $|\psi_{dist}(x_1, x_2)|^2$, $|\psi_{sym}(x_1, x_2)|^2$, 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 $0 < x_2 < L$. Note that these are 3D plots, as one axis is x_1, another is x_2 and the third axis is the quantity you want to plot. At this point, look at the plots carefully and **comment on** the difference between $|\psi_{sym}(x_1, x_2)|^2$ and $|\psi_{anti}(x_1, x_2)|^2$.

(b) Just to convince you that what you observe in part (a) is not accidental, **repeat the plots** in part (a) for one particle in the single-particle ground state $m = 1$ (thus ψ_1) and another in the 2nd excited state $n = 3$ (thus ψ_3).

Intermission: Let's review the essentials of the Helium Atom

The helium atom is the playground to learn the physics of multi-electron atoms. The helium atom Hamiltonian in SI units is

$$\hat{H}_{helium} = \underbrace{-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{2e^2}{4\pi\epsilon_0 r_1} - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{2e^2}{4\pi\epsilon_0 r_2}}_{\hat{H}_0} \underbrace{+\frac{e^2}{4\pi\epsilon_0 r_{12}}}_{troublesome\ term} , \qquad (1)$$

where $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$.

The idea is (i) to avoid doing many-electron problems and (ii) to reduce many-electron (2-electron) problems to single-electron problems. Carrying out this scheme and the picture that the two electrons are in the lowest 1s atomic orbital for the ground state emerged. With anti-symmetric requirement for many-electron wavefunctions, the helium atom ground state wavefunction is

$$\psi_{GS}(1,2) = \underbrace{\phi_{1s}(\mathbf{r}_1)\phi_{1s}(\mathbf{r}_2)}_{symmetric\ spatial\ part} \underbrace{\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \alpha(2)\beta(1)\right]}_{anti-symmetric\ spin\, part}, \tag{2}$$

where α represents the spin-up ($m_s = +1/2$) state and β represents the spin-down ($m_s = -1/2$) state. Equation (2) is the only proper form that satisfies the anti-symmetric requirement.

We encountered the form Eq. (2) twice in the following occasions.

- **Perturbation Theory** - We can take the first 4 terms in Eq. (1) as the unperturbed $\hat{H}_0$ and the electron-electron interaction term (last term) as $\hat{H}'$. In this case, $\phi_{1s}(\mathbf{r}_1)\phi_{1s}(\mathbf{r}_2)$ is the solution to $\hat{H}_0$ and thus each ϕ_{1s} is a hydrogen-like wavefunction, which is **known**. SQ14 takes on this viewpoint.
- **Variational Calculation** - Taking the charge in the states within $\phi_{1s}(\mathbf{r}_1)\phi_{1s}(\mathbf{r}_2)$ as a variational parameter, a better result can be obtained. SQ15 filled in the details.
- In **Hartree type approximation**, $\phi_{1s}(\mathbf{r})$ itself is an **unknown** wavefunction yet-to-be-determined. By including an average effect of one electron in ϕ_{1s} on the other electron also in ϕ_{1s}, an equation (Hartree equation) can be set up to solve for $\phi_{1s}(\mathbf{r})$ **self-consistently**. An Appendix in the class notes further discussed this point.

The following question is about the helium atom excited states.

4.4 (25 points) **Helium Atom - Excited States (1st order perturbation theory)**

This is another **must try/do** problem as it carries much physics.

The helium atom Hamiltonian is given in Eq. (1). The first four terms form the unperturbed Hamiltonian $\hat{H}_0$ and the last electron-electron interaction term is the perturbation term $\hat{H}'$. We discussed the idea in class notes. You will explore more here, based on the 1st order perturbation theory, (**without doing the integrals explicitly**).

We now explore the lowest excited states of two electrons. For $\hat{H}_0$ (the first four terms in Eq. (1)), 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}.] 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.

There are two spatial wavefunctions to be considered. They are

$$\psi^s(\mathbf{r}_1, \mathbf{r}_2) = \psi^{singlet}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}}\left[\phi_{1s}(\mathbf{r}_1)\phi_{2s}(\mathbf{r}_2) + \phi_{2s}(\mathbf{r}_1)\phi_{1s}(\mathbf{r}_2)\right] \tag{3}$$

$$\psi^t(\mathbf{r}_1, \mathbf{r}_2) = \psi^{triplet}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}}\left[\phi_{1s}(\mathbf{r}_1)\phi_{2s}(\mathbf{r}_2) - \phi_{2s}(\mathbf{r}_1)\phi_{1s}(\mathbf{r}_2)\right] \tag{4}$$

Eq. (3) will go with a spin singlet state and Eq. (4) will go with a spin triplet state; and thus the labels.

Your task is to examine the effect of the last term in the Hamiltonian using the two options Eq. (3) and Eq. (4).

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

$$\hat{H}' = \frac{e^2}{4\pi\epsilon_0 r_{12}} \tag{5}$$

Note that $\hat{H}'$ does not depend on spin explicitly. Don't worry about the first 4 terms forming the unperturbed Hamiltonian $\hat{H}_0$. It is given that $E_0 \equiv \langle\psi^s|\hat{H}_0|\psi^s\rangle = \langle\psi^t|\hat{H}_0|\psi^t\rangle = -5/2\,E_h$, where E_h is the Hartree (a unit of energy).

Your task is two consider the expectation value of $\hat{H}'$ using ψ^s and ψ^t. By applying the 1st order perturbation theory, **show explicitly** that the theory gives different estimates of the energy

$$E_{singlet} \approx E^{(0)} + J + K \tag{6}$$

$$E_{triplet} \approx E^{(0)} + J - K \tag{7}$$

and **write down explicitly from your derivations what the integrals J and K are.** **Give the interpretation** of the term J. The other integral K is called the indirect Coulomb or the **exchange integral**. Textbooks say that "the exchange integral is a quantum effect". **Explain what this phrase really means.**

(b) 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?

(c) The following statements are often made about the origin of ferromagnetism (FM) and anti-ferromagnetism (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), (ii) it is not the direct integral J that matters, and (iii) it is the exchange integral that matters. **Write a few sentences to illustrate your understanding** of these statements based on the calculations you carried out in this Problem.