PHYS3022 APPLIED QUANTUM MECHANICS

SAMPLE QUESTIONS FOR DISCUSSION IN WEEK 7 EXERCISE CLASSES (1 March - 5 March 2021)

The Sample Questions are designed to serve several purposes. They either review what you have learnt in previous courses, supplement our discussions in lectures, or closed related to the questions in an upcoming Problem Set. Students should be able to do the homework problems independently after attending the exercise class. **You should attend one exercise class session.** You are encouraged to think about (or work out) the sample questions before attending exercise class and ask the TA questions.

Progress in our course: We started to discuss the quantum mechanics of multi-electron atoms. For the many-electron Schrödinger Equation, the strategy is to reduce it to solving one-electron problems for the **atomic orbitals**. We used the helium atom ground state problem to illustrate the possibility of handling the effects of the other electron (electrons in bigger atoms) on one electron in an averaged way. It leads to an effective one-electron Schrödinger Equation problem, although solving the equation often requires **self-consistent calculations**. We also illustrated that a variational calculation using a product of one-electron (atomic) states gives reasonable result, thus further supporting the idea of approximating many-electron wavefunctions by a product of single-electron atomic states. These ideas eventually led to the **Independent Particle Approximation** (IPA). After solving for the single-electron states, the next step is to **fill the electrons into the atomic orbitals**. We know there is the **Pauli Exclusion Principle**. The more general principle is that the **many-electron wavefunctions must be anti-symmetric** with respect to interchanging any two electrons. It is due to the **indistinguishability of electrons**. Combining this requirement with IPA, the Pauli Exclusion Principle comes out. Filling the atomic orbitals with the Pauli Exclusion Principle explains the periodic table. These are the key points of Atomic Physics.

In discussing the helium atom ground state, we introduced the Hartree method of handling the electron-electron interaction. We **claimed the result of the Direct Coulomb Integral without prove**. A similar integral is also needed in the variational method. The TAs will fill in the mathematical details in evaluating the Direct Coulomb Integral here.

SQ14 Helium atom ground state energy - First order perturbation theory
SQ15 Helium atom ground state energy - Variational method

The Helium Atom

The helium atom is the simplest many-electron system and it is the playground to learn the physics of multi-electron atoms. The helium atom Hamiltonian in SI units is

$$\hat{H}_{helium} = \underbrace{\overbrace{-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{2e^2}{4\pi\epsilon_0 r_1}}^{\hat{h}_1} \overbrace{-\frac{\hbar^2}{2m}\nabla_2^2 - \frac{2e^2}{4\pi\epsilon_0 r_2}}^{\hat{h}_2}}_{\hat{H}_0} + \frac{e^2}{4\pi\epsilon_0 r_{12}}\ , \tag{1}$$

where $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$. Given $\hat{H}_{helium}$, we tried every tool we have in our box. We tried the first order perturbation theory and the variational method. More importantly, the results **illustrate** the way to move on to approximate a two-electron QM problem by one-electron problems by treating the effect of one electron on the other approximately.

When we invoke such approximation we will obtain single-electron states (atomic orbitals). It is the spirit of the Independent Particle Approximation (IPA). IPA is useful in atomic physics and nuclear physics. Let's consider the **ground state** of a helium atom. We know that the ground state has **two electrons** in the helium $1s$ atomic orbitals, with one electron being "spin-up" and another "spin-down". With two spin-1/2 particles, the total spin $\vec{S}$ has its quantum number being $S = 1$ (triplet spin states) or $S = 0$ (singlet spin state). In Week 7, we will discuss that quantum mechanical **many-electron wavefunctions must be antisymmetric** with respect to interchanging the coordinates of the two electrons. The proper helium atom ground state wavefunction is

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

The spin part is the $S = 0$ singlet state. Here, "1" (and "2") represents the coordinates (x,y,z, and spin) of electron #1 (and electron #2). We used α to represent the spin-up ($m_s = +1/2$) state and β the spin-down ($m_s = -1/2$) state. The spin part in Eq. (2) makes sure that the helium atom ground state wavefunction $\psi(1,2)$ is anti-symmetric with respect to interchanging the two electron's coordinates. What it means is that if we interchange $\mathbf{r}_1 \leftrightarrow \mathbf{r}_2$ and $1 \leftrightarrow 2$ in $\psi(1,2)$, we have $\psi(2,1) = -\psi(1,2)$. We will discuss more about Eq. (2) and the spin part later. Here, it is the spatial part that goes into the calculations.

We used $\psi(1,2)$ several times in our discussions.

- Perturbation Theory - The first 4 terms in Eq. (1) form the unperturbed problem $\hat{H}_0$ and the electron-electron interaction term (last term) is the perturbation $\hat{H}'$. 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 Method - The form of Eq. (2) and the hydrogen-like form of $\hat{H}_0 = \hat{h}_1 + \hat{h}_2$ motivate a trial wavefunction that can be used in a variational calculation. SQ15 takes on this viewpoint.

- In Hartree type approximation, $\phi_{1s}(\mathbf{r})$ is an **unknown** and yet-to-be-determined wavefunction. By including an averaged 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**.

SQ14 *Helium Ground State energy using first-order perturbation theory.* (Educational, but the techniques in evaluating the integrals are Optional for Exam Purposes)

In class notes, we claimed the result of the first-order perturbation approach, which needed the expectation value of $e^2/4\pi\epsilon_0 r_{12}$ for $\phi_{1s}(\mathbf{r}_1)\phi_{1s}(\mathbf{r}_2)$. Here, the TA will show the calculations.

The first four terms forming $\hat{H}_0 = \hat{h}_1 + \hat{h}_2$ gives an exactly solvable problem. The problem defined by

$$\hat{h} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{2e^2}{4\pi\epsilon_0 r} \tag{3}$$

is a **hydrogen-like** problem and thus its solutions are known. In this case, $\phi_{1s}(\mathbf{r})$ is a hydrogen-like $1s$ state of the form

$$\phi_{1s}(\mathbf{r}) = \phi_{100}(\mathbf{r}) = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-\frac{Z}{a_0}r} \tag{4}$$

where $Z = 2$ for $\hat{h}$ in Eq. (3). [Remark: $Z = 1$ gives the hydrogen atom $1s$ state].

(a) For $\phi_{1s}(\mathbf{r}_1)\phi_{1s}(\mathbf{r}_2)$ with $\phi_{1s}(\mathbf{r})$ given by Eq. (4), **what is the zeroth-order energy** of the helium atom problem in units of eV and in Hartree (atomic units).

(b) Using Eq. (2) (with $\phi_{1s}(\mathbf{r})$ in Eq. (4)) as the unperturbed wavefunction for the ground state, the first-order perturbation theory (in Hartree E_h and in eV) gives an integral over $\mathbf{r}_1$ and $\mathbf{r}_2$, i.e., integrating over 6 variables. **Evaluate the integral explicitly, with clear explanations**.

[Remark: The answer is $\frac{5}{8}Z = \frac{5\times 2}{8}\ E_h = \frac{5}{4}\ E_h$, as given in class notes. Here the TA will work out the not-too-easy integrals.]

(c) Hence, **obtain** the helium atom ground state energy in first order perturbation theory and compare it with the known value of $-2.9033\ E_h$.

SQ15 *Helium ground state energy using variational method.* (Techniques of evaluating the integrals are Optional for Exam Purposes)

Here is a twist on the problem and another way of using Eq. (2). Instead of using $Z = 2$ in the wavefunction $\phi_{1s}(\mathbf{r})$ in Eq. (4), let's turn Z into a **variational parameter** and call it ζ. So the variational problem is defined by

$$\hat{H}_{helium} = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{2e^2}{4\pi\epsilon_0 r_1} - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{2e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}}\ , \tag{5}$$

with the trial wavefunction

$$\psi_{trial}(\mathbf{r}_1,\mathbf{r}_2) = \left(\frac{1}{\sqrt{\pi}}\left(\frac{\zeta}{a_0}\right)^{3/2} e^{-\frac{\zeta}{a_0}r_1}\right)\cdot\left(\frac{1}{\sqrt{\pi}}\left(\frac{\zeta}{a_0}\right)^{3/2} e^{-\frac{\zeta}{a_0}r_2}\right) \tag{6}$$

(a) **Evaluate** $\langle\hat{H}_{helium}\rangle$ with respect to the trial wavefunction to obtain

$$\langle\hat{H}_{helium}\rangle = E(\zeta) = -\zeta^2 + 2\,\zeta(\zeta - \underbrace{2}_{nuclear\ charge}) + \frac{5}{8}\,\zeta = \zeta^2 - \frac{27}{8}\,\zeta \tag{7}$$

when the result is expressed in atomic units (in Hartree).

[Hints: The term $-\frac{2e^2}{4\pi\epsilon_0 r_1}$ in $\hat{H}_{helium}$ can be written as $-\frac{\zeta e^2}{4\pi\epsilon_0 r_1} - \frac{(2-\zeta)e^2}{4\pi\epsilon_0 r_1}$. The same goes for the term involving r_2. The integral in SQ14 will also be useful.]

(b) **Apply** the variational method, i.e., varying the value of ζ to search for the best value, to **obtain the best estimate** to the helium atom ground state energy.

[Remarks: Comparing the variational calculation result to the known value of helium ground state energy is $-2.9033\ E_h$, the approximation works quite well. Note that we only included one variational parameter ζ in the trial wavefunction in Eq. (6). This idea opens up wilder ideas. How about inserting more parameters? (Ans: Yes, it should work better.) How about **varying the whole function** $\phi_{1s}(\mathbf{r})$? (Ans: Yes! This can also be done!) And this is the formal mathematical approach to obtain the Hartree approximation with the self-consistent equation for $\phi_{1s}(\mathbf{r})$ as discussed in class. More formally, the mathematics invoked is functional derivatives, quite like what you did in varying the trajectory $x(t)$ (which is a function) of a particle from (x_1, t_1) to (x_2, t_2) in classical mechanics in discussing the less action principle.]