PHYS3022 APPLIED QUANTUM MECHANICS

SAMPLE QUESTIONS FOR DISCUSSION IN WEEK 6 EXERCISE CLASSES (18 Feb - 22 Feb 2019)

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 discussed 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**. These **Independent Particle Approximation** (IPA) can be carried out in different ways. A key idea is self-consistency, as we introduced through the Hartree approximation in the context of the helium atom ground state. For multi-electron atoms, the next step is to **fill the electrons into the atomic orbitals**. We know of the **Pauli Exclusion Principle**. But 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.

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 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 the problem defined by $\hat{H}_{helium}$, we try 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). 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, and one electron is "spin-up" and another is "spin-down". To write this physical picture down mathematically, the helium atom ground state wavefunction is

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

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 $\psi(2,1) = -\psi(1,2)$. This is a QM rule for multi-electron wavefunctions. We will discuss more about the spin part later. Here, it is the spatial part that goes into the calculations.

We encountered the form Eq. (2) several times.

- 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 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**.

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

In class notes, we discussed the first-order perturbation approach as as a first attempt to understand helium atom and claimed the result. Here, 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). For the hydrogen atom solved last term, $Z = 1$.

(a) For $\phi_{1s}(\mathbf{r}_1)\phi_{1s}(\mathbf{r}_2)$ with $\phi_{1s}(\mathbf{r})$ given in Eq. (4), **what is the zeroth-order energy** 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.

[Remark: The answer $\frac{5}{8}Z = \frac{5\times 2}{8}\ E_h = \frac{5}{4}\ E_h$ was 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.* (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.

[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 $\phi_{1s}(\mathbf{r})$ that we discussed in Appendix B of AP II. More formally, the mathematics invoked is functional derivatives, quite like what you did in varying the trajectory of a particle from (x_1, t_1) to (x_2, t_2) in classical mechanics in the discussion of the less action principle. When you tried different paths, you are trying different functions $x(t)$ with both ends fixed, thus varying the function $x(t)$.]