PHYS3022 APPLIED QUANTUM MECHANICS

SAMPLE QUESTIONS FOR DISCUSSION IN WEEK 9 EXERCISE CLASSES (23-27 March 2020)

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. **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 physics and QM behind multi-electron atoms and the periodic table. For the many-electron Schrödinger Equation, the Independent Particle Approximation (IPA) reduces it to an one-electron problem. Indistinguishability of electrons turn out to impose the requirement that **many-electron wavefunctions must be anti-symmetric** with respect to interchanging any two electrons. Combining this requirement with IPA, the Pauli Exclusion Principle comes out. Filling the IPA single-electron states, called atomic orbitals, following the Pauli Exclusion Principle explains the periodic table. These are the key points of Atomic Physics.

SQ21 Helium atom ground state energy - First order perturbation theory
SQ22 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 is (ignoring finer details such as spin-orbit interaction)

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

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

The whole idea is (i) to avoid doing many-electron problems and (ii) to reduce many-electron (2-electron here) problems to single-electron problems. Within the Independent Particle Approximation (IPA), the helium atom ground state can be considered to have its two electrons both in the 1s atomic orbital, but in different m_s state (usually thought to be one up and one down). QM consideration requires the ground state of the whole helium atom to be a spin singlet state with the wavefunction

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

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 a proper form. It is anti-symmetric with respect to interchanging the two electron's coordinates. This is a QM rule for multi-electron wavefunctions.

We used the spatial part in Eq. (2) in several discussions.

- Perturbation Theory - We can take the first 4 terms in Eq. (1) as $\hat{H}_0$ 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**. SQ21 takes on this viewpoint.
- We can introduce a variational parameter into $\phi_{1s}(\mathbf{r})$ and do variational calculation. SQ22 is related to this viewpoint.

- In Hartree type approximation, $\phi_{1s}(\mathbf{r})$ is an **unknown** and 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) for $\phi_{1s}(\mathbf{r})$ can be set up from which $\phi_{1s}(\mathbf{r})$ can be solved **self-consistently**.

SQ21 *Helium Ground State energy using first-order perturbation theory.* (Educational, but the integrals are Optional for Exam Purposes)

In class notes, we discussed the first-order perturbation approach as a first attempt to understand helium atom and claimed the result (without showing the calculation).

The first four terms forming $\hat{H}_0$ gives an exactly solvable problem. In this case, $\phi_{1s}(\mathbf{r})$ is a hydrogen-like 1s state of the form

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

where $\zeta = 1$ for hydrogen atom and it takes on other values for hydrogen-like atoms/ions.

(a) For the given $\hat{H}_0$, the parameter ζ in Eq. (3) is fixed at $\zeta = 2$. **Write down** the zeroth-order energy for the unperturbed wavefunction in Eq. (2) in both eV and in Hartree (atomic units).

(b) Using Eq.(2) as the unperturbed wavefunction, **estimate the ground state energy of helium** by the first-order perturbation theory (in Hartree E_h and in eV). The point here is to illustrate that the integrals can be done analytically, although not-too-easy. [Remark: The answer $\frac{5\times 2}{8}\ E_h = \frac{5}{4}\ E_h$ was given in class notes.]

SQ22 *Helium ground state energy using variational method.*

Here is a twist on the problem and another way of using Eq. (2). Instead of using $\zeta = 2$ in the wavefunction $\phi_{1s}(\mathbf{r})$, let's keep ζ undetermined and use it as a **variational parameter**. The Hamiltonian is given by Eq. (1). TA: Making use of the integrals already done (with minor changes to cope with ζ), **show that** the expectation value of the Hamiltonian (Eq. (1)) with the trial wavefunction is given by

$$E(\zeta) = -\zeta^2 + 2\,\zeta(\zeta - \underbrace{2}_{nuclear\ charge}) + \frac{5}{8}\zeta = \zeta^2 - \frac{27}{8}\zeta \tag{4}$$

in atomic units. Hence, apply the variational principle to **find the optimal value of** ζ and hence the **best estimate of helium ground state energy**.

[Remarks: (i) Plugging $\zeta = 2$ in Eq.(4) gives the result of first order perturbation as in SQ20. (ii) The known value of helium ground state energy is $-2.9033\ E_h$. (iii) Both first-order perturbation (SQ21) and variational method (SQ22) results are quite good, compared with the known value. (iv) Here, we insert one variational parameter ζ in the trial wavefunction. This idea opens up many 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 will give the Hartree approximation with the self-consistent equation for $\phi_{1s}(\mathbf{r})$! See class notes Appendix.]