PHYS3022 APPLIED QUANTUM MECHANICS

SAMPLE QUESTIONS FOR DISCUSSION IN WEEK 5 EXERCISE CLASSES (24-28 February 2020)

You are encouraged to think about (or work out) the sample questions before attending exercise class and ask questions. You should attend one exercise class session per week.

SQ11: Variational method estimation of ground state energy of hydrogen atom using a gaussian trial wavefunction

SQ12: Infinite well with V-shaped bottom - trial wavefunction of linear combination form and the art of guessing trial wavefunction

SQ11 *Variational Method estimation of ground state energy of a hydrogen atom by a student who only knows harmonic oscillator physics*

Background: We learned the analytic/exact solutions to the hydrogen atom (see class notes for a review). The allowed energies are determined by the equation governing the radial function $R(r)$. For the ground state ($1s$ state), the angular part is $Y_{00}(\theta,\phi)$, which is just a constant. Since $\ell = 0$ for s states, the term $\ell(\ell+1)/2\mu r^2$ in the radial equation vanishes, where μ is the effective mass (discussed in SQ6). The $1s$ ground state wavefunction and the ground state energy can be found by solving the radial equation

$$\hat{H}_r R(r) = \left[-\frac{\hbar^2}{2\mu}\left(\frac{1}{r^2}\frac{d}{dr}(r^2\frac{d}{dr})\right) - \frac{e^2}{4\pi\epsilon_0 r}\right] R(r) = E\,R(r)\ , \tag{1}$$

where $\hat{H}_r$ denotes the operator $[\cdots]$ in the radial equation. The range of r is $r > 0$ (there is no negative r in spherical coordinates). This can be solved analytically (Laguerre functions). Here, we pretend that we don't know the solutions.

A student learned QM and only learned the harmonic oscillator part well. Just picked up the variational method, the student proposes a trial wavefunction of the form (copying from oscillator ground state)

$$\phi(r) = A\,e^{-\lambda r^2} \quad \text{for } r > 0 \tag{2}$$

where λ will be used as the variational parameter. Here, the prefactor A is given by

$$A^2 = 8\sqrt{\frac{2\lambda^2}{\pi}}. \tag{3}$$

so that $\phi(r)$ is **normalized in the form** of

$$\int_0^\infty |\phi(r)|^2\, r^2 dr = \int_0^\infty A^2 e^{-2\lambda r^2}\, r^2 dr = 1 \tag{4}$$

There seems to be a missing factor of 4π in the integral, but we will also forget the same 4π factor in evaluating the energy expectation value. At the end, it makes no harm.

TA: **Evaluate** $\langle\hat{H}_r\rangle_\phi$ by working out

$$\langle\hat{H}_r\rangle_\phi = \int_0^\infty \phi^*(r)\hat{H}_r\,\phi(r)\, r^2 dr \stackrel{?}{=} \frac{3\lambda\hbar^2}{2\mu} - \frac{2e^2}{4\pi\epsilon_0}\sqrt{\frac{2\lambda}{\pi}} \tag{5}$$

It is alright to look up integral table for some integrals. Hence, **find** the value of λ_{best} that minimizes $\langle\hat{H}_r\rangle_\phi$ and the best estimate of the ground state energy. **Compare** the result with the exact value $E_{GS} = -\frac{\mu e^4}{2\hbar^2(4\pi\epsilon_0)^2}$.

SQ12 *Variational Method applied to Infinite well with V-shaped bottom - Trial wavefunction of linear combination form*

Background: The most useful applications of the variational method are related to using a trial wavefunction of the form $\phi_{trial} = c_1\psi_1 + c_2\psi_2 + c_3\psi_3 + \cdots$, i.e. **a linear combination of well-chosen functions**. The variational method is backed up by the theorem $\langle \hat{H}_r \rangle_\phi \geq E_{GS}$. So the trial wavefunction is meant to mimic the actual ground state wavefunction. Proposing a good trial wavefunction requires good physical sense.

Consider a 1D infinite well with a V-shaped bottom. The potential energy function $U(x)$ between $0 < x < a$ is that it drops linearly from zero to $-U_0$ at $x = a/2$ (middle of the well) and then increases linearly back to 0 at $x = a$. Outside the well ($x \leq 0$ and $x \geq a$), $U(x) = \infty$.

Writing down a good trial wavefunction ϕ_{trial} is an art and a science. If ϕ_{trial} captures the more of the key features of the actual ground state wavefunction (not known), the better will be the estimate.

Let's think like a physicist! The V-shaped $U(x)$ reminds us of the infinite well problem with a flat $U = 0$ bottom inside the well. This is the easiest QM problem and we know all the energy eigenvalues and the eigenstates. They are:

$$\phi_n = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) \quad \text{with} \quad E_n = \frac{n^2\pi^2\hbar^2}{2ma^2} \quad (n = 1, 2, 3, \ldots) \tag{6}$$

For the V-shaped problem, the ground state should *look like* ψ_1 of the flat-bottom problem. Of course, ψ_1 is not the correct ground state wavefunction. What else do we expect? It should be symmetric about the center ($x = a/2$) of the well because $U(x)$ is symmetric, and a bit higher at the middle (than ψ_1) so as to make use of the lower potential energy there. Mixing in a bit of ψ_2 (which is anti-symmetric about the center) is not a good idea, because it will ruin the symmetric feature of ψ_1 (which is a correct feature). Naturally, the next idea is to mix in a bit of ψ_3, which is symmetric about the center. This leads us to the following choice of a trial wavefunction

$$\begin{aligned} \phi_{trial}(x) &= c_1\ \psi_1(x) + c_3\ \psi_3(x) \\ &= c_1 \sqrt{\frac{2}{a}}\ \sin\left(\frac{\pi x}{a}\right) + c_3 \sqrt{\frac{2}{a}}\ \sin\left(\frac{3\pi x}{a}\right) \end{aligned} \tag{7}$$

for estimating the ground state energy. Here, c_1 and c_3 are used as the variational parameters.

TA: We discussed in class that ϕ_{trial} of the form in Eq. (7) leads to a 2×2 matrix problem. For the given ϕ_{trial}, **apply the variational method** to set up the problem, and **estimate** the ground state energy of a V-bottomed infinite well. [TA: Please do the math as plainly as possible.]

Optional: It will be interesting to see explicitly **why** $\phi_{trial} = c_1\psi_1 + c_2\psi_2$ **doesn't help** much.

[Remarks: Here we see an example of a trial wavefunction carrying two variational parameters. It can be more. If we want to do better by including one more $\psi_n(x)$, which one will you choose? If we include more and more terms, will the accuracy of the result improve? What if we include infinitely many terms? How will the result be connected to the exact formalism of changing TISE to a huge matrix problem?]