PHYS3022 Applied Quantum Mechanics Problem Set 3
Due: 3 March 2020 (Tuesday); "T+2" = 5 March 2020 (Thursday) (20% discount)
Note special arrangement for handing in Problem Set 3. To submit your homework, **email your work** to **cuhkphys3022@gmail.com by 23:00 on the due date**. TA will send you a reply confirming receipt of your work.
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.

3.0 **Reading Assignment.** It is a guide to supplementary reading. No need to hand in anything. We began the discussion on several approximation methods, as most real problems in QM cannot be solved analytically. The topics are covered in standard QM textbooks, such as Griffiths' *Introduction to Quantum Mechanics* and Rae's *Quantum Mechanics.* Softer (less math) discussions in books either on Modern Physics or Quantum Physics, e.g. *Modern Physics for Scientists and Engineers* by Taylor, Zafiratos, and Dubson, and *Modern Physics* by Randy Harris are also useful. The treatment in our course combines mathematics and physical sense.

In Week 4, we re-wrote TISE into a huge matrix problem. It is an exact approach. We will refer to the exact matrix formulation many times. The *variational method*, which is based on an one-sided guessing theorem, was then introduced. A particularly useful application is to use trial wavefunctions in the form of a linear combination of several functions. We showed that the variational method gives a matrix problem. The matrix elements are similar to the exact approach, only that the matrix is of smaller size. Thus, the variational method provides the conceptual back-up for truncating the exact big matrix. **This Problem Set is about the Variational Method.** In Week 5, we will develop the *time-independent non-degenerate perturbation theory* up to second order and the degenerate perturbation theory. They can also be understood in terms of making approximations on the huge matrix. Griffiths and Rae's books are both good on these topics. They presented the derivations (of the same results) slightly differently. It is interesting to see how two excellent authors look at a problem differently. The discussion so far points to the importance of **matrix mathematics** (a bit of it) in QM. Here, you will have the chance to re-do **simple matrix math**.

3.1 **Harmonic Oscillator - Insightful trial wavefunction could give excellent result**

Consider the one-dimensional harmonic oscillator problem with the Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\,\omega^2 x^2 \ . \tag{1}$$

We solved this problem exactly. Let's pretend that we don't know the answer.

Our task is to estimate the ground state energy using the variational method. Let's use a trial wavefunction of the form

$$\phi(x) = A\,e^{-\lambda x^2} \tag{2}$$

with λ being the variational parameter. Here, A is a normalization factor. **Apply the variational method to estimate the ground state energy** of the Hamiltonian in Eq. (1). Compare your result with the exact ground state energy and **comment on the reason behind the accuracy**.

3.2 **Quartic potential energy function - Variational Method**

[Hint: You just did some Gaussian integrals in Problem 3.1. Some of them are useful here. But there is one more Gaussian integral to do in this problem. You may work it by yourself or look it up from websites or tables (if you know what integral tables are).]

Consider a one-dimensional Hamiltonian in which the potential energy function is quartic in x, i.e.,

$$\hat{H} = \hat{T} + \hat{U} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + ax^4 \; , \tag{3}$$

which describes a particle of mass m under the influence of a potential energy of the form $\sim x^4$. Solving TISE is hard.

Let's take on the humble task of estimating the ground state energy based on the variational method. Proposing a trial wavefunction is an art and a science. The problem has $U(x) \sim x^4$, which is symmetric about $x = 0$, i.e., $U(x) = U(-x)$. We expect the ground state wavefunction to be symmetric about $x = 0$ and there is no node. Following this physical sense and our knowledge on the harmonic oscillator, let's use again a trial wavefunction of the form

$$\phi(x) = A\, e^{-\lambda x^2} \tag{4}$$

with λ being the variational parameter. **Apply the variational method to estimate the ground state energy** of the Hamiltonian in Eq. (3).

3.3 Harmonic oscillator with additional quartic term - Variational Method with trial wavefunction of linear combination form

Consider the Hamiltonian given by

$$\hat{H} = \left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2 \right] + ax^4 = \hat{H}_0 + \hat{H}' \; , \tag{5}$$

which is a harmonic oscillator characterized by $\hat{H}_0$ with an additional quartic term $\hat{H}'$. We want to set up a variational calculation. If there is $\hat{H}_0$ alone, we know the solutions. They are $\phi_n(x)$ for the **normalized energy eigenfunctions** with the corresponding $E_n^{(0)} = (n + \frac{1}{2})\hbar\omega$. Here, the superscript (0) emphasizes that these energies are those of $\hat{H}_0$.

Let's use the trial wavefunction

$$\phi(x) = c_0\, \phi_0(x) + c_2\, \phi_2(x) \tag{6}$$

with c_0 and c_2 being the variational parameters.

We discussed in class that such a linear combination form will lead to a 2×2 matrix problem of the form

$$\begin{pmatrix} H_{11} - E\, S_{11} & H_{12} - E\, S_{12} \\ H_{21} - E\, S_{21} & H_{22} - E\, S_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0 \tag{7}$$

(a) **Demonstrate** that for the trial wavefunction $\phi(x)$ in Eq. (6), Eq. (7) can be simplified to

$$\begin{pmatrix} E_0^{(0)} + H'_{00} - E & H'_{02} \\ H'_{20} & E_2^{(0)} + H'_{22} - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0 \tag{8}$$

where $E_0^{(0)} = \hbar\omega/2$ and $E_2^{(0)} = 5\hbar\omega/2$. Here, H'_{ij} are hard-to-do integrals. **Write down the form of the integrals** H'_{ij} (don't need to do the integral).

Hence, using the condition for non-trivial solutions, **solve for** E and **obtain an expression for the estimated ground state energy** of $\hat{H}$.

(b) **Explain why** the following trial wavefunction

$$\phi(x) = c_0\,\phi_0(x) + c_1\,\phi_1(x) \tag{9}$$

is a **bad choice** for this problem.

3.4 2×2 **matrices carry much physics and matrices ain't frightening. Street-fighting matrix math. (Must try)**

Background: From the general form Eq. (7) for a trial wavefunction of the form $\phi = c_1\phi_1 + c_2\phi_2$, we can solve for E by setting the determinant of the 2×2 matrix to zero. This **can be done exactly** as it is just a quadratic equation of E. In Problem 3.3, we saw that if the two functions in the linear combinations are normalized and orthogonal to each other, the matrix problem becomes:

$$\begin{pmatrix} H_{11} - E & H_{12} \\ H_{21} & H_{22} - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0 \tag{10}$$

In QM, we often encounter Eq. (10) or we make approximations so that Eq. (10) is what we want to deal with. Note that $H_{12} = H_{21}^*$ as the Hamiltonian is a Hermitian operator. [Remark: You solved it exactly in Problem 3.3.]

Therefore, we must acquire some mathematical sense about 2×2 matrix and its eigenvalue problem (as in Eq. (10)). This problem serves to illustrate that 2×2 stuffs are easy, and there is useful approximation with a clear physical picture although one can solve the problem exactly.

Inspecting Eq. (10), it is an eigenvalue problem of a 2×2 matrix defined by H_{ij}, with $i, j = 1, 2$. This leads us to consider a 2×2 matrix of the form

$$\begin{pmatrix} E_A & \Delta \\ \Delta & E_B \end{pmatrix} \tag{11}$$

where we simply take Δ to be a real number. [You may take one of them to be Δ^* if you like.] The corresponding eigenvalue problem is

$$\begin{pmatrix} E_A - E & \Delta \\ \Delta & E_B - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0 \tag{12}$$

(a) Easiest case! When $\Delta = 0$, **what are the eigenvalues** and the **corresponding eigenvectors**.

(b) Second easiest case. Now $\Delta \neq 0$. Consider the special case of $E_A = E_B = E_0$. **Find** the **eigenvalues**. For each eigenvalue, **find** the corresponding **normalized eigenvector**.

[**Physics Remarks**: This simple case is **very important**. For $\Delta = 0$, the two eigenvales are equal. We have two degenerate states $(1,0)^T$ representing ϕ_1 and $(0,1)^T$ representing ϕ_2. For $\Delta \neq 0$, you see the eigenvalues shift away from each other: one eigenvalue (energy in QM) goes down and another eigenvalue (energy) goes up. **Carry this result with you.** In classical physics, this is related to the coupling of two oscillators with identical fundamental frequency. In QM, it is related to the theory called LCAO (Linear Combinations of Atomic Orbitals) for bonding in diatomic molecules formed by two identical atoms. One result gives a bonding orbital (lower eigenvalue/energy) and the other an anti-bonding orbital (higher eigenvalue). You heard of them in CHEM1070.]

(c) Consider the **general case** of $E_A \neq E_B$. We assume $E_A < E_B$ without loss of generality. Let's call the eigenvalues E_1 and E_2. **Find the eigenvalues** by solving a quadratic equation **exactly**. [You may copy results from Problem 3.3.] For E_1 and E_2, **find the corresponding eigenvectors**. [Here, you solved the 2×2 eigenvalue problem exactly.]

(d) **Very important, poor person's perturbation theory, must do!** Let's assume that $|\Delta| \ll |E_B - E_A|$. The physical meaning is that E_A and E_B are well separated and Δ is much smaller than the separation. Then there is a **small parameter** in the problem. Starting with the exact expressions for the two eigenvalues in part (c), **expand the square root** (something like $(1+x)^{1/2}$ for small x) and **find approximate expressions** for the two eigenvalues E_1 and E_2. Identify E_1 as the eigenvalue that is closer to E_A and E_2 the one closer to E_B.

Hence, **make a sketch to illustrate** the following **physical picture** that emerges from the math: (i) the lower eigenvalue E_A is altered by an amount $\Delta^2/(E_A - E_B)$ and thus it is "pushed down"; (ii) the higher eigenvalue E_B is altered by an amount $\Delta^2/(E_B - E_A)$ and thus it is "pushed up"; and both shifts are due to the **small coupling** Δ (recall that $|\Delta| \ll |E_B - E_A|$ is assumed) between the two states of eigenvalues E_A and E_B.

[**Take-home picture/slogan:** Higher state is pushed up and lower state is pushed down, and take the approximated eigenvalue expressions with you. The coupling Δ "pushes" the two energies, originally well separated, further apart. This is street-fighting matrix math.]

(e) If all these are too abstract, **find the eigenvalues** of

$$\begin{pmatrix} 8 & \Delta \\ \Delta & 3 \end{pmatrix} \tag{13}$$

for $\Delta = 1$ and $\Delta = 0.1$. For each case, **compare** the exact eigenvalues with approximated values using the formulas in part (d).

3.5 Atomic polarizability of a hydrogen atom - Quantum Mechanics in action

Background: A hydrogen atom in ground state ($1s$) has the nucleus (proton) and the center of mass of the electron probability distribution $|\psi_{1s}(\mathbf{r})|^2$ overlapped. (Recall that $1s$ is like a sphere centered at the origin (nucleus).) Therefore, there is no electric dipole moment. When a **static electric field** $\vec{\mathcal{E}} = \mathcal{E}\hat{z}$ is applied to a hydrogen atom, the nucleus and the electron cloud will be shifted slightly in opposite directions along the z-direction, leading to an **induced electric dipole moment** $\vec{\mu} = \alpha\vec{\mathcal{E}}$, where α is **the atomic polarizability of the hydrogen atom**. This is discussed in Griffiths' *Introduction to Electrodynamics* (Chapter 4 in the 3rd edition). Griffiths even gave a number of $\alpha/(4\pi\epsilon_0) = 0.667 \times 10^{-30}$ m^3 for hydrogen. Note that the smallness 10^{-30} is actually related to a factor a_0^3, where a_0 is the Bohr radius. Classical electromagnetism then uses α to obtain the electric susceptibility χ_e and then the permittivity ϵ. But the origin of the atomic polarizability is quantum mechanical in nature. Here, we will calculate α using the variational method.

The situation is similar to that of Eq. (5), with a solvable part $\hat{H}_0$ plus a term due to the electric field. Let $\hat{H}_0$ be the hydrogen atom Hamiltonian. We solved it analytically. We know that the ground state wavefunction is ψ_{1s} and the energy $E_{1s} = -e^2/(2\kappa_0 a_0) = -13.6\ eV$, where $\kappa_0 = 4\pi\epsilon_0$. We also know an excited state called $2p_z$ state with wavefunction ψ_{2p_z} and energy $E_2 = -e^2/(8\kappa_0 a_0) = -13.6/4\ eV$.

The effect of a static electric field $\vec{\mathcal{E}} = \mathcal{E}\hat{z}$ is to introduce an addition term in the Hamiltonian. For this extra term, "think classical" gives an **interaction energy** $-\vec{\mu}\cdot\vec{\mathcal{E}} = -(-e\vec{r})\cdot\vec{\mathcal{E}} = ez\mathcal{E} = er\mathcal{E}\cos\theta$. Therefore, the full Hamiltonian of a hydrogen atom in an applied electric field is

$$\hat{H} = \hat{H}_0 + \hat{H}' = \hat{H}_0 + e\mathcal{E}r\cos\theta \tag{14}$$

The extra term $\hat{H}'$ in $\hat{H}$ is analogous to the quartic term added to a harmonic oscillator problem in Problem 3.3.

Since $\hat{H}'$ has the effect of shifting the $1s$ electron cloud a little bit in the z-direction, the resulting distribution can be mimicked by a combination of ψ_{1s} and ψ_{2p_z}. To study the effect of $\hat{H}'$, a trial wavefunction is

$$\phi = c_1\psi_{1s} + c_2\psi_{2p_z} \ , \tag{15}$$

which is a linear combination of functions. This will lead to a 2×2 matrix problem in variational method. We need to calculate H_{11}, H_{12}, and H_{22} in Eq. (7). I leave the S_{ij} to you. To help you out (actually rather obvious), **show that** $H_{11} = -e^2/(2\kappa_0 a_0)$ and $H_{22} = -e^2/(8\kappa_0 a_0)$. But H_{12} is harder, so I give you the result of

$$H_{12} = \frac{8}{\sqrt{2}}\left(\frac{2}{3}\right)^5 e\mathcal{E}a_0$$

Set up the 2×2 matrix problem and **solve for an estimated ground state energy** in the presence of the electric field $\mathcal{E}$. Hence, **show** that the energy is of the form

$$E \approx -\frac{e^2}{2\kappa_0 a_0} - (\textit{something})\, \kappa_0 a_0^3 \mathcal{E}^2 \tag{16}$$

and **find** that "something".

Going back to classical electromagnetism. The energy required to induce an electric dipole moment is given by $-\alpha\mathcal{E}^2/2$. This is what we see in Eq. (16). Apply this result to **demonstrate that the atomic polarizability** α is given by

$$\alpha = (\textit{number})\, \kappa_0 a_0^3 \tag{17}$$

and **give** the "number". [Note: The known/experimental value is $(4.5)\kappa_0 a_0^3$.] Now, you have applied QM and the variational method to calculate a measurable physical quantity of an atom. This is real stuff and Quantum Mechanics in Action.

[Remarks: Problems 3.3-3.5 form a set of problems related to 2×2 matrices in QM and the most useful way of applying the variational method in real QM problems. Problem 3.5 also forms part of the module on the "Physics of Atoms".]