PHYS3022 Applied Quantum Mechanics Problem Set 1
Due: 23 January 2019 (Wednesday); "T+2" = 25 January 2019 (Friday) (20% discount)
All problem sets should be handed in not later than 5pm on the due date. Drop your assignments in the box labelled PHYS3022 outside Rm.213.
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.

1.0 **Reading Assignment.** It is a guide to supplementary reading. No need to hand in anything. PHYS3022 started off with a 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. Our treatment combines mathematics and physical sense.

We first wrote TISE into a huge matrix problem as an exact treatment. 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, which can be regarded as a truncation of the huge matrix in the exact treatment. In Week 2, we will develop the *time-independent non-degenerate perturbation theory* up to second order and the degenerate perturbation theory as a by-product of approximating 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. Sample Questions in Week 2 illustrate how the variational method works. Here, you will do some problems by yourself.

1.1 **Reduced Mass μ, transformation, and separation of variables (Extending SQ2)**

Background: Hydrogen atom is a two-body problem with a proton and electron. In QM, we often fix the proton at the origin and then study it as a one-body problem. In doing so, a correction of replacing the bare electron mass m by the reduced mass μ is made. A H_2 molecule (ignoring the electrons) consists of two nuclei connected by a bond. This two-body problem can be treated as a freely motion center-of-mass (CM) motion plus a single-body vibrational motion. The same goes to the rotational rotation. In SQ2, TA showed that this is true for two identical masses by making transformation to the CM and relative coordinates. Here, you will extend the consideration to a heavier mass m_1 and a lighter mass m_2 interacting through $U(x_2 - x_1)$.

For simplicity, consider a two-particle system in 1D. The two-particle interaction is represented by a potential energy function $U(x_2 - x_1)$, i.e., depends only on the combination $(x_2 - x_1)$ of the positions x_1 of mass m_1 and x_2 of mass m. An example is that of two particles connected by a spring (as in a diatomic molecule). In 3D, the Coulomb interaction between a proton and an electron also depends on the separation between them. The time-independent Schrödinger equation (TISE) is

$$\underbrace{\left\{\left[-\frac{\hbar^2}{2m_1}\frac{\partial^2}{\partial x_1^2} - \frac{\hbar^2}{2m_2}\frac{\partial^2}{\partial x_2^2}\right] + U(x_1 - x_2)\right\}}_{\hat{H}}\psi(x_1, x_2) = E\,\psi(x_1, x_2)\ , \tag{1}$$

where the Hamiltonian $\hat{H}$ is marked.

(a) **(See SQ2)** We want to do a transformation from the variables x_1 and x_2 to two new variables X and x, where X is the center of mass coordinate and x is the relative coordinate. **Write down** (see classical mechanics book if necessary) X and x in terms of m_1, m_2, x_1 and x_2.

Carry out the transformation of the second derivatives and **show that** the Hamiltonian $\hat{H}$ becomes

$$\hat{H} = -\frac{\hbar^2}{2M}\frac{\partial^2}{\partial X^2} - \frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial x^2} + U(x) \ , \tag{2}$$

and **identify** what M and μ are in terms of m_1 and m_2. [Hint: The transformation involves carrying out several partial derivatives. See Math Skill books in book list if necessary.]

(b) Hence, writing $\psi = \Phi(X) \cdot \phi(x)$, apply the **method of separation of variables** to TISE to **obtain** two equations, one for $\Phi(X)$ and another for $\phi(x)$. **Check** whether $\Phi(X)$ has the form $\exp(iKX)$, indicating the center-of-mass motion is free with an energy $\hbar^2 K^2/2M$.

[Remarks: Important concept here. For a N_2 molecule in a gas, its energy has several contributions. The freely moving CM motion is the translational part. There are vibrational and rotational energies. The translational part gives the picture of point particles moving around in a gas as discussed in secondary school physics. In statistical mechanics, each part has a corresponding partition function.]

1.2 Variational Method: Harmonic oscillator

Consider a 1D harmonic oscillator for which the Hamiltonian is given by

$$\hat{H} = \hat{T} + \hat{V} = \frac{\hat{p}^2}{2m} + \frac{1}{2}k\hat{x}^2 = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2 \tag{3}$$

where the first term is the kinetic energy and the second term is the potential energy. The problem was solved exactly in QMI. Here, we pretend that we don't know the exact solution.

(a) Proposing a good trial wavefunction for the variational method is more an art than a science. Let's say we are not good at that. **A lousy proposal** of a trial wavefunction is

$$\phi_{trial}(x) = \begin{cases} \sin\lambda x & \text{for } -\frac{\pi}{\lambda} < x < \frac{\pi}{\lambda} \\ 0 & \text{otherwise} \end{cases} \tag{4}$$

which is not properly normalized. Pictorially, it is one wavelength of a sine wave, with λ adjusting the width. It is a bad proposal because it has a node at $x = 0$ and does not capture the key features of a ground state wavefunction. Nonetheless, the theorem $\langle\hat{H}\rangle_\phi \geq E_{GS}$ is valid.

Carry out a variational calculation using ϕ_{trial} to obtain the best estimate to E_{GS} and **contrast** your result with the exact value of $E_{GS} = \hbar\omega/2$.

(b) **A Twist that makes a lousy choice clever. Make an educated discussion** based on the symmetry of the trial wavefunction and argue that the estimated value in part (a) is actually a guess on the 1st excited state of the oscillator problem instead. Hence, **compare and comment** on the estimate value in light of the known energy of the 1st excited state $E_1 = 3\hbar\omega/2$.

[Remark: Here, you see a way how physicists have extended the variational method to go beyond guessing at the ground state energy.]

1.3 2×2 matrices are important in quantum physics and they can be treated exactly

Background: Two points here. Point #1: We showed in class that the time-independent Schrödinger Equation (TISE) can be turned into a huge matrix problem (typically $\infty \times \infty$ matrix problem) using a complete set of basis functions. Each matrix element is of the form $H_{ij} - ES_{ij}$. We also discussed that the practical approach is to *truncate* the problem to a smaller one. Point #2: In addition, when a trial wavefunction of a linear combination of functions is used in a variational calculation, a matrix problem of the same elements emerges, only that the size of the matrix is equal to that of the number of functions in the linear combination (thus smaller). Obviously, matrices are important in QM.

Let's truncate the huge matrix to retain only a 2×2 matrix problem. That is to say, what's left is one value of i and one value of j. Without loss of generality, the remaining 2×2 matrix equation takes on the form (see more on Approximation Methods in class notes):

$$\begin{pmatrix} H_{11} - E\,S_{11} & H_{12} - E\,S_{12} \\ H_{21} - E\,S_{21} & H_{22} - E\,S_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0 \tag{5}$$

with $H_{21} = H_{12}^*$ and $S_{21} = S_{12}^*$. The retention of S_{ij} implies that we have NOT assumed orthonormal properties of the basis functions. This form often appears in QM problems.

(a) For non-trivial solutions of c_1 and c_2, the determinant should vanish. Using this condition to **solve** for the allowed values for E exactly. [Hint: Recall what determinant is, then solve a quadratic equation for E.]

(b) There is a simpler form of Eq. (5) that appears in QM problems. First of all, if $S_{ij} = \delta_{ij}$, Eq. (5) becomes

$$\begin{pmatrix} H_{11} - E & H_{12} \\ H_{21} & H_{22} - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0 \tag{6}$$

Secondly, if $H_{11} = E^{(0)} + H'_{11}$, $H_{22} = E^{(0)} + H'_{22}$, (note the same $E^{(0)}$ appears in H_{11} and H_{22}), and $H_{12} = H'_{12}$, $H_{21} = H'_{21}$, Eq. (5) (or Eq. (6)) becomes

$$\begin{pmatrix} E^{(0)} + H'_{11} - E & H'_{12} \\ H'_{21} & E^{(0)} + H'_{22} - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0 \tag{7}$$

where $H'_{21} = H'^{*}_{12}$. In perturbation theory, these symbols have physical meanings. Typically, $E^{(0)} \gg H'_{11}$ and $E^{(0)} \gg H'_{22}$ in physics problems, but all these do not matter here. For Eq. (7), **find** the allowed values of E. [You may apply the results in (a) to this special case, or you may solve it again.]

[Important Remarks: Your answer to part (a) (the matrix in Eq. (5)) is important to the theory of bonding when two atoms come together to form a molecule. It is also related to non-degenerate perturbation theory up to 2nd order. Your answer in part (b) (the matrix in Eq. (7)) is related to the *time-independent* **degenerate** *perturbation theory.* The word "degenerate" is reflected in the same $E^{(0)}$ that appears in the "11" and "22" matrix elements in Eq. (7). Here, you did what the scary name of degenerate perturbation theory really means.]

1.4 **All CUHK students must do this.** 2×2 **matrices carry much physics and matrices ain't frightening. Street-fighting matrix math.**

Background: You solved exactly the 2×2 matrices that appear in QM problems in Problem 1.3. Sometimes, we don't need to do the mathematics exactly. This problem reminds you of the essential 2×2 stuffs and how useful/dirty approximation can be made. Inspecting Eq. (6) (above), 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

$$\begin{pmatrix} E_A & \Delta \\ \Delta & E_B \end{pmatrix} \tag{8}$$

where we simply take Δ to be a real number. The corresponding eigenvalue problem is

$$\begin{pmatrix} E_A - E & \Delta \\ \Delta & E_B - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0 \tag{9}$$

(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**. You see the eigenvalues become farther apart due to $\Delta \neq 0$: 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) of diatomic molecules formed by two identical atoms. This is an approximated form of Eq. (7) in Problem 1.3. One result gives a bonding orbital (lower eigenvalue) 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**. For E_1 and E_2, **find** the corresponding eigenvectors. At this point, we handled the 2×2 problem in Eq. (9) exactly (as you did in Problem 1.3). [Hint: Solving a quadratic equation, again.]

(d) **Very important, poor person's perturbation theory, must do!** Let's assume that $|\Delta| \ll |E_B - E_A|$, i.e., 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, **draw a picture to illustrate** the following **physical picture** that emerges from the math in your answer: (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** (recall that $|\Delta| \ll |E_B - E_A|$ is assumed) Δ between the two states of eigenvalues E_A and E_B.

[**Take-home picture:** Higher state pushed up and lower state pushed down, and take the approximated eigenvalue expressions with you. This is street-fighting matrix math.]

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

$$\begin{pmatrix} 10 & \Delta \\ \Delta & 3 \end{pmatrix} \tag{10}$$

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

1.5 **Variational Method: Tilted infinite well with trial wavefunction being a linear combination of functions (Closely resemble SQ5)**

Consider an infinite 1D well that $U(x) = \infty$ for $x \leq 0$ and $x \geq a$. Inside the well $0 < x < a$, the potential is tilted, with $U(x)$ increasing linearly from $U(0) = 0$ to $U(a) = U_0$. Here, you will estimate the ground state energy by the variational method.

See SQ5 for the art of proposing a reasonable trial wavefunction. Sketch $U(x)$ and inspect it. Think like a physicist. Make a guess (draw it out) on the shape of the ground state wavefunction AND think whether the ground state energy is higher or lower than that of an 1D infinite square well with a flat $U(x) = 0$ inside. These ideas will guide you through the variational calculation. As $U = \infty$ outside the well, the wavefunction vanishes there.

(a) A reasonable trial wavefunction *inside* the well for the tilted case is

$$\phi(x) = c_1\psi_1(x) + c_2\psi_2(x) = c_1\sqrt{\frac{2}{a}}\sin\frac{\pi x}{a} + c_2\sqrt{\frac{2}{a}}\sin\frac{2\pi x}{a}\ . \tag{11}$$

Obviously, $\psi_1(x)$ and $\psi_2(x)$ are the normalized ground state and first excited state of an infinite well with $U = 0$ inside the well.

Using c_1 and c_2 as the variational parameters for minimizing $\langle \hat{H} \rangle_\phi$, where $\hat{H}$ is the Hamiltonian operator (recall $\hat{H} = \hat{T} + \hat{U}$), the result is a 2×2 matrix problem. In general, it is of the form of Eq. (5) in Problem 1.3. You may use the result **without** re-driving it. There are a few integrals to do to set up the matrix. **Do them** and **estimate the ground state energy** of a tilted well based on the variational method.

(b) Consider two cases: a slightly tilted well, e.g. $U_0 = E_1/2$, where E_1 is the ground state energy of a flat infinite well; and a more tilted well, e.g. $U_0 = 2E_1$. Let's say we apply the result in part (a) to these two cases. [You need not do that explicitly.] For which case you believe the variational approach will give a more reliable result, and **why**? [**Give the argument behind your answer.**]

(c) A student wants to do a variational calculation with another trial wavefunction of the form

$$\widetilde{\phi}(x) = c_1\sqrt{\frac{2}{L}}\sin\frac{\pi x}{L} + c_3\sqrt{\frac{2}{L}}\sin\frac{3\pi x}{L} \tag{12}$$

instead of Eq. (11). **Comment on the appropriateness** of this choice.

(d) (Optional Extensions: No bonus points) A bit more work could also give you a rough estimate of the corresponding wavefunction, i.e., find the corresponding c_1 and c_2 and hence $\phi(x)$ for the estimated ground state energy. This can be checked against your guess of the ground state wavefunction. For students who want to do more, solve the TISE for the tilted well numerically. You may use a numerical package to solve TISE and compare results with variational calculation.

1.6 **Atomic polarizability of a hydrogen atom - Quantum Mechanics in action**

Background: A hydrogen atom in ground state has the nucleus (proton) and the center of mass of the electron probability distribution $|\psi_{1s}(\mathbf{r})|^2$ overlapped. 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 in 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 gives 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 electrodynamics then uses α to obtain the electric susceptibility χ_e and then the permittivity ϵ. This is all "Griffiths" EM. But the origin of the atomic polarizability is quantum mechanical in nature. Here, we apply the same method as in Problem 1.5 to calculate α of a hydrogen atom.

Let $\hat{H}_0$ be the hydrogen atom Hamiltonian. We solved it analytically last term. We know that 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} with energy $E_2 = -e^2/(8\kappa_0 a_0) = -13.6/4\ eV$.

The effect of $\vec{\mathcal{E}} = \mathcal{E}\hat{z}$ is 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

$$\hat{H} = \hat{H}_0 + \hat{H}' = \hat{H}_0 + e\mathcal{E}r\cos\theta \tag{13}$$

The extra term $\hat{H}'$ in $\hat{H}$ is analogous to the term that tilts the potential energy function in a 1D well.

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

$$\phi = c_1\psi_{1s} + c_2\psi_{2p_z} \tag{14}$$

This is analogous to Eq. (11) in Problem 1.5. The variational method requires us to calculate H_{11}, H_{12}, and H_{22} in Eq. (5). 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 the ground state energy in the presence of $\mathcal{E}$. Hence, **show** that the energy is of the form

$$E \approx -\frac{e^2}{2\kappa_0 a_0} - (\textit{something})\,\kappa_0 a_0^3\mathcal{E}^2 \tag{15}$$

and **find** that "something".

Going back to classical electrodynamics. The energy required to induce an electric dipole moment is given by $-\alpha\mathcal{E}^2/2$. This is what we see in Eq. (15). Applying this result to **identify** an expression for the atomic polarizability α to be

$$\alpha = (\textit{number})\,\kappa_0 a_0^3 \tag{16}$$

and **give** the "number". [Note: The known/experimental value is $(4.5)\kappa_0 a_0^3$.] At this point, you applied the variational method to a real QM problem in atomic physics. Problems 1.3-1.6 form a set of problems related to 2×2 matrices in QM and the most useful way of applying the variational method.

[Remark: This problem is also part of the module on the "Physics of Atoms".]