PHYS3022 Applied Quantum Mechanics Problem Set 1
Due: 25 January 2021 (Monday); "T+2" = 27 January 2021 (Wednesday) (20% discount)

You should submit your work in **ONE PDF file via Blackboard** to the appropriate submission folder no later than 23:59 on the due date. Follow Blackboard → Course Contents → Problem Sets → **Problem Set Submission Folder**.

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.** This is a guide to supplementary reading as the course proceeds. No need to hand in anything. PHYS3022 started off with a discussion on several approximation methods, as most real and interesting 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.

In Week 1, we wrote TISE into a huge matrix problem as an exact treatment. We will use this exact matrix formulation many times later. 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.

1.1 (16 points) **Reduced Mass μ, transformation, and separation of variables (See SQ3)**

Background: Hydrogen atom is formally a two-body problem with a proton and electron, as you learned in QMI last term. 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 needed. Here is another example. A H_2 molecule (ignoring the electrons) consists of two nuclei connected by a bond (due to the electrons). 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 SQ3, TA showed that the classical equations of motion and a linear molecule (in 1D motion) can be turned into CM part and a relative motion part, by making transformation to the CM and relative coordinates.

Here, you will repeat the consideration for general $U(x_2 - x_1)$ and see what the Schrödinger Equation turns out to be. For simplicity, consider a two-particle system in 1D, with a two-particle interaction represented by a potential energy function $U(x_2 - x_1)$, i.e., depending 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). 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 SQ3)** You will carry out 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. The first step is to **write down** (see classical mechanics book if necessary) X and x in terms of m_1, m_2, x_1 and x_2. Then **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.]

(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 $\hbar^2K^2/2M$. [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 rotational and vibrational energies. The translational part gives the picture of point particles moving around in a gas as discussed in secondary school physics (ideal gas). You saw the rotational part in QM I as the 3D rotor problem. You have worked out the vibrational part here. In statistical mechanics, each part has a corresponding partition function, giving rise to a steps-like structure in the heat capacity as a function of temperature.]

1.2 (16 points) 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 in the form 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.

Start Here. 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 in class notes under Approximation Methods):

$$\begin{pmatrix} H_{11}-E\,S_{11} & H_{12}-E\,S_{12} \\ H_{21}-E\,S_{21} & H_{22}-E\,S_{22}\end{pmatrix}\begin{pmatrix} c_1 \\ c_2\end{pmatrix}=0 \tag{3}$$

with $H_{21}=H_{12}^*$ and $S_{21}=S_{12}^*$. The retention of S_{ii} and S_{ij} in Eq. (3) implies that we have NOT assumed orthonormal properties of the basis functions yet. 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: It is just a quadratic equation for E.]

(b) Very often, Eq. (3) takes on even simpler form in QM problems. Firstly, when the basis functions are orthonormal, then $S_{ij} = \delta_{ij}$ and Eq. (3) becomes

$$\begin{pmatrix} H_{11} - E & H_{12} \\ H_{21} & H_{22} - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0 \tag{4}$$

Secondly, in some problems $H_{11} = E^{(0)} + H'_{11}$, $H_{22} = E^{(0)} + H'_{22}$, (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

$$\begin{pmatrix} E^{(0)} + H'_{11} - E & H'_{12} \\ H'_{21} & E^{(0)} + H'_{22} - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0 \tag{5}$$

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. From Eq. (5), **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. (3)) is important to the **theory of bonding** when two atoms come together to form a molecule. It is also related to **time-independent non-degenerate perturbation theory** up to 2nd order. Your answer in part (b) (the matrix in Eq. (5)) 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. (5). Here, you have done what the scary name of **degenerate perturbation theory** really means.]

1.3 (25 points) 2×2 **matrices carry much physics and matrices ain't frightening. Street-fighting matrix math.**

Background: You solved the 2×2 matrices that appear in QM problems in Problem 1.2 **exactly**. Sometimes (quite often), we don't even need to do the mathematics exactly. This problem serves to remind you of the essential 2×2 stuffs and how useful/dirty approximation can be made. Inspecting Eq. (4) (see above), it is an eigenvalue problem of a 2×2 matrix defined by the matrix elements H_{ij}, with $i, j = 1, 2$. This leads us to consider a 2×2 matrix of the form

$$\begin{pmatrix} E_A & \Delta \\ \Delta & E_B \end{pmatrix} \tag{6}$$

where we simply take Δ to be a real number. [More generally, the off-diagonal elements should be Δ and Δ^*.] The corresponding eigenvalue problem is defined by

$$\begin{pmatrix} E_A - E & \Delta \\ \Delta & E_B - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0 \tag{7}$$

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

(b) Second easiest case. Now consider $\Delta \neq 0$ and 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. (Actually related to Problem 1.1, do you see that!) 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. (5) in Problem 1.3. In molecular physics, one result gives a bonding molecular orbital (lower eigenvalue) and the other an anti-bonding molecular 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. **Find the eigenvalues** and call them 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. For E_1 and E_2, **find** the corresponding eigenvectors. At this point, we handled the 2×2 problem in Eq. (7) exactly (as you did in Problem 1.2).

(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 exists 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.

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 it is "pushed down"; (ii) the higher eigenvalue E_B is altered by an amount $\Delta^2/(E_B - E_A)$ and 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 message:** Higher state being pushed up (by lower state) and lower state being pushed down (by higher state), and memorize the approximated eigenvalue expressions. This is street-fighting matrix math.]

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

$$\begin{pmatrix} 12 & \Delta \\ \Delta & 3 \end{pmatrix} \tag{8}$$

for $\Delta = 2$ and $\Delta = 0.5$. For each case, **compare** the exact eigenvalues with the approximated values using the formulas in part (d).

1.4 (23 points) **Variational Method: Harmonic oscillator**

Background: The variational theorem says that $\langle H \rangle_\phi \geq E_{GS}$, i.e., the energy expectation value of any trial wavefunction is higher or at best equal to the actual ground state energy of a given problem (given Hamiltonian). Depending on the trial wavefunction, $\langle H \rangle_\phi$ can be way above or very close to E_{GS}.

Consider a 1D harmonic oscillator. The Hamiltonian is

$$H = -\frac{\hbar^2}{2m}\frac{d}{dx} + \frac{1}{2}m\omega^2 x^2 \tag{9}$$

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. We will use the variational method and at the same time try to gain some quantum sense.

(a) Exercising good physics sense, we expect the ground state wavefunction to (i) be even about $x = 0$ (center of potential) as the potential energy is even, (ii) have no node, and (iii) have a peak at $x = 0$ and fall off on both sides. So, it will be reasonable to start with a trial wavefunction of the form

$$\phi_{trial}(x) = A\, e^{-\lambda x^2}\ , \tag{10}$$

where A is a prefactor (normalization), and λ can be used as a variational parameter.

Evaluate the energy expectation value $\langle \hat{H} \rangle$ as a function of the parameter λ using ϕ_{trial}. Hence, **identify** from the answer which term is the expectation value of the kinetic energy $\langle \hat{T} \rangle$ and which term is the expectation value of the potential energy $\langle \hat{V} \rangle$.

(b) **Discuss** the role of the parameter λ in Eq. (10) in tuning the form of the wavefunction, i.e., how does the form change when λ goes from big to small?

(c) **Discuss** how $\langle \hat{T} \rangle$ and $\langle \hat{V} \rangle$ vary as λ changes. In particular why do the two terms behave differently? With this understanding, **argue** that there exists an optimal (best) value of λ for which $\langle \hat{H} \rangle = \langle \hat{T} \rangle + \langle \hat{V} \rangle$ is a minimum. [Hint: A sketch may help.]

(d) By varying λ, **find** the best estimate of the ground state energy. Hence, **write down** the trial wavefunction using the determined best value of λ. **Comment** on your answer in light of the exact solution.

1.5 (20 points) **Potential energy of Quartic form - Variational Method**

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

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + ax^4\ , \tag{11}$$

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

Following the physical sense conveyed in Problem 1.4, let's use a trial wavefunction of the form

$$\phi(x) = Ae^{-\lambda x^2} \tag{12}$$

again, with λ being the variational parameter. **Apply the variational method** to estimate the ground state energy.

[Hint: This problem may be harder. You need to do integrals involving x^4 between the trial wavefunctions. You may find some useful integrals in the chapter on harmonic oscillators in your PHYS 3021 last term (see your class notes). Of course, we may look up some formulas (Gaussian integrals) for similar integrals and apply them here instead of doing the integrals from scratch.]