PHYS3022 Applied Quantum Mechanics   Problem Set 2
Due Date: 30 January 2019 (Wednesday); "T+2" = 1 February 2019

All problem sets should be handed in not later than 5pm on the due date. Drop your assignments in the PHYS3022 box 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.

2.0 **Reading Assignment.** We developed time-independent perturbation theories. The 1st and 2nd order perturbation in the energy and the 1st order perturbation in the wavefunction of the **non-degenerate perturbation theory** were derived. These methods will be used repeatedly in later parts of our course. They form the standard coverage of undergraduate QM on approximation methods. I extended the discussion to look at the perturbation results in the huge matrix viewpoint. The discussion also illustrated that many results could be understood/obtained in terms of 2 × 2 matrices. The **degenerate perturbation theory** emerged as a by-product in that it amounts to focusing on the smaller-size matrix formed by the few degenerate unperturbed (or nearly degenerate) states and treating the matrix exactly. For references, see Chapter 6 of Griffiths' *Introduction to Quantum Mechanics* and Rae's *Quantum Mechanics* Chapter 7. A very practical discussion can be found in McQuarrie's *Quantum Chemistry* Chapter 8. All of them covered almost the same contents. **Here is your turn to practice.**

2.1 **Tilted infinite well - Perturbation Theory**

Background: In perturbation theory, we need to identify an unperturbed problem $\hat{H}_0\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)}$ that the energy eigenvalues $\{E_n\}$ and eigenstates $\{\psi_n^{(0)}\}$ are known. These exactly known quantities are then used to solve a new problem $\hat{H}\psi = E\psi$ approximately, where $\hat{H} = \hat{H}_0 + \hat{H}'$ doesn't allow exact solutions and $\hat{H}'$ is the perturbation term of the Hamiltonian.

Let's consider the titled infinite well again. It is an infinite well with $V(x) = \infty$ for $x \leq 0$ and $x \geq a$. Inside the well $0 < x < a$, the potential is tilted, with $V(x)$ increasing linearly from $V(0) = -V$ to $V(a) = 0$.

An obvious choice of the unperturbed problem of $\hat{H}_0$ is a 1D particle-in-a-box problem with a flat floor $V(x) = 0$ for $0 < x < a$.

(a) **Identify** $\hat{H}'$ and apply **first-order perturbation theory to find** the perturbed energies E_n and the perturbed wavefunctions ψ_n approximately. [The perturbed wavefunctions are in the form of an infinite sum.]

(b) From the answer to (a), **write down** explicitly the perturbation results for the ground state energy E_1 and wavefunction ψ_1. If you only include the correction term of $\psi_2^{(0)}$ into ψ_1 , **write down** ψ_1 again. Hence, **comment** on the connection between the answer with only two terms and a trial wavefunction (for variational method) that carries the same two terms. [Hint: You may discuss in words (simpler), or carry out the variational calculation and compare results.]

(c) Apply **second-order perturbation theory** to find an expression for the perturbed energies E_n up to second order, i.e., the final expression should include zeroth, first, and second-order terms.

2.2 **Integrals involving eigenstates of harmonic oscillator**

Background: There are many important problems in physics for which the unperturbed problem $\hat{H}_0$ is an 1D harmonic oscillator. We solved it exactly in QMI. What if $\hat{H} = \hat{H}_0 + \hat{H}'$ with $\hat{H}' = \beta x$ or $\hat{H}' = \frac{1}{6}\gamma x^3$ or $\hat{H}' = \frac{1}{24}bx^4$? In applying perturbation theory, we need to evaluate integrals like

$\langle\psi_n^{(0)}|\hat{H}'|\psi_n^{(0)}\rangle$ and $\langle\psi_m^{(0)}|\hat{H}'|\psi_n^{(0)}\rangle$, where $\psi_n^{(0)}$ are the energy eigenstates of harmonic oscillator. This problem prepares you for some of these integrals.

(a) Now look at all eigenstates $\psi_n^{(0)}(x)$, where n is the quantum number that labels the states and also the energies $E_n^{(0)} = (n+\frac{1}{2})\hbar\omega$. **Argue** or **show** clearly that the expectation values of x and x^3 are **zero** for **all** $\psi_n^{(0)}(x)$, i.e.,

$$x_{nn} \equiv \langle\psi_n^{(0)}|x|\psi_n^{(0)}\rangle = \int \psi_n^{*(0)}(x)\,x\,\psi_n^{(0)}(x)dx = 0 \tag{1}$$

and a similar expression with x^3 in the middle. The symbol x_{nn} emphasizes that the entities in Eq. (1) can be regarded as the nn-th matrix element of the operator $\hat{x}$ with respect to the basis set of harmonic oscillator states $\{\psi_i^{(0)}\}$.

(b) The harder ones are the expectation values of x^2 and x^4 with respect to **any** $\psi_n^{(0)}(x)$.
In PHYS3021 (2018-19 Term 1), we considered the recursive relation of the Hermite Polynomials and used it to evaluate the integrals of x between **different** eigenstates

$$x_{nm} \equiv \langle\psi_n^{(0)}|x|\psi_m^{(0)}\rangle = \int \psi_n^{*(0)}(x)\,x\,\psi_m^{(0)}(x)dx \tag{2}$$

for $n \neq m$. We found, after doing the integral,

$$x_{nm} \equiv \langle\psi_n^{(0)}|x|\psi_m^{(0)}\rangle = \int \psi_n^{*(0)}(x)\,x\,\psi_m^{(0)}(x)dx = \delta_{m,n+1}\sqrt{\frac{n+1}{2\alpha}} + \delta_{m,n-1}\sqrt{\frac{n}{2\alpha}}\,, \tag{3}$$

where $\alpha \equiv (m\omega)/\hbar$ and $\delta_{i,j}$ is the Kronecker delta function, i.e., it is 1 for $i=j$ and vanishes otherwise. In fact, Eq.(3) covers the result in Eq.(1).
It is important to note what Eq.(3) implies is that x_{nm} is nonzero ONLY when the two states are different by $\Delta n = \pm 1$, i.e., a state n (of energy $E_n^{(0)}$) is "connected" through the position operator $\hat{x}$ only to the nearest higher state $n+1$ (of energy $E_{n+1}^{(0)}$) and the nearest lower state $n-1$ (of energy $E_{n-1}^{(0)}$), and nothing else. Eq. (3) is important in understanding the selection rule in vibrational spectrum.
Your task is to evaluate

$$x_{nn}^2 \equiv \langle\psi_n^{(0)}|x^2|\psi_n^{(0)}\rangle = \int \psi_n^{*(0)}(x)\,x^2\,\psi_n^{(0)}(x)dx \tag{4}$$

Hint: It will be useful to start with some matrix thinking, i.e., taking

$$x_{nn}^2 \equiv \langle\psi_n^{(0)}|x^2|\psi_n^{(0)}\rangle = \sum_i \langle\psi_n^{(0)}|x|\psi_i^{(0)}\rangle\langle\psi_i^{(0)}|x|\psi_n^{(0)}\rangle = \cdots \tag{5}$$

where the summation $\sum_i$ is over all states i. Eq. (5) says that the matrix elements $(x^2)_{nn}$ is given by $\sum_i (x)_{ni}(x)_{in}$, which is the usual way of multiplying two matrices. Thus, x_{nn}^2 is taken to be the $(nn)th$ (diagonal) matrix element of a matrix x^2 which can be found by multiplying two matrices each corresponding to the position operator $\hat{x}$. **Then use Eq. (5) and apply Eq. (3) to get at** x_{nn}^2. The same trick in Eq. (5) allows you to evaluate all the other things like x_{nm}^3 and x_{nn}^4.

Remark: There is another way to understand what is being done in Eq. (5). Recall that for any function $\Psi(x)$, it can be expanded by the complete set $\{\psi_n^{(0)}\}$ as

$$\Psi = \sum_i a_i \psi_i^{(0)} = \sum_i \left(\int \psi_i^{*(0)}(x)\Psi(x)dx \right) \psi_i^{(0)} = \sum_i \langle \psi_i^{(0)} | \Psi \rangle | \psi_i^{(0)} \rangle = \underbrace{\sum_i | \psi_i^{(0)} \rangle \langle \psi_i^{(0)} |}_{\hat{1}} \Psi \rangle \quad (6)$$

It follows that

$$\hat{1} = \sum_i | \psi_i^{(0)} \rangle \langle \psi_i^{(0)} | \quad (7)$$

where $\hat{1}$ is an identity operator. So in Eq. (5), we have inserted the identity operator $\hat{1}$ in between x^2, i.e., $x\hat{1}x$.

2.3 Anharmonic oscillator - First order perturbation theory

Background – Harmonic oscillator carries a potential energy function $U(x) \sim x^2$, i.e., quadratic in x. The answer to the question"Why do we need harmonic oscillator physics?" is that one can do a Taylor expansion around the minimum of any form $U(x)$ and near the minimum, $U(x)$ has a leading quadratic term. Nice and OK! Let's take the Taylor expansion more seriously and keep the cubic and quartic terms. These are the **anharmonic effects**. For one thing, if we only have the $\sim x^2$ term, the position expectation value is always at $x = 0$ for all states, and there will be no thermal expansion.

Generally, the Hamiltonian of an oscillator including anharmonic effects is given by

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}k\,x^2 + \frac{1}{6}\gamma_3\,x^3 + \frac{1}{24}\gamma_4\,x^4 = \hat{H}_0 + \frac{1}{6}\gamma_3\,x^3 + \frac{1}{24}\gamma_4\,x^4 \,, \quad (8)$$

where the cubic x^3 term and quartic x^4 term are included. The symbols γ_3 and γ_4 are just coefficients. The pre-factors 1/2, 1/6, and 1/24 are 1/2!, 1/3! and 1/4! in a Taylor expansion about a minimum of $U(x)$.

Action: Using the harmonic oscillator $\hat{H}_0$ as the known (unperturbed) problem and the rest as the perturbation $\hat{H}'$, **calculate the first-order correction to the ground state energy** due to the anharmonic effects. [Hint: Some integrals here are called the Gaussian integrals. Their evaluations are easier than you think. You may look up integral tables, but cite the source.]

Extension (Optional and No bonus points): For those who like to do integrals, how about first-order correction in energy to **any state** labelled by the quantum number n?

[**Physics remarks**: The results here are useful in that (i) anharmonic effects are always there when we keep more terms in the Taylor expansion around a minimum, (ii) they give a better understanding of the vibrational states (vibrational spectrum) of molecules, (iii) they give an understanding of why a solid expands as it is heated up, and (iv) they give an understanding of thermal conduction, i.e., what is the mechanism that heat goes from a hotter end of a system to the colder end. Items (iii) and (iv) will be discussed in Solid State Physics. So carry the results with you to other courses.]

2.4 Potential energy of Quartic form - Perturbation Theory

Consider the Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + ax^4 \,, \quad (9)$$

which describes a particle of mass m under the influence of a potential energy of the form $\sim x^4$. Let's say we would like to find an approximation to the ground state energy. A physical sense is that the ground state wavefunction will have a shape rather like that of a harmonic oscillator. In thinking so, we are taking

$$\hat{H} = \left(-\frac{\hbar^2}{2m} + \frac{1}{2}kx^2 \right) - \frac{1}{2}kx^2 + ax^4 = \hat{H}_0 - \frac{1}{2}kx^2 + ax^4 \,. \tag{10}$$

Apply first-order perturbation theory to estimate the ground state energy.

(Optional: No Bonus Point, but educational.) Use the method in Problem 2.2 to obtain the first order correction in energy to all states. Here, you will need x^4_{nn}.

2.5 Harmonic Oscillator with a linear term - Exact solutions versus perturbation treatment

Must Try! Here is a classic QM problem that is exactly solvable and one can compare exact results with perturbative results. The problem is to add in a linear $\sim x$ term into a harmonic oscillator. The physical situation is that of a particle of mass m and charge $-e$ under the influence of a parabolic potential as well as a **static electric field** $\mathcal{E}$ in the x-direction. The Hamiltonian reads

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2 + e\,\mathcal{E}x \,, \tag{11}$$

where the last term is treated as the perturbation and it comes from the electrostatic potential energy. It is **linear** in x.

Let's do it by perturbation theory

(a) For the given context, **explain** why do we have such a perturbative term in the Hamiltonian?

(b) For any unperturbed states $\psi_n^{(0)}$, **find** the first order correction to the energy.

(c) For any unperturbed states $\psi_n^{(0)}$, **find** the second order correction to the energy and **show** that all the states are shifted by the same amount. Hence, **write down** the modified energy E_n up to second order.

(d) (Optional for students and TAs - NO bonus points.) For those who want to do more, work out the modified wavefunctions to first order.

Let's do it exactly

(e) Consider $x^2 + ax$. Once upon a time, you learned a trick called "completing the square", i.e., we want to write $x^2 + ax$ into $(x+b)^2 + c$. Show that we can always do that and **express** b and c in terms of a.

(f) Consider the Hamiltonian in Eq.(11) again. Completing the square and defining a new variable x' to replace x, **show** that the problem represented by $\hat{H}$ in Eq. (11) is **just another harmonic oscillator** problem! Hence, **give** the exact values of the energies of $\hat{H}$. [Morale of the story is: a linear plus a quadratic term in the potential is exactly solvable.]

(g) **Compare** your perturbation result up to 2nd order with the exact result and comment. [Hint: You will see a happy coincidence.]

2.6 2D harmonic oscillator plus a perturbation - Degenerate perturbation theory

Recall that in higher dimensions, degenerate states are common. Here is an example based on harmonic oscillator. Consider a two-dimensional (2D) harmonic oscillator given by the Hamiltonian

$$\hat{H}_0 = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) + \frac{1}{2}m\omega^2(x^2 + y^2)\ . \tag{12}$$

You don't need to solve it. Just go through in your mind the standard procedure of **separation of variables** and then using the results of a 1D harmonic oscillator. The eigenvalues add and the wavefunctions multiply. [If you think you want to practice the calculations again, do it! No points though.]

(a) The ground state energy is $\hbar\omega$ and it is non-degenerate. Let's consider the first excited states. **Show** that there are two different states (different wavefunctions) corresponding to the first excited states' energy $E^{(0)} = 2\hbar\omega$. **Write** down the two wavefunctions. [So, we have two states that are degenerate.]

(b) Now consider the 2D oscillator problem given by the Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) + \frac{1}{2}m\omega^2(x^2 + y^2) + \beta\, x\, y = \hat{H}_0 + \beta\, x\, y\ , \tag{13}$$

where the last term $\beta x\, y$ can be treated as a perturbation. Here, β is a constant parameter that tunes the strength of the perturbation.

We want to study how the perturbation $\beta\, x\, y$ affects the two degenerate unperturbed states corresponding to $E^{(0)} = 2\hbar\omega$. **Set up** the 2×2 matrix that is important in $\hat{H}$ when we consider the effect of the perturbation on the two degenerate states. [Hint: See Problem 2.2 for useful integrals.]

(c) Hence, **solve** for the new eigenenergies and **show** explicitly that the perturbation term $\beta\, x\, y$ removes/lifts the degeneracy of the originally degenerate states and splits them into two states of different energies. [Hint: 2×2 matrices in Problem Set 1 are again useful.]

(d) (Harder) Finally, **find** the modified wavefunctions for the two states, in terms of the originally degenerate states in part (a). [Hint: Find eigenvector of each eigenvalue.]