PHYS3022 Applied Quantum Mechanics Problem Set 4
Due Date: 17 March 2020 (Tuesday) "T+2" = 19 March 2020

Submission: 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.

Assessment Scheme – As face-to-face classes cannot resume by 10 March 2020, the alternative Assessment Scheme becomes effective. The Scheme is: Problem Sets (30%), Mid-Term Exam (30%), Final Exam (40%)

4.0 **Reading Assignment.** We developed the 1st and 2nd order non-degenerate perturbation theory and degenerate perturbation theory. The results were interpreted using matrix mathematics. We also developed degenerate perturbation theory as a by-product. Here, you will do some exercises on perturbation theory, using harmonic oscillator plus perturbation terms as the context. For reading into approximation methods, see chapters in Griffiths' *Introduction to Quantum Mechanics* and Rae's *Quantum Mechanics.* A more practical discussion can be found in McQuarrie's *Quantum Chemistry.* Liboff's *Introductory Quantum Mechanics* also has a good chapter. They covered almost the same contents.

We started the module on the Physics of Atoms. We covered/will cover orbital and spin angular momenta, total angular momentum, spin-orbit interaction, relativistic correction (see SQ in Week 6), fine structure, Zeeman effect, and hyperfine structure, using the hydrogen atom as the focus of our discussion. There are two levels of understanding. Level 1 is the big picture (key ideas). They are covered in standard textbooks on *Modern Physics* (e.g. by Taylor, Zafiratos, Dubson; and by Harris) or *Quantum Physics* (e.g. by Eisberg and Resnick). These books **describe** the physics clearly. For applying QM mathematical and approximation methods to these topics (Level 2), see the references in the last paragraph. But I stress that these QM treatments should be seasoned by the physics discussions. For a more focused and serious study of Atomic Physics, see Mark Fox, *A student's Guide to Atomic Physics* (Cambridge Univ. Press) and C.J. Foot, *Atomic Physics* (Oxford Univ. Press). The latter is a textbook that takes you to the beginning graduate level.

Here, you will practice perturbation theories with $\hat{H}_0$ being an harmonic oscillator. You may want to read the class notes on harmonic oscillator in PHYS3021 (QM I) and related Problem Sets last term for a review. Problem 2.1 fills in some background and takes you through the calculations of some matrix elements between harmonic oscillator eigenstates. The results are then used in the other problems.

4.1 **Oscillator physics is important and Integrals involving eigenstates of harmonic oscillator**

Background: Let $\hat{H}_0$ be an 1D harmonic oscillator. It is exactly solvable. It is often said that most physics is harmonic oscillator physics. This refers to the fact that when many particles interact and they find their equilibrium positions (e.g. atoms in a molecule or in a solid), the potential energy function in the vicinity of the equilibrium position behaves like a harmonic oscillator. Further away from the equilibrium position, the form is like a harmonic oscillator plus some correction terms. These correction terms can be treated as perturbations.

(a) Let $V(x)$ be a potential energy function that has a minimum at $x = 0$ and $V(0) = 0$. Using

Taylor expansion, **show** that $V(x)$ around $x = 0$ takes on the form

$$V(x) \approx \frac{1}{2}k\,x^2 + \frac{1}{6}\gamma\,x^3 + \frac{1}{24}\,b\,x^4 \tag{1}$$

and **find the relations** between $V(x)$ and the coefficients k, γ, and b.

[Remark: Ignoring the $\sim x^3$ and $\sim x^4$ terms reduces the problem to the exactly solvable **harmonic oscillator**. What about including a linear $\sim x$ term? See Problem 4.3.]

(b) **(1st order perturbation theory for ground state.)** We are, therefore, motivated to consider the Hamiltonian of a 1D **anharmonic oscillator** of the form

$$\hat{H} = \left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}k\,x^2\right) + \frac{1}{6}\gamma\,x^3 + \frac{1}{24}\,b\,x^4 = \hat{H}_0 + \frac{1}{6}\gamma\,x^3 + \frac{1}{24}\,b\,x^4 \tag{2}$$

Let's **find the first order perturbation theory for the ground state energy**. Let $\psi_0^{(0)}$ be the ground state wavefunction of an harmonic oscillator $\hat{H}_0$. **Evaluate** (or **argue at an answer**) the expectation values of x^3, and x^4 for the **harmonic oscillator ground state** $\psi_0^{(0)}$. Hence, **give** the anharmonic oscillator ground state energy using first order perturbation theory.

[Hint: You did the x^4 integral in Problem 3.2 in a variational calculation. You may look up the integrals there or from Tables or websites (cite the source).]

(c) As a by-product, **evaluate** (or **argue at an answer**) the expectation values of x and x^2 with respect to $\psi_0^{(0)}$.

[Hint: You did the x^2 integral in Problem 3.1 in a variational calculation.]

(d) Going beyond the ground state, **argue clearly** that the expectation values of x and x^3 are **zero** for **all** harmonic oscillator states $\psi_n^{(0)}$.

(e) This leads us to consider the expectation values $\langle\psi_n^{(0)}|x^2|\psi_n^{(0)}\rangle$ and $\langle\psi_n^{(0)}|x^4|\psi_n^{(0)}\rangle$ for any unperturbed states $\psi_n^{(0)}$. More generally, when you do perturbation theory, we need the **matrix elements** $\langle\psi_n^{(0)}|x^k|\psi_m^{(0)}\rangle$ for $k = 1$, 2, 3, and 4 **between eigenstates labelled** n **and** m.

In PHYS3021, we did the matrix element $\langle\psi_n^{(0)}|x|\psi_m^{(0)}\rangle$ based on the recursive relation of the Hermite Polynomials, which are part of $\psi_n^{(0)}$. The result for the matrix element x_{nm} is

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

$\delta_{i,j}$ is the Kronecker delta function, i.e., it is 1 for $i = j$ and vanishes otherwise. Here

$$\alpha \equiv \frac{m\omega}{\hbar} \tag{4}$$

and $\omega = \sqrt{k/m}$. [You are NOT asked to verify Eq.(3).] We take Eq. (3) as given and it is important to note that Eq. (3) says that x_{nm} is nonzero ONLY between two neighboring unperturbed energy eigenstates, i.e., a state n (of energy $E_n^{(0)}$) is connected through 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. This is the most important information of Eq.(3). [Remark: This is related to some selection rule in transitions in molecules.]

Action: Apply Eq.(3) to evaluate

$$x^2_{nn} \equiv \langle \psi_n^{(0)} | x^2 | \psi_n^{(0)} \rangle = \int \psi_n^{*(0)}(x)\, x^2\, \psi_n^{(0)}(x) dx \tag{5}$$

Hint: The set $\{\psi_n^{(0)}\}$ is complete. The mathematical way to say this is

$$\hat{1} = \sum_i |\psi_i^{(0)}\rangle\langle\psi_i^{(0)}| \,, \tag{6}$$

where $\hat{1}$ is an identity operator. That Eq. (6) is correct can be seen by operating on both sides an arbitrary function $|\psi\rangle$. We have

$$|\psi\rangle = \sum_i |\psi_i^{(0)}\rangle\langle\psi_i^{(0)}|\psi\rangle \,, \tag{7}$$

which is a fancy way of writing the expansion of $\psi(x)$ in terms of the orthonormal basis set $\{\psi_n^{(0)}\}$ of functions, i.e.,

$$\psi(x) = \sum_i c_i \psi_i^{(0)} = \sum_i \left(\int \psi_i^{(0)*} \psi(x) dx \right) \psi_i^{(0)} \tag{8}$$

after solving for c_i.
Now we use Eq. (6) to help us evaluate x^2_{nn}. We start with

$$x^2_{nn} \equiv \langle \psi_n^{(0)} | x^2 | \psi_n^{(0)} \rangle = \langle \psi_n^{(0)} | x\, \hat{1}\, x | \psi_n^{(0)} \rangle = \sum_i \langle \psi_n^{(0)} | x | \psi_i^{(0)} \rangle \langle \psi_i^{(0)} | x | \psi_n^{(0)} \rangle = \cdots \tag{9}$$

where the summation $\sum_i$ is over all states i. First understand for yourself that we have taken x^2_{nn} as the $(nn)th$ (diagonal) matrix element of a matrix x^2 and it in turn is found by multiplying two matrices each corresponding to the position operator $\hat{x}$. Hence, **use Eq. (9) and apply Eq. (3) to obtain x^2_{nn}.**
[Remark: The same trick in Eq. (9) allows you to evaluate all the other things like x^2_{nm}, x^3_{nm} and x^4_{nn}.]

4.2 **Anharmonic oscillator with a quartic term as perturbation**

Consider an **anharmonic oscillator** with the Hamiltonian

$$\hat{H} = \left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2 \right) + \frac{1}{24}bx^4 = \hat{H}_0 + \hat{H}' \,, \tag{10}$$

where the quartic term is taken to be the perturbation.

(a) Consider **any unperturbed states** $\psi_n^{(0)}$ of $\hat{H}_0$, **evaluate the modified energy to first-order** due to the quartic terms $\hat{H}'$. [Hint: Here you need x^4_{nn} and the approach/result in Problem 4.1 is useful. The answer has a nice and simple closed form.]

(b) This part is quiet hard – Consider the **ground state**. **Find the leading correction term**, i.e., one term that is the most important, to the **ground state wavefunction** due to the quartic perturbative term.

4.3 Harmonic Oscillator with a linear term - Exact solutions versus perturbative treatment

Background: Here is a classic QM problem that all CUHK students are asked to try. It can be solved exactly. Therefore, one can compare the perturbative results with the exact results. The problem is adding a linear $\sim x$ term to 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 can be treated as the perturbation.

Let's do it by perturbation theory

(a) **Explain the physics** behind the perturbative term in the Hamiltonian based on how a charged particle at position x and an electric field interact (EM theory).

(b) For any unperturbed states $\psi_n^{(0)}$, **find the first order correction to the energy**. [Hint: See Problem 4.1]

(c) For any unperturbed states $\psi_n^{(0)}$, **find the second order correction to the energy** and **show** that the energies are shifted by the same amount for all states. Hence, **write down** the modified energy E_n of any state n up to second order. [Eq. (3) may be useful.]

(d) (Optional for students and TAs - NO bonus points.) For those who want to practice 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 $(x+b)^2 + c$. **Do that** and **express** b and c in terms of a.

(f) Consider the Hamiltonian in Eq.(11). Completing the square and replacing x by a new variable x', **show** that the problem represented by $\hat{H}$ in Eq. (11) is nothing but **another harmonic oscillator** problem! Hence, **give the exact values** of the energies of $\hat{H}$.

[Moral of the story is: a linear plus a quadratic term in the potential is exactly solvable.]

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

4.4 $\hat{H}_0$ is a 2D harmonic oscillator - Degenerate perturbation theory

Degenerate states are common in higher dimensional QM problems. Here is an example based on harmonic oscillators. 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. You are more skillful than that. 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**.

(a) The ground state energy is $\hbar\omega$. **Write down** the 2D ground state wavefunction.

(b) Consider the **first excited states**. **Show** that the corresponding energy is $E^{(0)} = 2\hbar\omega$ and **write down** the two corresponding wavefunctions. So, these two states are degenerate and the energy $2\hbar\omega$ has a degeneracy of 2.

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

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

where the last term $\gamma\, x\, y$ can be treated as a perturbation. Here, γ is a parameter representing the strength of the perturbation.

The question is to investigate the effect of the perturbation $\gamma\, x\, y$ on the two degenerate unperturbed states corresponding to $E^{(0)} = 2\hbar\omega$. Applying the **degenerate perturbation theory**, **set up** the 2×2 matrix for $\hat{H}$ with respect to the two unperturbed degenerate states. [You have worked out the integrals earlier.]

(d) Hence, **solve for the new eigen-energies** and **show explicitly** that the perturbation term $\gamma\, x\, y$ removes the degeneracy of the originally degenerate states and splits them into two states of different energies. **Make a sketch** showing the two new energies as a function of γ. [Hint: Here, you are using the 2×2 matrix math in Problem Set 3.]

(e) **Find the two new wavefunctions** corresponding to the two eigen-energies, in terms of the originally degenerate states in part (b). [Hint: 2×2 matrix math again. You will see them mixed strongly.]

Intermission: Read through Problems 4.1 to 4.4 again. They cover oscillator physics, evaluations of matrix elements, and perturbation theories.

Physics of Atoms

4.5 **Normal Zeeman Effect** (See SQ15)

Consider transitions from an upper d-states ($\ell = 2$) to a lower f-states ($\ell = 3$). When an external magnetic field $\mathbf{B}_{ext} = B_{ext}\hat{z}$ is applied, the degeneracy behind the quantum number m_ℓ is removed. **Sketch a diagram** showing how the d-states and f-states split in the presence of $\mathbf{B}_{ext}$. Hence, by applying the selection rule that $\Delta m_\ell = 0, \pm1$, **indicate the allowed transitions** from d states to f states in the sketch and **find the relations** between the frequencies involved in the transitions with the frequency when $\mathbf{B}_{ext} = 0$.

4.6 **The rule of adding two angular momenta gives the right number of states.** (See SQ16)

Consider two angular momenta with one characterized by the quantum number $j_1 = 3$ and the other by $j_2 = 1$. Using $(j_1, m_{j_1}, j_2, m_{j_2})$, **count** all the states given by the system of two angular momenta.

We can add the two angular momenta into a total angular momentum. The total angular momentum is characterized by the quantum number j. Applying the rule of getting the values of j, **label and count** all the states using (j_1, j_2, j, m_j).