PHYS3022 Applied Quantum Mechanics Problem Set 2
Due Date: 10 February 2021 (Wednesday) "T+2" (plus holidays) = 16 February 2021

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.

2.0 **Reading Assignment.**

Approximation Methods: In the first module of the course, we did approximation methods including the variational method (Problem Set 1), 1st and 2nd order non-degenerate perturbation theory and degenerate perturbation theory. We also discussed the results in the viewpoint of approximations starting from an exact but huge matrix representing the TISE problem. For those who want to read more on the topics, see chapters in Griffiths' *Introduction to Quantum Mechanics*, Rae's *Quantum Mechanics*, and Liboff's *Introductory Quantum Mechanics*. A very practical and lucid discussion can be found in McQuarrie's *Quantum Chemistry*. You can do much physics with these tools.

Physics of Atoms: We started the module in Week 3. We covered/will cover orbital and spin angular momenta, total angular momentum, spin-orbit interaction, (relativistic correction), 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 **describes** the key ideas very clearly. For applying QM mathematical and approximation methods to these topics, see the books list in the last paragraph. I stress that these QM treatments should be seasoned by the physical sense discussed in the Modern Physics books. Students who want to read more on Atomic Physics may consult (undergraduate level) M. Fox, *A Student's Guide to Atomic Physics*, and (beginning postgraduate level) C.J. Foot, *Atomic Physics*. We covered more QM than Fox's book, but the book covers more topics than we can do.

This Problem Set covers the Applications of Perturbation Theories.

2.1 (25 points) **Matrix elements $x^3_{mn} \equiv \langle m|\hat{x}^3|n\rangle$ and $x^4_{mn} \equiv \langle m|\hat{x}^4|n\rangle$ for harmonic oscillator eigenstates**

Background: Harmonic oscillator physics is everywhere. A reason is that when basic entities bind and form a bigger object (atoms forming molecules/solids), the fact that they bind and have a preferred separation R_0 at equilibrium implies that the potential energy function $V(r)$, where r is the separation between the two basic entities (e.g. atoms), has a minimum at the $r = R_0$. In the vicinity of the minimum, $V(r)$ is approximately quadratic and thus of the harmonic oscillator form. An immediate implication is that there are anharmonic terms when r is away from R_0.

(a) For simplicity, let's consider the 1D case, shift the minimum of $V(r)$ to $r = 0$ and let the minimum value be $V(0) = 0$. **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.

(b) The Hamiltonian of a particle of mass m under the influence of $V(x)$ around $x = 0$ can be written as

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

where $\omega^2 = k/m$. Here, $\hat{H}_0$ is the harmonic oscillator problem with exact solutions, i.e.,

$$\hat{H}_0 = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2 \tag{3}$$

with TISE being

$$\hat{H}_0 \psi_n^{(0)} = \left(n + \frac{1}{2}\right)\hbar\omega\; \psi_n^{(0)} \tag{4}$$

or

$$\hat{H}_0 |n\rangle = \left(n + \frac{1}{2}\right)\hbar\omega\; |n\rangle \tag{5}$$

where $\psi_n^{(0)}(x)$ or $|n\rangle$ is the n-th energy eigenstate with eigenvalue $(n + \frac{1}{2})\hbar\omega$.

Let's start with the simplest case of the **ground state** energy of $\hat{H}$ in Eq. (2). **Applying first-order perturbation theory** to estimate $E_0^{(1)}$ (first order correction in energy) due to $\hat{H}'$.

[Hint: You might have done the integral in Problem Set 1.]

(c) In **SQ7**, TA worked out the integrals (matrix elements) $x_{mn} \equiv \langle m|\hat{x}|n\rangle$ and $x^2_{mn} \equiv \langle m|\hat{x}^2|n\rangle$ between harmonic oscillator eigenstates. For example,

$$x_{mn} \equiv \langle \psi_m^{(0)}|x|\psi_n^{(0)}\rangle = \int \psi_m^{*(0)}(x)\, x\, \psi_n^{(0)}(x) dx = \delta_{n-1,m}\sqrt{\frac{n}{2\alpha}} + \delta_{n+1,m}\sqrt{\frac{n+1}{2\alpha}} \,, \tag{6}$$

where $\alpha \equiv (m\omega)/\hbar$ and $\delta_{i,j}$ is the Kronecker delta function. Physically, Eq. (6) says that the operator $\hat{x}$ can only connect the oscillator state $\psi_n^{(0)}$ to $\psi_{n+1}^{(0)}$ and $\psi_{n-1}^{(0)}$, and nothing else. Eq. (6) can be derived by either using the recursive relation of the Hermite Polynomials or the operator method. From Eq. (6), one can also find $x^2_{mn} \equiv \langle m|\hat{x}^2|n\rangle$ (**See SQ7**).

Following the approach in SQ7 or otherwise, **evaluate the following matrix elements**

$$x^3_{mn} \equiv \langle m|\hat{x}^3|n\rangle \tag{7}$$

and

$$x^4_{mn} \equiv \langle m|\hat{x}^4|n\rangle \tag{8}$$

2.2 (22 points) $\hat{H}_0$ **is a harmonic oscillator - with a quartic anharmonic term**

Let's make use of the results in Problem 2.1. Consider the **anharmonic oscillator** problem with the quartic term as the perturbation

$$\hat{H} = \left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2\right) + \frac{1}{24}\, b\, x^4 = \hat{H}_0 + \hat{H}' \,, \tag{9}$$

where the perturbation is taken to be the quartic $\sim x^4$ term.

(a) For **any unperturbed states** $\psi_n^{(0)}$ or $|n\rangle$ of $\hat{H}_0$, **evaluate** the modified energy to **first-order** in $\hat{H}'$ using perturbation theory.

[Hint: Use your answer in Problem 2.1 for the special case of x_{nn}^4. The answer has a nice and simple closed form. Note that you have generalized the result in Problem 2.1(b) to arbitrary unperturbed states.]

(b) Let's consider only the ground state. **Find the leading correction term** (the first non-vanishing term that has the biggest effect) to the **ground state wavefunction** due to the quartic perturbative term.

2.3 (25 points) **Must Do! Harmonic Oscillator with a linear term - Exact solutions versus perturbation treatment**

Here is a classic QM problem that is exactly solvable and one can compare exact results with perturbative results. The problem is to add 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

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2 + e\,\mathcal{E}x \ , \tag{10}$$

where the last term is treated as the perturbation and it comes from the electrostatic potential energy. It is **linear** in x. Note that the integral $x_{mn} \equiv \langle \psi_m^{(0)}|x|\psi_n^{(0)}\rangle$ (see Eq. (6) and SQ7) will be useful.

Perturbation theory

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

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

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

Solve the TISE problem exactly

(d) 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.

(e) Consider the Hamiltonian in Eq.(10) again. Completing the square and defining a new variable x' to replace x, **show that** the problem represented by $\hat{H}$ in Eq. (10) is just **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 energy function is exactly solvable**.]

Comparing results

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

2.4 (28 points) **2D harmonic oscillator with a βxy type coupling - Degenerate perturbation theory**

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

$$\hat{H}_0 = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) + \frac{1}{2}m\omega^2(x^2 + y^2)\ . \qquad (11)$$

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 bonus points though.]

(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 $2\hbar\omega$ has a degeneracy of 2.

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

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

where the last term $\beta\, x\, y$ can be treated as a perturbation. Here, β is a constant serving as a 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 $E^{(0)} = 2\hbar\omega$. We need to apply the **degenerate perturbation theory**. **Set up** a 2×2 matrix representing $\hat{H}$ using the two degenerate wavefunctions.

[Hint: You will see some familiar integrals again.]

Hence, **solve for the new eigenenergies** and **make a sketch** illustrating how the two new energies behave as the parameter β varies.

(d) (Slightly harder) Finally, **find the modified wavefunctions** for the two states, in terms of the originally degenerate states in part (b).

[Hint: Find the eigenvector of each eigenvalue.]