
Department of Physics, IIT-Kanpur
Tarun Kanti Ghosh

Quantum Mechanics-II (PHY626) AY 2025-26, SEM-II
 Homework-1: time-independent perturbation theory

1. Consider an infinite square well potential as

$$\begin{aligned} V(x) &= 0, \quad 0 < x < L \\ &= \infty, \quad \text{otherwise}. \end{aligned}$$

Applying a δ -perturbation as $V_1(x) = V_0 L \delta(x - L/2)$, where V_0 has the dimension of energy.

- Show that the first-order corrections to the energies are

$$E_n^{(1)} = V_0 [1 - (-1)^n].$$

- Show that the first-order correction to the ground state wave function is

$$\psi_1^{(1)}(x) \simeq \frac{V_0}{4E_1^{(0)}} \sqrt{\frac{2}{L}} \left[\sin\left(\frac{3\pi x}{L}\right) - \frac{1}{3} \sin\left(\frac{5\pi x}{L}\right) + \frac{1}{6} \sin\left(\frac{7\pi x}{L}\right) - \frac{1}{10} \sin\left(\frac{9\pi x}{L}\right) + \dots \right],$$

where $E_1^{(0)} = (\pi\hbar)^2/(2ML^2)$.

- Plot $\psi_1^{(0)}(x)$, $\psi_1^{(1)}(x)$ and $\psi(x) = \psi_1^{(0)}(x) + \psi_1^{(1)}(x)$.

- Show that the second-order energy corrections for odd n are

$$E_n^{(2)} = \frac{(2V_0)^2}{E_1^{(0)}} \sum_{l \neq n, l: \text{odd}} \frac{1}{n^2 - l^2}.$$

2. Consider two identical spin-zero bosons kept in one-dimensional harmonic potential well. The interaction between two bosons is given by $V(x_1, x_2) = -V_0 a_0 \delta(x_1 - x_2)$. Here V_0 is a constant having dimension of energy and $a_0 = \sqrt{\hbar/(m\omega)}$ is the oscillator length scale.

- For non-interacting case, obtain the ground and first excited state energies and the corresponding eigenfunctions (in terms of the oscillator functions).
- Calculate the first-order correction to the ground state and excited state energies, due to the two-body interaction $V(x_1, x_2)$.
- Calculate the first-order correction to the ground state and first excited state wavefunctions, due to the two-body interaction $V(x_1, x_2)$.

3. Consider a charge particle (mass m and charge q) is performing a simple harmonic motion with the oscillation frequency ω along x -axis. It is subjected to a constant electric field $\mathbf{E} = E_0 \hat{x}$. The quantum mechanical Hamiltonian for this system is

$$H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} m\omega^2 x^2 - qE_0 x.$$

- (a) Solve this problem exactly.
- (b) Treat the dipole interaction energy term as a perturbation and solve the problem perturbatively (up to second-order energy correction and first-order correction to the eigenstates).
- (c) Show that the perturbative results are in agreement with the series expansion of the exact results.
4. **The Morse potential:** The Morse potential is very useful to study vibrational energy levels of diatomic molecules. It is given as

$$\begin{aligned} V(r) &= D_e [1 - e^{-\beta(r-r_e)}]^2 - D_e \\ &= D_e [e^{-2\beta(r-r_e)} - 2e^{-\beta(r-r_e)}]. \end{aligned}$$

Here $\beta = \beta_0/r_e$, r is the intermolecular distance and D_e is the depth of the well. The dissociation energy can be calculated by subtracting the zero-point energy from D_e . Also, r_e is the equilibrium distance at which the potential energy is minimum and β controls effective width of the well. This is a real example of an anharmonic potential.

- (a) Plot $V(r)$ (in units of D_e) vs r/r_e for three different values of $\beta : 0.5, 1, 1.5$.
- (b) We are interested in the small amplitude oscillation, which can be obtained from the Taylor series expansion of the Morse potential $V(r)$ around the equilibrium position r_e . Show that the Morse potential $V(r)$ can be approximated around r_e as

$$V(r) \simeq -D_e + D_e\beta^2(r - r_e)^2 - D_e\beta^3(r - r_e)^3 + \frac{7}{12}D_e\beta^4(r - r_e)^4 - \dots$$

- (c) The bond stiffness (force constant) is the coefficient of the second derivative of the potential at the equilibrium position and it is $k = 2D_e\beta^2$.

Since the vibration is occurring along the intermolecular separation, the motion is one dimensional. So the kinetic energy will be simply

$$T = -\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2}.$$

Here μ is the reduced mass of the two particles.

Shifting the origin to the equilibrium position r_e , so the new variable is $x = r - r_e$. Show that the total Hamiltonian for a diatomic molecule around the equilibrium position is

$$\begin{aligned} H &= -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + D_e\beta^2x^2 - D_e\beta^3x^3 + \frac{7}{12}D_e\beta^4x^4 \\ &= -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + \frac{1}{2}\mu\omega^2x^2 - D_e\beta^3x^3 + \frac{7}{12}D_e\beta^4x^4. \end{aligned}$$

where $\omega = \sqrt{2D_e\beta^2/\mu} = \beta\sqrt{2D_e/\mu}$ and $a_0 = \sqrt{\hbar/(\mu\omega)} = \sqrt{\hbar/(\beta\sqrt{2\mu D_e})}$.

5. Consider an anharmonic oscillator as described by

$$H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2}m\omega^2x^2 + \frac{1}{2}\lambda \frac{m^{3/2}\omega^{5/2}}{\hbar^{1/2}}x^3,$$

where $\lambda \ll 1$ so that the cubic term can be treated as a perturbative term.

- (a) Express the Hamiltonian H in terms of dimensionless variable $\eta = x/a_0$ with $a_0 = \sqrt{\hbar/(m\omega)}$.
- (b) Plot the potential energy $V(\eta)$ for $\lambda = 0.1, 0.15, 0.5$:

$$V(\eta) = \frac{1}{2}\hbar\omega [\eta^2 + \lambda\eta^3].$$

The sign of λ does not alter the results since it flips the effective potential with respect to y axis.

Comment on the behaviour of the potential energy on the negative η axis side for three different λ values. Under what condition on λ , the perturbative analysis will be valid?

- (c) Obtain first-order and second-order energy corrections to the n -th energy levels.

$$\begin{aligned} E_n^{(1)} &= 0 \\ E_n^{(2)} &= -\frac{\lambda^2\hbar\omega}{32}(30n^2 + 30n + 11) \\ &= -\frac{\lambda^2 15\hbar\omega}{16} \left[(n + 1/2)^2 + \frac{7}{60} \right]. \end{aligned}$$

The second-order corrections to the energy levels do not depend on the sign of λ , as expected.

Validity of the approximation: The approximation will be good if $|E_{n+1} - E_n| \gg |E_n^{(1)} + E_n^{(2)} + \dots|$. In this case, we have to choose λ and n such that $\hbar\omega \gg |E_n^{(2)}|$.

- (d) Obtain the first-order correction to the eigenstates.

$$\begin{aligned} \phi_n^{(1)}(x) &= \frac{\lambda}{12\sqrt{2}} \left[\sqrt{n(n-1)(n-2)}\phi_{n-3}^{(0)}(x) + 9n\sqrt{n}\phi_{n-1}^{(0)}(x) \right] \\ &\quad - \frac{\lambda}{12\sqrt{2}} \left[9(n+1)\sqrt{n+1}\phi_{n+1}^{(0)}(x) + \sqrt{(n+1)(n+2)(n+3)}\phi_{n+3}^{(0)}(x) \right]. \end{aligned}$$

- (e) For the ground state, the correction is

$$\phi_0^{(1)}(x) = -\frac{\lambda}{12\sqrt{2}} \left[9\phi_1^{(0)}(x) + \sqrt{6}\phi_3^{(0)}(x) \right].$$

Plot $\phi_0^{(1)}(x)$.

6. Consider another anharmonic oscillator as described by

$$H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2 + \frac{1}{2}\lambda \frac{m^2\omega^3}{\hbar} x^4,$$

where $0 < \lambda \ll 1$ so that the quartic term can be treated as a perturbative term. For the inverted parabolic potential plus quartic potential, $V(x) = (1/2)(-m\omega^2 x^2 + \lambda \frac{m^2\omega^3}{\hbar} x^4)$, the effective potential will have double-well structure.

- (a) Express the Hamiltonian H in terms of dimensionless variable $\eta = x/a_0$ with $a_0 = \sqrt{\hbar/(m\omega)}$.

- (b) Plot the effective potential energy $V(\eta)$ for $\lambda = 0.5$ and $\lambda = 1.5$:

$$V(\eta) = \frac{1}{2}\hbar\omega [\eta^2 + \lambda\eta^4].$$

- (c) Show that the first-order energy correction to the n -th level is

$$E_n^{(1)} = \frac{3\lambda\hbar\omega}{8}(2n^2 + 2n + 1) = \frac{3\lambda\hbar\omega}{4} \left[(n + 1/2)^2 + \frac{1}{4} \right].$$

The first-order energy correction depends on the sign of λ . Note that the energy levels are enhanced for $\lambda > 0$ case because the quartic potential compressed the harmonic potential. On the other hand, the energy levels are decreased for $\lambda < 0$ case because the quartic potential flattens the harmonic potential. For $\lambda < 0$ case, the effective potential has finite depth (it has local maximum). Therefore, the perturbative result is valid as long as $E_n = E_n^{(0)} + E_n^{(1)}$ is less than the local maximum.

- (d) Show that the second-order energy correction to the ground state is

$$E_0^{(2)} = -\frac{21\lambda^2\hbar\omega}{32}.$$

Note that the second-order energy correction to the ground state is negative, as it should be and it is independent of the sign of λ .

- (e) Show that the second-order energy correction to the n -th level is

$$E_n^{(2)} = -\frac{21\lambda^2\hbar\omega}{32} [34n^3 + 51n^2 + 59n + 21]$$

NOTES: Bender and Wu [PR 184, 1231 (91969)] computed higher-order energy correction for the quartic perturbation. The modified ground state energy turns out to be

$$\begin{aligned} E_0(\lambda) &= \frac{\hbar\omega}{2} \left[1 + \frac{3}{2} \left(\frac{\lambda}{2} \right) - \frac{21}{4} \left(\frac{\lambda}{2} \right)^2 + \frac{333}{8} \left(\frac{\lambda}{2} \right)^3 - \frac{30885}{64} \left(\frac{\lambda}{2} \right)^4 \right] \\ &\quad + \frac{\hbar\omega}{2} \left[\frac{916731}{128} \left(\frac{\lambda}{2} \right)^5 - \frac{65518401}{512} \left(\frac{\lambda}{2} \right)^6 + \dots \right] \end{aligned}$$

The coefficients of λ^k is growing with the increase of powers of λ . The series does not converge for any non-zero λ . It does not imply that the series expansion is not useful. For a given small value of λ , the magnitude of the successive terms generally decrease. At some point, it starts growing again. What will be the good approximation? Keep only the part of the series where the terms are decreasing.

For example, set $\lambda = 0.2$. In this case,

$$E_0(\lambda = 0.2) = \frac{\hbar\omega}{2} \left[\underbrace{1 + 0.15 - 0.0525 + 0.041625}_{\text{decreasing}} - \underbrace{0.04825 + 0.07161 - 0.1279\dots}_{\text{increasing}} \right].$$

Note that $E_0^{(3)} < E_0^{(2)} < E_0^{(1)} < E_0^{(0)}$, but $E_0^{(4)} > E_0^{(3)}$. So we can safely take upto third-order correction for $\lambda = 0.2$.

- (f) Show that the first-order correction to the ground state wavefunction is

$$\phi_0^{(1)}(x) = -\frac{\lambda}{16} \left[6\sqrt{3}\phi_2^{(0)}(x) + \sqrt{6}\phi_4^{(0)}(x) \right],$$

where $\phi_n^{(0)}(x)$ are the normalized oscillator states.

- (g) Plot $\phi_0^{(0)}(x)$, $\phi_0^{(1)}(x)$ and $\phi_0(x) = \phi_0^{(0)}(x) + \phi_0^{(1)}(x)$.

- (h) **Exact diagonalization method:** Exact diagonalization is a numerical technique for obtaining the eigenvalues and the eigenstates of a given quantum Hamiltonian. For $\lambda = 0$, the system reduces to the simple harmonic oscillator problem whose eigenvalues and eigenfunctions are exactly known: $E_n^{(0)} = \hbar\omega(n + 1/2)$ and the normalized oscillator wavefunctions $\phi_n(x)$:

$$\phi_n^{(0)}(x) = \frac{1}{\sqrt{\sqrt{\pi}2^n n! a_0}} e^{-x^2/(2a_0^2)} H_n(x/a_0),$$

where $a_0 = \sqrt{\hbar/(m\omega)}$.

The unperturbed wavefunctions $\phi_n^{(0)}(x)$ can be used as a basis states and the most general wavefunction for $\lambda \neq 0$ can be assumed to be of the form

$$\phi(x) = \sum_{n=0}^{\infty} c_n \phi_n^{(0)}(x).$$

Here the unknown expansion coefficients $c_n \equiv c_n(\lambda)$ can be obtained from the time-independent Schrödinger equation $H\phi(x) = E\phi(x)$.

Acting the total Hamiltonian H on $\phi(x)$ given above, multiplying $\phi_m^*(x)$ from left and integrating over all space, you will get

$$[(m + 1/2) - \epsilon]c_m + \sum_{n=0,..} c_n M_{mn} = 0,$$

where the energy $\epsilon = E/(\hbar\omega)$ is dimensionless energy and the matrix elements M_{nm} are given by

$$M_{mn} = \frac{\lambda}{2} \int_{-\infty}^{\infty} \phi_m^{(0)}(\eta) \eta^4 \phi_n^{(0)}(\eta) d\eta.$$

In order to obtain low energy levels, construct a square matrix by running the quantum numbers n, m . For example, construct a 50×50 matrix, diagonalize it to obtain the eigenvalues and the corresponding eigenfunctions for a given λ (say $\lambda = 0.1$). For different values of λ , you will get different values of c_n . Thus coefficients c_n are λ -dependent.

- (i) Obtain the ten lowest energy eigenvalues for $\lambda = 0.1$ and $\lambda = 0.3$. Compare the numerical results with that of the perturbative results.
 - (ii) Plot the probability density of the ground state and the first excited state. Finally compare with the perturbative results.
7. Consider a two-dimensional anisotropic harmonic oscillator

$$H = -\frac{\hbar^2}{2m} \left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right] + \frac{1}{2}m\Omega^2(x^2 + y^2) + m\omega^2 xy.$$

- (a) Obtain the energy levels and the corresponding eigenstates exactly for $\Omega > \omega$.

Hints: Rotate the xy plane around z -axis by $\phi = \pi/4$ angle, so the new coordinates (x_+, x_-) are

$$x_{\pm} = \frac{\pm x + y}{\sqrt{2}},$$

and the rotated Hamiltonian is now

$$\mathcal{H} = -\frac{\hbar^2}{2m} \left[\frac{\partial^2}{\partial x_+^2} + \frac{\partial^2}{\partial x_-^2} \right] + \frac{1}{2}m(\gamma_+\Omega)^2 x_+^2 + \frac{1}{2}m(\gamma_-\Omega)^2 x_-^2,$$

where the dimensionless factors $\gamma_{\pm} = \sqrt{1 \pm \omega^2/\Omega^2}$ renormalize the oscillation frequency Ω differently in two orthogonal directions.

Answer: The energy eigenvalues are

$$E_{n_x, n_y} = [(n_x + 1/2)\gamma_+ + (n_y + 1/2)\gamma_-] \hbar\Omega, \quad n_x, n_y : 0, 1, 2, \dots,$$

where $\gamma_{\pm} = \sqrt{1 \pm \omega^2/\Omega^2}$ and the wavefunctions are

$$\psi_{n_x, n_y}(x, y) = \phi_{n_x}(x/a_+) \phi_{n_y}(y/a_-),$$

where $\phi_{n_x}(x/a_+), \phi_{n_y}(y/a_-)$ are the oscillator wavefunctions and $a_{\pm} = \sqrt{\hbar/(m\Omega\gamma_{\pm})} = a_0/\sqrt{\gamma_{\pm}}$ with $a_0 = \sqrt{\hbar/(m\Omega)}$.

- (b) Obtain the first three lowest energy levels and their corresponding wavefunctions.

Answer: Ground state: $n_x = 0, n_y = 0$. First excited state: $n_x = 0, n_y = 1$ and Second excited state: $n_x = 1, n_y = 0$.

Second excited state:

$$E_{1,0} = \frac{(3\gamma_+ + \gamma_-)}{2} \hbar\Omega, \quad \psi_{1,0}(x, y) = \phi_1(x/a_+) \phi_0(y/a_-).$$

- (c) Assuming $\omega \ll \Omega$ and treat the term $H' = m\omega^2 xy$ as a perturbation.

- (i) Obtain energies and the corresponding eigenstates for $H' = 0$.

Answer:

$$\epsilon_{n_x, n_y} = (n_x + n_y + 1)\hbar\Omega, \quad \psi_{n_x, n_y} = \phi_{n_x}(x/a_0) \phi_{n_y}(y/a_0).$$

- (ii) Obtain the first-order and second order energy corrections to the ground state.

Answer: $\epsilon_{0,0}^{(1)} = 0$ and

$$\epsilon_{0,0}^{(2)} = -\frac{\hbar\omega^4}{8\Omega^3}.$$

- (iii) Obtain the energy corrections to the first-excited state (two-fold degenerate) and their wavefunctions.

$$\epsilon_1^{(1)} = \pm \frac{\hbar\omega^2}{2\Omega}.$$

- (iv) Compare the perturbative results with the series expansion of the exact results.

8. Consider an electron's spin is interacting with the static magnetic field $\mathbf{B} = B_x \hat{x} + B_z \hat{z}$ with $B_x < B_z$. The Hamiltonian for the spin degree of freedom can be written as

$$H = \hbar\omega_z\sigma_z + \hbar\omega_x\sigma_x,$$

where $\omega_z = eB_z/(2m)$ and $\omega_x = eB_x/(2m)$ with $\omega_z > \omega_x$. Here σ_z and σ_x are the usual Pauli matrices.

- (a) Obtain energy levels and the corresponding eigenstates exactly.

Answer:

$$E_{\pm} = \pm\hbar\sqrt{\omega_z^2 + \omega_x^2}.$$

$$|\chi_+\rangle = \begin{bmatrix} \cos(\theta/2) \\ \sin(\theta/2) \end{bmatrix}, \quad |\chi_-\rangle = \begin{bmatrix} -\sin(\theta/2) \\ \cos(\theta/2) \end{bmatrix}, \quad \theta = \tan^{-1}(\omega_x/\omega_z).$$

- (b) For $\omega_x \ll \omega_z$, show that

$$E_{\pm} \simeq \pm\hbar\omega_z \left[1 + \frac{\omega_x^2}{2\omega_z^2} + \dots \right],$$

and

$$|\chi_+\rangle \simeq \begin{bmatrix} 1 \\ \frac{\omega_x}{2\omega_z} \end{bmatrix}, \quad |\chi_-\rangle \simeq \begin{bmatrix} -\frac{\omega_x}{2\omega_z} \\ 1 \end{bmatrix}, \quad \theta = \tan^{-1}(\omega_x/\omega_z).$$

- (c) Treat the term $\omega_x\sigma_x$ as a perturbation and obtain energy corrections up to second-order and the eigenstates up to first-order.

Answer: The first-order energy corrections: $E_{\pm}^{(1)} = 0$.

The second-order energy corrections:

$$E_{\pm}^{(2)} = \pm\frac{\hbar\omega_x^2}{2\omega_z}.$$

$$|\psi_+\rangle = \begin{bmatrix} 1 \\ \frac{\omega_x}{2\omega_z} \end{bmatrix}, \quad |\psi_-\rangle = \begin{bmatrix} -\frac{\omega_x}{2\omega_z} \\ 1 \end{bmatrix}$$

- (d) Show that the perturbative results are in agreement with the series expansion of the exact results.

9. Fine structure electronic energy levels of hydrogenic atoms:

- (a) Write down the relativistic expression for the kinetic energy in terms of the relativistic momentum \mathbf{p} and $m_e c$. Here m_e is the mass of the electron and c is the velocity of light. In the non-relativistic limit ($|\mathbf{p}| \ll m_e c$), show that the lowest-order relativistic correction to the kinetic energy in one-electron atom is

$$E_{\text{kin}} = -E_n \left(\frac{Z\alpha}{n} \right)^2 \left[\frac{3}{4} - \frac{n}{l+1/2} \right].$$

- (b) The spin-orbit interaction term is given as

$$H_{\text{so}} = \frac{1}{2m_e^2 c^2} \frac{1}{r} \frac{dV(\mathbf{r})}{dr} \mathbf{L} \cdot \mathbf{S}.$$

Show that components of \mathbf{L} and \mathbf{S} do not commute with H_{so} , but the total angular momentum of the electron $\mathbf{J} = \mathbf{L} + \mathbf{S}$ does commute with the H_{so} .

Show that $[\mathbf{J}^2, \mathbf{L} \cdot \mathbf{S}] = 0$, $[\mathbf{L}^2, \mathbf{L} \cdot \mathbf{S}] = 0$ and $[\mathbf{S}^2, \mathbf{L} \cdot \mathbf{S}] = 0$.

- (c) Show that the spin-orbit correction to the electronic energy levels are

$$\begin{aligned} E_{\text{so}} &= -E_n \left(\frac{Z\alpha}{n} \right)^2 \left[\frac{n}{2(l+1/2)(l+1)} \right]; \quad j = l + 1/2 \\ &= E_n \left(\frac{Z\alpha}{n} \right)^2 \left[\frac{n}{2l(l+1/2)} \right]; \quad j = l - 1/2 \end{aligned}$$

- (d) **Darwin term:** For a relativistic particle, its position rapidly oscillates with the amplitude $\lambda_c = \hbar/(m_e c)$, (λ_c is the Compton wavelength) due to interference between positive and negative energy states. In other words, the instantaneous position of the relativistic particle can not be defined more precisely than within the volume $V_c = (4\pi/3)\lambda_c^3$. Therefore, the Coulomb potential $V(r)$ can not be the actual potential. It must be modified to take into account of the intrinsic oscillation of the particle's position.

Show that the smeared average of the potential $V(\mathbf{r})$ over a sphere of radius λ_c is

$$\bar{V}(\mathbf{r}) = \frac{3}{4\pi\lambda_c^3} \int_{V_c} V(\mathbf{r} + \mathbf{r}') d^3 r' \simeq V(\mathbf{r}) + \frac{\lambda_c^2}{10} \nabla_{\mathbf{r}}^2 V(\mathbf{r}) + \dots$$

The second term on the right hand side is the Darwin term, but the factor 1/10 should be replaced by 1/8 if we obtain the term from the Dirac equation.

- (e) Show that the Darwin correction to the electronic energy levels is

$$E_D = -E_n \frac{(Z\alpha)^2}{n}, \quad l = 0.$$

- (f) Show that the total energy correction is

$$E_{nj} = (E_{\text{kin}} + E_{\text{so}} + E_D) = E_n \left(\frac{Z\alpha}{n} \right)^2 \left[\frac{n}{j+1/2} - \frac{3}{4} \right]$$

for **all** values of l . Note that the individual corrections depend on l , but the total correction does not depend on l . [Hint: Note that $j = l \pm 1/2$; treat the $j = l + 1/2$ and $j = l - 1/2$ separately. You will get the same final answer either way.]

- (g) The exact fine-structure energy for hydrogenic atom obtained by solving the relativistic Dirac equation is

$$E_{nj}^{\text{exact}} = m_e c^2 \left(\left[1 + \left(\frac{Z\alpha}{n - (j+1/2) + \sqrt{(j+1/2)^2 - Z^2\alpha^2}} \right)^2 \right]^{-1/2} - 1 \right).$$

Expand in powers of $Z\alpha$ [upto order $(Z\alpha)^4$] and show that you get

$$E_{nj}^{\text{exact}} \simeq E_n \left[1 + \left(\frac{Z\alpha}{n} \right)^2 \left[\frac{n}{j+1/2} - \frac{3}{4} \right] \right],$$

which matches exactly with the perturbative results. Note that $Z\alpha < 1$ as long as $Z < 137$.

- 10. Isotope Shifts:** The protons in the nucleus are distributed in a finite volume. The electrostatic potential inside the nucleus is different from $1/r$ law. Actual potential depends on the proton distribution within the nucleus. For simplicity, consider the nuclear charge is distributed uniformly within a sphere of radius $R = r_0 A^{1/3}$, where A is the atomic mass number and $r_0 \sim 1.2 \times 10^{-15}$ fm.

- (a) Show that, in this simple model, the electrostatic potential due to the nucleus of charge Ze is

$$\begin{aligned} V_0(r) &= \frac{Ze^2}{4\pi\epsilon_0 2R} \left(\frac{r^2}{R^2} - 3 \right), & r \leq R \\ &= -\frac{Ze^2}{4\pi\epsilon_0 r}, & r \geq R. \end{aligned}$$

- (b) Calculate the first-order energy correction E_1^{finite} to the ground state of hydrogenic atoms. We can rewrite the potential $V_0(r)$ as

$$V_0(r) = V(r) + U(r),$$

where

$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r}, \quad r > 0.$$

and

$$\begin{aligned} U(r) &= \frac{Ze^2}{4\pi\epsilon_0 2R} \left(\frac{r^2}{R^2} - 3 \right) + \frac{Ze^2}{4\pi\epsilon_0 r}, & r \leq R \\ &= 0, & r \geq R. \end{aligned}$$

Or

$$\begin{aligned} U(r) &= \frac{Ze^2}{4\pi\epsilon_0 2R} \left(\frac{r^2}{R^2} - 3 + \frac{2R}{r} \right) & r \leq R \\ &= 0, & r \geq R. \end{aligned}$$

The range of the perturbation is within the nuclear size, rest is zero.

$$\psi_{100} = \frac{Z^{3/2}}{\sqrt{\pi a_0^3}} e^{-Zr/a_0}.$$

Here a_0 is the Bohr radius of hydrogen atom.

Estimating order of magnitude: Maximum value of r can be taken to be R . Replace r by R in $U(r)$ as well as in $|\psi_{100}|^2 \sim \frac{1}{a_0^3}$ since $R \ll a_0$. Also, $4\pi r^2 dr \rightarrow R^3$.

$$U(r)|\psi_{100}|^2 4\pi r^2 dr \rightarrow \frac{e^2}{4\pi\epsilon_0} \left(\frac{R}{a_0}\right)^2.$$

$$E_1^{\text{finite}} = 4\pi \int_0^R dr r^2 \frac{1}{\pi a_0^3} e^{-2Zr/a_0} U(r).$$

Use the fact that $R \ll a_0$ and expand the exponential and perform the integral:

$$E_1^{\text{finite}} \simeq = \frac{2Z^4 e^2 R^2}{5a_0^3} \simeq \frac{4Z^4}{5} |E_{100}| \left(\frac{R}{a_0}\right)^2.$$

Here E_{100} is the ground state energy of a hydrogen atom. Thus the effect of the finite size of nucleus is to shift the energy upward and the scale of the shift is determined by $\left(\frac{R}{a_0}\right)^2$.

- (c) Estimate ΔE for hydrogen atom and muonic atom.
- 11. Show that in the linear Stark effect the $n = 3$ level of a hydrogenic atom is splitting into five equally spaced levels. Calculate the expression for the level separation as a function of the electric field strength.
- 12. **Quenching of orbital angular momentum:** In a crystal, the electric field of neighboring ions perturbs the energy levels of an atom. As a crude model, imagine that a hydrogen atom in $n = 2, l = 1$ state is surrounded by three pairs of point charges. Ignore spin of the electron. Now the potential energy of the electron due to the field arising from the atom's surroundings is of the following form:

$$H' = ax^2 + by^2 - (a + b)z^2,$$

where a and b are two constants with $a > b$. Show that the $l = 1$ level of a hydrogenic atom splits into three distinct levels for $a \neq b$. Show that each state has a wave function of the form

$$\Psi(\mathbf{r}) = (\alpha x + \beta y + \gamma z)f(r),$$

where $f(r)$ is a common function and each level has its own set of constants α , β , and γ . Show that $\langle \Psi(\mathbf{r}) | \mathbf{L} | \Psi(\mathbf{r}) \rangle = 0$ for all the three states. This is known as the **quenching of orbital angular momentum** due to the strong crystal fields.

[Answer: The splitted energy levels are $\epsilon_1 = -12a_0^2(a + b)$, $\epsilon_2 = 12a_0^2b$ and $\epsilon_3 = 12a_0^2a$. Here a_0 is the Bohr radius. The corresponding (α, β, γ) are $(1, 0, 0)$, $(0, 1, 1)$ and $(0, -1, 1)$, respectively].

- 13. Consider an electron ($q = -e$) moving on xy plane subjected to the uniform magnetic field $\mathbf{B} = B\hat{z}$.
 - (a) Using the Landau gauge for the vector potential $\mathbf{A} = Bx\hat{y}$, show that its Hamiltonian is

$$H_0 = \frac{p_x^2}{2m} + \frac{(p_y + eBx)^2}{2m}.$$

- (b) Since the Hamiltonian H_0 commutes with the momentum operator p_y , $[H_0, p_y] = 0$, the total wave function can be decomposed as $\psi(x, y) = \phi(x)e^{ik_y y}$, where k_y is a number. Using this fact, show that the two-dimensional Hamiltonian H_0 reduces to the following one-dimensional Hamiltonian:

$$H_0 = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2}m\omega_c^2(x + k_y l_0)^2.$$

Here $\omega_c = eB/m$ and $l_0 = \sqrt{\hbar/(eB)}$.

Introducing the bosonic ladder operators as

$$b = \frac{1}{\sqrt{2}} \left[\frac{\xi}{l_0} + i \frac{p_\xi}{p_0} \right], \quad b^\dagger = \frac{1}{\sqrt{2}} \left[\frac{\xi}{l_0} - i \frac{p_\xi}{p_0} \right],$$

where $\xi = x + k_y l_0^2$ and $p_0 = \sqrt{\hbar m \omega_c}$. Note that the origin of the coordinate system has been shifted along x -axis by a constant amount $k_y l_0$, such that the minimum of effective potential is at $\xi = 0$.

Show that the Hamiltonian can be expressed as

$$H_0 = \left(b^\dagger b + \frac{1}{2} \right) \hbar \omega_c.$$

Therefore its energy levels are $E_n = (n + 1/2)\hbar \omega_c$ and the corresponding eigenfunctions are the oscillator wavefunctions $\phi_n(\xi/l_0)$.

- (c) Applying an in-plane electric field $\mathbf{E} = E_x \hat{x}$, so the dipole interaction term is $V = eE_x x$. Now the total Hamiltonian is $H = H_0 + V$ which can be solved exactly. Show that the energy levels are

$$E_n = (n + 1/2)\hbar \omega_c - \hbar k_y v_d + \frac{1}{2}mv_d^2,$$

where $v_d = E_x/B$ and the corresponding eigenfunctions are

- (d) Treat the dipole potential energy $V = eE_x x$ as a perturbative term in the total Hamiltonian H .

Calculate the first-order and second-order energy corrections and compare with the exact result.

Calculate the first-order correction to the unperturbed eigenstate ϕ_n and compare with the exact result.

14. **A Dirac electron subjected to crossed magnetic and electric fields:** Consider the Dirac electron (on a graphene sheet) in xy plane subject to constant magnetic field ($\mathbf{B} = B\hat{z}$) is described by the Hamiltonian

$$H_0 = \hbar v_f \boldsymbol{\sigma} \cdot (\mathbf{k} + e\mathbf{A}/\hbar), \quad (1)$$

where $\boldsymbol{\sigma}$ is the Pauli matrices and \mathbf{A} is the vector potential. For convenience, we choose $\mathbf{A} = Bx\hat{y}$. One can solve this Hamiltonian exactly [see “Graphene: Carbon in Two Dimensions” by M. I. Katsnelson, Cambridge University Press]. The energy levels are

$$E_n^{(0)} = \hbar \omega_c \sqrt{2n}, \quad n = 0, 1, 2, \dots$$

and the corresponding eigenstates are

$$\psi_{n,k_y}^{(0)}(x, y) = \frac{e^{ik_y y}}{\sqrt{2L_y}} \begin{pmatrix} \phi_{n-1}(\xi/l_0) \\ i\phi_n(\xi/l_0) \end{pmatrix}.$$

Here $\omega_c = v_f/l_0$ with $l_0 = \sqrt{\hbar/(eB)}$ and $\phi_n(\xi)$ are the normalized oscillator wavefunctions with $\xi = (x + k_y l_0^2)$. Note that $\phi_{-1}(\xi) = 0$.

Applying an in-plane electric field $\mathbf{E} = E_x \hat{x}$, so the dipole interaction term is $V = eE_x x \sigma_0$, where σ_0 is the 2×2 identity matrix. Now the total Hamiltonian is $H = H_0 + V$ which can be solved exactly using the Lorentz boost transformation [V Lukose, R. Shankar and G. Baskaran, Phys. Rev. Lett. **98**, 116802 (2007)]. The exact energy levels of the Hamiltonian H are given by

$$E_n = \hbar\omega_c \sqrt{2n}(1 - \beta^2)^{3/4} - \hbar v_f k_y \beta,$$

where $\beta = v_d/v_f = E_x/(v_f B)$. For typical experimental parameters, $\beta \ll 1$. Therefore we can have Taylor series expansion (keeping upto quadratic in β) of the exact energy levels as

$$\begin{aligned} E_n &\simeq \hbar\omega_c \sqrt{2n} - \hbar v_f k_y \beta - \hbar\omega_c \sqrt{2n} \frac{3}{4} \beta^2 + \dots \\ &\simeq E_n^{(0)} - \hbar v_f k_y \beta - \frac{3E_n^{(0)}}{4} \beta^2 + \dots \end{aligned} \quad (2)$$

- (a) Treat the dipole energy term $V = eE_x x \sigma_0 = \sigma_0 \hbar\omega_c (x/l_0) \beta$ as a perturbation to H_0 . Obtain the first-order and second-order energy corrections for $n > 0$ and compare with the series expansion of the exact result for $n = 1, 2, 3$ and 4 .

Answers:

$$\begin{aligned} E_n^{(1)} &= -\hbar v_f k_y \beta. \\ E_n^{(2)} &= \beta^2 \hbar\omega_c \left[\frac{4n(\sqrt{n-1} - \sqrt{n+1}) - 6\sqrt{n} - \sqrt{n-1} - \sqrt{n+1}}{8\sqrt{2}} \right]. \end{aligned}$$

- (b) Show that for large n ($n \rightarrow \infty$),

$$E_n^{(2)} \sim -E_n^{(0)} \frac{\beta^2}{2}.$$

15. **The Aharonov-Bohm ring geometry subjected to crossed magnetic and electric fields:** Consider an electron of charge e and mass M is free to move on a circle of radius R and negligible width. This ring is lying on xy plane and subjected to the uniform magnetic field $\mathbf{B} = B\hat{z}$ perpendicular to the ring. We will consider the magnetic vector potential $\mathbf{A} = (Br/2)\hat{\phi}$ in the circular gauge owing to the circular symmetry of the given problem.

- (a) Show that the Hamiltonian for the electron is

$$H_0 = \frac{\hbar^2}{2MR^2} \left(i \frac{\partial}{\partial \phi} + \frac{\Phi}{\phi_0} \right)^2.$$

Here $\Phi = B\pi R^2$ is the total magnetic flux passing through the ring and $\phi_0 = h/e$ is the unit of magnetic flux quanta.

- (b) Show that you will get the same Hamiltonian if you consider an infinitely long solenoid of radius $R_s (< R)$ oriented along z axis placed at the center of the ring. In this case, Φ will be replaced by $\Phi_s = \pi R_s^2 B_s$, where $B_s = \mu_0 n_s I$ is the magnetic field inside the solenoid. Here n_s is the number of turns per unit length and I is the current flowing along the wire of the solenoid. The vector potential correspond to the magnetic field of a solenoid is given by

$$\begin{aligned}\mathbf{A} &= \frac{B_s r}{2} \hat{\phi}, \quad r \leq R_s \\ &= \frac{\Phi_s}{2\pi r} \hat{\phi}, \quad r \geq R_s.\end{aligned}\tag{3}$$

- (c) Show that the energy levels are

$$E_m^{(0)} = \frac{\hbar^2}{2MR^2} \left(m - \frac{\Phi}{\phi_0} \right)^2$$

and the corresponding normalized eigenstates

$$\langle \phi | m \rangle = \frac{1}{\sqrt{2\pi}} e^{im\phi}, \quad m \in \mathbb{Z}.$$

- (d) Sketch/plot E_m (in units of $\epsilon_0 = \hbar^2/(2MR^2)$) vs Φ/ϕ_0 for different values of m . Identify the ground state and first excited state for a given $\frac{\Phi}{\phi_0}$.

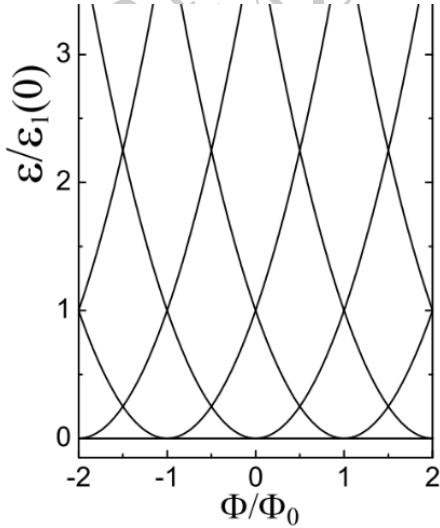


Figure 1: Plots of the energy spectrum of a quantum ring in presence of the magnetic field versus Φ_s/ϕ_0 . Each parabola represents for a particular value of the angular quantum m .

Important observations: Two successive angular momentum states $|m\rangle$ and $|m+1\rangle$ are crossing whenever $\Phi/\phi_0 = m + 1/2$.

In presence of the magnetic field, $E_{+|m|}^{(0)} < E_{-|m|}^{(0)}$, implying the magnetic field breaks the degeneracy.

For $\mathbf{B} = 0$, the ground state ($m = 0$) has zero angular momentum. For $\mathbf{B} \neq 0$, the ground state ($m = 0$) has finite angular momentum which gives rise to a persistent current.

- (e) Choosing magnetic field such that $\Phi/\phi_0 = (m + 1/2) + \delta$ with $\delta \ll 1$, representing two energy levels slightly away from the degeneracy at $\Phi/\phi_0 = (m + 1/2)$. Show that energies and the corresponding eigenvectors of the two states near $\Phi/\phi_0 = (m + 1/2) + \delta$ are

$$\begin{aligned} E_m^{(0)} &= \epsilon_0 \left(\frac{1}{2} + \delta \right)^2, \quad |m\rangle = \frac{1}{\sqrt{2\pi}} e^{im\phi} \\ E_{(m+1)}^{(0)} &= \epsilon_0 \left(\frac{1}{2} - \delta \right)^2, \quad |m+1\rangle = \frac{1}{\sqrt{2\pi}} e^{i(m+1)\phi}. \end{aligned} \quad (4)$$

- (f) Constructing a subspace spanned by the vectors $|m\rangle$ and $|m+1\rangle$. What will be the matrix representation of H_0 in this subspace? Express in terms of the Pauli matrices and identity matrix.

$$\begin{aligned} H_0 &= \begin{bmatrix} \epsilon_0 \left(\frac{1}{2} + \delta \right)^2 & 0 \\ 0 & \epsilon_0 \left(\frac{1}{2} - \delta \right)^2 \end{bmatrix} \\ &= \epsilon_0 \left[\frac{\left(\frac{1}{2} + \delta \right)^2 + \left(\frac{1}{2} - \delta \right)^2}{2} \right] \sigma_0 + \epsilon_0 \left[\frac{\left(\frac{1}{2} + \delta \right)^2 - \left(\frac{1}{2} - \delta \right)^2}{2} \right] \sigma_z \\ &= a_0 \sigma_0 + a_z \sigma_z. \end{aligned}$$

where

$$\begin{aligned} a_0 &= \frac{\epsilon_0}{4} + \epsilon_0 \delta^2 \approx \frac{\epsilon_0}{4} \quad \text{as } \delta \rightarrow 0 \\ a_z &= \epsilon_0 \delta. \end{aligned}$$

Note that the Hamiltonian H_0 is independent of m . Therefore, this Hamiltonian is valid around any degeneracy between any two states $|m\rangle$ and $|m+1\rangle$. This is an example of a two-level system having angular momentum m and $m+1$.

- (g) Now we apply an in-plane weak electric field $\mathbf{E} = \hat{i}E_x \cos \beta + \hat{j}E_y \sin \beta$, where β is a fixed azimuthal angle. This can be also written as $\mathbf{E} = \hat{i}E_1 + \hat{j}E_2$, where $E_1 = E_x \cos \beta$ and $E_2 = E_y \sin \beta$.

Plot the electric field vector \mathbf{E} on the ring for three different cases: (i) $E_1 = E_2$, (ii) $E_1 = 0.5E_2$ and $E_1 = 1.5E_2$.

Show that the dipole interaction energy due to electric field is

$$H_1 = -eR(E_1 \cos \phi + E_2 \sin \phi).$$

What will be the matrix representation of H_1 in the subspace defined earlier. Express in terms of the Pauli matrices and identity matrix.

$$H_1 = -\frac{eR}{2} \begin{bmatrix} 0 & E_1 + iE_2 \\ E_1 - iE_2 & 0 \end{bmatrix} = -\frac{eR}{2} (\sigma_x E_1 - \sigma_y E_2).$$

- (h) Express the full Hamiltonian $H = H_0 + H_1$ in a matrix form. Obtain eigenvalues and the eigenvectors.

$$E_{\pm} = \frac{\epsilon_0}{4} + \epsilon_0 \delta^2 \pm \sqrt{(\epsilon_0 \delta)^2 + \left(\frac{eRE}{2} \right)^2},$$

where $E = \sqrt{E_1^2 + E_2^2}$.

- (i) Show that there is an energy gap at the level crossing is $eR\sqrt{E_1^2 + E_2^2}$, independent of m .

16. Jaynes-Cummings model: The Jaynes-Cummings (JC) Hamiltonian describes a two-level system interacting with the quantized electromagnetic field of a single mode. This model Hamiltonian has great importance in atomic physics, solid state physics, and quantum optics.

The JC model Hamiltonian is given by $H_{JC} = H_0 + H_{int}$, where

$$\begin{aligned} H_0 &= \hbar\omega_c \left(a^\dagger a + \frac{1}{2} \right) + \hbar\omega_a \frac{\sigma_z}{2} \\ H_{int} &= \frac{\hbar g}{2} (a\sigma_+ + a^\dagger\sigma_-). \end{aligned}$$

The first term in the free Hamiltonian H_0 describes the quantized electromagnetic field with the energy $\hbar\omega_c$, whereas the second term describes a two-level system (TLS) with the energy separation $\hbar\omega_a$. Finally, H_{int} describes the interaction between TLS and the EM field. Here a^\dagger and a are the EM field mode creation and annihilation operators respectively, acting on the n -th oscillator states $|n\rangle$ satisfying the properties: $a^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle$ and $a|n\rangle = \sqrt{n}|n-1\rangle$. Also, $\sigma_\pm = (\sigma_x \pm i\sigma_y)/2$ represent raising and lowering operators in the Hilbert space spanned by $(1, 0)^\mathcal{T}$ and $(0, 1)^\mathcal{T}$, where \mathcal{T} represents the transpose operation.

Physical interpretation of H_{int} : The term $a\sigma_+$: the operator a destroy a photon in the ground state and so the system goes to the excited state which is possible only when the operator σ_+ acts on the ground state.

Similarly, the operator a^\dagger creates a photon which will be released in the system and the system goes to the ground state which is possible only when the operator σ_- acts on the excited state.

We are interested in the two regimes: (i) at resonance, $\omega_c = \omega_a = \omega$ and (ii) nearly resonance, $\omega_c \sim \omega_a$.

- (a) Show that at resonance $H_0 = \hbar\omega\mathcal{N}$, where $\mathcal{N} = a^\dagger a + \sigma_+\sigma_-$.
- (b) Show that $[H_0, H_{int}] = 0$ and $[H_0, H_{JC}] = 0$ at resonance.
- (c) Show that the total number of excitation quanta is conserved, $[\mathcal{N}, H] = 0$, where $\mathcal{N} = a^\dagger a + \sigma_+\sigma_-$ is a constant of motion even at off-resonant.
- (d) Show that doubly degenerate eigenvalues of H_0 at resonance are $E_n = (n+1)\hbar\omega$ and the corresponding eigenstates are

$$|\chi_n^+\rangle = |n\rangle \otimes \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} |n\rangle \\ 0 \end{pmatrix}, \quad |\chi_n^-\rangle = |n+1\rangle \otimes \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} 0 \\ |n+1\rangle \end{pmatrix}$$

for all the harmonic oscillator states $|n\rangle$. Here $|\chi_n^+\rangle$ represents the TLS is in the excited state and n photons and $|\chi_n^-\rangle$ represents the TLS is in the ground state and $(n+1)$ photons.

Show that the ground state energy of the whole system is $\epsilon_0 = 0$ and the corresponding state is $(0, |0\rangle)$.

- (e) In the off-resonant condition, the Hamiltonian H_0 can be written as

$$H_0 = \hbar\omega_c \left(a^\dagger a + \frac{1}{2} + \frac{\sigma_z}{2} \right) + \frac{\hbar\delta}{2} \sigma_z,$$

where $\delta = \omega_a - \omega_c$ is the detuning frequency. Show that the two eigenstates $|\chi_n^\pm\rangle$ now have different eigenvalues

$$\tilde{E}_n^\pm = (n+1)\hbar\omega_c \pm \hbar\frac{\delta}{2}.$$

So the degeneracy is removed due to non-zero δ . It provides n dimensional orthogonal Hilbert sub-spaces of dimension 2×2 .

- (f) The interacting part H_{int} is an unique entangled state of TLS and EM field: H_{int} couples only those states that belong to a single subspace of dimension 2×2 . It is sufficient to consider eigenspace of H_0 at a given number of photons n : $\{|\chi_n^+\rangle, |\chi_n^-\rangle\}$ with $n = 0, 1, 2, \dots$. Within each of these subspaces, show that the matrix representation of H_{JC} is

$$[H_{JC}]_n = \hbar \begin{pmatrix} (n+1)\omega_c + \frac{\delta}{2} & \frac{g}{2}\sqrt{n+1} \\ \frac{g}{2}\sqrt{n+1} & (n+1)\omega_c - \frac{\delta}{2} \end{pmatrix}$$

Show that the energy eigenvalues of H_{JC} for a given n are

$$E_n^\pm = (n+1)\hbar\omega_c \pm \frac{1}{2}\hbar\Omega_n,$$

where $\Omega_n = \sqrt{\delta^2 + (n+1)g^2}$ is the Rabi frequency. At resonance ($\delta = 0$), the splitting energy is

$$\Delta E_n = E_n^+ - E_n^- = \hbar g \sqrt{n+1}.$$

So $\Delta E_n \propto \sqrt{n}$, not n .

- (g) Plot E_n^\pm vs δ for $g = 0$ and $g \neq 0$ cases. You will see that E_n^\pm levels are nearly-degenerate when $\delta \rightarrow 0$.

- (h) Show that the corresponding eigenvectors are

$$\begin{aligned} |n, +\rangle &= \cos(\theta_n/2)|\chi_n^+\rangle + \sin(\theta_n/2)|\chi_n^-\rangle, \\ |n, -\rangle &= \sin(\theta_n/2)|\chi_n^+\rangle - \cos(\theta_n/2)|\chi_n^-\rangle, \end{aligned} \quad (5)$$

where $\theta_n = \tan^{-1}(\sqrt{n+1}g/\delta)$.

- (i) Near the resonance $\omega_a \sim \omega_c$, so $\delta \rightarrow 0$, Assuming that $g \ll \omega_c$ and H_{int} can be treated as a perturbation. Calculate first-order and second-order energy corrections to the unperturbed energy levels. Compare with the series expansion of the exact results.