CHAPTER - 10

Perturbation

Time Independent perturbation theory:

The potential energy of most of the real systems are different from the standard potentials that have been considered till now, and an exact solution is not possible. A slight change in the potential of the system can be treated as a perturbation. The perturbation may be time dependent or time independent. In this chapter, we shall only discuss time independent perturbation theory.

Non-degenerate Perturbation Theory:

In this section, we consider that the perturbation is applied on a system which is not degenerate. In the time independent perturbation approach, the Hamiltonian of the system can be written as: $\hat{H} = \hat{H}_0 + \hat{H}^{'}$,

where $\hat{H}_0$ is the unperturbed Hamiltonian, whose nondegenerate energy eigenvalues $E_n^0\ (n = 0,1,2......)$ and corresponding eigenfunctions $\psi_n^0\ (n = 0,1,2......)$ are assumed to be known. The functions $\psi_n^0\ (n = 0,1,2......)$ form a complete orthonormal basis and $\hat{H}^{'}$ is the time independent perturbing Hamiltonian.

First order correction to energy of the n^{th} state = $E_n^{(1)} = \left\langle \psi_n^0 \middle| H^{'} \middle| \psi_n^0 \right\rangle$

First order correction to wave function of the n^{th} state = $\psi_n^{(1)} = \sum_{m \neq n} \dfrac{\left\langle \psi_m^0 \middle| H^{'} \middle| \psi_n^0 \right\rangle}{E_n^0 - E_m^0} \left| \psi_m^0 \right\rangle$

Second order correction to energy of the n^{th} state = $E_n^{(2)} = \sum_{m \neq n} \dfrac{\left| \left\langle \psi_m^0 \middle| H^{'} \middle| \psi_n^0 \right\rangle \right|^2}{E_n^0 - E_m^0}$

SOLVED PROBLEMS

1. If a perturbation of the form $H' = \dfrac{v}{a}x$ is added in a 1-D box having length 0 to *a*, find the total energy of the system corrected upto first order.

Soln. The non-perturbed states are: $\psi = \sqrt{\dfrac{2}{a}} \sin \dfrac{n\pi x}{a}$ and $H' = \dfrac{v}{a}x$ (Given)

$$\therefore \qquad \Delta E = \int_0^a \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a} \frac{v}{a} x \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a} dx = \frac{2}{a} \cdot \frac{v}{a} \int_0^a x \sin^2 \frac{n\pi x}{a} dx = \frac{2v}{a.a} \cdot \frac{a^2}{4} = \frac{v}{2}$$

The unperturbed energy spectrum is $\dfrac{n^2 h^2}{8m\ell^2}$.

Therefore, the corrected total energy upto first order $= \left(\dfrac{n^2 h^2}{8m\ell^2} + \dfrac{v}{2} \right)$.

2. Consider an anharmonic oscillator whose potential is $\frac{1}{2}kx^2+\frac{1}{6}\gamma x^3$. Calculate the 1st order correction to the ground state harmonic oscillator energy.

Soln. As we know, $\Delta E=\int_{-\infty}^{+\infty}\psi_0^*\frac{1}{6}\gamma x^3\psi_0$

Since, the integrand of the above integral is odd and it is integrated over a symmetric interval, it is equal to zero. Therefore, $\Delta E=0$

3. Calculate the First order correction to the ground state energy of an anharmonic oscillator whose potential energy is $\frac{1}{2}kx^2+\frac{\gamma}{6}x^3+bx^4$

Soln. The first order correction is, $\Delta E=\int_{-\infty}^{\infty}\left(\frac{\beta}{\pi}\right)^{1/4}e^{-\beta x^2/2}\left(\frac{\gamma}{6}x^3+bx^4\right)\left(\frac{\beta}{\pi}\right)^{1/4}e^{-\beta x^2/2}dx$

$$=\int_{-\infty}^{\infty}\left(\frac{\beta}{\pi}\right)^{1/4}e^{-\beta x^2/2}\frac{\gamma}{6}x^3\left(\frac{\beta}{\pi}\right)^{1/4}e^{-\beta x^2/2}dx+\int_{-\infty}^{\infty}\left(\frac{\beta}{\pi}\right)^{1/4}e^{-\beta x^2/2}bx^4\left(\frac{\beta}{\pi}\right)^{1/4}e^{-\beta x^2/2}dx$$

$$=\left(\frac{\beta}{\pi}\right)^{1/2}\frac{\gamma}{6}\int_{-\infty}^{\infty}x^3\,e^{-\beta x^2}dx+\int_{-\infty}^{\infty}\left(\frac{\beta}{\pi}\right)^{1/2}bx^4\,e^{-\beta x^2}dx$$

$$=\left(\frac{\beta}{\pi}\right)^{1/2}b\int_{-\infty}^{\infty}x^4e^{-\beta x^2}dx\qquad\left[\text{Since, }\left(\frac{\beta}{\pi}\right)^{1/2}\frac{\gamma}{6}\int_{-\infty}^{\infty}x^3\,e^{-\beta x^2}dx=0\right]$$

$$=\frac{\sqrt{\beta}}{\sqrt{\pi}}\times 2b\times\frac{1}{2\beta^{\frac{4+1}{2}}}\Gamma\left(\frac{4+1}{2}\right)=\frac{\sqrt{\beta}}{\sqrt{\pi}}\times 2b\times\frac{1}{2\beta^{5/2}}\times\frac{3}{2}\times\frac{1}{2}\times\sqrt{\pi}=\frac{3\,b}{4\,\beta^2}\qquad\left[\text{Since, }\beta=\frac{\sqrt{mk}}{\hbar}\right]$$

Since, we know that $E'=E_0+\Delta E$

Therefore, total ground energy is $\frac{3b}{4\left(\frac{\sqrt{mk}}{\hbar}\right)^2}+\frac{1}{2}h\nu+\text{high order term}$

4. A particle of mass 'm' is confined in a one-dimensional box of length L. Using the first order perturbation theory, the energy of the particle in the ground state in presence of the perturbation

$$V_p(x)=\begin{cases}-V_0\left(1-\frac{x}{L}\right), & 0\le x\le\frac{L}{2}\\ 0, & \text{elsewhere}\end{cases}$$

is,

(a) $\left(\frac{4+3\pi^2}{8\pi^2}\right)V_0$ (b) $\left(\frac{4+3\pi^2}{8\pi^2}\right)V_0-\frac{V_0}{3}$ (c) $\left(\frac{4-3\pi^2}{8\pi^2}\right)V_0$ (d) $+\frac{V_0}{2}$

Soln. The ground state function of the particle in a box is

$$\psi=\sqrt{\frac{2}{L}}\sin\left(\frac{\pi x}{L}\right)$$

And the ground state energy $E_1 = \frac{\pi^2\hbar^2}{2mL^2}$.

Therefore, the first order correction of energy in the ground state

$$\Delta E_0^{(1)} = \langle \psi | V_p | \psi \rangle = -\frac{V_0 2}{L}\int_0^{L/2}\left(1-\frac{x}{L}\right)\sin^2\left(\frac{\pi x}{L}\right)dx$$

$$= -\frac{V_0}{L}\int_0^{L/2}\left(1-\frac{x}{L}\right)\left(1-\cos\left(\frac{2\pi x}{L}\right)\right)dx$$

$$= -\frac{V_0}{L}\left[\int_0^{L/2}dx - \int_0^{L/2}\cos\frac{2\pi x}{L}dx - \int_0^{L/2}\frac{x}{L}dx + \frac{1}{L}\int_0^{L/2}x\cos\frac{2\pi x}{L}dx\right]$$

$$= -\frac{V_0}{L}\left[x\Big|_0^{L/2} - \frac{L}{2\pi}\sin\frac{2\pi x}{L}\Big|_0^{L/2} - \frac{1}{L}\cdot\frac{x^2}{2}\Big|_0^{L/2} + \frac{1}{L}\left\{x\cdot\frac{L}{2\pi}\sin\frac{2\pi x}{L}\Big|_0^{L/2} - \int_0^{L/2}1\cdot\frac{L}{2\pi}\sin\frac{2\pi x}{L}\right\}\right]$$

$$= -\frac{V_0}{L}\left[\frac{L}{2} - 0 - \frac{1}{2L}\left(\frac{L^2}{4}\right) + \frac{1}{2\pi}\frac{L}{2\pi}\cos\frac{2\pi x}{L}\Big|_0^{L/2}\right]$$

$$= -\frac{V_0}{L}\left[\frac{L}{2} - \frac{L}{8} + \frac{L}{4\pi^2}(-1-1)\right]$$

$$= -V_0\left[\frac{4\pi^2 - \pi^2 - 4}{8\pi^2}\right]$$

$$= \left(\frac{4-3\pi^2}{8\pi^2}\right)V_0$$

Correct option is (c)

5. Consider a particle of mass '*m*' subjected to a one dimensional potential $V(x) = \frac{1}{2}m\omega^2 x^2$. Then we applied a potential $V_p(x) = \lambda x$, where λ is very less and independent of *x*. The first order energy correction to ground state for positive value of *x* is (Given : $\alpha = \sqrt{\frac{\hbar}{m\omega}}$)

(a) 0 (b) $\frac{\lambda\alpha^2}{4\sqrt{\pi}}$ (c) $\frac{\lambda\alpha^2}{\sqrt{\pi}}$ (d) $\frac{\lambda\alpha^2}{2\sqrt{\pi}}$

Soln. The ground state wave function of 1-D SHM is $\psi = \left(\frac{1}{\sqrt{\pi}\alpha^2}\right)^{1/4} e^{-x^2/2\alpha^2}$, where $\alpha = \sqrt{\frac{\hbar}{m\omega}}$.

Therefore, first order energy correction to the ground state

$$\Delta E_0^{(1)} = \langle \psi | V_p | \psi \rangle = \lambda\left(\frac{1}{\sqrt{\pi}\alpha^2}\right)^{1/2}\int_{-\infty}^{\infty} x e^{-x^2/\alpha^2}dx = 0 \quad \text{(Since, the integral is odd)}$$

Correct option is (a)

6. The perturbation, $H' = \begin{cases} b(a-x) & -a < x < a \\ 0 & \text{otherwise} \end{cases}$

acts on a particle of mass 'm' confined in an infinite square well potential

$$V(x) = \begin{cases} 0 & -a < x < a \\ \infty & \text{otherwise} \end{cases}$$

The first order correction to the ground state energy of the particle is

(a) $\frac{ba}{2}$ (b) $\frac{ba}{\sqrt{2}}$ (c) $2ba$ (d) ba

Soln. The ground state wavefunction for the given potential $\psi(x) = \sqrt{\frac{2}{2a}}\cos\left(\frac{\pi x}{2a}\right) = \frac{1}{\sqrt{a}}\cos\left(\frac{\pi x}{2a}\right)$

The perturbation, $H' = \begin{cases} b(a-x) & -a < x < a \\ 0 & \text{otherwise} \end{cases}$

The first order correction in energy,

$$E' = \int \psi^* H \psi \, dx$$

$$= \int_{-a}^{+a} \frac{1}{\sqrt{a}}\cos\left(\frac{\pi x}{2a}\right) b(a-x) \frac{1}{\sqrt{a}}\cos\left(\frac{\pi x}{2a}\right) dx = \frac{b}{a}\int_{-a}^{+a} \cos^2\left(\frac{\pi x}{2a}\right)(a-x)\,dx$$

$$= \frac{b}{a}\int_{-a}^{+a} \frac{\left(1+\cos\frac{\pi x}{a}\right)}{2}(a-x)\,dx = \frac{b}{2a}\left[\int_{-a}^{+a}(a-x)\,dx + \int_{-a}^{+a} a\cos\frac{\pi x}{a}\,dx - \underbrace{\int_{-a}^{+a} x\cos\frac{\pi x}{a}\,dx}_{0}\right] \text{ (as integral is odd)}$$

$$= \frac{b}{2a}\left[\left\{ax - \frac{x^2}{2}\right\} + \frac{a\sin\left(\frac{\pi x}{a}\right)}{\frac{\pi}{a}}\right]_{-a}^{+a} = \frac{b}{2a}\left[2a^2 + 0\right] = ab$$

Correct option is (d)

PRACTICE SET

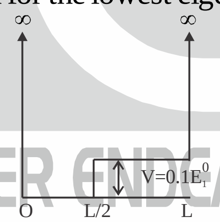
1. For the n = 2 states of a hydrogen atom in a uniform electric field of strength F,
(a) the first-order correction to the energy equals zero for all four states.
(b) there are four different values of the energy to first order
(c) the first-order correction to the energy is proportional to F for two states.
(d) the first-order correction to the energy is proportional to F^2 for two states.

2. Which one of the following statements is true for a hydrogen atom in its ground state that is placed in a uniform z-directed electric field?
(a) The first-order correction to the energy equals zero
(b) the proper zeroth-order wavefunctions are $\left(1/\sqrt{2}\right)\left(1s \pm 2p_z\right)$
(c) the second-order correction to the energy is positive
(d) the first-order correction to the wavefunction contains some 2s AO.

3. The hydrogen atom transition $3d_{xy} \leftarrow 2p_x$ is
(a) dipole allowed and *z*-polarized
(b) dipole allowed and *x*-polarized
(c) dipole allowed and *y*-polarized
(d) dipole allowed and *xy*-polarized

4. Which of the following integrals over all space vanish by symmetry for a hydrogen atom with nucleus at the coordinate origin?
(1) $\int 1s\ y\ 2p_z dv$
(2) $\int 2p_z\ z\ 3d_{xy} dv$
(3) $\int 2p_z\ x\ 3d_{xz} dv$
(a) 1 only
(b) 1 and 2 only
(c) 1 and 3 only
(d) 2 and 3 only
(e) 1, 2 and 3

5. A particle in a one-dimensional infinite potential box is perturbed as shown in figure.
(i) Find out the first order energy of the system.
(ii) Calculate the second order correction for the lowest eigenvalue



6. An electron moving in a simple harmonic potential $V = \frac{1}{2}kx^2$ is subjected to a perturbation $\hat{H}' = Ex$ where E is the strength of the electric field which is applied in the *x*-direction. Determine the effect of first and second order perturbation on the energy.

7. A hydrogen atom is exposed to an electric field of strength F applied in the *z*-direction. Calculate the first order and the second order effects for the ground state of the atom (Stark effect).

ANSWER KEY

1. (c) **2. (a)** **3. (c)** **4. (b)**

5. (i) $\frac{1.05\,h^2}{8m\ell^2}$, **(ii)** $-6.196\times10^{-4}\left(\frac{h^2}{8m\ell^2}\right)$ **6. (zero)**

7. $(i)\ E_2^{(1)} = 0, (ii)\ E_2^0 = -\frac{1}{8}au, (iii)\ E_1^2 = -\left(\frac{2^{18}}{3^{11}}\right)F^2$