Second order perturbation: To calculate correction in second order, we will make use of λ^2 equation (11),

$$(\hat{H}_0 - E_n^{(0)})\,\psi_n^{(2)} \;=\; -(\hat{H}' - E_n^{(1)})\,\psi_n^{(1)} + E_n^{(2)}\,\psi_n^{(0)} \tag{19}$$

and go straight for expansion of $\psi_n^{(2)}$ and $\psi_n^{(1)}$ in terms of unperturbed wavefunction $\psi_n^{(0)}$,

$$\psi_n^{(1)} \;=\; \sum_m c_m^{(1)}\,\psi_m^{(0)} \quad \text{and} \quad \psi_n^{(2)} \;=\; \sum_m c_m^{(2)}\,\psi_m^{(0)}. \tag{20}$$

Substituting the above expression for $\psi_n^{(2)}$ and $\psi_n^{(1)}$ in (19), we obtain,

$$\begin{aligned}(\hat{H}_0 - E_n^{(0)})\sum_m c_m^{(2)}\,\psi_m^{(0)} &= -(\hat{H}' - E_n^{(1)})\sum_m c_m^{(1)}\,\psi_m^{(0)} + E_n^{(2)}\,\psi_n^{(0)} \\ \sum_m (E_m^{(0)} - E_n^{(0)})\,c_m^{(2)}\,\psi_m^{(0)} &= -\sum_m (\hat{H}' - E_n^{(1)})\,c_m^{(1)}\,\psi_m^{(0)} + E_n^{(2)}\,\psi_n^{(0)}.\end{aligned}$$

As before, we take inner product with the unperturbed wavefunction $\psi_k^{(0)}$,

$$\begin{aligned}&\sum_m (E_m^{(0)} - E_n^{(0)})\,c_m^{(2)}\left(\psi_k^{(0)},\,\psi_m^{(0)}\right) = \\ &\qquad -\sum_m \left(\psi_k^{(0)},\,\hat{H}'\psi_m^{(0)}\right)\,c_m^{(1)} + \sum_m E_n^{(1)}\,c_m^{(1)}\left(\psi_k^{(0)},\,\psi_m^{(0)}\right) + E_n^{(2)}\left(\psi_k^{(0)},\,\psi_n^{(0)}\right) \\ \text{or,}\quad &\sum_m (E_m^{(0)} - E_n^{(0)})\,c_m^{(2)}\,\delta_{km} = -\sum_m c_m^{(1)}\,\hat{H}'_{km} + \sum_m E_n^{(1)}\,c_m^{(1)}\,\delta_{km} + E_n^{(2)}\,\delta_{kn} \\ \text{or,}\quad &(E_k^{(0)} - E_n^{(0)})\,c_k^{(2)} = -\sum_m c_m^{(1)}\,\hat{H}'_{km} + E_n^{(1)}\,c_k^{(1)} + E_n^{(2)}\,\delta_{kn}.\end{aligned} \tag{21}$$

For $k = n$ we get the second order correction to energy, keeping in mind that $c_n^{(1)} = 0$,

$$E_n^{(2)} \;=\; \sum_{m\neq n} c_m^{(1)}\,\hat{H}'_{nm} \;=\; \sum_{m\neq n}\frac{\hat{H}'_{mn}\,\hat{H}'_{nm}}{E_n^{(0)} - E_m^{(0)}} \;=\; \sum_{m\neq n}\frac{|\hat{H}'_{mn}|^2}{E_n^{(0)} - E_m^{(0)}}. \tag{22}$$

For $k \neq n$, we will get $c_k^{(2)}$ knowing $E_n^{(1)}$ (13) and $c_m^{(1)}$ (17),

$$\begin{aligned}c_k^{(2)}(E_k^{(0)} - E_n^{(0)}) &= -\sum_m c_m^{(1)}\,\hat{H}'_{km} + c_k^{(1)}\,\hat{H}'_{nn} \\ \text{or,}\quad c_k^{(2)}(E_k^{(0)} - E_n^{(0)}) &= -\sum_{m\neq n}\frac{\hat{H}'_{mn}\,\hat{H}'_{km}}{E_n^{(0)} - E_m^{(0)}} + \frac{\hat{H}'_{kn}\,\hat{H}'_{nn}}{E_n^{(0)} - E_k^{(0)}} \\ \text{or,}\quad c_k^{(2)} &= \sum_{m\neq n}\frac{\hat{H}'_{km}\,\hat{H}'_{mn}}{(E_n^{(0)} - E_m^{(0)})(E_n^{(0)} - E_k^{(0)})} - \frac{\hat{H}'_{kn}\,\hat{H}'_{nn}}{(E_n^{(0)} - E_k^{(0)})^2}.\end{aligned} \tag{23}$$

Therefore, the energy E_n and wavefunction ψ_n of the full Hamiltonian (1) to second order in perturbation theory are,

$$E_n \;=\; E_n^{(0)} + \hat{H}'_{nn} + \sum_{m\neq n}\frac{|\hat{H}'_{mn}|^2}{E_n^{(0)} - E_m^{(0)}} + \cdots \tag{24}$$

$$\begin{aligned}\psi_n \;=\; &\psi_n^{(0)} + \sum_{m\neq n}\left[\frac{\hat{H}'_{mn}}{E_n^{(0)} - E_m^{(0)}}\right]\psi_m^{(0)} \\ &+ \sum_{m\neq n}\left[\sum_{k\neq n}\frac{\hat{H}'_{mk}\,\hat{H}'_{kn}}{(E_n^{(0)} - E_k^{(0)})(E_n^{(0)} - E_m^{(0)})} - \frac{\hat{H}'_{mn}\,\hat{H}'_{nn}}{(E_n^{(0)} - E_m^{(0)})^2}\right]\psi_m^{(0)} + \cdots\end{aligned} \tag{25}$$

For perturbation theory to work, the corrections it produces must be small (not wildly different from $E_n^{(0)}$). But onward second order corrections in energy (24) and first order in wavefunction (25) contain the term that must be small,

$$\left| \frac{\hat{H}'_{mn}}{E_n^{(0)} - E_m^{(0)}} \right| \ll 1, \qquad n \neq m$$

otherwise it has potential to grow large if $E_n^{(0)} \approx E_m^{(0)}$, *i.e.* when the energy levels are about to be degenerate. Therefore, degenerate energy levels have to be treated differently in perturbation theory.

Examples

1. Using first order perturbation theory, calculate the energy of the n-th state for a particle of mass m moving in an infinite potential well of length $2L$ with wall at $x = 0$ and $x = 2L$, which is modified at the bottom by the perturbations: (i) $\lambda V_0 \sin(\pi x/2L)$ and (ii) $\lambda V_0 \delta(x - L)$, where $\lambda \ll 1$.

2. Calculate the energy of the n-th excited state to first order perturbation for a 1-dim infinite potential well of length $2L$, with walls at $x = -L$ and $x = L$, which is modified at the bottom by the following perturbations with $V_0 \ll 1$,

$$\hat{H}' = \begin{cases} -V_0 & -L \leq x \leq L \\ 0 & \text{elsewhere} \end{cases} \qquad \hat{H}' = \begin{cases} -V_0 & -L/2 \leq x \leq L/2 \\ 0 & \text{elsewhere} \end{cases}$$

$$\hat{H}' = \begin{cases} -V_0 & -L/2 \leq x \leq 0 \\ 0 & \text{elsewhere} \end{cases} \qquad \hat{H}' = \begin{cases} V_0 & 0 \leq x \leq L/2 \\ 0 & \text{elsewhere} \end{cases}$$

3. For a 1-dim harmonic oscillator, the spring constant changes from k to $k(1 + \epsilon)$, where ϵ is small. Calculate the first order perturbation in the energy.

4. Calculate the first order perturbation in the energy for n-th state of a 1-dim harmonic oscillator subjected to perturbation βx^4, β is a constant.

5. Consider a quantum charged 1-dim harmonic oscillator, of charge q, placed in an electric field $\vec{E} = E\hat{x}$. Find the exact expression for the energy and then use perturbation theory to calculate the same.

6. For the following set of Hamiltonians, with $\lambda \ll 1$,

$$(i)\ E_0 \begin{pmatrix} 1 & \lambda \\ \lambda & 3 \end{pmatrix} \qquad (ii)\ E_0 \begin{pmatrix} 1+\lambda & 0 & 0 & 0 \\ 0 & 8 & 0 & 0 \\ 0 & 0 & 3 & -2\lambda \\ 0 & 0 & -2\lambda & 7 \end{pmatrix}$$

$$(iii)\ E_0 \begin{pmatrix} -5 & 3\lambda & 0 & 0 \\ 3\lambda & 5 & 0 & 0 \\ 0 & 0 & 8 & -\lambda \\ 0 & 0 & -\lambda & -8 \end{pmatrix} \qquad (iv)\ E_0 \begin{pmatrix} 3 & 2\lambda & 0 & 0 \\ 2\lambda & -3 & 0 & 0 \\ 0 & 0 & -7 & \sqrt{2}\lambda \\ 0 & 0 & \sqrt{2}\lambda & 7 \end{pmatrix},$$

(a) find the eigenvalues and eigenvectors of the unperturbed Hamiltonian, (b) diagonalize the full Hamiltonian to find the exact eigenvalues and expand each eigenvalue to the second power of λ and (c) using the first and second order perturbation theory find the approximate energy eigenvalues and eigenstates of the full Hamiltonian.