Time - independent Perturbation Theory

Perturbation theory

- It is based on the assumption that the problem we wish to solve is, in some sense, only slightly different from a problem that can be solved exactly.
- Perturbation means disturbance.
- Perturbation theory builds on the known exact solutions to obtain approximate solutions.
- There are systems whose Hamiltonian cannot be reduced to an exactly solvable part plus a small correction.
- For these, we may consider the variational method or the WKB approximation.
- The variational method is particularly useful in estimating the energy eigenvalues of the ground state and the first few excited states of a system for which one has only a qualitative idea about the form of the wave function.
- The WKB method is useful for finding the energy eigenvalues and wave functions of systems for which the classical limit is valid.
- Unlike perturbation theory, the variational and WKB methods do not require the existence of a closely related Hamiltonian that can be solved exactly.

Basic concepts

In the time - dependent perturbation approach, a known solution of a system whose Hamiltonian is only slightly different from that of the system under consideration is used as the starting point. The Hamiltonian operator H representing the total energy of the system can be written as

$$H = H^0 + H'$$

Where H^0 is called unperturbed Hamiltonian, whoes nondegenerate eigenvalues $E^0{}_n =$ 1, 2, ... and eigenfunctions $\Psi_n{}^0$ are assumed to be known and the time - independent operator H', called perturbation, is small. These corresponds to the eigenvalue equation.

$$H^0\Psi_n{}^0 = E_n{}^0\ \Psi^0{}_n \qquad n = 1, 2, ...$$

We have to solve the schrodinger equation

$$H\Psi_n = E_n\Psi_n \rightarrow (1)$$

If the Hamiltonian of the perturbed system as

$$H = H^0 + \lambda H'$$

The parameter λ changes from 0 to 1 , the Hamiltonian changes from H^0 to H and the eigenfunction changes from $\Psi^0{}_n$ to Ψ_n . Expanding E_n and Ψ_n in terms of λ

$$E_n = E_n{}^0 + \lambda E^{(1)}{}_n + \lambda^2 E_n{}^{(2)} + \ldots\ldots \rightarrow (2)$$

$$\Psi_n = \Psi_n{}^0 + \lambda \Psi^{(1)}{}_n + \lambda^2 \Psi_n{}^{(2)} + \ \ldots\ldots \rightarrow (3)$$

In the above equation terms independent of λ are called zeroth order terms, those in λ are first order, those in λ^2 second order, and so on. Thus $E^{(1)}{}_n$ and $\Psi^{(1)}{}_n$ are respectively the first order correction to the energy and wave function. $E_n{}^{(2)}$ and $\Psi_n{}^{(2)}$ the respective second order correction and so on.

Substituting the values in equ (1) and equating the coefficients we get .

$$H^0\Psi_n{}^0 = E_n{}^0\Psi_n{}^0 \rightarrow (5)$$

$$H'\Psi^0{}_n + H^0\Psi^{(1)}{}_n = E_n{}^{(1)}\,\Psi^0{}_n + E_n{}^0\,\Psi^{(1)}{}_n \rightarrow (6)$$

$$H'\Psi^{(1)}{}_n + H^0\Psi_n{}^2 = E_n{}^{(2)}\,\Psi^0{}_n + E_n{}^{(1)}\Psi_n{}^{(1)} + E_n{}^0\,\Psi^{(2)}{}_n \rightarrow (7)$$

Nondegenerate Energy Levels

First-order Correction to the Energy

Multiplying Equ (6) from the left by $\langle\Psi_n{}^0|$, we get

$$\langle\Psi_n{}^0|H'|\Psi^0{}_n\rangle + \langle\Psi_n{}^0\ H^0|\Psi^{(1)}{}_n\rangle = E_n{}^{(1)}\,\langle\Psi_n{}^0|\,\Psi^0{}_n\rangle + E_n{}^0\,\langle\Psi_n{}^0|\Psi^{(1)}{}_n\,\rangle \rightarrow (8)$$

Since H^0 is Hermitian , the second term on the left reduces to $E_n{}^0\,\langle\Psi_n{}^0|\Psi^{(1)}{}_n\,\rangle$ and Equ (8) gives

$$E_n{}^1 = \langle\Psi_n{}^0|H'\,|\Psi^{(1)}{}_n\,\rangle \rightarrow (9)$$

Or $\quad E_n{}^1 = \langle n|H'|n\rangle$

Which is often referred to as matrix elements. The first order correction to the energy is thus the average value of the perturbation over the corresponding unperturbed states of the system.

ENTRI

First-order correction to Wave Function

The first-order correction to the wave function is written as a linear combination of the unperturbed wave functions of the system.

$$\Psi_n{}^{(1)} = \sum_{l=1}^{\infty} a_l \Psi^0{}_l \rightarrow (10)$$

Substituting Equ (8) in Equ (6) and multiplying from the left by $\langle\Psi_m{}^0|$ gives

$$\langle\Psi_m{}^0|H'|\Psi_n{}^0\rangle + \sum_{l=1}^{\infty} a_l\, E^0{}_l\langle\Psi^0{}_m|H'|\Psi_l{}^0\rangle = E_n{}^{(1)}\, \langle\Psi_m{}^0|\Psi_n{}^0\rangle + \sum_{l=1}^{\infty} a_l\, E^0{}_n\, \langle\Psi_m{}^0|\Psi_l{}^0\rangle$$

Or $$\langle\Psi_m{}^0|H'|\Psi_n{}^0\rangle + a_m E^0{}_m = a_m E^0{}_n$$

$$a_m = \frac{\langle\Psi_m{}^0|H'|\Psi_n{}^0\rangle}{E^0{}_n - E^0{}_m} \longrightarrow (11)$$

All the a's except a_n in Equ (10) can be calculated using Equ (11) . The coefficient a_n is found to be zero from the normalization condition $\langle\Psi_n|\Psi_n\rangle = 1$. It follows that

$$\Psi_n{}^{(1)} = \sum_m{}' \frac{\langle m|H'|n\rangle}{E^0{}_n - E_m{}^0}\, |\Psi_m{}^0\rangle$$

Consequently, the energy and wave function corrected first order are

$$E_n = E_n{}^0 + \langle n|\ H'\ |n\rangle$$

$$\Psi_n = \Psi_n{}^0 + \sum_m{}' \frac{\langle m|H'|n\rangle}{E^0{}_n - E_m{}^0}\, |\Psi_m{}^0\rangle$$

Second order Correction to the Energy

Multiplying Equ (7) from left by $\langle\Psi_n{}^0|$ and using the Hermitian nature of H^0 , we get

$$\langle\Psi_n{}^0|H'|\Psi^{(1)}{}_n\rangle = E_n{}^{(2)}\langle\, \Psi^0{}_n|\, \Psi^0{}_n\rangle + E_n{}^{(1)}\langle\, \Psi^0{}_n|\Psi_n{}^{(1)}\rangle \rightarrow (7)$$

Here the second term on the right side vanishes

$$(7) \rightarrow E_n{}^{(2)} = \langle\, \Psi^0{}_n|H'|\Psi_n{}^{(1)}\rangle$$

Substituting the value of $\Psi_n{}^{(1)}$ in above equation and also H' is Hermitian

$$\langle n|\ H'\ |n\rangle = \langle m|\ H'\ |n\rangle *$$

Then we get

$$E_n{}^{(2)} = \sum_m{}' \frac{\langle m|H'|n\rangle^2}{E^0{}_n - E_m{}^0} \longrightarrow (8)$$

Since $\langle m|\ H'\ |n\rangle^2$ is always positive, the sign of the correction is determined by the denominator. The second-order correction in energy to level n due to levels for which $E_n{}^0 > E_m{}^0$ is positive whereas that due to levels for which $E_n{}^0 < E_m{}^0$ is negative.

Second-order Correction to Wave Function

The second order correction to wave function $\Psi_n{}^{(2)}$ is written as a linear combination of unperturbed wave function of the system.

$$\Psi_n{}^{(2)} = \sum_k b_k \Psi^0{}_k$$

Substituting the above value in Equ (7) and multiplying from left by $\langle \Psi_l{}^0|$ gives

$$\sum_m' a_m \langle l|H'|m\rangle + \sum_k b_k \langle l|\, H^0\, |k\rangle = E_n{}^{(2)}\langle l|n\rangle + \sum_m' a_m E_n{}^{(1)} \langle l|m\rangle + \sum_k b_k \, E_n{}^0\langle l\,|k\rangle$$

The first term on the right is zero and substituting the values of the a's and $E^{(1)}{}_n$ we get

$$b_l = \sum_m' \frac{\langle n|\; H'\;|n\rangle\; \langle l|H'|m\rangle}{(E^0{}_l - E^0{}_n)(E^0{}_n - E^0{}_l)} - \frac{\langle n|\; H'\;|n\rangle\,\langle l|H'|m\rangle}{(E^0{}_n - E^0{}_l)^2} \longrightarrow (9)$$

The normalization condition of the wave function shows that the coefficient b_n is zero. It follows that the energy and the wave function of the system corrected to second order in the perturbation is

$$E_n = E_n{}^0 + \langle n|\; H'\;|n\rangle + \sum_m' \frac{\langle n|H'|m\rangle^2}{E^0{}_n - E_m{}^0} \rightarrow (10)$$

$$\Psi_n = \Psi_n{}^0 + \sum_m' a_m\, \Psi_m{}^0 + \sum_l' b_l\, \Psi_l{}^0 \rightarrow (11)$$

Degenerate Energy Levels

The unperturbed wave function $\Psi_n{}^0$ is a unique one in the nongenerate case. When a degeneracy exists, a linear combination of the degenerate wave functions can be taken as the unperturbed wave function. For simplicity, consider a case in which $E_n{}^0$ is two fold degenerate. Let $\Psi_n{}^0$ and $\Psi_l{}^0$ be eigenfunctions corresponding to eigenvalues $E_n{}^0 = E_l{}^0$ and linear combination of the two be

$$\emptyset = c_n \Psi_n{}^0 + c_l \Psi^0{}_l \rightarrow (12)$$

Where c_n and c_l are constants

First-Order Correction

Replacing $\Psi_n{}^0$ in Equ (6) by Ø we get

$$H'\, |c_{n\,\Psi_n{}^0} + c_l\, \Psi_l{}^0\rangle + H^0|\Psi_n{}^{(1)}\rangle = E_n{}^{(1)}|c_{n\,\Psi_n{}^0} + c_l\, \Psi_l{}^0\rangle + E_n{}^0|\Psi_n{}^{(1)}\rangle \rightarrow (13)$$

Multiplying Equ (13) from left by $\langle \Psi_n{}^0|$, we get

$c_n \langle \Psi_n{}^0 | H' | \Psi_n{}^0 \rangle + l \langle \Psi_n{}^0 | H' | \Psi_l{}^0 \rangle + \langle \Psi_n{}^0 | H' | \Psi_n{}^{(1)} \rangle = c_n E_n{}^{(1)} + E_n{}^0$

$\langle \Psi_n{}^0 | \Psi_n{}^{(1)} \rangle \rightarrow (13)$

Since H^0 is Hermitian

$$\langle \Psi_n{}^0 | H^0 | \Psi_n{}^{(1)} \rangle = E_n{}^0 \langle \Psi_n{}^0 | \Psi_n{}^{(1)} \rangle$$

Equ (13) reduces to

$(H_{nn}{}' - E_n{}^{(1)})\, c_n = H_{nl}{}'\, c_l = 0 \rightarrow (14)$

Operating Equ (13) from left by $\langle \Psi_l{}^0 |$, we get

$H_{lm}{}'\, c_n + (H_{ll}{}' - E_n{}^{(1)})\, c_l = 0 \rightarrow (15)$

Equations (14) and (15) together form a set of simultaneous equations for the coefficients c_n and c_l . A nontrivial solution of these equations exists only if the determinant of the coefficients vanish.

$$\begin{vmatrix} H_{nn}{}' - E_n{}^{(1)} & H_{nl}{}' \\ H_{ln}{}' & H_{ll}{}' - E_n{}^{(1)} \end{vmatrix} = 0$$

This is called secular equation and its two solutions are ;

$E_{n\mp}{}^{(1)} = \frac{1}{2}(H_{nn}{}' + H_{ll}{}') \mp \frac{1}{2} [(H_{nn}{}' - H_{ll}{}')^2 + 4 |H_{nl}{}'|^2]^{(1/2)}$

Now , the corrected energies are ;

$$E_n = E_n{}^0 + E_{n+}{}^{(1)} \text{ and } E_l = E_n{}^0 + E_{n-}{}^{(1)}$$