First Order Perturbation Theory

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1. Time Independent Perturbation Theory

The purpose of time independent perturbation theory is to estimate the energy levels and wavefunctions for a system which is perturbed from an initial Hamiltonian system with known energy levels and energy eigenstates. Suppose the unperturbed Hamiltonian is $\hat{H}_0$ and has eigenstates $\hat{H}_0|u_n\rangle = E_n|u_n\rangle$. The perturbation is an additional term in the Hamiltonian, $\lambda\hat{H}_I$, where λ is a dimensionless parameter small compared with unity. It is convenient to introduce this parameter as a clear indication that the perturbation is small. We write the eigenstates of the perturbed Hamiltonian as,

$$\hat{H}|\psi_n\rangle = \tilde{E}_n|\psi_n\rangle \qquad \text{where, } \hat{H} = \hat{H}_0 + \lambda\hat{H}_I \tag{1}$$

The new wavefunctions can be expanded in terms of the unperturbed eigenfunctions,

$$|\psi_n\rangle = \sum_m a_{nm}|u_m\rangle \tag{2}$$

The expansion coefficients can in turn be expanded in powers of the perturbation parameter, λ,

$$a_{nm} = a_0\delta_{nm} + \lambda a^1_{nm} + \lambda^2 a^2_{nm} + \ldots \tag{3}$$

And the perturbed energy levels can also be so expanded,

$$\tilde{E}_n = E_n + \lambda E^1_n + \lambda^2 E^2_n + \ldots \tag{4}$$

[NB: The superscripts in (3) and (4) denote different terms, not squares, etc.]. Hence,

$$\hat{H}|\psi_n\rangle = \left(\hat{H}_0 + \lambda\hat{H}_I\right)\sum_m a_{nm}|u_m\rangle = \sum_m a_{nm}\left(E_m + \lambda\hat{H}_I\right)|u_m\rangle = \tilde{E}_n|\psi_n\rangle \tag{5}$$

Hence, taking the scalar product, the LHS of (5) becomes, (6)

$$\langle u_k|\sum_m a_{nm}\left(E_m + \lambda\hat{H}_I\right)|u_m\rangle = \sum_m a_{nm}\left(E_m\delta_{km} + \lambda\langle u_k|\hat{H}_I|u_m\rangle\right) = a_{nk}E_k + \lambda\sum_m a_{nm}\langle u_k|\hat{H}_I|u_m\rangle$$

$$= \left(a_0\delta_{nk} + \lambda a^1_{nk}\right)E_k + \lambda\sum_m a_0\delta_{nm}\langle u_k|\hat{H}_I|u_m\rangle + O\left(\lambda^2\right)$$

$$= \left(a_0\delta_{nk} + \lambda a^1_{nk}\right)E_k + \lambda a_0\langle u_k|\hat{H}_I|u_n\rangle + O\left(\lambda^2\right)$$

Whilst the RHS becomes,

$$\begin{aligned}\langle u_k|\tilde{E}_n|\psi_n\rangle &= \langle u_k|\tilde{E}_n\sum_m a_{nm}|u_m\rangle \\ &= \langle u_k|\left(E_n + \lambda E^1_n\right)\sum_m\left(a_0\delta_{nm} + \lambda a^1_{nm}\right)|u_m\rangle + O\left(\lambda^2\right) \\ &= \left(E_n + \lambda E^1_n\right)\left(a_0\delta_{nk} + \lambda a^1_{nk}\right) + O\left(\lambda^2\right)\end{aligned} \tag{7}$$

The leading terms, independent of λ, are equal in (6) and (7), as they should be. Equating the coefficients of λ gives,

$$E^1_n a_0\delta_{nk} + E_n a^1_{nk} = E_k a^1_{nk} + a_0\langle u_k|\hat{H}_I|u_n\rangle \tag{8}$$

When $k = n$ (8) becomes,

$$E_n^1 = \langle u_n | \hat{H}_I | u_n \rangle \tag{9}$$

This means that the first approximation to the energy of the nth state, after perturbation by the additional interaction $\lambda \hat{H}_I$ is,

$$\tilde{E}_n = E_n + \lambda \langle u_n | \hat{H}_I | u_n \rangle = \langle u_n | \hat{H} | u_n \rangle \tag{10}$$

In other words, to first order, the new energy level is just the expectation value of the new (total) Hamiltonian with respect to the *unperturbed* eigenstate.

When $k \neq n$ (8) becomes,

$$\frac{a_{nk}^1}{a_0} = \frac{\langle u_k | \hat{H}_I | u_n \rangle}{E_n - E_k} \tag{11}$$

At this point we can drop the parameter λ, provided that the perturbing Hamiltonian $\hat{H}_I$ is small compared with $\hat{H}_0$. The nth eigenstate is thus given by the expansion (2) where, to first order,

$$a_{nn} = a_0 \qquad \text{and} \qquad a_{nm} = a_0 \frac{\langle u_m | \hat{H}_I | u_n \rangle}{E_n - E_m} \text{ for } m \neq n \tag{12}$$

Finally, the value of a_0 is found from the normalisation requirement. In practice we can just put $a_0 = 1$ to a good enough approximation, since the validity of the perturbation approach means that $a_{nm} << a_0$ for $m \neq n$.

The salient feature of (12) is that those states which are close in energy to the unperturbed state, so that $E_n - E_m$ is small, are the most significant in the perturbed wavefunction.

2. Time Dependent Perturbation Theory

Time dependent perturbation theory addresses the time dependent solution to,

$$\hat{H} | \psi \rangle = i\hbar \frac{\partial}{\partial t} | \psi \rangle \tag{13}$$

We again assume that the Hamiltonian consists of an unperturbed part plus a relatively small perturbation, $\hat{H} = \hat{H}_0 + \hat{H}_I$. Moreover, we assume that the perturbation is switched on only at time zero, so more exactly we may write,

$$\hat{H} = \hat{H}_0 + \Theta(t) \hat{H}_I \tag{14}$$

where Θ is the step function. At any time, t, the wavefunction is given in terms of the unperturbed energy eigenstates, $\hat{H}_0 | u_n \rangle = E_n | u_n \rangle$, by,

$$| \psi \rangle = \sum_n a_n(t) | u_n \rangle \exp\{-iE_n t / \hbar\} \tag{15}$$

The coefficients, $a_n(0)$, are given at time zero (defined by the initial state). If there were no perturbation, the time dependent state would be given by,

$$| \psi \rangle_{unperturbed} = \sum_n a_n(0) | u_n \rangle \exp\{-iE_n t / \hbar\} \tag{16}$$

Note that this means, in general, that the unperturbed state would have been non-

trivially time dependent. Substituting (14,15) into (13) gives, for t > 0,

$$\begin{aligned}&\left(\hat{H}_0+\hat{H}_I\right)\sum_n a_n(t)\left|u_n\right\rangle\exp\{-iE_nt/\hbar\}=\sum_n a_n(t)\left[E_n+\hat{H}_I\right]\left|u_n\right\rangle\exp\{-iE_nt/\hbar\}\\&=i\hbar\frac{\partial}{\partial t}\left(\sum_n a_n(t)\left|u_n\right\rangle\exp\{-iE_nt/\hbar\}\right)=\sum_n\left[a_n(t)E_n+i\hbar\frac{\partial a_n}{\partial t}\right]\left|u_n\right\rangle\exp\{-iE_nt/\hbar\}\end{aligned}\tag{17}$$

The first terms cancel, leaving,

$$\sum_n a_n(t)\hat{H}_I\left|u_n\right\rangle\exp\{-iE_nt/\hbar\}=\sum_n i\hbar\frac{\partial a_n}{\partial t}\left|u_n\right\rangle\exp\{-iE_nt/\hbar\}\tag{18}$$

Taking the scalar product gives,

$$\sum_n a_n(t)\left\langle u_k\left|\hat{H}_I\right|u_n\right\rangle\exp\{-iE_nt/\hbar\}=i\hbar\frac{\partial a_k}{\partial t}\exp\{-iE_kt/\hbar\}\tag{19}$$

Hence,
$$\frac{\partial a_k}{\partial t}=\frac{1}{i\hbar}\sum_n\left\langle u_k\left|\hat{H}_I\right|u_n\right\rangle\exp\{i(E_k-E_n)t/\hbar\}a_n(t)\tag{20}$$

Equ.(20) is exact. It gives a coupled set of first order differential equations for the expansion coefficients in terms of the matrix elements of the perturbing interaction with respect to the unperturbed eigenstates, and a phase factor dependent upon the unperturbed energy levels. Numerical integration of (20) would form a means of solving the time dependent problem.

First order perturbation theory consists of approximating the coefficients on the LHS of (20) by their initial values, i.e.,

$$\frac{\partial a_k}{\partial t}\approx\frac{1}{i\hbar}\sum_n\left\langle u_k\left|\hat{H}_I\right|u_n\right\rangle\exp\{i\omega_{kn}t\}a_n(0)\tag{21}$$

where we have written $\omega_{kn}=(E_k-E_n)/\hbar$. (21) will always be true for sufficiently short times. If the initial state is the nth energy eigenstate of the unperturbed Hamiltonian, (21) becomes,

$$\frac{\partial a_k}{\partial t}\approx\frac{\exp\{i\omega_{kn}t\}}{i\hbar}\left\langle u_k\left|\hat{H}_I\right|u_n\right\rangle\tag{22}$$

In many problems of interest, the interaction Hamiltonian will have an explicit time dependence, e.g., the time dependence of an incident electromagnetic wave. In such cases the integration of (22) depends upon the nature of this time dependence. However, if the interaction Hamiltonian is time independent, integration gives,

$$a_k=\delta_{kn}-\frac{e^{i\omega_{kn}t}-1}{\hbar\omega_{kn}}\left\langle u_k\left|\hat{H}_I\right|u_n\right\rangle\tag{23}$$