Static Perturbation Theory

Static perturbation theory is concerned with getting corrections to bound state energies and wave functions due to a perturbing potential, V. The total Hamiltonian is written

$$H = H_0 + V.$$

It is assumed that H_0 is a soluble Hamiltonian whose eigenstates and energies are known. An eigenstate of H_0 satisfies

$$H_0|\Psi^{(0)} >= E^{(0)}|\Psi^{(0)} >,$$

while a eigenstate of the full Hamiltonian satisfies

$$H|\Psi >= (H_0 + V)|\Psi >= E|\Psi > .$$

The eigenstates of H_0 are a complete set, in which the eigenstates of H may be expanded,

$$|\Psi_n >= \sum_m |\Psi_m^{(0)} > c_{mn}.$$

The coefficients c_{mn} are overlaps of exact and unperturbed eigenstates,

$$c_{mn} =< \Psi_m^{(0)}|\Psi_n > .$$

Using this expansion, consider the nth exact eigenstate,

$$H|\Psi_n >= E_n|\Psi_n > .$$

We have

$$H_0|\Psi_m^{(0)} >= E_m^{(0)}|\Psi_m^{(0)} >,$$

so

$$H|\Psi_n >= \sum_m E_n|\Psi_m^{(0)} > c_{mn}$$

$$= \sum_m (H_0 + V)|\Psi_m^{(0)} > c_{mn}$$

$$= \sum_m (E_m^{(0)} + V)|\Psi_m^{(0)} > c_{mn}.$$

Re-arranging this equation, we have

$$\sum_m (E_n - E_m^{(0)})|\Psi_m^{(0)} > c_{mn} = \sum_m V|\Psi_m^{(0)} > c_{mn}$$

Taking the matrix element of this equation with $< \Psi_l^{(0)}|$, we have

$$(E_n - E_l^{(0)})c_{ln} = \sum_m V_{lm}c_{mn}, \tag{1}$$

where

$$V_{lm} = < \Psi_l^{(0)}|V|\Psi_m^{(0)} > .$$

Eq.(1) is still exact and is equivalent to the original Schrödinger equation. At this point, we introduce the perturbation expansion. Quantities are classified in terms of their order in the perturbing potential, V. V is regarded as first order, so of course the matrix elements V_{mn} are also first order. The coefficients and the energy eigenvalues are expanded in orders or powers of V,

$$\begin{aligned} c_{mn} &= c_{mn}^{(0)} + c_{mn}^{(1)} + \dots \\ E_n &= E_n^{(0)} + E_n^{(1)} + \dots \end{aligned}$$

Non Degenerate Case   At this point, we assume the spectrum of H_0 is non-degenerate, meaning that for each energy eigenvalue there is only one quantum state. Each of these states goes over into an eigenstate of the full Hamiltonian. At $0th$ order the potential is absent, so the eigenstates of H_0 are the eigenstates of the Hamiltonian, which implies

$$c_{mn}^{(0)} = \delta_{mn}$$

Writing Eq.(1) to first order, we have

$$(E_n^{(0)} - E_l^{(0)})c_{ln}^{(1)} + E_n^{(1)}c_{ln}^{(0)} = \sum_m V_{lm}c_{mn}^{(0)}.$$

The index l is arbitrary. Choosing $l = n$ we have

$$n = l \quad \rightarrow \quad E_n^{(1)} = V_{nn}. \tag{2}$$

This is probably the most useful result in perturbation theory, and says that to first order the shift in an energy eigenvalue is the expected value of the potential in the unperturbed state.

Taking $n \neq l$, we have

$$n \neq l \quad \rightarrow \quad c_{ln}^{(1)} = \frac{1}{(E_n^{(0)} - E_l^{(0)})}V_{ln}.$$

The $c_{ln}^{(1)}$ determine the first order change in the eigenfunction. To maintain normalization of the perturbed eigenstate to $O(V)^2$, we set

$$c_{nn}^{(1)} = 0.$$

We finally have for the first order perturbation in the nth eigenstate,

$$|\Psi_n^{(1)} >= \sum_m' \frac{1}{(E_n^{(0)} - E_m^{(0)})}|\Psi_m^{(0)} > V_{mn}.$$

For perturbation theory to be valid, this must be a small correction, so we need

$$\left|\frac{V_{mn}}{(E_n^{(0)} - E_m^{(0)})}\right| << 1.$$

Going to second order, from Eq.(1) we have

$$E_n^{(2)} c_{ln}^{(0)} + E_n^{(1)} c_{ln}^{(1)} + (E_n^{(0)} c_{ln}^{(1)} - E_l^{(0)}) c_{ln}^{(2)} = \sum_m V_{lm} c_{mn}^{(1)}.$$

Choosing $l = n$ and using $c_{nn}^{(0)} = 1$, and $c_{nn}^{(1)} = 0$, we have an equation for the second order shift,

$$E_n^{(2)} = \sum_m{}' \frac{V_{nm} V_{mn}}{(E_n^{(0)} - E_m^{(0)})}.$$

This is also a very useful equation, particularly in the case (which happens often) when the first order shift vanishes. Note that the second order shift for the ground state is *always negative.*

Degenerate Case   When there is more than one state for a given energy in the unperturbed Hamiltonian, H_0, our previous treatment needs modification. The potential V may have matrix elements between several of these unperturbed states, and our previous formula for the first order shift, Eq.(2) no longer makes sense.

Suppose that for the nth eigenvalue of H_0, we have d states, all with the same eigenvalue $E_n^{(0)}$ of H_0. **In what follows, we will suppress the index n and only keep an index $1, 2, \ldots d$ which labels the d different states of H_0 that exist with the same energy.** Our goal is to replace the original basis of degenerate states, $|\Psi_j^{(0)} >$ with a new basis, $|\Psi_j^{(0)\prime} >$, where $j = 1, 2, \ldots, d$. We expand the new basis in terms of the old as follows:

$$|\Psi_j^{(0)\prime} > = \sum_{k=1}^d |\Psi_k^{(0)} > c_{kj}^{(0)} \tag{3}$$

From this equation, we have

$$c_{kj}^{(0)} = < \Psi_k^{(0)} | \Psi_j^{(0)\prime} >, \tag{4}$$

so the left index of $c_{kj}^{(0)}$ is in the old basis, and the right index is in the new basis. The defining property of the new basis is that in it, the potential is diagonal. Writing this out we have

$$< \Psi_k^{(0)\prime} | V | \Psi_j^{(0)\prime} > = E_j^{(1)} < \Psi_k^{(0)\prime} | \Psi_j^{(0)\prime} > = E_j^{(1)} \delta_{kj}, \tag{5}$$

where $E_j^{(1)}$, $j = 1, 2, \ldots, d$ are the d new values of the first order shift in the energy. To find the energy shifts and new basis, we rewrite the previous equation as an operator equation, in the $d \times d$ space of degenerate states. We have

$$V | \Psi_j^{(0)\prime} > = E_j^{(1)} | \Psi_j^{(0)\prime} >, \tag{6}$$

which merely states that $|\Psi_j^{(0)\prime}>$ is an eigenstate of V with eigenvalue $E_j^{(1)}$. Now taking the matrix element with an unperturbed state $< \Psi_k^{(0)}|$, we obtain

$$< \Psi_k^{(0)}|V|\Psi_j^{(0)\prime} >= E_j^{(1)} < \Psi_k^{(0)}|\Psi_j^{(0)\prime} >= E_j^{(1)} c_{kj}^{(0)} \tag{7}$$

Using the expansion of Eq.(3), we obtain

$$\sum_{l=1}^{d} < \Psi_k^{(0)}|V|\Psi_l^{(0)} > c_{lj}^{(0)} = E_j^{(1)} c_{kj}^{(0)}, \tag{8}$$

or

$$\sum_{l=1}^{d} (V_{kl} - E_j^{(1)} \delta_{kl}) c_{lj}^{(0)} = 0. \tag{9}$$

Eq.(9) is an equation for the eigenvalues of V_{kl}. It is customary in solving such an equation to suppress the index j on $E_j^{(1)}$ and $c_{lj}^{(0)}$, so we would have

$$\sum_{l=1}^{d} (V_{kl} - E^{(1)} \delta_{kl}) c_l^{(0)} = 0. \tag{10}$$

This is a set of d homogeneous equations for the unknowns $c_l^{(0)}$. The only solution other than all the $c_l^{(0)} = 0$ is found by setting the determinant of the coefficients equal to zero. This gives

$$\det \begin{pmatrix} V_{11} - E^{(1)} & V_{12} & . \\ V_{21} & V_{22} - E^{(1)} & . \\ \vdots & \vdots & \vdots \\ . & . & V_{dd} - E^{(1)} \end{pmatrix} = 0. \tag{11}$$

Eq.(11) is a dth order equation for the $E^{(1)}$, which will determine d different eigenvalues $E_1^{(1)}, E_2^{(1)}, \ldots, E_d^{(1)}$. After solving this equation, a specific $E_j^{(1)}$ is chosen. We then return to Eq.(9). There are d equations, but only $d-1$ are independent. Using these $d-1$ equations, allows a solution for the *ratios* of the $c_{lj}^{(0)}$. The last step is normalization. The normalization condition is

$$\sum_{l=1}^{d} |c_{lj}^{(0)}|^2 = 1. \tag{12}$$

At this point, $|\Psi_j^{(0)\prime} >$ is completely determined. Then another value of j is chosen and the process is repeated until all the states in the new basis are found.

The case of a two-fold degeneracy is an important special case, and provides an illustration of the formalism. Writing out Eq.(11) for this case, we have

$$\det \begin{pmatrix} V_{11} - E^{(1)} & V_{12} \\ V_{21} & V_{22} - E^{(1)} \end{pmatrix} = 0. \tag{13}$$

The resulting quadratic equation is solved by

$$E^{(1)} = \frac{1}{2}\left(V_{11} + V_{22} \pm \sqrt{(V_{11} - V_{22})^2 + 4V_{12}V_{21}}\right). \tag{14}$$

Restoring the index j, we assign $j = 1$ to the lower eigenvalue and $j = 2$ to the upper one, so

$$E_1^{(1)} = \frac{1}{2}\left(V_{11} + V_{22} - \sqrt{(V_{11} - V_{22})^2 + 4V_{12}V_{21}}\right)$$

$$E_2^{(1)} = \frac{1}{2}\left(V_{11} + V_{22} + \sqrt{(V_{11} - V_{22})^2 + 4V_{12}V_{21}}\right)$$

Choosing $j = 1$, returning to Eq.(8), and writing out the equation for $k = 1$, we have

$$\frac{1}{2}\left(V_{11} - V_{22} + \sqrt{(V_{11} - V_{22})^2 + 4V_{12}V_{21}}\right) c_{11}^{(0)} + V_{12}c_{21}^{(0)} = 0. \tag{15}$$

(Eq.(8) for $k = 2$ gives an equation equivalent to Eq.(15).) Eq.(15) is then used to determine a ratio of coefficients, say $c_{21}^{(0)}/c_{11}^{(0)}$, and finally the normalization condition

$$|c_{11}^{(0)}|^2 + |c_{21}^{(0)}|^2 = 1 \tag{16}$$

finishes the determination of $c_{j1}^{(0)}$ up to an unimportant phase factor. With the $c_{j1}^{(0)}$ in hand, the new basis eigenfunction $|\Psi_1^{(0)\prime}>$ is determined;

$$|\Psi_1^{(0)\prime}> = |\Psi_1^{(0)}> c_{11}^{(0)} + |\Psi_2^{(0)}> c_{21}^{(0)}. \tag{17}$$

Similar steps determine $|\Psi_2^{(0)\prime}>$.

Restoring the index n, we now have for a two-fold degeneracy, that $E_n^{(0)}$ is split by V into two levels with energies $E_n^{(0)} + E_{n1}^{(1)}$, and $E_n^{(0)} + E_{n2}^{(1)}$. In the new basis at level n, V is diagonal, and its matrix elements are $E_{n1}^{(1)}$, and $E_{n2}^{(1)}$.