Higher-Order Perturbation Theory for a Degenerate Level Completely Split by a Perturbation

Our hamiltonian H is

$$H = H_0 + \lambda V \qquad (1)$$

with g states $|m^0\rangle$ that have the same H_0 energy

$$H_0 |m^0\rangle = E_D^0 |m^0\rangle. \qquad (2)$$

These g states $|m^0\rangle$ span a space D.

We assume that the perturbation V completely lifts the degeneracy.

Let P_D be the projection operator onto the space D

$$P_D = \sum_{m=1}^{g} |m^0\rangle\langle m^0| . \qquad (3)$$

We have seen in our treatment of first-order perturbation theory for a degenerate level that the first-order shift Δ_1 in the energies is given by the eigenvalues of the truncated potential

$$V_D = P_D V P_D . \qquad (4)$$

We assume that these eigenvalues $\Delta_{Dl}^{(1)}$

$$V_D |l^0\rangle = \Delta_{Dl}^{(1)} |l^0\rangle \tag{5}$$

are all different for the g linear combinations

$$|l^0\rangle = \sum_{m=1}^{g} |m^0\rangle\langle m^0|l^0\rangle . \tag{6}$$

Note that

$$P_D = \sum_{l=1}^{g} |l^0\rangle\langle l^0| = \sum_{m=1}^{g} |m^0\rangle\langle m^0| . \tag{7}$$

Since V_D splits the g degenerate levels, the hamiltonian

$$H_0^D = H_0 + \lambda V_D \tag{8}$$

has g eigenstates $|l^0\rangle$

$$\begin{aligned} H_0^D |l^0\rangle &= \left(E_D^0 + \Delta_{Dl}^{(1)}\right)|l^0\rangle \\ &= E_l^0 \, |l^0\rangle \end{aligned} \tag{9}$$

all with different eigenvalues $E_l^0 = E_D^0 + \Delta_{Dl}^{(1)}$. So if we write our hamiltonian H as

$$\begin{aligned} H = H_0 + \lambda V &= H_0 + \lambda V_D + \lambda V_D' \\ &= H_{0D} + \lambda V_D' \end{aligned} \tag{10}$$

with $H_{0D} = H_0 + \lambda V_D$ (11)

and
$$V'_D = V - V_D \tag{12}$$

then we may apply non-degenerate perturbation theory to
$$H = H_{0D} + \lambda V'_D . \tag{13}$$

We recall that with $E^0_\ell = E^0_D + \Delta^{(1)}_{D\ell}$

$$|\ell\rangle = |\ell^0\rangle + \lambda|\ell^1\rangle + \lambda^2|\ell^2\rangle + \cdots \tag{14}$$

$$\Delta_\ell = E_\ell - E^0_\ell = \lambda\Delta^{(1)}_\ell + \lambda^2\Delta^{(2)}_\ell + \cdots \tag{15}$$

$$\Delta^{(k)}_\ell = \langle \ell^0 | V'_D | \ell^{k-1}\rangle, \quad \Delta_\ell = \lambda\langle \ell^0 | V'_D | \ell\rangle \tag{16}$$

and

$$|\ell\rangle = \left[1 - \frac{A_\ell}{E^0_\ell - H_{0D}}\left(\lambda V'_D - \Delta_\ell\right)\right]^{-1} |\ell^0\rangle \tag{17}$$

where A_ℓ is the projection operator that avoids the state $|\ell^0\rangle$ and is a sum

$$A_\ell = \sum_{k\neq\ell} |k^0\rangle\langle k^0| \tag{18}$$

over all the eigenstates of H_{0D} except $|\ell^0\rangle$.

Our formula (17) for $|\ell\rangle$ is

$$|\ell\rangle = |\ell^0\rangle + \frac{A_\ell}{E^0_\ell - H_{0D}} (\lambda V'_D - \Delta_\ell) |\ell^0\rangle \qquad (19)$$

or to first order in λ

$$|\ell\rangle = |\ell^0\rangle + \lambda \sum_{k^0 \neq \ell^0} \frac{|k^0\rangle}{E^0_\ell - E^0_k} \langle k^0 | V'_D - \Delta^{(1)}_\ell | \ell^0 \rangle . \quad (20)$$

Not surprisingly, the first-order term $\Delta^{(1)}_\ell$ vanishes, for by (16) it is

$$\Delta^{(1)}_\ell = \langle \ell^0 | V'_D | \ell^0 \rangle = \langle \ell^0 | V - P_D V P_D | \ell^0 \rangle \qquad (21)$$

or since $P_D |\ell^0\rangle = |\ell^0\rangle$

$$\Delta^{(1)}_\ell = \langle \ell^0 | V - V | \ell^0 \rangle = 0 . \qquad (22)$$

So now our formula (20) for $|\ell\rangle$ to order λ is

$$|\ell\rangle = |\ell^0\rangle + \lambda \sum_{k^0 \neq \ell^0} \frac{|k^0\rangle}{E^0_\ell - E^0_k} \langle k^0 | V'_D | \ell^0 \rangle . \qquad (23)$$

States $|k^0\rangle \in D$ do not contribute to this sum because for them $P_D |k^0\rangle = |k^0\rangle$ as $P_D |\ell^0\rangle = |\ell^0\rangle$, so

$$\langle k^0 | V'_D | \ell^0 \rangle = \langle k^0 | V - P_D V P_D | \ell^0 \rangle = \langle k^0 | V - V | \ell^0 \rangle = 0 . \quad (24)$$

To order λ then, our formula (23) for $|\ell\rangle$ is now

$$|\ell\rangle = |\ell^0\rangle + \lambda \sum_{k^0 \notin D} \frac{|k^0\rangle\langle k^0|V_D'|\ell^0\rangle}{E_\ell^0 - E_k^0}. \quad (25)$$

For states $|k^0\rangle \notin D$, the matrix element $\langle k^0|V_D'|\ell^0\rangle$ simplifies because $P_D|k^0\rangle = 0$

$$\langle k^0|V_D'|\ell^0\rangle = \langle k^0|V - P_D V P_D|\ell^0\rangle = \langle k^0|V|\ell^0\rangle \quad (26)$$

and so

$$|\ell\rangle = |\ell^0\rangle + \lambda \sum_{k^0 \notin D} \frac{|k^0\rangle\langle k^0|V|\ell^0\rangle}{E_\ell^0 - E_k^0}. \quad (26)$$

Incidentally, the states $|k^0\rangle \notin D$ are eigenstates of both H_0 and $H_{0D} = H_0 + \lambda P_D V P_D$

$$H_{0D}|k^0\rangle = H_0|k^0\rangle + \lambda P_D V P_D|k^0\rangle = H_0|k^0\rangle = E_k^0|k^0\rangle. \quad (27)$$

Because E_ℓ^0 includes the order-λ correction to the energy, the term $\Delta_\ell^{(1)} = 0$ as we've seen (22). By (16), the order-λ^2 correction is

$$\Delta_\ell^{(2)} = \langle \ell^0|V_D'|\ell'\rangle = \sum_{k^0 \notin D} \frac{\langle \ell^0|V_D'|k^0\rangle\langle k^0|V|\ell^0\rangle}{E_\ell^0 - E_k^0} \quad (28)$$

in which by (26) $\langle \ell^0|V_D'|k^0\rangle = \langle \ell^0|V|k^0\rangle$.

Thus $\Delta_\ell^{(2)}$ is

$$\Delta_\ell^{(2)} = \sum_{k^0 \notin D} \frac{|\langle k^0 | V | \ell^0 \rangle|^2}{E_\ell^0 - E_k^0} \tag{29}$$

and the energy of the state $|\ell\rangle$ is

$$\begin{aligned} E_\ell &= E_\ell^0 + \lambda^2 \Delta_\ell^{(2)} \\ &= E_D^0 + \lambda \Delta_{D\ell}^{(1)} + \lambda^2 \Delta_\ell^{(2)} \end{aligned} \tag{30}$$

where by (5), $\Delta_{D\ell}^{(1)}$ is the eigenvalue of $|\ell^0\rangle$ and the truncated potential $V_D = P_D V P_D$

$$P_D V P_D |\ell^0\rangle = \Delta_{D\ell}^{(1)} |\ell^0\rangle . \tag{31}$$