Higher-Order Degenerate Perturbation Theory

Let me write our hamiltonian H in the odd form

$$H = h_0 + \lambda V \tag{1}$$

in which the level of h_0 we want to study has g eigenstates $|m_i^0\rangle$

$$h_0|m_i^0\rangle = E_D^0|m_i^0\rangle \tag{2}$$

which span the subspace D. As we saw when we studied first-order perturbation theory, the first step is to define a projection operator P_0 on D

$$P_0 = \sum_{i=1}^{g} |m_i^0\rangle\langle m_i^0| \tag{3}$$

which, like all projection operators, satisfies $P_0^2 = P_0$. The next step is to diagonalize the $g \times g$ matrix H_0

$$H_0 = h_0 + \lambda P_0 V P_0 \tag{4}$$

and to find its g e-vecs $|n_i^0\rangle$ and e-vals

$$E_{n_i}^0 = E_D^0 + \lambda v_i \tag{5}$$

by solving the system

$$H_0|n_i^0\rangle = (h_0 + \lambda P_0 V P_0)\,|n_i^0\rangle = E_{n_i}^0|n_i^0\rangle = \left(E_D^0 + \lambda v_i\right)|n_i^0\rangle. \tag{6}$$

The projection operator P_0 also is a sum of the dyadics of these e-vecs

$$P_0 = \sum_{i=1}^{g} |n_i^0\rangle\langle n_i^0| \,. \tag{7}$$

We shall assume that the $E_{n_i}^0$ are all different. In this case, we may apply non-degenerate perturbation theory to each of the g states $|n_i^0\rangle$. We write our hamiltonian H in the form

$$H = H_0 + \lambda W. \tag{8}$$

In terms of the projection operator P_1 that is complementary to P_0

$$P_1 = I - P_0 = \sum_{k \notin D} |k^0\rangle\langle k^0| \tag{9}$$

the perturbation W is

$$W = V - P_0 V P_0 = (P_0+P_1)V(P_0+P_1) - P_0 V P_0 = P_0 V P_1 + P_1 V P_0 + P_1 V P_1. \tag{10}$$

We now apply non-degenerate perturbation theory to each of the g states $|n_i^0\rangle$. We define the "safe" identity operator

$$\phi_{n_i} = I - |n_i^0\rangle\langle n_i^0| \tag{11}$$

and obtain from Sakurai's (5.1.34) an equation for the exact e-vec $|n_i\rangle$ of H

$$|n_i\rangle = |n_i^0\rangle + \frac{\phi_{n_i}}{E_{n_i}^0 - H_0}(\lambda W - \Delta_{n_i})|n_i\rangle \tag{12}$$

which implies that $|n_i\rangle$ is an exact e-vec of H

$$H|n_i\rangle = E_{n_i}|n_i\rangle \tag{13}$$

with energy

$$E_{n_i} = E_{n_i}^0 + \Delta_{n_i} \tag{14}$$

We temporarily normalize the state $|n_i\rangle$ in such a way that

$$\langle n_i^0|n_i\rangle = 1. \tag{15}$$

Since Eq.(13) is equivalent to

$$(E_{n_i}^0 - H_0)|n_i\rangle = (\lambda W - \Delta_{n_i})|n_i\rangle \tag{16}$$

Eqs.(6) & 15) imply that

$$0 = \langle n_i^0|(E_{n_i}^0 - H_0)|n_i\rangle = \langle n_i^0|(\lambda W - \Delta_{n_i})|n_i\rangle = \lambda\langle n_i^0|W|n_i\rangle - \Delta_{n_i} \tag{17}$$

or

$$\Delta_{n_i} = \lambda\langle n_i^0|W|n_i\rangle. \tag{18}$$

Now we expand the e-state $|n_i\rangle$ in powers of the small parameter λ

$$|n_i\rangle = |n_i^0\rangle + \lambda|n_i^1\rangle + \lambda^2|n_i^2\rangle + \dots \tag{19}$$

so that by (18) the power series

$$\Delta_{n_i} = \sum_{k=1}^{\infty} \lambda^k \Delta_{n_i}^{(k)} \tag{20}$$

for the change $\Delta_{n_i} = E_{n_i} - E^0_{n_i}$ in the energy is

$$\Delta_{n_i} = \lambda\langle n_i^0|W|n_i\rangle = \lambda\langle n_i^0|W|n_i^0\rangle + \lambda^2\langle n_i^0|W|n_i^1\rangle + \lambda^3\langle n_i^0|W|n_i^2\rangle + \ldots. \tag{21}$$

But by (10) the operator W has no non-zero matrix elements between states in D, and so Δ_{n_i} is just

$$\Delta_{n_i} = +\lambda^2\langle n_i^0|W|n_i^1\rangle + \lambda^3\langle n_i^0|W|n_i^2\rangle + \ldots. \tag{22}$$

The first-order correction $\Delta_{n_i}^{(1)}$ to the energy is λv_i, and it is included in $E^0_{n_i}$. The second-order correction is, by our formula (10) for W,

$$\Delta_{n_i}^{(2)} = \langle n_i^0|W|n_i^1\rangle = \langle n_i^0|VP_1|n_i^1\rangle. \tag{23}$$

We now substitute this expansion and the one (19) for the e-state $|n_i\rangle$ into the e-value equation (12)

$$\begin{aligned} &|n_i^0\rangle + \lambda|n_i^1\rangle + \lambda^2|n_i^2\rangle + \cdots = \\ &\quad |n_i^0\rangle + \frac{\phi_{n_i}}{E^0_{n_i} - H_0}\left(\lambda W - (\lambda^2\Delta_{n_i}^{(2)} + \lambda^3\Delta_{n_i}^{(3)} + \ldots)\right) \\ &\qquad\qquad \times \left(|n_i^0\rangle + \lambda|n_i^1\rangle + \lambda^2|n_i^2\rangle + \ldots\right) \end{aligned} \tag{24}$$

and identify equal powers of λ. By Eq.(10), the perturbation W is

$$W = P_0VP_1 + P_1VP_0 + P_1VP_1. \tag{25}$$

and so after canceling the $|n_i^0\rangle$-terms one has

$$\begin{aligned} \lambda|n_i^1\rangle + \lambda^2|n_i^2\rangle + \ldots &= \frac{\phi_{n_i}}{E^0_{n_i} - H_0}\lambda P_1V|n_i^0\rangle \\ &\quad + \frac{\phi_{n_i}}{E^0_{n_i} - H_0}\left[\lambda(P_0VP_1 + P_1VP_0 + P_1VP_1)\right. \\ &\qquad \left. -\lambda^2\Delta_{n_i}^{(2)} - \lambda^3\Delta_{n_i}^{(3)} - \ldots\right] \\ &\qquad\quad \times \left(\lambda|n_i^1\rangle + \lambda^2|n_i^2\rangle + \ldots\right). \end{aligned} \tag{26}$$

So the first-order correction $|n_i^1\rangle$ to the e-state is

$$|n_i^1\rangle = \frac{\phi_{n_i}}{E_{n_i}^0 - H_0} P_1 V |n_i^0\rangle + \frac{\phi_{n_i}}{E_{n_i}^0 - H_0} \lambda P_0 V P_1 |n_i^1\rangle \tag{27}$$

or

$$\begin{aligned} |n_i^1\rangle &= \frac{1}{E_{n_i}^0 - H_0} P_1 V |n_i^0\rangle + \sum_{\substack{j\in D \\ j\neq i}} \frac{|n_j^0\rangle}{E_{n_i}^0 - E_{n_j}^0} \lambda \langle n_j^0 | V P_1 | n_i^1\rangle \\ &= \frac{1}{E_{n_i}^0 - H_0} P_1 V |n_i^0\rangle + \sum_{\substack{j\in D \\ j\neq i}} \frac{|n_j^0\rangle}{v_i - v_j} \langle n_j^0 | V P_1 | n_i^1\rangle. \end{aligned} \tag{28}$$

By Eq.(23), the second-order correction to the energy is

$$\Delta_{n_i}^{(2)} = \langle n_i^0 | V P_1 | n_i^1\rangle = \langle n_i^0 | V P_1 \frac{1}{E_{n_i}^0 - H_0} P_1 V | n_i^0\rangle. \tag{29}$$

If one now expresses the projection operator P_1 in terms of dyadics, as in Eq.(9), then one has

$$\Delta_{n_i}^{(2)} = \sum_{k\notin D} \langle n_i^0 | V | k^0\rangle \frac{1}{E_{n_i}^0 - E_k^0} \langle k^0 V | n_i^0\rangle = \sum_{k\notin D} \frac{|\langle k^0 | V | n_i^0\rangle|^2}{E_{n_i}^0 - E_k^0}. \tag{30}$$

Since by (5) the energy $E_{n_i}^0$ itself contains the first-order correction $E_{n_i}^0 = E_D^0 + \lambda v_i$, our formula (30) for the second-order correction contains a term of order λ

$$\Delta_{n_i}^{(2)} = \sum_{k\notin D} \frac{|\langle k^0 | V | n_i^0\rangle|^2}{E_D^0 + \lambda v_i - E_k^0}. \tag{31}$$

If we drop it, then we get Sakurai's (5.2.15)

$$\Delta_{n_i}^{(2)} = \sum_{k\notin D} \frac{|\langle k^0 | V | n_i^0\rangle|^2}{E_D^0 - E_k^0} \tag{32}$$

(with his typo corrected).

Finally, let's cast our formulas (27 & 28) for $|n_i^1\rangle$ in the more explicit form

$$\left[1 - \frac{\phi_{n_i}}{E_{n_i}^0 - H_0} \lambda P_0 V P_1\right] |n_i^1\rangle = \frac{1}{E_{n_i}^0 - H_0} P_1 V |n_i^0\rangle \tag{33}$$

or

$$|n_i^1\rangle = \left[1 - \frac{\phi_{n_i}}{E_{n_i}^0 - H_0}\lambda P_0 V P_1\right]^{-1} \frac{1}{E_{n_i}^0 - H_0} P_1 V |n_i^0\rangle \tag{34}$$

or

$$|n_i^1\rangle = \left[1 - \sum_{\substack{j\in D \\ j\neq i}} \frac{|n_j^0\rangle}{v_i - v_j}\langle n_j^0| V P_1\right]^{-1} \frac{1}{E_{n_i}^0 - H_0} P_1 V |n_i^0\rangle. \tag{35}$$