Higher-Order Non-Degenerate Perturbation Theory

We want to use our knowledge of the e-vecs $|n^0\rangle$ of H_0

$$H_0 |n^0\rangle = E_n^0 |n^0\rangle \tag{1}$$

to find those of

$$H = H_0 + \lambda V \tag{2}$$

as power-series expansions in λ:

$$(H_0 + \lambda V)|n\rangle = E_n |n\rangle. \tag{3}$$

Let

$$\Delta_n = E_n - E_n^0 \tag{4}$$

be the exact energy shift of the nth level.
We want to solve

$$(H_0 + \lambda V)|n\rangle = E_n|n\rangle = \left(\Delta_n + E_n^0\right)|n\rangle \tag{5}$$

or

$$(E_n^0 - H_0)|n\rangle = (\lambda V - \Delta_n)|n\rangle, \tag{6}$$

which implies that $(\lambda V - \Delta_n)|n\rangle$ is $\perp$ to $|n^0\rangle$

$$0 = \langle n^0|(E_n^0 - H_0)|n\rangle = \langle n^0|(\lambda V - \Delta_n)|n\rangle. \tag{7}$$

We can't just invert (6) because $1/(E_n^0 - H_0)$ has an infinite diagonal matrix element.

But we can use the projection operator

$$\phi_n = 1 - |n^0\rangle\langle n^0|$$

$$= \sum_{k \neq n} |k^0\rangle\langle k^0| \qquad (8)$$

on the subspace orthogonal to $|n^0\rangle$ to form

$$\frac{1}{E_n^0 - H_0}\phi_n = \phi_n \frac{1}{E_n^0 - H_0} = \frac{\phi_n}{E_n^0 - H_0} = \sum_{k \neq n} \frac{|k^0\rangle\langle k^0|}{E_n^0 - E_k^0} \qquad (9)$$

in which the non-degeneracy of H_0 is crucial.

Since by (7) $\langle n^0 | \lambda V - \Delta_n | n\rangle = 0$, the state $(\lambda V - \Delta_n)|n\rangle$ lies in the orthogonal subspace and so

$$(\lambda V - \Delta_n)|n\rangle = \phi_n(\lambda V - \Delta_n)|n\rangle. \qquad (10)$$

So we could try

$$|n\rangle \overset{?}{=} \frac{1}{E_n^0 - H_0}\phi_n(\lambda V - \Delta_n)|n\rangle,$$

but we know that $|n\rangle \to |n^0\rangle$ as $\lambda \to 0$.

So a smarter guess is

$$|n\rangle = C_n(\lambda)|n^0\rangle + \frac{1}{E_n^0 - H_0}\phi_n(\lambda V - \Delta_n)|n\rangle \quad (11)$$

$$= C_n(\lambda)|n^0\rangle + \phi_n \frac{1}{E_n^0 - H_0}\phi_n(\lambda V - \Delta_n)|n\rangle . \quad (12)$$

We expect that as $\lambda \to 0$

$$\langle n^0|n\rangle = C_n(\lambda)\langle n^0|n^0\rangle = C_n(\lambda) \to 1 . \quad (13)$$

To simplify what follows, we'll set

$$C_n(\lambda) = 1 \quad (14)$$

and worry later about how to normalize $|n\rangle$.

So we now want to solve

$$|n\rangle = |n^0\rangle + \frac{\phi_n}{E_n^0 - H_0}(\lambda V - \Delta_n)|n\rangle . \quad (15)$$

By (7)

$$0 = \langle n^0|(\lambda V - \Delta_n)|n\rangle = \lambda\langle n^0|V|n\rangle - \Delta_n$$

so the energy shift Δ_n is

$$\Delta_n = \lambda \langle n^0|V|n\rangle . \quad (16)$$

Before going on, let's verify that (15) does imply $H|n\rangle = E_n|n\rangle$. By (10), we see that (15) implies

$$(E_n^0 - H_0)|n\rangle = \phi_n(\lambda V - \Delta_n)|n\rangle = (\lambda V - \Delta_n)|n\rangle$$

$$= (\lambda V - (E_n - E_n^0))\,|n\rangle$$

or

$$-H_0|n\rangle = (\lambda V - E_n)\,|n\rangle$$

or

$$(H_0 + \lambda V)|n\rangle = E_n|n\rangle . \qquad (17)$$

So (15) is what we need.

We now want to solve (15) & (16) as power series in the small parameter λ:

$$|n\rangle = |n^0\rangle + \lambda|n^1\rangle + \lambda|n^2\rangle + \cdots \qquad (18)$$

$$\Delta_n = \lambda\Delta_n^1 + \lambda^2\Delta_n^2 + \cdots \qquad , \qquad (19)$$

We put (18) in (16) to get

$$\Delta_n = \lambda\langle n^0|V\left(|n^0\rangle + \lambda|n^1\rangle + \lambda^2|n^2\rangle + \cdots\right)$$

$$= \sum_{k=0}^{\infty}\lambda^{k+1}\langle n^0|V|n^k\rangle . \qquad (20)$$

So

$$\Delta_n^k = \langle n^0|V|n^{k-1}\rangle , \qquad (21)$$

e.g.

$$\Delta_n^1 = \langle n^0|V|n^0\rangle, \quad \Delta_n^2 = \langle n^0|V|n^1\rangle, \text{ etc.} \qquad (22)$$

Now we put (18) and (20) in (15) to get

$$\sum_{k=0}^{\infty} \lambda^k |n^k\rangle = |n^0\rangle + \frac{\phi_n}{E_n^0 - H_0} \left(\lambda V - \sum_{\ell=1}^{\infty} \lambda^\ell \Delta_n^\ell\right) \times \sum_{j=0}^{\infty} \lambda^j |n^j\rangle. \qquad (23)$$

But since

$$\phi_n \Delta_n |n^0\rangle = 0 \qquad (24)$$

(23) is

$$\sum_{k=0}^{\infty} \lambda^k |n^k\rangle = |n^0\rangle + \frac{\phi_n}{E_n^0 - H_0} \lambda V |n^0\rangle + \frac{\phi_n}{E_n^0 - H_0} \left(\lambda V - \sum_{\ell=1}^{\infty} \lambda^\ell \Delta_n^\ell\right) \sum_{j=1}^{\infty} \lambda^j |n^j\rangle. \qquad (25)$$

To zeroth order

$$|n^0\rangle = |n^0\rangle. \qquad (26)$$

To first order

$$\lambda |n^1\rangle = \frac{\phi_n}{E_n^0 - H_0} \lambda V |n^0\rangle \qquad (27)$$

or

$$|n^1\rangle = \frac{\phi_n}{E_n^0 - H_0} V |n^0\rangle. \qquad (28)$$

This last (28) for $|n'\rangle$ together with (22) gives

$$\Delta^2_n = \langle n^0|V|n'\rangle = \langle n^0|V \frac{\phi_n}{E_n^0 - H_0} V|n^0\rangle \qquad (29)$$

$$= \sum_{k \neq n} \frac{\langle n^0|V|k^0\rangle\langle k^0|V|n^0\rangle}{E_n^0 - E_k^0} \qquad (30)$$

$$\Delta^2_n = \sum_{k \neq n} \frac{|V_{kn}|^2}{E_n^0 - E_k^0} \qquad (31)$$

where

$$V_{kn} = \langle k^0|V|n^0\rangle. \qquad (32)$$

Suppose $n = 1$ is the ground state. Then $E_1^0 - E_k^0 < 0$ for all k since there is no degeneracy by assumption. Thus the second-order correction Δ^2_1 the ground-state energy is negative

$$\Delta^2_1 = \sum_{k \neq n} \frac{|V_{kn}|^2}{E_1^0 - E_k^0} < 0 \qquad (33)$$

when the system is non-degenerate.

We now use (28) for $|n^1\rangle$ in (25) to find $|n^2\rangle$

$$\lambda^2 |n^2\rangle = \frac{\phi_n}{E_n^0 - H_0} \left(\lambda V - \lambda \Delta_n^1\right) \lambda |n^1\rangle \tag{34}$$

or

$$|n^2\rangle = \frac{\phi_n}{E_n^0 - H_0} V \frac{\phi_n}{E_n^0 - H_0} V |n^0\rangle$$

$$- \frac{\phi_n}{E_n^0 - H_0} \langle n^0 | V | n^0 \rangle \frac{\phi_n}{E_n^0 - H_0} V |n^0\rangle \tag{35}$$

or

$$|n^2\rangle = \sum_{k,\ell \neq n} \frac{|k^0\rangle}{E_n^0 - E_k^0} \frac{V_{k\ell} V_{\ell n}}{E_n^0 - E_\ell^0} - \sum_{k \neq n} \frac{|k^0\rangle V_{nn} V_{kn}}{(E_n^0 - E_k^0)^2} \tag{36}$$

$$= \sum_{k \neq n} \frac{|k^0\rangle}{E_n^0 - E_k^0} \left(\sum_{\ell \neq n} \frac{V_{k\ell} V_{\ell n}}{E_n^0 - E_\ell^0} - \frac{V_{nn} V_{kn}}{E_n^0 - E_k^0} \right). \tag{37}$$

One can go on if necessary.

To order λ^2 then

$$E_n = E_n^0 + \lambda \langle n^0 | V | n^0 \rangle + \lambda^2 \sum_{k \neq n} \frac{|\langle k^0 | V | n^0 \rangle|^2}{E_n^0 - E_k^0} \quad (34)$$

and (apart from normalization)

$$|n\rangle = |n^0\rangle + \lambda \frac{\phi_n}{E_n^0 - H_0} V |n^0\rangle$$

$$+ \lambda^2 \frac{\phi_n}{E_n^0 - H_0} V \frac{\phi_n}{E_n^0 - H_0} V |n^0\rangle$$

$$- \lambda^2 \frac{\phi_n}{E_n^0 - H_0} \langle n^0 | V | n^0 \rangle \frac{\phi_n}{E_n^0 - H_0} V |n^0\rangle \quad (35)$$

$$|n\rangle = |n^0\rangle + \frac{\lambda \phi_n V |n^0\rangle}{E_n^0 - H_0} + \lambda^2 \left(\frac{\phi_n}{E_n^0 - H_0} V \right)^2 |n^0\rangle - \lambda^2 \langle n^0 | V | n^0 \rangle \left(\frac{\phi_n}{E_n^0 - H_0} \right)^2 V |n^0\rangle .$$

Suppose t & b are two levels coupled by $\langle t^0 | V | b^0 \rangle$ with $E_t^0 > E_b^0$. Then

$$\Delta^2_{t_b} = \frac{|\langle b^0 | V | t^0 \rangle|^2}{E_t^0 - E_b^0} > 0 \quad (36)$$

while

$$\Delta^2_{b_t} = \frac{|\langle t^0 | V | b^0 \rangle|^2}{E_b^0 - E_t^0} < 0 \quad , \quad (37)$$

That is, the correction Δ^2_t due to b is positive while Δ^2_b due to t is negative. The levels repel each other.

We may normalize $|n\rangle$

$$|n\rangle_N = Z_n^{1/2} \, |n\rangle \tag{38}$$

So that

$$1 = {}_N\langle n|n\rangle_N = Z_n^{1/2} \, {}_N\langle n|n\rangle . \tag{39}$$

By (14)

$$C_n(\lambda) = \langle n^0|n\rangle = 1 \tag{40}$$

so

$$\langle n^0|n\rangle_N = Z_n^{1/2} \, \langle n^0|n\rangle = Z_n^{1/2} \tag{41}$$

or

$$Z_n^{1/2} = \langle n^0|n\rangle_N . \tag{42}$$

Now

$$1 = {}_N\langle n|n\rangle_N = Z_n \, \langle n|n\rangle \tag{43}$$

which implies

$$Z_n^{-1} = \langle n|n\rangle = \left(\langle n^0| + \lambda\langle n'| + \cdots\right)\left(|n^0\rangle + \lambda|n'\rangle + \cdots\right)$$

$$= 1 + \lambda^2 \langle n'|n'\rangle \tag{44}$$

since $\langle n^0|n'\rangle = 0$ by (28).

Using (28) for $|n'\rangle$ we have

$$Z_n^{-1} = 1 + \lambda^2 \langle n^0 | V \left(\frac{\phi_n}{E_n^0 - H_0}\right)^2 V | n^0 \rangle$$

$$= 1 + \lambda^2 \sum_{k \neq n} \frac{|V_{nk}|^2}{(E_n^0 - E_k^0)^2} + \cdots \qquad (45)$$

or

$$Z_n \approx 1 - \lambda^2 \sum_{k \neq n} \frac{|V_{nk}|^2}{(E_n^0 - E_k^0)^2}, \qquad (46)$$

By (24), $Z_n = |{}_N\langle n | n^0 \rangle|^2$ is the probability that $|n\rangle_N$ is in the state $|n\rangle_N$. The stronger the coupling V_{kn} to other levels, the smaller this probability is.

Using (34) we have

$$\frac{\partial E_n}{\partial E_0} = 1 - \lambda^2 \sum \frac{|V_{kn}|^2}{(E_n^0 - E_k^0)^2} = Z_n. \qquad (47)$$

Finally, it may be worth comparing this theory of perturbations to the usual way one diagonalizes a (simpler) hamiltonian H. There one finds the roots of the equation

$$0 = \det(\hat{H} - EI) \tag{48}$$

in which I is the $N \times N$ identity matrix and $\hat{H}$ is the (truncated) $N \times N$ matrix

$$\hat{H}_{k\ell} = \langle \overset{\circ}{k} | H | \overset{\circ}{\ell} \rangle \tag{49}$$

and the N basis states $|\overset{\circ}{k}\rangle$. One must choose these basis states so that one can compute the N^2 matrix elements (49). Computer programs (e.g., LINPACK) then can find all the e-vals E and all the e-vecs for this truncated $\hat{H}$. One first finds a given e-val E_n, and then one finds its e-vec $|n\rangle$ satisfying

$$\hat{H}|n\rangle = E_n|n\rangle. \tag{50}$$

As $N \to \infty$, one gets all the solutions.

In perturbation theory, by contrast, one iteratively finds the energy shift Δ_n^1 and then the correction $|n^1\rangle$ to the e-vec and then Δ_n^2 and $|n^2\rangle$ etc.

But suppose somehow one knew

the exact value of E_n and so too of $\Delta_n = E_n - E_n^0$. Then one could cast (15)

$$|n\rangle = |n^0\rangle + \frac{\phi_n}{E_n^0 - H_0}(\lambda V - \Delta_n)|n\rangle \qquad (51)$$

into the form

$$\left(1 - \frac{\phi_n}{E_n^0 - H_0}(\lambda V - \Delta_n)\right)|n\rangle = |n^0\rangle \qquad (52)$$

and find

$$|n\rangle = \left[1 - \frac{\phi_n}{E_n^0 - H_0}(\lambda V - \Delta_n)\right]^{-1} |n^0\rangle \qquad (53)$$

$$= \sum_{k=0}^{\infty} \left[\frac{\phi_n}{E_n^0 - H_0}(\lambda V - \Delta_n)\right]^n |n^0\rangle \qquad (54)$$

as long as the matrix elements of the operator inside the [ ] are suitably small.