Higher-Order Non-Degenerate Perturbation Theory

We want to use our knowledge of the exact \( |n^0\rangle \) 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 \( \lambda \):

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

Let

\[
\Delta_n = E_n - E_n^0 \tag{4}
\]

be the exact energy shift of the \( n \)th level.

We want to solve

\[
(H_0 + \lambda V) |n\rangle = E_n |n\rangle = (\Delta_n + E_n^0) |n\rangle \tag{5}
\]

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 insert (6) because $1/(E_n^0 - H_0)$ has an infinite diagonal matrix element.

But we can use the projection operator

$$\phi_n = 1 - 1m^0 \times m^0$$

$$= \sum_{k+n} 1k^0 \times k^0$$

on the subspace orthogonal to $1m^0$. To form

$$\frac{1}{E_n^0 - H_0} \phi_n = \frac{1}{E_n^0 - H_0} \phi_n = \sum_{k+n} \frac{1k^0 \times k^0}{E_n^0 - E_k^0}$$

in which the non-degeneracy of $H_0$ is crucial.

Since by (7), $<n^0 | \lambda v - \Delta m | n^0> = 0$, the state $(\lambda v - \Delta m)1n >$ lies in the orthogonal subspace and so

$$(\lambda v - \Delta m)1n > = \phi_n (\lambda v - \Delta m)1n >.$$ (10)

So we could try

$$|n> \equiv \frac{1}{E_n^0 - H_0} \phi_n (\lambda v - \Delta m)1n >,$$

but we know that $|n> \rightarrow |m^0>$ as $\lambda \rightarrow 0.$
So a smart guess is

\[ |m\rangle = C_m(\lambda) |m^0\rangle + \frac{1}{E_m - H_0} \phi_m(\lambda V - \Delta n) |m\rangle \]  (11)

\[ = C_m(\lambda) |m^0\rangle + \phi_m \frac{1}{E_m - H_0} \phi_m(\lambda V - \Delta n) |m\rangle \]  (12)

We expect that as \( \lambda \to 0 \)

\[ \langle m^0 | m \rangle = C_m(\lambda) \langle m^0 | m^0 \rangle = C_m(\lambda) \to 1 \]  (13)

To simplify what follows, we'll set

\[ C_m(\lambda) = 1 \]  (14)

and worry later about how to normalize \( |m\rangle \).

So we now want to solve

\[ |m\rangle = |m^0\rangle + \frac{\phi_m}{E_m - H_0} (\lambda V - \Delta n) |m\rangle \]  (15)

By (7)

\[ \Delta n = \lambda \langle m^0 V | m \rangle - \Delta n \]

so the energy shift \( \Delta n \) is

\[ \Delta n = \lambda \langle m^0 V | m \rangle \]  (16)

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

\[(E_m^0 - H_0) |m\rangle = \varphi_m (\lambda V - \Delta m) |m\rangle = (\lambda V - (E_n - E_m^0)) |m\rangle\]

or

\[-H_0 |m\rangle = (\lambda V - E_n) |m\rangle\]

or

\[(H_0 + \lambda V) |m\rangle = E_n |m\rangle.\]

so (15) is what we need.

We now want to solve (15) & (16)

in power series in the small parameter \(\lambda:\)

\[|m\rangle = |m^0\rangle + \lambda |m^1\rangle + \lambda^2 |m^2\rangle + \cdots \]  

\[\Delta n = \lambda \Delta n^i + \lambda^2 \Delta n^2 + \cdots \]

We put (18) in (16) to get

\[\Delta n = \lambda \langle m^0 | V | m^0\rangle + \lambda |m^1\rangle + \lambda^2 |m^2\rangle + \cdots \]

\[= \sum_{k = 0}^{\infty} \frac{\lambda^{k+1}}{k!} \langle m^0 | V | m^k\rangle,\]

so

\[\Delta_n^k = \langle m^0 | V | m^{k-1}\rangle,\]

e.g.,

\[\Delta_1^n = \langle m^0 | V | m^0\rangle, \quad \Delta_2^n = \langle m^0 | V | m^1\rangle, \quad \text{etc.}\]
Now we put (18) and (20) in (15) to get
\[
\sum_{k=0}^{\infty} \lambda^k |m^k\rangle = |m^0\rangle + \phi_m \left( \lambda V - \sum_{k=1}^{\infty} \lambda^k \Delta m \frac{\sum_{j}^{\infty} \chi_j |m_j\rangle}{E_{m^0} - H_0} \right)
\]
\[
\times \sum_{j=0}^{\infty} \chi_j |m_j\rangle.
\] (23)

But since
\[
\phi_m \Delta m |m^0\rangle = 0
\] (24)

(23) is
\[
\sum_{k=0}^{\infty} \lambda^k |m^k\rangle = |m^0\rangle + \frac{\phi_m}{E_{m^0} - H_0} \lambda V |m^0\rangle
\]
\[
+ \frac{\phi_m}{E_{m^0} - H_0} \left( \lambda V - \sum_{k=1}^{\infty} \lambda^k \Delta m \frac{\sum_{j=1}^{\infty} \chi_j |m_j\rangle}{E_{m^0} - H_0} \right) \sum_{j=1}^{\infty} \chi_j |m_j\rangle.
\] (25)

To zeroth order
\[
|m^0\rangle = |m^0\rangle.
\] (26)

To first order
\[
\lambda |m^1\rangle = \frac{\phi_m}{E_{m^0} - H_0} \lambda V |m^0\rangle
\] (27)
\[
\text{or}
\]
\[
|m^1\rangle = \frac{\phi_m}{E_{m^0} - H_0} \lambda V |m^0\rangle.
\] (28)
This last (28) for \( | m \rangle \) together with (22) gives
\[
\Delta^2_n = \langle n^0 | V | m \rangle = \langle n^0 | V | \frac{\phi_n}{E_n^0 - E_0} V | m^0 \rangle \tag{29}
\]

\[
= \sum_{k \neq n} \frac{\langle n^0 | V | k^0 \rangle \langle k^0 | V | m^0 \rangle}{E_n^0 - E_k^0} \tag{30}
\]

\[
\Delta^2_n = \sum_{k \neq n} \frac{1}{E_n^0 - E_k^0} | V_{kn} |^2 \tag{31}
\]

where
\[
V_{kn} = \langle k^0 | V | m^0 \rangle. \tag{32}
\]

Suppose \( m = 1 \) 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 \( \Delta^2 \) of the ground-state energy is negative
\[
\Delta^2 = \sum_{k \neq n} \frac{1}{E_n^0 - E_k^0} | V_{kn} |^2 < 0 \tag{33}
\]
when the system is non-degenerate.
We now use (28) for \( |m'\rangle \) in (25) to find \( |m^2\rangle \)

\[
\chi^2 |m^2\rangle = \frac{\phi_m}{E_{m} - H_0} (\lambda V - \lambda \Delta m^1 \lambda |m'\rangle.
\]

or

\[
|m^2\rangle = \frac{\phi_m}{E_{m} - H_0} V \frac{\phi_m}{E_{m} - H_0} V |m^0\rangle
\]

\[
= \frac{\phi_m}{E_{m} - H_0} \langle m^0 | V |m^0\rangle \frac{\phi_m}{E_{m} - H_0} V |m^0\rangle.
\]

or

\[
|m^2\rangle = \sum_{k \neq m} \frac{|k^0\rangle}{E_{m} - E_k} \frac{V_{km} V_{m} - \sum |k^0\rangle V_{nm} V_{mn}}{E_{m} - E_k \sum_{k \neq m} (E_{m} - E_k)^2}
\]

\[
= \sum_{k \neq m} \frac{|k^0\rangle}{E_{m} - E_k} \left( \sum_{m \neq n} \frac{V_{km} V_{m}}{E_{m} - E_k} - \frac{V_{mn} V_{km}}{E_{m} - E_k} \right).
\]

One can go on if necessary.
To order $x^2$ then

$$E_n = E_m^0 + \lambda \langle n^0 | V | m^0 \rangle + \lambda^2 \sum_{k \neq m} \frac{1}{E_n^0 - E_k^0} \langle \phi_{n^0} | V | \phi_{m^0} \rangle$$

(34)

and (apart from normalization)

$$|m^0\rangle = |m^0\rangle + \lambda \frac{\phi_m}{E_m^0 - H_0} V |m^0\rangle$$

$$+ \lambda^2 \frac{\phi_m}{E_m^0 - H_0} \frac{\phi_m}{E_m^0 - H_0} V |m^0\rangle$$

(35)

$$\langle n^0 | V | \langle n^0 | V | m^0 \rangle \rangle - \lambda^2 \langle n^0 | V | \langle n^0 | V | m^0 \rangle \rangle$$

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

$$\Delta_{tb}^2 = \frac{1}{E_t^0 - E_b^0} < 0$$

(36)

while

$$\Delta_{bt}^2 = \frac{1}{E_b^0 - E_t^0} > 0$$

(37)

That is, the correction $\Delta_t^2$ due to $b$ is positive while $\Delta_b^2$ due to $t$ is negative. The levels repel each other.
We may normalize $1_n$

$$1_n \rangle = \frac{1}{\sqrt{2}} 1_n \rangle$$

so that

$$1 = N \langle n | 1_n \rangle_N = \frac{1}{\sqrt{2}} \langle 2 | n \rangle_N \langle n | n \rangle_N$$

By (4)

$$C_n(x) = \langle n^0 | 1_n \rangle = 1$$

so

$$\langle n^0 | 1_n \rangle_N = \frac{1}{\sqrt{2}} \langle n^0 | n \rangle = \frac{1}{\sqrt{2}} \langle n^0 | 1_n \rangle_N$$

or

$$\frac{1}{\sqrt{2}} = \langle n^0 | 1_n \rangle_N.$$ 

Now

$$1 = N \langle n | 1_n \rangle_N = \frac{1}{\sqrt{2}} \langle n^0 | 1_n \rangle_N$$

which implies

$$\frac{1}{\sqrt{2}} = \langle n^0 | 1_n \rangle = \langle n^0 | 1_n \rangle (\langle n^0 | 1_n \rangle + N \langle n^0 | 1_n \rangle + \ldots) \rangle$$

$$= 1 + \frac{1}{2} \langle n^1 | n^1 \rangle$$

since $\langle n^0 | 1_n \rangle = 0$ by (28).
Using (28) for $|n\rangle$ we have
\[ Z_n = 1 + \lambda^2 <n^0|V|n^0> \]
\[ = 1 + \lambda^2 \sum_{k \neq n} \frac{|V_{nk}|^2}{(E_n^0 - E_k^0)^2} + \cdots \quad (45) \]

Or
\[ Z_n \approx 1 - \lambda^2 \sum_{k \neq n} \frac{|V_{nk}|^2}{(E_n^0 - E_k^0)^2} \quad (46) \]

By (24), $Z_n = \frac{1}{N} \langle m|n^0 \rangle^2$ is the probability that $|n^0 \rangle$ is in the state $|m \rangle$. The stronger the coupling $V_{nk}$ to other levels, the smaller this probability is.

Using (34) we have
\[ \frac{\partial E_n}{\partial E_0} = 1 - \lambda^2 \sum_{k \neq n} \frac{|V_{nk}|^2}{(E_n^0 - E_k^0)^2} = \frac{Z_n}{N} \quad (47) \]

Finally, it may be worth comparing this theory of perturbations to the usual way one diagonalizes a (simpler) Hamiltonian $H$. Then one finds the roots of the equation
\[ 0 = \det (\hat{H} - EI) \]  

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

\[ \hat{H}_{kl} = <k|H|l> \]  

and the \( N \) basis states \( |k> \). 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-values \( E \) and all the e-vectors for this truncated \( \hat{H} \). One first finds a given e-val \( E_m \) and then one finds its e-vector \( |n> \), satisfying

\[ \hat{H}|n> = E_n|n> \]  

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

In perturbation theory, by contrast, one iteratively finds the energy shift \( \Delta^1 \) and then the correction \( |n'> \) to the e-vec and then \( \Delta^2 \) and \( |n''> \) etc.

But suppose somehow one knew
the exact value of $E_n$. and so for

if

$$\Delta_n = E_n - E_n^0.$$ Then one could express

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

into the form

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

and find

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

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

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