Higher-Order Non-Degenerate Perturbation Theory

We want to use our knowledge of the exact \( |m^0\rangle \) of \( H_0 \)

\[ H_0 |m^0\rangle = E^0_m |m^0\rangle \]  

(1)

to find those of

\[ H = H_0 + \lambda V \]  

(2)

as power-series expansions in \( \lambda \):

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

(3)

Let

\[ \Delta_m = E_m - E^0_m \]

(4)

be the exact energy shift of the \( m \)th level. We want to solve

\[ (H_0 + \lambda V) |m\rangle = E_m |m\rangle = (\Delta_m + E^0_m) |m\rangle \]  

(5)

\[ (E^0_m - H_0) |m\rangle = (\lambda V - \Delta_m) |m\rangle , \]  

(6)

which implies that \( (\lambda V - \Delta_m) |m\rangle \) is \( \perp \) to \( |m^0\rangle \)

\[ 0 = \langle m^0 | (E^0_m - H_0) |m\rangle = \langle m^0 | (\lambda V - \Delta_m) |m\rangle . \]  

(7)
We can't just invert (5) because \(1/(E_n^0 - H_0)\) has an infinite diagonal matrix element.

But we can use the projection operator

\[
\phi_n = 1 - 1_{m^0} \times m^0
\]

\[
= \sum_{k \neq n} 1_{k^0} \times k^0
\]

on the subspace orthogonal to \(1_{m^0}\) to form

\[
\frac{1}{E_n^0 - H_0} \phi_n = \frac{1}{E_n^0 - H_0} \cdot \frac{1}{E_n^0 - H_0} = \sum_{k \neq n} \frac{1_{k^0} \times k^0}{E_n^0 - E_k^0}
\]

in which the non-degeneracy of \(H_0\) is crucial.

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

\[
(\chi V - \Delta m) | n \rangle = \phi_n (\chi V - \Delta m) | n \rangle.
\]

So we could try

\[
| n \rangle = \frac{1}{E_n^0 - H_0} \phi_n (\chi V - \Delta m) | n \rangle,
\]

but we know that \(| n \rangle \rightarrow | m^0 \rangle\) as \(\chi \rightarrow 0\).
So a smarter guess is

\[ |n> = C_n(x) |n^0> + \frac{1}{E_n^0 - H_0} \phi_n (\lambda \nu - \Delta \eta) |n> \]  

(11)

\[ = C_n(x) |n^0> + \phi_n \frac{1}{E_n^0 - H_0} \phi_n (\lambda \nu - \Delta \eta) |n> \]  

(12)

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

\[ \langle n^0 | n > = C_n(x) \langle n^0 | n^0 > = C_n(x) \to 1 \]  

(13)

To simplify what follows, we'll set

\[ C_n(x) = 1 \]  

(14)

and worry later about how to normalize \( |n> \).

So we now want to solve

\[ |n> = |n^0> + \phi_n \frac{1}{E_n^0 - H_0} (\lambda \nu - \Delta \eta) |n> \]  

(15)

By (7)

\[ \Delta \eta = \lambda \langle n^0 | \nu 1 n > - \Delta \eta \]  

(16)

Before moving on, let's verify that (15) does in fact imply \( M |n> = E_n |n> \).

By (10),
we see that (15) implies

$$(E^0_m - H_0) |n\rangle = \delta_n (\lambda V - \Delta_n) |n\rangle = (\lambda V - (E_n - E^o_n)) |n\rangle$$

or

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

or

$$(H_0 + \lambda V) |n\rangle = E_n |n\rangle.$$  \hspace{1cm} (17)

So (15) is what we need.

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

as power series in the small parameter $\lambda$:

$$|n\rangle = |n^0\rangle + \lambda |n^1\rangle + \lambda^2 |n^2\rangle + \cdots$$  \hspace{1cm} (18)

$$\Delta_n = \lambda \Delta^1_n + \lambda^2 \Delta^2_n + \cdots.$$  \hspace{1cm} (19)

We put (18) in (16) to get

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

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

So

$$\Delta^k_n = \langle n^0 | V | n^{k-1}\rangle.$$  \hspace{1cm} (21)

eg.

$$\Delta^1_n = \langle n^0 | V | n^0\rangle, \quad \Delta^2_n = \langle n^0 | V | n^1\rangle, \quad \text{etc}.$$  \hspace{1cm} (22)
Now we put (18) and (20) in (15) to get
\[
\sum_{k=0}^{\infty} \chi^k |m^k> = |m^0> + \frac{\phi_m}{E_m - H_0} (\chi V - \sum_{l=1}^{\infty} \chi^l \Delta_{lm}^l) \sum_{j=1}^{\infty} \chi^j |m_j>
\]
\[
\text{But since} \quad \phi_m \Delta_m |m^0> = 0 \quad \text{(24)}
\]
(23) is
\[
\sum_{k=0}^{\infty} \chi^k |m^k> = |m^0> + \phi_m \chi V |m^0> \frac{1}{E_m - H_0}
\]
\[
+ \frac{\phi_m}{E_m - H_0} (\chi V - \sum_{l=1}^{\infty} \chi^l \Delta_{lm}^l) \sum_{j=1}^{\infty} \chi^j |m_j>
\]
\text{To zeroth order}
\[
|m^0> = |m^0>
\]
(26)
\text{To first order}
\[
\chi |m'> = \frac{\phi_m}{E_m - H_0} \chi V |m^0>
\]
(27)
\text{or}
\[
|m'> = \frac{\phi_m}{E_m - H_0} \chi V |m^0>
\]
(28)
This last (28) for \( |\psi^1\rangle \) together with (22) gives

\[
\Delta^2_m = \langle n^0| V |m^1\rangle = \langle n^0| V \frac{\phi_m}{E_n - H_0} V |m^0\rangle \quad (29)
\]

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

\[
\Delta^2_m = \sum_{k \neq n} \frac{1}{E_n - E_k} |V_{kn}|^2 \quad (31)
\]

where

\[
V_{kn} = \langle k^0| V |m^0\rangle. \quad (32)
\]

Suppose \( m = k \) is the ground state. Then \( E_n^0 - E_k^0 < 0 \) for all \( k \) since there is no degeneracy by assumption. Thus the second-order correction \( \Delta^2 \) to the ground-state energy is negative

\[
\Delta^2 = \sum_{k \neq n} \frac{1}{E_n - E_k} |V_{kn}|^2 < 0 \quad (33)
\]

when the system is non-degenerate.
We now use (28) for $|m'|$ in (25) to find $|m^2>$

\[ \lambda^2 |m^2> = \frac{\phi_m}{E_{n}^{0} - H_0} \right) \lambda |m'> \]  \quad (34)

or

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

- \[ \frac{\phi_m}{E_{n}^{0} - H_0} \left< m^0 | V | m^0 \right> \frac{\phi_m}{E_{n}^{0} - H_0} |m^0> \]  \quad (35)

or

\[ |m^2> = \sum_{k \neq n} \frac{|k^0>}{E_{n}^{0} - E_k^0} \frac{V_{km} V_{mn}}{E_{m}^{0} - E_k^0} \left[ \sum_{k+n} \frac{|k^0>}{E_{n}^{0} - E_k^0} \left( \frac{V_{km} V_{nm}}{E_{n}^{0} - E_k^0} - \frac{V_{mn} V_{km}}{E_{m}^{0} - E_k^0} \right) \right] \]  \quad (36)

\[ = \sum_{k+n} \frac{|k^0>}{E_{n}^{0} - E_k^0} \left( \frac{\sum V_{ke} V_{en}}{E_{n}^{0} - E_e^0} - \frac{V_{mn} V_{km}}{E_{m}^{0} - E_k^0} \right) \]  \quad (37)

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

$$E_n = E_n^0 + \lambda \langle m^0 | V | m^0 \rangle + \lambda^2 \sum_{k \neq n} \frac{1 \langle k^0 | V | m^0 \rangle^2}{E_n^0 - E_k^0} \quad (3.4)$$

and (apart from normalization)

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

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

$$- \lambda^2 \frac{\phi_m}{E_n^0 - H_0} \frac{\langle m^0 | V | m^0 \rangle \phi_m}{E_m^0 - H_0} \frac{V |m^0\rangle}{E_n^0 - H_0} \quad (3.5)$$

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

Suppose $\alpha$ and $\beta$ are two levels coupled by $\langle \alpha^0 | V | \beta^0 \rangle$ with $E_\alpha^0 > E_\beta^0$. Then

$$\Delta_{\alpha \beta}^2 = \frac{|\langle \alpha^0 | V | \beta^0 \rangle|^2}{E_\alpha^0 - E_\beta^0} > 0 \quad (3.6)$$

while

$$\Delta_{\beta \alpha}^2 = \frac{|\langle \beta^0 | V | \alpha^0 \rangle|^2}{E_\beta^0 - E_\alpha^0} < 0 \quad (3.7)$$

That is, the correction $\Delta_{\alpha \beta}$ due to $\beta$ is positive while $\Delta_{\beta \alpha}$ due to $\alpha$ is negative. The levels repel each other.
We may normalize \( \ket{m} \)
\[
\ket{m}_N = \frac{1}{\sqrt{Z}} \sum_n \ket{m}_n
\] (38)

so that
\[
1 = \langle m | m \rangle_N = \frac{1}{Z} \sum_n \langle m | n \rangle.
\] (39)

By (14)
\[
C_n(x) = \langle m | m \rangle_n = 1
\] (40)

so
\[
\langle m | m \rangle_N = \frac{1}{Z} \sum_n \langle m | m \rangle = \frac{1}{Z} \sum_n \langle m | m \rangle
\] (41)

or
\[
\frac{1}{Z} \sum_n \langle m | m \rangle = \langle m | m \rangle_N.
\] (42)

Now
\[
1 = \langle m | m \rangle_N = \frac{1}{Z} \sum_n \langle m | m \rangle
\] (43)

which implies
\[
\frac{1}{Z} = \langle m | m \rangle = \langle m | m \rangle \sum_n \langle m | m \rangle
\] (44)

which \( \Rightarrow \)
\[
\sum_n \langle m | m \rangle = 0 \quad \text{by (28)}.
\]
Using (28) for $|\psi\rangle$ we have
\[
Z_n^{-1} = 1 + \chi^2 \langle n | V \langle \phi_n \rangle \rangle_n^2 \langle \psi | n \rangle 
\]
\[
= 1 + \chi^2 \sum_{k+n} \frac{|V_{nk}|^2}{(E_n - E_k)^2} + \cdots
\]
(45)

or
\[
Z_n \approx 1 - \chi^2 \sum_{k+n} \frac{|V_{nk}|^2}{(E_n - E_k)^2}
\]
(46)

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

Using (34) we have
\[
\frac{\partial \langle n | m \rangle}{\partial \phi_n} = 1 - \chi^2 \sum_{k+n} \frac{|V_{nk}|^2}{(E_n - E_k)^2} = Z_n
\]
(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
\[ 0 = \det (\hat{H} - EI) \]  

(48)

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

\[ \hat{H}_{kk} = \langle k^0 | H | k^0 \rangle \]  

(49)

and the \( N \) basis states \( | k^0 \rangle \). 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 \( | \rangle \)-vecs \( | \rangle \) for this truncated \( \hat{H} \). One must choose a given \( E \)-val \( E_n \) and then one finds its \( | \rangle \)-vec \( | n \rangle \), satisfying

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

(50)

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

In perturbation theory, by contrast, one iteratively finds the energy shift \( \Delta \) and then the connection \( | n \rangle \) to the \( | \rangle \)-vec and then \( \Delta^2 \) and \( | n \rangle \) etc.

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

$$\left| n \right> = \left| n^0 \right> + \frac{\phi_n}{E_n^0 - \lambda} (\lambda V - \Delta_n) \left| n \right>$$

(51)

into the form

$$\left( 1 - \frac{\phi_n}{E_n^0 - \lambda} \right) \left| n \right> = \left| n^0 \right>$$

(52)

and find

$$\left| n \right> = \left[ 1 - \frac{\phi_n}{E_n^0 - \lambda} \right]^{-1} \left| n^0 \right>$$

(53)

$$= \sum_{k = 0}^{\infty} \left[ \frac{\phi_n}{E_n^0 - \lambda} \right]^k \left| n^0 \right>$$

(54)

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