Perturbation Theory

We begin with
\[ H^0 \psi^0_n = E^0 \psi^0_n \]
where the \( \psi^0_n \) constitute a complete set of orthonormal functions
\[ \langle \psi^0_n | \psi^0_m \rangle = \delta_{nm} \]

Next we perturb the systems so that we find new functions and eigenvalues
\[ H \psi_n = E_n \psi_n \]
The new \( H \) can be written as the sum of two terms
\[ H = H^0 + \lambda H' \]
Dirac liked to refer to \( H^0 \) and \( H' \) as the “simple and small parts” of the Hamiltonian, respectively.

where \( \lambda \equiv \text{small number} \). \( \psi_n \) and \( E_n \) can then be expressed as power series in \( \lambda \).
\[ \psi_n = \psi^0_n + \lambda \psi^1_n + \lambda^2 \psi^2_n + \ldots \]
\[ E_n = E^0_n + \lambda E^1_n + \lambda^2 E^2_n + \ldots \]

where \( E^1_n \) is the first order correction to the \( n \)th eigenvalue, \( E^2_n \) is the second order correction to the \( n \)th eigenvalue, and so forth!

Inserting \( \psi_n \) and \( E_n \) into equations above yields ...

\[ \left( H^0 + \lambda H' \right) \left[ \psi^0_n + \lambda \psi^1_n + \lambda^2 \psi^2_n + \ldots \right] = \left( E^0_n + \lambda E^1_n + \lambda^2 E^2_n + \ldots \right) \left[ \psi^0_n + \lambda \psi^1_n + \lambda^2 \psi^2_n + \ldots \right] \]

Collecting terms in like powers of \( \lambda \) yields ...

\[ H^0 \psi^0_n + \lambda \left( H^0 \psi^1_n + H' \psi^0_n \right) + \lambda^2 \left( H^0 \psi^2_n + H' \psi^1_n + \ldots \right) = E^0_n \psi^0_n + \lambda \left( E^0_n \psi^1_n + E^1_n \psi^0_n \right) + \lambda^2 \left( E^0_n \psi^2_n + E^1_n \psi^1_n + E^2_n \psi^0_n \right) + \ldots \]

Lowest order yields ....

\[ H^0 \psi^0_n = E^0_n \psi^0_n \]
\[ \lambda^1 \text{--first order term} \ldots \]
\[ H^0 \psi^1_n + H' \psi^0_n = E^0_n \psi^1_n + E^1_n \psi^0_n \]
\[ \lambda^2 \text{--second order term} \ldots \]
\[ H^0 \psi^2_n + H' \psi^1_n = E^0_n \psi^2_n + E^1_n \psi^1_n + E^2_n \psi^0_n \]
1st Order Theory - Corrections to $E_0$ and to $\Psi$

Multiple the equation in $\lambda^1$ on the left by $(\psi_n^0)^*$

$$\langle \psi_n^0 | H^0 | \psi_n^1 \rangle + \langle \psi_n^0 | H' | \psi_n^0 \rangle = E_n^0 \langle \psi_n^0 | \psi_n^1 \rangle + E_n^1 \langle \psi_n^0 | \psi_n^0 \rangle$$

evaluate the first term

$$\langle \psi_n^0 | H^0 | \psi_n^1 \rangle = \langle H_0^0 \psi_n^0 | \psi_n^1 \rangle = E_n^0 \langle \psi_n^0 | \psi_n^1 \rangle$$

therefore first terms on the lhs and the rhs cancel.

This leaves

$$E_n^1 = \langle \psi_n^0 | H' | \psi_n^0 \rangle$$

$E_n^{(1)}$ -- FIRST ORDER CORRECTION TO ENERGY

To obtain first order corrections to $\psi_n^0$ we rearrange the $\lambda^1$ equations as

$$(H^0 - E_n^0) \psi_n^1 = -(H' - E_n^1) \psi_n^0$$

Express $\psi_n^1$ as expansion of $\psi_m^0$ is

$$\psi_n^1 = \sum_{m \neq n} c_m^{(n)} \psi_m^0$$

Substituting into the above

$$(H^0 - E_n^0) \psi_n^1 = (H^0 - E_n^0) \sum_{m \neq n} c_m^{(n)} \psi_m^0 = -(H' - E_n^1) \psi_n^0$$

$$\sum_{m \neq n} (E_m^0 - E_n^0) c_m^{(n)} \psi_m^0 = -(H' - E_n^1) \psi_n^0$$

left multiple by $\psi_n^0$ and integrate

$$\sum_{m \neq n} (E_m^0 - E_n^0) c_m^{(n)} \langle \psi_n^0 | \psi_m^0 \rangle = -\langle \psi_n^0 | H' | \psi_n^0 \rangle + E_n^1 \langle \psi_n^0 | \psi_n^0 \rangle$$

- For $l=n$ the left side is zero ...ie the lhs is

$$\sum_{m \neq n} (E_m^0 - E_n^0) c_m^{(n)} \langle \psi_n^0 | \psi_m^0 \rangle$$

and since $m \neq n$ then $\langle \psi_n^0 | \psi_m^0 \rangle = 0$, and we recover the formula above for $E_n^1$.

- If $l \neq n$ we obtain
\[ (E_i^0 - E_n^0) c_l^{(n)} = -\langle \psi_i^0 | H' | \psi_n^0 \rangle \]

For \( l \Rightarrow m \)

\[ c_m^{(n)} = -\frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{E_m^0 - E_n^0} \]

And \( \psi_n^1 \), the first order correction to \( \psi_n^0 \) is

\[ \psi_n^1 = \sum_{m \neq n} \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle \langle \psi_n^0 | \psi_n^0 \rangle}{E_n^0 - E_m^0} \]

The denominator is "well behaved" since \( m \neq n \). When \( m = n \), then two energy levels are degenerate, the denominator goes to zero, and the expression blows-up. To treat this case you need degenerate perturbation theory (a topic discussed in graduate quantum mechanics courses).

**Second Order Energies**

Taking the inner product with \( \psi_n^0 \)

\[ \langle \psi_n^0 | H^0 \psi_n^2 \rangle + \langle \psi_n^0 | H' \psi_n^1 \rangle = E_n^0 \langle \psi_n^0 | \psi_n^2 \rangle + E_n^1 \langle \psi_n^0 | \psi_n^1 \rangle + E_n^2 \langle \psi_n^0 | \psi_n^0 \rangle \]

\( H^0 \) is Hermitian therefore

\[ \langle \psi_n^0 | H^0 | \psi_n^2 \rangle = \langle H^0 \psi_n^0 | \psi_n^2 \rangle = E_n^0 \langle \psi_n^0 | \psi_n^2 \rangle \]

So

\[ E_n^2 = \langle \psi_n^0 | H' \psi_n^1 \rangle - E_n^1 \langle \psi_n^0 | \psi_n^1 \rangle \]

But

\[ \langle \psi_n^0 | \psi_n^1 \rangle = \sum_{m \neq n} c_m^{(n)} \langle \psi_n^0 | \psi_m^0 \rangle = 0 \]

Therefore

\[ E_n^2 = \langle \psi_n^0 | H' \psi_n^1 \rangle = \sum_{m \neq n} c_m^{(n)} \langle \psi_n^0 | H' | \psi_m^0 \rangle \]

\[ E_n^2 = \sum_{m \neq n} \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle \langle \psi_n^0 | H' | \psi_m^0 \rangle}{E_n^0 - E_m^0} = \sum_{m \neq n} \frac{H'_{nm} H'_{mn}}{E_n^0 - E_m^0} \]

\[ E_n^{(2)} -- \text{SECOND ORDER CORRECTION TO ENERGY} \]