Perturbation Theory

We begin with

$$H^0\psi_n^0 = E^0\psi_n^0$$

where the $\psi_n^0 \equiv$ constitutes a complete set of orthonormal functions

$$\langle \psi_n^0 | \psi_m^0 \rangle = \delta_{nm}$$

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 $\lambda \equiv$ small number. ψ_n and E_n can the be expressed as power series in λ.

$$\psi_n = \psi_n^0 + \lambda\psi_n^1 + \lambda^2\psi_n^2 + \ldots$$

$$E_n = E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \ldots$$

where E_n^1 is the <u>first order correction</u> to the *nth* eigenvalue, E_n^2 is the <u>second order correction</u> to the *nth* eigenvalue, and so forth !

Inserting ψ_n and E_n into equations above yields …

$$\left(H^0 + \lambda H'\right)\left[\psi_n^0 + \lambda\psi_n^1 + \lambda^2\psi_n^2 + \cdots\right] = \left(E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \cdots\right)\left[\psi_n^0 + \lambda\psi_n^1 + \lambda^2\psi_n^2 + \cdots\right]$$

Collecting terms in like powers of λ yields …

$$\begin{aligned} &H^0\psi_n^0 + \lambda\left(H^0\psi_n^1 + H'\psi_n^0\right) + \lambda^2\left(H^0\psi_n^2 + H'\psi_n^1 + \cdots\right) \\ &= E_n^0\psi_n^0 + \lambda\left(E_n^0\psi_n^1 + E_n^1\psi_n^0\right) + \lambda^2\left(E_n^0\psi_n^2 + E_n^1\psi_n^1 + E_n^2\psi_n^0\right) + \cdots \end{aligned}$$

Lowest order yields ….

$$H^0\psi_n^0 = E_n^0\psi_n^0$$

λ^1 --first order term ….

$$H^0\psi_n^1 + H'\psi_n^0 = E_n^0\psi_n^1 + E_n^1\psi_n^0$$

λ^2 --second order term….

$$H^0\psi_n^2 + H'\psi_n^1 = E_n^0\psi_n^2 + E_n^1\psi_n^1 + E_n^2\psi_n^0$$

1st Order Theory – Corrections to E_0 and to Ψ

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

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

evaluate the first term

$$\left\langle\psi_n^0\middle|H^0\psi_n^1\right\rangle=\left\langle H^0\psi_n^0\middle|\psi_n^1\right\rangle=E_n^0\left\langle\psi_n^0\middle|\psi_n^1\right\rangle$$

therefore first terms on the *lhs* and the *rhs* cancel.

This leaves

$$\boxed{E_n^1=\left\langle\psi_n^0\middle|H'\middle|\psi_n^0\right\rangle}$$

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

To obtain first order corrections to ψ_n^0 we rearrange the λ^1 equations as

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

Express ψ_n^1 as expansion of ψ_m^0 is

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

Substituting into the above

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

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

left multiple by ψ_l^0 and integrate

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

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

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

  and since $m\neq n$ then $\left\langle\psi_n^0\middle|\psi_m^0\right\rangle=0$, and we recover the formula above for $E^{1.}$

- If $l\neq n$ we obtain

$$\left(E_l^0 - E_n^0\right)c_l^{(n)} = -\left\langle \psi_l^0 \middle| H' \middle| \psi_n^0 \right\rangle$$

For $l \Rightarrow m$

$$c_m^{(n)} = -\frac{\left\langle \psi_m^0 \middle| H' \middle| \psi_n^0 \right\rangle}{E_m^0 - E_n^0}$$

And ψ_n^1, the first order correction to ψ_n^0 is

$$\boxed{\psi_n^1 = \sum_{m \neq n} \frac{\left\langle \psi_m^0 \middle| H' \middle| \psi_n^0 \right\rangle}{E_n^0 - E_m^0} \Psi_m^0}$$

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 ψ_n^0

$$\left\langle \psi_n^0 \middle| H^0 \psi_n^2 \right\rangle + \left\langle \psi_n^0 \middle| H' \psi_n^1 \right\rangle = E_n^0 \left\langle \psi_n^0 \middle| \psi_n^2 \right\rangle + E_n^1 \left\langle \psi_n^0 \middle| \psi_n^1 \right\rangle + E_n^2 \left\langle \psi_n^0 \middle| \psi_n^0 \right\rangle$$

H^0 is Hermitian therefore

$$\left\langle \psi_n^0 \middle| H^0 \middle| \psi_n^2 \right\rangle = \left\langle H^0 \psi_n^0 \middle| \psi_n^2 \right\rangle = E_n^0 \left\langle \psi_n^0 \middle| \psi_n^2 \right\rangle$$

So

$$E_n^2 = \left\langle \psi_n^0 \middle| H' \middle| \psi_n^1 \right\rangle - E_n^1 \left\langle \psi_n^0 \middle| \psi_n^1 \right\rangle$$

But

$$\left\langle \psi_n^0 \middle| \psi_n^1 \right\rangle = \sum_{m \neq n} c_m^{(n)} \left\langle \psi_n^0 \middle| \psi_m^0 \right\rangle = 0$$

Therefore

$$E_n^2 = \left\langle \psi_n^0 \middle| H' \middle| \psi_n^1 \right\rangle = \sum_{m \neq n} c_m^{(n)} \left\langle \psi_n^0 \middle| H' \middle| \psi_m^0 \right\rangle$$

$$\boxed{E_n^2 = \sum_{m \neq n} \frac{\left\langle \psi_m^0 \middle| H' \middle| \psi_n^0 \right\rangle \left\langle \psi_n^0 \middle| H' \middle| \psi_m^0 \right\rangle}{E_n^0 - E_m^0} = \sum_{m \neq n} \frac{H'_{mn} H'_{nm}}{E_n^0 - E_m^0}}$$

$E_n^{(2)}$ --SECOND ORDER CORRECTION TO ENERGY