SECOND-ORDER PERTURBATION THEORY (TIME-INDEPENDENT)

We need to at least take a look at how we can continue our approximation of E_n and ψ_n, by adding one more term to the λ expansion. Again, the problem is as follows:

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

: ψ_n^0 is (non-degenerate) eigenstate of unperturbed Hamiltonian H^0 with eigenvalue E_n^0

We add a perturbation $\lambda H'$ and now want to know the ψ_n and E_n that satisfy:

$$H \psi_n = E_n \psi_n \qquad \text{where} \quad H = H^0 + \lambda H'$$

We write:

$$\psi_n = \psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \dots$$
$$E_n = E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \dots$$

and, upon substitution onto Schroedinger's equation, we can collect terms with the same power of λ:

λ^0 : $H^0 \psi_n^0 = E_n^0 \psi_n^0 \implies$ Schroedinger's equation with unperturbed Hamiltonian

λ^1 (power) : $H' \psi_n^0 + H^0 \psi_n^1 = E_n^1 \psi_n^0 + E_n^0 \psi_n^1 \implies E_n^1 = \langle \psi_n^0 | H' | \psi_n^0 \rangle$

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

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

Let us write the last equation in Dirac's notation, and take its direct product with $\langle \psi_n^0 |$:

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

H^0 is Hermitian : $\langle \psi_n^0 | H^0 | \psi_n^2 \rangle = \langle H^0 \psi_n^0 | \psi_n^2 \rangle = E_n^0 \langle \psi_n^0 | \psi_n^2 \rangle$

We therefore have :

$$\langle \psi_n^0 | H' | \psi_n^1 \rangle = E_n^2 + E_n^1 \underbrace{\langle \psi_n^0 | \psi_n^1 \rangle}_{=0}$$

$= 0$: remember, we choose $\psi_n^1 = \underline{\underline{\sum_{m \neq n}}} (\dots)\, \psi_m^0$

$$\| $$

$$\sum_{m \neq n} C_m^{(n)} \langle \psi_n^0 | H' | \psi_m^0 \rangle$$

I used $|\psi_n^1\rangle = \sum_{m \neq n} C_m^{(n)} |\psi_m^0\rangle$

$$\|$$

$$\sum_{m \neq n} \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{E_n^0 - E_m^0} \cdot \langle \psi_n^0 | H' | \psi_m^0 \rangle = \sum_{m \neq n} \frac{|\langle \psi_m^0 | H' | \psi_n^0 \rangle|^2}{E_n^0 - E_m^0}$$

Finally:

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

Explicitly:

third-order correction

$$E_n = E_n^0 + \lambda \langle \psi_n^0 | H' | \psi_n^0 \rangle + \lambda^2 \sum_{m \neq n} \frac{|\langle \psi_m^0 | H' | \psi_n^0 \rangle|^2}{E_n^0 - E_m^0} + \dots$$

$\lambda = 1$ if I write

$H = H^0 + H'$