The eigenvalue equation is

$$H\psi_n = E_n \psi_n.$$

Assuming that the n-th eigenstate ψ_n and eigenvalue E_n can be expand as a power series in λ:

$$E_n = \sum_i \lambda^i E_n^{(i)} = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots$$

$$\psi_n = \sum_i \lambda^i \psi_n^{(i)} = \psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \cdots$$

where

$E_n^{(0)}$ — nth eigenenergy of H_0

$\psi_n^{(0)}$ — n-th eigenstate of H_0.

The other terms $E_n^{(1)}, E_n^{(2)}, E_n^{(3)}, \ldots$ are the first, second, third, ... order corrections to the unperturbed eigenenergy $E_n^{(0)}$. Similarly $\psi_n^{(1)}, \psi_n^{(2)}, \psi_n^{(3)}, \ldots$ are the first, second, third, ... order corrections to $\psi_n^{(0)}$. For physically exactable problems the perturbation series expansion should be convergent.

1) Non-Degenerate Case.

The time-independent schrodinger equ is

$$H \psi_n = E_n \psi_n.$$

$$(H_0 + \lambda H_1) \psi_n = E_n \psi_n.$$

$$(H_0 + \lambda H_1)(\psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \cdots)$$

$$= (E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 \psi_n^{(2)} + \cdots)($$

$$(\psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \cdots)$$

By comparing the co-efficients of $\lambda^0, \lambda^1, \lambda$ ..., one obtains

$O(\lambda^0)$: $H_0 \psi_n^{(0)} = E_n^{(0)} \psi_n^{(0)}$

$O(\lambda^1)$: $H_0 \psi_n^{(1)} + H_1 \psi_n^{(0)} = E_n^{(0)} \psi_n^{(1)} + E_n^{(1)} \psi_n^{(0)}$

$O(\lambda^2)$: $H_0 \psi_n^{(2)} + H_1 \psi_n^{(1)} = E_n^{(0)} \psi_n^{(2)} + E_n^{(1)} \psi_n^{(1)} + E_n^{(2)} \psi_n^{(0)}$.

It is convenient to fix the normalization of ψ_n by

$$(\psi_n^{(0)}, \psi_n) = \int \psi_n^{*(0)} \psi_n \, d^3\underline{x} = 1$$

i.e

$$\lambda(\psi_n^{0}, \psi_n) + \lambda^2(\psi_n^{(0)}, \psi_n^{(2)}) + \cdots = 0.$$

or equivalently

$$(\psi_n^{(0)}, \psi_n^{(1)}) = (\psi_n^{(0)}, \psi_n^{(2)}) = \cdots = 0.$$

First Order Correction:

The first order perturbation is obtained by the equation

$$H_0 \psi_n^{(1)} + H_1 \psi_n^{(0)} = E_n^{(0)} \psi_n^{(1)} + E_n^{(1)} \psi_n^{(0)}$$

Since the exact states $\psi_n^{(0)}$ form a complete orthonormal set, the states $\psi_n^{(i)}$ $i \geq 1$, can be expanded as a linear combination of $\psi_n^{(0)}$.

$$\psi_n^{(i)} = \sum_m C_{nm}^{(i)} \psi_m^{(0)} \quad i \geq 1$$

For $i=1$, we have.

$$\psi_n^{(1)} = \sum_m C_{nm}^{(1)} \psi_m^{(0)}.$$

So the first order approximation is now expressed as.

$$\sum_m C_{nm}^{(1)} \underbrace{H_0 \psi_m^{(0)}}_{} + H_1 \psi_n^{(0)} = \sum_m C_{nm}^{(1)} E_n^{(0)} \psi_m^{(0)} + E_n^{(1)} \psi_n^{(0)}$$

$$H_0 \psi_m^{(0)} = E_m^{(0)} \psi_m^{(0)}$$

$$\sum_m C_{nm}^{(1)} E_m^{(0)} \psi_m^{(0)} + H_1 \psi_n^{(0)} = \sum_m C_{nm}^{(1)} E_n^{(0)} \psi_m^{(0)} + E_n^{(1)} \psi_n^{(0)}$$

or

$$\sum_m C_{nm}^{(1)} \left(E_m^{(0)} - E_n^{(0)}\right) \psi_m^{(0)} + H_1 \psi_n^{(0)} = E_n^{(1)} \psi_n^{(0)} \quad \rightarrow (1)$$

By taking the inner product with $\psi_k^{(0)}$, we gi

$$\sum_m C_{nm}^{(1)} \left(E_m^{(0)} - E_n^{(0)}\right)\left(\psi_k^{(0)}, \psi_m^{(0)}\right) + \left(\psi_k^{(0)}, H_1 \psi_n^{(0)}\right) = E_n^{(1)} \left(\psi_k^{(0)}, \psi_n^{(0)}\right) \quad \rightarrow (2)$$

when $K = n$, equation (2) gives

$$E_n^{(1)} = \left(\psi_n^{(0)}, H_1 \psi_n^{(0)}\right)$$

$$E_n^{(1)} = (H_1)_{nn}$$

where $(H_1)_{nn}$ is the matrix element of H_1.

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The first order correction in the n-th energy eigenvalue due to perturbation "H_1" is the expectation value of H_1 in the unperturbed n-th eigenstate.

when $k \neq n$, the only non-zero terms are

$(k = m)$.

$$C_{nk}^{(1)} \left(E_k^{(0)} - E_n^{(0)} \right) = -\left(\psi_k^{(0)}, H_1 \psi_n^{(0)} \right)$$

this gives.

$$C_{nk}^{(1)} = \frac{(H_1)_{kn}}{\left(E_n^{(0)} - E_k^{(0)} \right)} \qquad (k \neq n)$$

Let us consider the state.

$$\psi_n \simeq \psi_n^{(0)} + \lambda \psi_n^{(1)}$$

The normalization of ψ_n gives.

$$1 = (\psi_n, \psi_n)$$

$$\simeq 1 + \lambda \left(C_{nn}^{(1)*} + C_{nn}^{(1)} \right)$$

or.

$$C_{nn}^{(1)*} + C_{nn}^{(1)} = 0.$$

Let.

$$C_{nn}^{(1)} = \alpha + i\beta.$$

$$C_{nn}^{(1)*} + C_{nn}^{(1)} = 2\alpha$$

$$\boxed{\alpha = 0.}$$

The normalization implied that the real part of $C_{nn}^{(1)}$ Vanishes i.e.

$$C_{nn}^{(1)} = i\beta.$$

The first order nth ~~correct~~ wavefn. ψ_n can be written as.

$$\psi_n = \psi_n^{(0)} + \lambda \psi_n^{(1)}$$

$$= \psi_n^{(0)} + \lambda \left[\sum_{m \neq n} C_{nm}^{(1)} \psi_m^{(0)} + C_{nn}^{(1)} \psi_n^{(0)} \right]$$

$$= \psi_n^{(0)} + \lambda \left[\sum_{m \neq n} C_{nm}^{(1)} \psi_m^{(0)} + i\beta \psi_n^{(0)} \right]$$

$$= (1 + i\lambda\beta) \psi_n^{(0)} + \lambda \sum_{m \neq n} C_{nm}^{(1)} \psi_m^{(0)}$$

Since we are interested in normalization to the first order in λ, therefore, we may write.

$$1 + i\lambda\beta \simeq \exp(i\beta\lambda)$$

so that.

$$\psi_n = e^{i\beta\lambda}\psi_n^{(0)} + \lambda \sum_{m\neq n} C_{nm}^{(1)}\psi_m^{(0)}$$

Let us look at the probability density:

$$P = |\psi_n \psi_n^{*}|$$

$$= \left(e^{i\beta\lambda}\psi_n^{(0)} + \lambda \sum_{m\neq n} C_{nm}^{(1)}\psi_m^{(0)}\right)\left(e^{-i\beta\lambda}\psi_n^{*(0)} + \lambda \sum_{m\neq n} C_{nm}^{*(1)}\psi_m^{*(0)}\right)$$

$$= \psi_n^{(0)}\psi_n^{*(0)} + \lambda \sum_{m\neq n} C_{nm}^{(1)*} e^{i\beta\lambda}\psi_n^{(0)}\psi_m^{(0)*} + \lambda \sum_{m\neq n} C_{nm}^{(1)} e^{-i\beta\lambda}\psi_m^{(0)}\psi_n^{*(0)} + \lambda^2$$

or.

$$(\psi_n, \psi_n) = (\psi_n^{(0)}, \psi_n^{(0)}) + 0 + 0 + \dots$$

This says that the total probability does not depend on the phase β. Therefore we can make any choice of phase, say, $\beta = 0$.

This gives $\boxed{C_{nn}^{(1)} = 0.}$

So, the n-th wavefunction ψ_n and energy eigenvalue E_n with first order correction are respectively.

$$\psi_n = \psi_n^{(0)} + \sum_{m\neq n} \frac{(H_1)_{mn}}{E_n^{(0)} - E_m^{(0)}} \psi_m^{(0)}$$

$\lambda = 1.$

$$E_n = E_n^{(0)} + (H_1)_{nn}$$

Second Order Correction:

For the 2nd order correction, we take

$$H_0 \psi_n^{(2)} + H_1 \psi_n^{(1)} = E_n^{(0)} \psi_n^{(2)} + E_n^{(1)} \psi_n^{(1)} + E_n^{(2)} \psi_n^{(0)}$$

we know

$$\psi_n^{(2)} = \sum_m C_{nm}^{(2)} \psi_m^{(0)} \quad , \; 2 = 2$$

$$\sum_m C_{nm}^{(2)} H_0 \psi_m^{(0)} + \sum_m C_{nm}^{(1)} H_1 \psi_m^{(0)}$$

$E_m^{(0)} \psi_m^{(0)}$

$$= \sum_m C_{nm}^{(2)} E_n^{(0)} \psi_m^{(0)} + \sum_m C_{nm}^{(1)} E_n^{(1)} \psi_m^{(0)} + E_n^{(2)} \psi_n^{(0)}$$

or

$$\sum_m C_{nm}^{(2)} \left(E_m^{0} - E_n^{(0)}\right) \psi_m^{(0)} = \sum_m C_{nm}^{(1)} (E_n^{(1)} - H_1) \psi_m^{(0)} + E_n^{(2)} \psi_n^{(0)}$$

Multiplying from the Left by $\psi_n^{*(0)}$ and integrate over whole space:

$$\sum_m C_{nm}^{(2)} (E_m^{(0)} - E_n^{(0)}) (\psi_n^{(0)}, \psi_m^{(0)})$$

$$= \sum_m C_{nm}^{(1)} E_n^{(1)} (\psi_n^{(0)}, \psi_m^{(0)}) - \sum_m C_{nm}^{(1)} (\psi_n^{(0)}, H_1 \psi_m^{(0)})$$

$$+ E_n^{(2)} (\psi_n^{(0)}, \psi_n^{(0)})$$

$\Rightarrow$

$$\sum_m C_{nm}^{(2)} (E_m^{(0)} - E_n^{(0)}) \delta_{nm} = \sum_m C_{nm}^{(1)} E_n^{(1)} \delta_{nm}$$

$$- \sum_m C_{nm}^{(1)} (\psi_n^{(0)}, H_1 \psi_m^{(0)}) + E_n^{(2)}$$

we know, when

$$C_{nn}^{(1)} = 0 \quad , \quad m = n$$

$$C_{nm}^{(1)} = \frac{(H_1)_{mn}}{(E_n^{(0)} - E_m^{(0)})} \quad , m \neq n.$$

therefore, when $m \neq n$.

$$E_n^{(2)} = \sum_{m \neq n} C_{nm}^{(1)} (\psi_n^{(0)}, H_1 \psi_m^{(0)})$$

$$E_n^{(2)} = \sum_{m \neq n} C_{nm}^{(1)} (H_1)_{nm}$$

$$E_n^{(2)} = \sum_{m \neq n} \frac{(H_1)_{nm} (H_1)_{mn}}{E_n^{(0)} - E_m^{(0)}}$$

The required 2nd order correction in E_n.

The 2nd order Correction to ψ_n:

we know the equ.

$$\sum_m C_{nm}^{(2)} \left(E_m^{(0)} - E_n^{(0)}\right) \psi_m^{(0)} = \sum_m C_{nm}^{(1)} \left(E_n^{(1)} - H_1\right) \psi_m^{(0)} + E_n^{(2)} \psi_n^{(0)}.$$

Taking the inner product with $\psi_k^{(0)}$ $k \neq n$, $k = m$.

$$\Rightarrow \sum_m C_{nm}^{(2)} \left(E_m^{(0)} - E_n^{(0)}\right) \left(\psi_k^{(0)}, \psi_m^{(0)}\right)^{=1}$$

$$= \sum_m C_{nm}^{(1)} E_n^{(1)} \left(\psi_k^{(0)}, \psi_m^{(0)}\right) - \sum_m C_{nm}^{(1)} \left(\psi_k^{(0)}, H_1 \psi_m^{(0)}\right) + E_n^{(2)} \left(\psi_k^{(0)}, \psi_n^{(0)}\right)^{=0}$$

or

$$C_{nk}^{(2)} \left(E_k^{(0)} - E_n^{(0)}\right) = \sum_m C_{nm}^{(1)} E_n^{(1)} \delta_{km} - \sum_m C_{nm}^{(1)} (H_1)_{km}.$$

$$C_{nk}^{(2)} = \frac{1}{\left(E_k^{(0)} - E_n^{(0)}\right)} \sum_m C_{nm}^{(1)} \left(E_n^{(1)} \delta_{km} - (H_1)_{km}\right)$$

Since

$$C^{(1)}_{nm} = \frac{(H_1)_{mn}}{E^{(0)}_n - E^{(0)}_m} \qquad m \neq n$$

$$E^{(1)}_n = (H_1)_{nn}$$

One can therefore get

$$C^{(2)}_{nk} = \frac{1}{\left(E^{(0)}_k - E^{(0)}_n\right)} \sum_{m \neq n} \frac{(H_1)_{mn}}{E^{(0)}_n - E^{(0)}_m} \left[(H_1)_{nn} \delta_{km} - (H_1)_{km}\right]$$

for $n = k$.

Let us consider the state

$$\psi_n \simeq \psi^{(0)}_n + \lambda \psi^{(1)}_n + \lambda^2 \psi^{(2)}_n$$

It is convenient to

we know from the normalization condition that

$$\left(\psi^{(0)}_n, \psi_n\right) = 1$$

and

$$\lambda \left(\psi^{(1)}_n, \psi_n\right) + \lambda^2 \left(\psi_n, \psi_n\right) + \cdots = 0$$

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The normalization condition gives

$$1 = (\psi_n, \psi_n)$$

$$= 1 + \lambda(C_{nn}^{(1)*} + C_{nn}^{(1)}) + \lambda^2 \left(C_{mn}^{(1)*} C_{mn}^{(1)} + C_{nn}^{(2)} + C_{nn}^{(2)*} \right)$$

($C_{nn}^{(1)*} + C_{nn}^{(1)} = 0$; $C_{mn}^{(1)*} C_{mn}^{(1)} = \sum_{m \neq n} |C_{nm}^{(1)}|^2$)

Also when $n = k \neq m$, then the term $\sum_{m \neq n} |C_{nm}^{(1)}|^2$

The co-efficient of λ^2 is zero, i.e

$$C_{nn}^{(2)} + C_{nn}^{(2)*} = -\sum_{m \neq n} |C_{nm}^{(1)}|^2$$

The phase is chosen such that

$$C_{nn}^{(2)} = C_{nn}^{(2)*}, \quad C_{nn}^{(2)} - \text{real}$$

So

$$C_{nn}^{(2)} = -\frac{1}{2} \sum_{m \neq n} \left| \frac{(H_1)_{mn}}{E_n^{(0)} - E_m^{(0)}} \right|^2$$

Since the 2nd order correction in wavefn ψ_n is

$$\psi_n^{(2)} = \sum_{m \neq n} C_{nm}^{(2)} \psi_m^{(0)} + C_{nn}^{(2)} \psi_n^{(0)}$$

$$\psi_n^{(2)} = \sum_{m \neq n} \left[\sum_{k \neq n} \frac{(H_1)_{mk} (H_1)_{km}}{\left(E_n^{(0)} - E_m^{(0)}\right)\left(E_n^{(0)} - E_k^{(0)}\right)_{n \neq m}} - \frac{(H_1)_{nn} (H_1)_{nm}}{\left(E_n^{(0)} - E_m^{(0)}\right)^2} \right] \psi_m^{(0)}$$

$$- \frac{1}{2} \sum_{m \neq n} \left| \frac{(H_1)_{mn}}{E_n^{(0)} - E_m^{(0)}} \right|^2 \psi_n^{(0)}$$

The n-th wavefn ψ_n to the 2nd order correction is

$$\psi_n = \psi_n^{(0)} + \sum_{m \neq n} \left[\frac{(H_1)_{nm}}{E_n^{(0)} - E_m^{(0)}} - \frac{(H_1)_{nn} (H_1)_{nm}}{\left(E_n^{(0)} - E_m^{(0)}\right)^2} + \sum_{k \neq n} \frac{(H_1)_{nk} (H_1)_{km}}{\left(E_n^{(0)} - E_m^{(0)}\right)\left(E_n^{(0)} - E_k^{(0)}\right)} \right] \psi_m^{(0)}$$

$$- \frac{1}{2} \sum_{m \neq n} \left| \frac{(H_1)_{mn}}{E_n^{(0)} - E_m^{(0)}} \right|^2 \psi_n^{(0)}$$

and the energy is

$$E_n = E_n^{(0)} + (H_1)_{nn} + \sum_{m \neq n} \frac{(H_1)_{nm} (H_1)_{mn}}{E_n^{(0)} - E_m^{(0)}}$$