Perturbation Theory

Hamiltonian: $H(\lambda) = H_0 + \lambda H_1$

solution to eigenvalue problem for H_0 is known

$$H_0 |n\rangle = E_n |n\rangle$$

discrete energies E_n

complete set of orthonormal eigenstates

$$\langle n|m\rangle = \delta_{mn}$$

$$\sum_n |n\rangle\langle n| = 1$$

eigenvalue equation for $H(\lambda)$:

$$H(\lambda)|n(\lambda)\rangle = E_n(\lambda)\,|n(\lambda)\rangle$$

assume that $E_n(\lambda)$ and $|n(\lambda)\rangle$
have expansions in powers of λ

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

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

solve eigenvalue problem order-by-order in λ

insert expansions in powers of λ
into eigenvalue equation for H

$$(H_0 + \lambda H_1)\left(|n\rangle + \lambda |n\rangle^{(1)} + \lambda^2 |n\rangle^{(2)} + \cdots\right)$$

$$= \left(E_n + \lambda E_n^{(1)} + \lambda^2 E_n^{(1)} + \cdots\right)\left(|n\rangle + \lambda|n\rangle^{(1)} + \lambda^2 |n\rangle^{(2)} + \cdots\right)$$

expand in powers of λ

match powers of λ on both sides:

λ^0: $H_0 |n\rangle = E_n |n\rangle$

(eigenvalue equation for H_0)

λ^1: $H_0 |n\rangle^{(1)} + H_1 |n\rangle = E_n |n\rangle^{(1)} + E_n^{(1)} |n\rangle$

must solve for $E_n^{(1)}$, $|n\rangle^{(1)}$

λ^2: $H_0 |n\rangle^{(2)} + H_1 |n\rangle^{(1)} = E_n |n\rangle^{(2)} + E_n^{(1)} |n\rangle^{(1)} + E_n^{(2)} |n\rangle$

must solve for $E_n^{(2)}$, $|n\rangle^{(2)}$

1^{st} order perturbation theory

order-λ terms in eigenvalue equation for $H(\lambda)$

$$H_0 |n\rangle^{(1)} + H_1 |n\rangle = E_n |n\rangle^{(1)} + E_n^{(1)} |n\rangle$$

left-multiply by bet $\langle n|$:

$$\underbrace{\langle n| H_0 |n\rangle^{(1)}}_{\langle n| E_n} + \langle n| H_1 |n\rangle = E_n \langle n|n\rangle^{(1)} + E_n^{(1)} \underbrace{\langle n|n\rangle}_{1}$$

$$E_n \cancel{\langle n|n\rangle^{(1)}} + \langle n| H_1 |n\rangle = E_n \cancel{\langle n|n\rangle^{(1)}} + E_n^{(1)}$$

1^{st} order perturbation to energies

$$\boxed{E_n^{(1)} = \langle n| H_1 |n\rangle}$$

left-multiply by bet $\langle m|$ where $m \neq n$:

$$\underbrace{\langle m| H_0 |n\rangle^{(1)}}_{\langle m| E_m} + \langle m| H_1 |n\rangle = E_n \langle m|n\rangle^{(1)} + E_n^{(1)} \underbrace{\langle m|n\rangle}_{0}$$

$$E_m \langle m|n\rangle^{(1)} + \langle m| H_1 |n\rangle = E_n \langle m|n\rangle^{(1)}$$

$$(E_n - E_m) \langle m|n\rangle^{(1)} = \langle m| H_1 |n\rangle$$

can solve for $\langle m|n\rangle^{(1)}$ only if $E_m \neq E_n$

if $E_m \neq E_n$,

$$\boxed{\langle m|n\rangle^{(1)} = \frac{\langle m|H_1|n\rangle}{E_n - E_m} \qquad m \neq n}$$

1st order perturbation to eigenstate: $|n\rangle^{(1)}$

insert completeness relation

$$|n\rangle^{(1)} = \hat{1}\,|n\rangle^{(1)} = \left(\sum_m |m\rangle\langle m|\right)|n\rangle^{(1)}$$

$$= \sum_m |m\rangle \left(\langle m|n\rangle^{(1)}\right) = \sum_m \langle m|n\rangle^{(1)}\,|m\rangle$$

$$= \langle n|n\rangle^{(1)}\,|n\rangle + \sum_{m\neq n} \langle m|n\rangle^{(1)}\,|m\rangle$$

$$\boxed{|n\rangle^{(1)} = \langle n|n\rangle^{(1)}\,|n\rangle + \sum_{m\neq n} \frac{\langle m|H_1|n\rangle}{E_n - E_m}\,|m\rangle}$$

coefficient $\langle n|n\rangle^{(1)}$ of $|n\rangle$ is undetermined, because it can be changed by multiplying $|n(\lambda)\rangle$ by an overall constant

$$[1 + \lambda(a+ib)]\,|n(\lambda)\rangle = |n\rangle + \lambda\left(|n\rangle^{(1)} + (a+ib)|n\rangle\right) + O(\lambda^2)$$

changes coefficient of $|n\rangle$ to $\langle n|n\rangle^{(1)} + a + ib$

can choose a and b to cancel real and imaginary part of $\langle n|n\rangle^{(1)}$

The equation for the 1st order coefficients $\langle m|n\rangle^{(1)}$ is

$$(E_n - E_m)\langle m|n\rangle^{(1)} = \langle m|H_1|n\rangle$$

If $E_m = E_n$, this equation is satisfied if $\langle m|H_1|n\rangle = 0$.

$$\boxed{\begin{array}{l}\text{1st order perturbation to energies} \\ \qquad E_n^{(1)} = \langle n|H_1|n\rangle\end{array}}$$

The general condition for its validity is either

- the state $|n\rangle$ is nondegenerate (no other state $|m\rangle$ with $E_m = E_n$)

OR

- the state $|n\rangle$ is degenerate but the degenerate states $|m\rangle$ with $E_m = E_n$ are chosen so that $\langle m'|H_1|m\rangle = 0$ for any two states $|m\rangle$ and $|m'\rangle$ with energy E_n.

2^{nd} order perturbation theory

order-λ terms in eigenvalue problem for $H(\lambda)$

$$H_0|n\rangle^{(2)} + H_1|n\rangle^{(1)} = E_n|n\rangle^{(2)} + E_n^{(1)}|n\rangle^{(1)} + E_n^{(2)}|n\rangle$$

left-multiply by $\langle n|$:

$$\underbrace{\langle n|H_0}_{\langle n|E_n}|n\rangle^{(2)} + \langle n|H_1|n\rangle^{(1)} = E_n\langle n|n\rangle^{(2)} + E_n^{(1)}\langle n|n\rangle^{(1)} + E_n^{(2)}\underbrace{\langle n|n\rangle}_{1}$$

$$E_n\cancel{\langle n|n\rangle^{(2)}} + \langle n|H_1|n\rangle^{(1)} = E_n\cancel{\langle n|n\rangle^{(2)}} + E_n^{(1)}\langle n|n\rangle^{(1)} + E_n^{(2)}$$

$$E_n^{(2)} = \langle n|H_1|n\rangle^{(1)} - E_n^{(1)}\langle n|n\rangle^{(1)}$$

insert solution for $|n\rangle^{(1)}$:

$$E_n^{(2)} = \langle n|H_1\left(\langle n|n\rangle^{(1)}|n\rangle + \sum_{m\neq n}\frac{\langle m|H_1|n\rangle}{E_n-E_m}|m\rangle\right) - E_n^{(1)}\langle n|n\rangle^{(1)}$$

$$= \cancel{\langle n|H_1|n\rangle\langle n|n\rangle^{(1)}} + \sum_{m\neq n}\frac{\langle m|H_1|n\rangle}{E_n-E_m}\langle n|H_1|m\rangle - \cancel{E_n^{(1)}\langle n|n\rangle^{(1)}}$$

2^{nd} order perturbation to energies

$$\boxed{E_n^{(2)} = \sum_{m:E_m\neq E_n}\frac{\langle n|H_1|m\rangle\langle m|H_1|n\rangle}{E_n-E_m}}$$

sum over "virtual states"