Perturbation Theory

Time-independent Perturbation Theory:

This set of problems are related to causing a perturbation into the Hamiltonean and seeing how this affects the energy levels and the differents wave functions.

We have our original problem (solved) and ad an extra potential to see how the system reacts to it: for instances we have a quantum harmonic osciltor but what happens if we apply some external eletric field? In most cases we can't solve completely this new problem, so we search for approximate solutions for the perturbated energy levels - wave functions.

Our Hamiltonean is written as: $\underbrace{H = H^0 + \lambda H'}$

→ perturbation / new potential
λ is a small number $(0,1]$ which measures the intensity of the perturbation (in most cases $\lambda = 1$ but is a important factor to the theory)

original Hamiltonean (already solved)

We already know all solutions for: $H^0|n^0\rangle = E_n^0|n^0\rangle$ (eigen-energy functions / values)

We want to solve $H|n\rangle = E_n|n\rangle$

power series of λ and then set $\lambda = 1$

hypothesis: $|n\rangle$ and E_n can be written as a sum of perturbated terms:

for each n
$$\begin{cases} |n\rangle = |n^0\rangle + \lambda|n^1\rangle + \lambda^2|n^2\rangle + \dots \\ E_n = \underbrace{E_n^0}_{\text{come from } H^0} + \underbrace{\lambda E_n^1 + \lambda^2 E_n^2 + \dots}_{\text{Come from } H'} \end{cases}$$

→ aproximation order / Series of λ order

So $H|n\rangle = E_n|n\rangle \Rightarrow (H^0 + \lambda H')[|n^0\rangle + \lambda|n^1\rangle + \lambda^2|n^2\rangle + \dots] = [E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \dots][|n^0\rangle + \lambda|n^1\rangle + \lambda^2|n^2\rangle + \dots]$

Organizing the equation by powers of λ:

$$H^0|n^0\rangle + \lambda(H^0|n^1\rangle + H'|n^0\rangle) + \lambda^2(H^0|n^2\rangle + H'|n^1\rangle) + \dots = E_n^0|n^0\rangle + \lambda(E_n^0|n^1\rangle + E_n^1|n^0\rangle) + \lambda^2(E_n^0|n^2\rangle + E_n^1|n^1\rangle + E_n^2|n^0\rangle) + \dots$$

The coeficients of each order of λ^m must be equal which leed us to order corrections equations:

Order zero: $H^0|n^0\rangle = E_n^0|n^0\rangle$ independent of perturbation H'

First Order: $H^0|n^1\rangle + H'|n^0\rangle = E_n^0|n^1\rangle + E_n^1|n^0\rangle$

Second Order: $H^0|n^2\rangle + H'|n^1\rangle = E_n^0|n^2\rangle + E_n^1|n^1\rangle + E_n^2|n^0\rangle$

We usually calcute the perturbation up to the second order.

The zero order equation it's just the eigen vector equation for H^0 our original Hamiltonean. The first order is:

$$H^0|n^1\rangle + H'|n^0\rangle = E_n^0|n^1\rangle + E_n^1|n^0\rangle \xrightarrow{*\langle n^0|} \langle n^0|\underbrace{H^0|n^1\rangle}_{E_n^0\langle n^0|n^1\rangle} + \langle n^0|H'|n^0\rangle = \underbrace{\langle n^0|E_n^0|n^1\rangle}_{E_n^0\langle n^0|n^1\rangle} + \underbrace{\langle n^0|E_n^1|n^0\rangle}_{E_n^1\langle n^0|n^0\rangle}$$

$$E_n^0\cancel{\langle n^0|n^1\rangle} + \langle n^0|H'|n^0\rangle = E_n^0\cancel{\langle n^0|n^1\rangle} + E_n^1 \Rightarrow \boxed{E_n^1 = \langle n^0|H'|n^0\rangle}$$

First Order Correction to the energy

Expectation Value of the perturbed Hamiltonean on our original state.

Let us dot now our first order equation by another eigen-state of our original Hamiltonean H^0; $|m^0\rangle$; $m\neq n$ doting the eq by $\langle m^0|$ we have:

$$\langle m^0|H^0|n^1\rangle + \langle m^0|H'|n^0\rangle = E_n^0\langle m^0|n^1\rangle + E_n^1\cancel{\langle m^0|n^0\rangle}^{\,0 \text{ orthogonal}}$$

$E_m^0\langle m^0|n^1\rangle$

$$\hookrightarrow E_m^0\langle m^0|n^1\rangle + \langle m^0|H'|n^0\rangle = E_n^0\langle m^0|n^1\rangle \longrightarrow \boxed{\langle m^0|n^1\rangle = \frac{\langle m^0|H'|n^0\rangle}{E_n^0 - E_m^0}}$$

Components of the first order state corection into our original state basis of H^0

$\rightarrow$ for all $m\neq n$

but what about the component in $|n^0\rangle$?

Our perturbed state will be: $|n\rangle = |n^0\rangle + |n^1\rangle$:

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

$\rightsquigarrow$ Perturbed state correction up to first order

Looking at the second order equation now: $H^0|n^2\rangle + H'|n^1\rangle = E_n^0|n^2\rangle + E_n^1|n^1\rangle + E_n^2|n^0\rangle$ doting $\langle n^0|$ we have:

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

; however $|n^0\rangle$ and $|n^1\rangle$ are orthogonal

$\cancel{E_n^0\langle n^0|n^2\rangle}$

$\Rightarrow E_n^2 = \langle n^0|H'|n^1\rangle$ opening $|n^1\rangle$ we have:

$$E_n^2 = \sum_m \frac{\langle n^0|H'|m^0\rangle\langle m^0|H'|n^0\rangle}{E_m^0 - E_n^0}$$

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

Second Order energy correction

$\hookrightarrow$ This theory is for the case of non degenerate energy spectrum. If we came across degenerancy we must turn ourselfes to degenerate perturbation theory which will be tackled next.

But what if our energy spectrum is degenerated?

Degenerate Perturbation Theory:

→ The correction $\frac{1}{E_m^0 - E_n^0}$ blows up and does not make sense anymore.

What happens if our original unperturbed states are degenerate and different states shares the same energy levels? Suppose for instance we have a two-fold degenerancy for levels a, b;

$$H^0 \psi_a^0 = E^0 \psi_a^0 \; ; \; H^0 \psi_b^0 = E^0 \psi_b^0$$ and of corse since both are eigenstates: $\langle \psi_a^0 | \psi_b^0 \rangle = 0$

We can write the unpertubed states (with eigen value E^0) as $\psi^0 = \alpha \psi_a^0 + \beta \psi_b^0$ with same Eigenvalue E^0. But how do we construct this state and apply perturbation?

Looking at the first order equation: $H^0 \psi^1 + H^1 \psi^0 = E^0 \psi^1 + E^1 \psi^0$ doting by $\langle \psi_a^0 |$ we have:

$$\langle \psi_a^0 | H^0 | \psi^1 \rangle + \langle \psi_a^0 | H^1 | \psi^0 \rangle = E^0 \langle \psi_a^0 | \psi^1 \rangle + E^1 \langle \psi_a^0 | \psi^0 \rangle$$ remembering that $\psi^0 = \alpha \psi_a^0 + \beta \psi_b^0$

$$\alpha \cancel{\langle \psi_a^0 | \psi^1 \rangle} + \langle \psi_a^0 | H^1 | \alpha \psi_a^0 + \beta \psi_b^0 \rangle = E^0 \cancel{\langle \psi_a^0 | \psi^1 \rangle} + E^1 \langle \psi_a^0 | \alpha \psi_a^0 + \beta \psi_b^0 \rangle$$

$$\alpha \underbrace{\langle \psi_a^0 | H^1 | \psi_a^0 \rangle}_{W_{aa}} + \beta \underbrace{\langle \psi_a^0 | H^1 | \psi_b^0 \rangle}_{W_{bb}} = E^1 \alpha \Rightarrow \underline{\alpha W_{aa} + \beta W_{ab} = \alpha E^1} \; ; \text{ where } \boxed{W_{ij} \equiv \langle \psi_i^0 | H^1 | \psi_j^0 \rangle}$$

If we return to first order equation and dot it by $\langle \psi_b^0 |$ we will get: $\underline{\alpha W_{ba} + \beta W_{bb} = \beta E^1}$

$$\boxed{\begin{pmatrix} W_{aa} & W_{ab} \\ W_{ba} & W_{bb} \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = E^1 \begin{pmatrix} \alpha \\ \beta \end{pmatrix}}$$

In the states which not presents degenerancy we can use non degenerade perturbation theory

→ W-Matrix; $E^{1's}$ are its eigenvalues and thus the first order correction to the degenerate energy levels.

Mathmatically speaking we are constructing an eigenbasis into the degenerate subspace. In the case of a n-fold degenerancy we will have a similar thing but with a $n \times n$ matrix whose elements are $W_{ij} = \langle \psi_i^0 | H^1 | \psi_j^0 \rangle$

The eigenvalues $E_\pm^1$ are in this 2x2 case:

$$\boxed{E_\pm^{(1)} = \frac{1}{2} \left[W_{aa} + W_{bb} \pm \sqrt{(W_{aa} - W_{bb})^2 + 4 |W_{ab}|^2} \right]}$$ First order energy correction

→ if $\alpha = 0$ or $\beta = 0$ we fall in non-degenerade perturbation theory

The process would be something like:

$$H^0 = \begin{pmatrix} \epsilon_1 & & & \\ & \boxed{\begin{matrix} \epsilon & \\ & \epsilon \end{matrix}} & & \\ & & \ddots & \\ & & & \epsilon_n \end{pmatrix}$$ → states ψ_a^0 and ψ_b^0 such that $E_a^0 = E_b^0 = \epsilon$

Subspace $\vec{v}$ considered; we construc W by $W_{ij} = \langle \psi_i^0 | H^1 | \psi_j^0 \rangle$ now diagonalize W

→ $\det(W - \mu \mathbb{1}) = 0$ → $\mu_a, \; \vec{V}_a = \begin{pmatrix} A \\ B \end{pmatrix}$ → $\psi_I = A \psi_a + B \psi_b$; $\underline{E_I = \epsilon + \mu_a}$

$\mu_b, \; \vec{V}_b = \begin{pmatrix} C \\ D \end{pmatrix}$ → $\psi_{II} = C \psi_a + D \psi_b$; $\underline{E_{II} = \epsilon + \mu_b}$

state correction to first order

energy up to first order

if $\mu_a \neq \mu_b$ → no more degenerancy

The second order correction to the energy will be:

$$E_I^{(2)} = \sum_{k \neq I, II} \frac{|\langle \psi_k^0 | H^1 | \psi_I \rangle|^2}{\epsilon - E_k^0} \; ; \; E_{II}^{(2)} = \sum_{k \neq I, II} \frac{|\langle \psi_k^0 | H^1 | \psi_{II} \rangle|^2}{\epsilon - E_k^0}$$