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now take adjoint of term.

$$V^{\dagger}_{nm} = \int (\psi_n^{*(0)} V \psi_m^{(0)})^{\dagger} d\tau$$

$$V^{\dagger}_{nm} = \int \psi_m^{*(0)} V \psi_n^{(0)} d\tau$$

$$= V_{mn}$$

As we have $V^{\dagger}_{nm} = V_{mn}$. So it satisfies the following property -

$$V^{*}_{nm} = V_{mn}$$

So we can take $V_{nm} = |V_{nm}|$

substitue it in eq (5) - then we have 2nd order energy.

$$E_n^{(2)} = -\sum_m \frac{|V_{nm}|^2}{(E_m^{(0)} - E_n^{(0)})}$$

this is the 2nd order correction in energy where we have taken the condition $m \neq n$ where 's' is the intermideat state and at ground state there is no variation in energy.

Now Write the energy in the form of series

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

substitute value of Ist and 2nd order

equations and put $\lambda = 1$, so we have

$$E_n = E_n^{(0)} + V_{nn} + \sum_m \frac{(-1)\,|V_{nm}|^2}{(E_m^{(0)} - E_n^{(0)})}$$

This is the variation in Ist and 2nd order equation of energy due to ~~pert~~ variation potential.

Lec #9:

21-5-15

Second order correction to wave function:

write the 2nd order equation:

$$H^{(0)}\psi_n^{(2)} + V\psi_n^{(1)} = E_n^{(0)}\psi_n^{(2)} + E_n^{(1)}\psi_n^{(1)} + E_n^{(2)}\psi_n^{(0)}$$

$$(H^{(0)} - E_n^{(0)})\psi_n^{(0)} = E_n^{(2)}\psi_n^{(0)} + E_n^{(1)}\psi_n^{(1)} - V\psi_n^{(1)}$$

Now rearrange this equation:

$$(H^{(0)} - E_n^{(0)})\psi_n^{(0)} = E_n^{(2)}\psi_n^{(0)} + E_n^{(1)}\psi_n^{(1)} - V\psi_n^{(1)}$$

Now xing this equation by $\psi_m^{(0)*}$ on both sides and integrate wrt all coordinates.

$$\int \psi_m^{(0)*}(H^{(0)} - E_n^{(0)})\psi_n^{(2)}\,d\tau = \int \psi_m^{(0)*} E_n^{(2)}\psi_n^{(0)}\,d\tau + \int \psi_m^{(0)*} E_n^{(1)}\psi_n^{(1)} - \int \psi_m^{(0)*} V\psi_n^{(1)}\,d\tau$$

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Now take Ist L.H.S and solve it.

$$\int \psi_m^{(0)*}(H^{(0)} - E_n^{(0)})\psi_n^{(2)}\,d\tau$$

as $H^{(0)}$ operator can not operate on $\psi_n^{(2)}$ it

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can operate only on $\psi_m^{(0)*}$ so we take only the 1st term:

$$\psi_m^{(0)*} H^{(0)} = H^{(0)} \psi_m^{(0)*}$$

$$\psi_m^{(0)*} H^{(0)} = E_m^{(0)*} \psi_m^{(0)*}$$

$$\because E_m^{*(0)} = E_m^{(0)}$$

so we have $H^{(0)} \psi_m^{(0)*} = E_m^{(0)} \psi_m^{(0)*}$

as energy is a constant value so we can change its order again.

$$H^{(0)} \psi_m^{(0)*} = \psi_m^{(0)*} E_m^{(0)}$$

Now substitute this value in the integral.

$$\int \psi_m^{(0)*} (E_m^{(0)} - E_n^{(0)}) \psi_n^{(2)} d\tau = \int \psi_m^{(0)*} E_n^{(2)} \psi_n^{(0)} d\tau + \int \psi_m^{(0)*} E_n^{(1)} \psi_n^{(1)} d\tau - \int \psi_m^{(0)*} V \psi_n^{(1)} d\tau \quad \text{— 6a}$$

On the R.H.S take out the energy terms out side the integral.

$$= E_n^{(2)} \int \psi_m^{(0)*} \psi_n^{(0)} d\tau + E_n^{(1)} \int \psi_m^{(0)*} \psi_n^{(1)} d\tau - \int \psi_m^{(0)*} V \psi_n^{(1)} d\tau \quad \text{— 6b}$$

in the first term write the integral in the form of cronomical delta:

$$\because \int \psi_m^{(0)} \psi_n^{(0)} d\tau = \delta_{mn}$$

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$$\int \psi_m^{(0)*}(E_m^{(0)}-E_n^{(0)})\psi_n^{(1)}\,d\tau = E_n^{(2)}\delta_{mn} + E_n^{(1)}\int \psi_m^{(0)*}\psi_n^{(1)}\,d\tau - \int \psi_m^{(0)*} V \psi_n^{(1)}\,d\tau \quad \text{— 6c}$$

we take the condition that $n \neq m$ so the cronanical delta becomes zero so $\delta_{mn} = 0$

$$\int \psi_m^{(0)*}(E_m^{(0)}-E_n^{(0)})\psi_n^{(1)}\,d\tau = 0 + E_n^{(1)}\int \psi_m^{(0)*}\psi_n^{(1)}\,d\tau - \int \psi_m^{(0)*} V \psi_n^{(1)}\,d\tau \quad \text{— 6d}$$

substitute $\psi_n^{(1)}$ and $\psi_n^{(2)}$ in eq (6d).
where we take

$$\psi_n^{(1)} = \sum_s C_{ns}^{(1)} \psi_s^{(0)}$$

$$\psi_n^{(2)} = \sum_s C_{ns}^{(2)} \psi_s^{(0)}$$

Now putting value in integral.

$$\int \psi_m^{(0)*}(E_m^{(0)} - E_n^{(0)}) \sum_s C_{ns}^{(2)} \psi_s^{(0)}\,d\tau = E_n^{(1)} \int \psi_m^{(0)*} \sum_s C_{ns}^{(1)} \psi_s^{(0)}\,d\tau - \int \psi_m^{(0)*} V \sum_s C_{ns}^{(1)} \psi_s^{(0)}\,d\tau$$

take out the constants out side of integral.

$$(E_m^{(0)} - E_n^{(0)}) \sum_s C_{ns}^{(2)} \int \psi_m^{(0)*} \psi_s^{(0)}\,d\tau = E_n^{(1)} \sum_s C_{ns}^{(1)} \int \psi_m^{(0)*} \psi_s^{(0)}\,d\tau - \sum_s C_{ns}^{(1)} \int \psi_m^{(0)*} V \psi_s^{(0)}\,d\tau$$

write the integrals in the form of cronomical delta.

$$(E_m^{(0)} - E_n^{(0)}) \sum_s C_{ns}^{(2)} \delta_{ms} = E_n^{(1)} \sum_s C_{ns}^{(1)} \delta_{ms} - \sum_s C_{ns}^{(1)} \int \psi_m^{(0)*} V \psi_s^{(0)}\,d\tau$$

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Now apply the condition that m=s, then due to normalization condition crononical delta $\delta_{ms}=1$.

$$(E_m^{(0)}-E_n^{(0)})\sum_s C_{ns}^{(2)} = E_n^{(1)}\sum_s C_{ns}^{(1)} - \sum_s C_{ns}^{(1)}\int \psi_m^{(0)*} V \psi_s^{(0)} d\tau$$

Now remove sigma notation.

$$(E_m^{(0)}-E_n^{(0)}) C_{ns}^{(2)} = E_n^{(1)} C_{ns}^{(1)} - C_{ns}^{(1)}\int \psi_m^{(0)*} V \psi_s^{(0)} d\tau$$

Now write the potential terms in terms of symbol.

i.e $\int \psi_m^{(0)*} V \psi_s^{(0)} d\tau = V_{ms}$

$$(E_m^{(0)}-E_n^{(0)}) C_{ns}^{(2)} = E_n^{(1)} C_{ns}^{(1)} - C_{ns}^{(1)} V_{ms}$$

As we have applied the condition that s=m so replace the value of s by m for relations having cronoical delta previously only.

$$(E_m^{(0)}-E_n^{(0)}) C_{nm}^{(2)} = E_n^{(1)} C_{nm}^{(1)} = C_{ns}^{(1)} V_{ms} \quad \text{— 7}$$

Divide on both sides by $(E_m^{(0)}-E_n^{(0)})$

$$C_{nm}^{(2)} = E_n^{(1)} C_{nm}^{(1)} \frac{1}{E_m^{(0)}-E_n^{(0)}} - \frac{C_{ns}^{(1)}}{E_m^{(0)}-E_n^{(0)}} V_{ms} \quad \text{— 8}$$

Substitute $C_{nm}^{(1)}$ $E_m^{(1)}$ and $C_{ns}^{(1)}$ in eq 8.

$$C_{nm}^{(1)} = \frac{-V_{nm}}{(E_m^{(0)}-E_n^{(0)})}$$

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