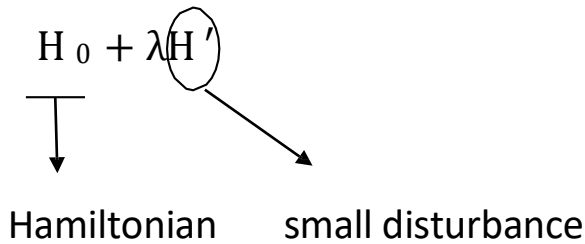


## Disturbances in the Hamiltonian during the Schrödinger equation :



For example when we have one electron that us “ shield” another electron.

$(H_0 + \lambda H') | \phi_n \rangle = E_n | \phi_n \rangle$  when  $\lambda=0$  we are in one undisturbed state.

According to HILBERT:

$$H_0 | \phi_n^{(0)} \rangle = E_n^{(0)} | \phi_n^{(0)} \rangle \text{ and } | \phi_n \rangle = \sum_m \alpha_{nm} | \phi_n^{(0)} \rangle$$

The perturbative method is based on expressing  $E_n$  as Taylor expansions; when at  $E_n^{(0)}$ , we have only one “eigenvector” :

$| \phi_n^{(0)} \rangle$ . Then:

$$\lim_{\lambda \rightarrow 0} E_n(\lambda) = E_n^{(0)} \text{ and } \lim_{\lambda \rightarrow 0} | \phi_n(\lambda) \rangle = | \phi_n^{(0)} \rangle$$

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

$$| \phi_n(\lambda) \rangle = | \phi_n \rangle = | \phi_n^{(0)} \rangle + \lambda | \phi_n^{(1)} \rangle + \lambda^2 | \phi_n^{(2)} \rangle + \dots$$

Since the components of  $| \phi_n(\lambda) \rangle$  are integral members of it, they comply with the rules of the group: distinct elements independent of each other.

Its norm is 1:  $\langle \Phi_n^{(0)} | \Phi_n(\lambda)^{(0)} \rangle = 1, \lambda = 0$

If  $\lambda \neq 0$ , such as  $\langle \Phi_n^{(0)} | \Phi_n^{(1)} \rangle$  the result is  $= 0$

Let's remember, I repeat, to Taylor and the headquarters developments of series functions based on derivatives.

$$\begin{aligned} (H_0 + \lambda H') (|\phi_n^{(0)} \rangle + \lambda |\phi_n^{(1)} \rangle + \lambda^2 |\phi_n^{(2)} \rangle + \dots) = \\ = (E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots) (|\phi_n^{(0)} \rangle + \lambda |\phi_n^{(1)} \rangle \\ + \lambda^2 |\phi_n^{(2)} \rangle + \dots) \end{aligned}$$



"a"

Yes now we separate the equations in order 0 from the in order 1 and from those of order 2 and so on... we obtain each of the terms that make up the  $E_n$  global.

Regarding the term  $\lambda^0: H_0 |\phi_n^{(0)} \rangle = E_n^{(0)} |\phi_n^{(0)} \rangle$

Regarding the  $\lambda^1: H_0 |\phi_n^{(1)} \rangle + H' |\phi_n^{(0)} \rangle = E_n^{(0)} |\phi_n^{(1)} \rangle + E_n^{(1)} |\phi_n^{(0)} \rangle$  expression that we will call (\*)

$$\text{I respecte a } \lambda^2: H_0 |\phi_n^{(2)} \rangle + H' |\phi_n^{(1)} \rangle = E_n^{(0)} |\phi_n^{(2)} \rangle + E_n^{(1)} |\phi_n^{(1)} \rangle + E_n^{(2)} |\phi_n^{(0)} \rangle$$



"b"

If we now take  $\lambda^1$  and multiply  $\langle \Phi_n^{(0)} |$ :

$$0 = \langle \Phi_n^{(0)} | H_0 - E_n^{(0)} | \Phi_n^{(1)} \rangle + \langle \Phi_n^{(0)} | H' - E_n^{(1)} | \Phi_n^{(0)} \rangle$$

Considering that the scalar product of unit vectors is = 1 if they are linearly dependent and = 0 if they are linearly independent. We solve that:

$$E_n^{(1)} = \langle \Phi_n^{(0)} | H' | \Phi_n^{(0)} \rangle = H'_{nn}$$

As the terms of  $E_n$  and of  $|\Phi_n(\lambda)\rangle$  increase from  $\lambda^0$  to  $\lambda^n \dots$  they become less and less likely to occur.

Now I will establish the framework to deduce the aspect of  $|\Phi^{(1)}\rangle$  and that of  $E_n^{(2)}$ ; first we represent

$$|\Phi_n^{(1)}\rangle = \sum_k |\Phi_k^{(0)}\rangle \langle \Phi_k^{(0)} | \Phi_n^{(1)} \rangle$$

Knowing that normalization is:

$$\langle \Phi_k^{(0)} | \Phi_k^{(0)} \rangle = 1 = \langle \Phi_k^{(0)} | \Phi_k^{(0)} \rangle$$

If we then multiply the order expression  $\lambda^1$  by  $\langle \Phi_k^{(0)} |$ :

$$0 = \langle \Phi_k^{(0)} | (H_0 - E_n^{(0)}) | (\sum_k |\Phi_k^{(0)}\rangle \langle \Phi_k^{(0)} | \Phi_n^{(1)} \rangle) + \langle \Phi_k^{(0)} | (H' - E_n^{(1)}) | \Phi_n^{(0)} \rangle$$

And now I expand this as follows:

$$E_k^{(0)} = H_0$$

$$0 = \sum_k (E_k^{(0)} - E_n^{(0)}) \langle \Phi_k^{(0)} | \Phi_n^{(1)} \rangle + H'_{kn} - \delta_{kn} \cdot E_n^{(1)}$$

$$\text{Since } \langle \Phi_k^{(0)} | \Phi_n^{(1)} \rangle = \sum_k \frac{H'_{kn} - \delta_{kn} \cdot E_n^{(1)}}{(E_k^{(0)} - E_n^{(0)})}$$

If  $k = n$ , I retrieve a previous expression to formulate:

$$|\Phi_n^{(1)}\rangle = \sum_k \frac{H'_{kn} - \delta_{kn} E_n^{(1)}}{(E_k^{(0)} - E_n^{(0)})} |\Phi_k^{(0)}\rangle.$$

To elucidate  $E_n^{(2)}$  we can take “a” and expand it and then isolate the terms that contain  $\lambda^2$  (“b”):

$$\begin{aligned} & H_0 |\Phi_n^{(0)}\rangle + \lambda H_0 |\Phi_n^{(1)}\rangle + \lambda^2 H_0 |\Phi_n^{(2)}\rangle + \lambda H' |\Phi_n^{(0)}\rangle + \\ & + \lambda^2 H' |\Phi_n^{(1)}\rangle + \lambda^3 H' |\Phi_n^{(2)}\rangle = E_n^{(0)} |\Phi_n^{(0)}\rangle + \lambda E_n^{(0)} |\Phi_n^{(1)}\rangle + \\ & + \lambda^2 E_n^{(0)} |\Phi_n^{(2)}\rangle + \lambda E_n^{(1)} |\Phi_n^{(0)}\rangle + \lambda^2 E_n^{(1)} |\Phi_n^{(1)}\rangle + \\ & + \lambda^3 E_n^{(1)} |\Phi_n^{(2)}\rangle + \lambda^2 E_n^{(2)} |\Phi_n^{(0)}\rangle + \lambda^3 E_n^{(2)} |\Phi_n^{(1)}\rangle + \dots \end{aligned}$$

And now we will multiply “b” by  $\langle \Phi_k^{(0)} |$  and we will obtain:

$$\begin{aligned} & \langle \Phi_n^{(0)} | H_0 | \Phi_n^{(2)} \rangle + \langle \Phi_n^{(0)} | H' | \Phi_n^{(1)} \rangle = \\ & = \langle \Phi_n^{(0)} | E_n^{(0)} | \Phi_n^{(2)} \rangle + \langle \Phi_n^{(0)} | E_n^{(1)} | \Phi_n^{(1)} \rangle + \\ & \langle \Phi_n^{(0)} | E_n^{(2)} | \Phi_n^{(0)} \rangle \end{aligned}$$

Only the following terms are plausible:  $\langle \Phi_n^{(0)} | H' | \Phi_n^{(1)} \rangle$   
 $\langle \Phi_n^{(0)} | E_n^{(1)} | \Phi_n^{(1)} \rangle$  and  $\langle \Phi_n^{(0)} | E_n^{(2)} | \Phi_n^{(0)} \rangle$  if  $n=k$

$$\begin{aligned} \text{And we will obtain: } E_n^{(2)} &= \langle \Phi_n^{(0)} | H' - E_n^{(1)} | \Phi_n^{(1)} \rangle = \\ &= \langle \Phi_n^{(0)} | (H' - E_n^{(1)}) \sum_k \frac{H'_{kn} - \delta_{kn} E_n^{(1)}}{(E_k^{(0)} - E_n^{(0)})} | \Phi_k^{(0)} \rangle. \end{aligned}$$

Now we will focus the study on **degenerate states** :

When  $\lambda^0$  (zero order):  $E_{nr} = E_n^{(0)}$

When  $\lambda^1$  (order u):  $|\Phi_n^{(0)}\rangle = \sum_r \alpha_r |\Phi_{nr}^{(0)}\rangle$ , which we will replace in (\*) and we will obtain  $\sum_r \alpha_r H' |\Phi_{nr}^{(0)}\rangle + H_0 |\Phi_{nr}^{(0)}\rangle = \sum_r \alpha_r E_n^{(1)} |\Phi_{nr}^{(0)}\rangle + E_n^{(0)} |\Phi_{nr}^{(1)}\rangle$

And if we now multiply this expression by  $\langle \Phi_{kn}^{(0)} |$  we will see everything in the form:

$$\begin{aligned} \sum_r \langle \Phi_{kn}^{(0)} | \alpha_r \cdot H' | \Phi_{nr}^{(0)} \rangle + \langle \Phi_{kn}^{(0)} | H_0 | \Phi_n^{(1)} \rangle &= \\ = \sum_r \langle \Phi_{kn}^{(0)} | E_n^{(1)} \cdot \alpha_r | \Phi_{nr}^{(0)} \rangle + \langle \Phi_{kn}^{(0)} | E_n^{(0)} | \Phi_n^{(1)} \rangle & \end{aligned}$$

Where  $\alpha_r \cdot H' = \mathbb{H}_{kr}$  and

$$\begin{aligned} \sum_r \langle \Phi_{kn}^{(0)} | E_n^{(1)} \alpha_r | \Phi_{nr}^{(0)} \rangle &= \delta_{kr} E_n^{(1)} \alpha_r \\ \text{and } \langle \Phi_{kn}^{(0)} | H_0 | \Phi_n^{(1)} \rangle - \langle \Phi_{kn}^{(0)} | E_n^{(0)} | \Phi_n^{(1)} \rangle &= \\ = \langle \Phi_{kn}^{(0)} | H_0 - E_n^{(0)} | \Phi_n^{(1)} \rangle & \end{aligned}$$

Deducing that  $\langle \Phi_{kn}^{(0)} | H_0 = \langle \Phi_{kn}^{(0)} | E_{kn}^{(0)}$

$$\begin{aligned} E_{nr} &= E_{nr}^{(0)} + \lambda E_{nr}^{(1)} + \lambda^2 E_{nr}^{(2)} + \dots \\ |\Phi_{nr}(\lambda)\rangle &= |\Phi_{nr}\rangle = |\Phi_{nr}^{(0)}\rangle + \lambda |\Phi_n^{(1)}\rangle + \lambda^2 |\Phi_n^{(2)}\rangle + \dots \end{aligned}$$

$$\begin{aligned} |\Phi_{nr}^{(1)}\rangle &= \sum_k \langle \Phi_{kn}^{(0)} | \Phi_{nr}^{(0)} \rangle \langle \Phi_{kn}^{(0)} | \Phi_n^{(1)} \rangle \\ |\Phi_n^{(1)}\rangle &= \sum_p \alpha_p |\Phi_{np}^{(1)}\rangle \text{ assuming that } p=r \end{aligned}$$

We can express  $|\Phi_{nr}^{(1)}\rangle$  in terms of  $|\Phi_{kn}^{(0)}\rangle$   $r \neq k$

$$\langle \Phi_{kn}^{(0)} | H_0 - E_n^{(0)} | \Phi_n^{(1)} \rangle : \langle \Phi_{kn}^{(0)} | H_0 - E_n^{(0)} | \sum_p \alpha_p |\Phi_{np}^{(1)}\rangle = \\ = \langle \Phi_{kn}^{(0)} | H_0 - E_n^{(0)} | \sum_p \alpha_p | \sum_k \langle \Phi_{kn}^{(0)} | \Phi_{np}^{(1)} \rangle$$

Continuing to remember that  $r = p$

$$\alpha_r. H' = \mathbb{H}_{kr} \text{ and } H_0 = E_{kn}^{(0)} \text{ and} \\ \sum_r \langle \Phi_{kn}^{(0)} | E_n^{(1)} \alpha_r | \Phi_{nr}^{(0)} \rangle = \delta_{kr} E_n^{(1)} \alpha_r$$

$$\text{To end up obtaining: } \langle \Phi_{kn}^{(0)} | \Phi_{nr}^{(1)} \rangle = \sum_r \sum_k \frac{(H' - E_n^{(1)}) \delta_{kn} \alpha_r}{(E_{kn}^{(0)} - E_n^{(0)})}$$

$$\text{If we multiply it by } |\Phi_{kn}^{(0)}\rangle : \\ |\Phi_{nr}^{(1)}\rangle = \sum_r \sum_k \frac{(H' - E_n^{(1)}) \delta_{kn} \alpha_r}{(E_{kn}^{(0)} - E_n^{(0)})} |\Phi_{kn}^{(0)}\rangle$$

And now, until tomorrow!

If we have had a good morning, now it's time to isolate  $E_{nr}^{(2)}$ :

$$\text{We multiply "b" by } \langle \Phi_{kn}^{(0)} | : \\ \langle \Phi_{kn}^{(0)} | H_0 \alpha_r | \Phi_n^{(1)} \rangle = \langle \Phi_{kn}^{(0)} | E_{nr}^{(1)} \alpha_r | \Phi_n^{(1)} \rangle + \\ + \langle \Phi_{kn}^{(0)} | E_{nr}^{(2)} \alpha_r | \Phi_n^{(0)} \rangle$$

$$\text{Where I have taken the liberty of deleting } \langle \Phi_{kn}^{(0)} | E_n^{(2)} | \\ \Phi_n^{(2)} \rangle \text{ and} \\ \langle \Phi_{kn}^{(0)} | H_0 | \Phi_n^{(2)} \rangle$$

$$|\Phi_{nr}^{(1)}\rangle = \sum_k |\Phi_{kn}^{(0)}\rangle \langle \Phi_{kn}^{(0)} | \Phi_{nr}^{(1)} \rangle \\ \text{and } |\Phi_n^{(1)}\rangle = \sum_p \alpha_p |\Phi_{np}^{(1)}\rangle \quad r = p \neq k$$

$$\sum_r \langle \Phi_{kn}^{(0)} | H' . \alpha_r | \Phi_{nr}^{(1)} \rangle = \sum_r \langle \Phi_{kn}^{(0)} | E_{nr}^{(1)} \alpha_r | \Phi_{nr}^{(1)} \rangle + \langle \Phi_{kn}^{(0)} | E_{nr}^{(2)} | \Phi_{nr}^{(0)} \rangle$$

$$| \Phi_{nr}^{(1)} \rangle = \sum_r \sum_k \frac{(H' - E_n^{(1)}) \delta_{kn} \alpha_r}{(E_{kn}^{(0)} - E_n^{(0)})} | \Phi_{kn}^{(0)} \rangle \text{ where } H_0 = E_{kn}^{(0)}$$

From which we will know:

$$E_{nr}^{(2)} = \langle \Phi_{kn}^{(0)} | (H' - E_{nr}^{(1)}) . \alpha_r | \Phi_{nr}^{(1)} \rangle$$

$$E_{nr}^{(2)} = \langle \Phi_{kn}^{(0)} | (H' - E_{nr}^{(1)}) \alpha_r | \sum_r \sum_k \frac{(H' - E_n^{(1)}) \delta_{kn} \alpha_r}{(E_{kn}^{(0)} - E_n^{(0)})} | \Phi_{kn}^{(0)} \rangle$$

To finish insulating

$$E_{nr}^{(2)} = \sum_r \sum_k \frac{(H' - E_n^{(1)}) \delta_{kn})^2 . (\alpha_r)^2}{(E_{kn}^{(0)} - E_n^{(0)})}$$