Non-degenerate perturbat° theory

$$\hat{H} = \hat{H}_0 + \hat{H}'$$

$\hat{H}' << \hat{H}_0$ = perturbat°

$$\hat{H}_0 |\phi_{0n}\rangle = E_{0n} |\phi_{0n}\rangle$$

Effect of $\hat{H}'$ on E_{0n} & ϕ_{0n}

$$\hat{H} = \hat{H}_0 + \lambda \hat{H}'$$

$$\hat{H} |\phi_n\rangle = E_n |\phi_n\rangle$$

$$E_n = E_{0n} + \lambda E_{1n} + \lambda^2 E_{2n} + \dots$$

2nd order correct°

$$|\phi_n\rangle = |\phi_{0n}\rangle + \lambda |\phi_{1n}\rangle + \lambda^2 |\phi_{2n}\rangle + \dots$$

1st order correct°

λ^0 terms : $\hat{H}_0 |\phi_{0n}\rangle = E_{0n} |\phi_{0n}\rangle$

λ^1 terms : $\hat{H}' |\phi_{0n}\rangle + \hat{H}_0 |\phi_{1n}\rangle = E_{0n} |\phi_{1n}\rangle + E_{1n} |\phi_{0n}\rangle$

λ^2 terms : $\hat{H}' |\phi_{1n}\rangle + \hat{H}_0 |\phi_{2n}\rangle = E_{0n} |\phi_{2n}\rangle + E_{1n} |\phi_{1n}\rangle + E_{n}|\phi_{0}$

$$\boxed{\lambda^a \text{ terms} : \quad \hat{H} |\phi_{(a-1)n}\rangle + \hat{H}_0 |\phi_{an}\rangle = \sum_{i=0}^{a} E_{in} |\phi_{(a-i)n}\rangle}$$

1st correct° $|\phi_{1n}\rangle$: $|\phi_{1n}\rangle = \sum_k a_{nk} |\phi_{0k}\rangle$

$$(\hat{H}' - E_{1n}) |\phi_{0n}\rangle = \sum_k a_{nk} (E_{0n} - E_{0k}) |\phi_{0k}\rangle$$

$$\Big\downarrow \; \langle \phi_{0n} | \phi_{0k}\rangle = \delta_{nk}$$

$$E_{1n} = \langle \phi_{0n} | \hat{H}' | \phi_{0n}\rangle$$

1D $\quad E_{1n} = \int \phi_{0n}^* \hat{H}' \phi_{0n} \, dx$

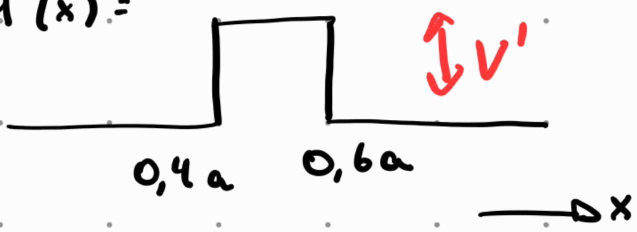
3D $E_{1n} = \iiint \phi_{on}^{*} \hat{H}' \phi_{on} \, d^3r$

$$E_n = E_{on} + \underbrace{\langle \phi_{on} | \hat{H}' | \phi_{on} \rangle}_{1^{st} \text{ order}} + \underbrace{\sum_{k \neq n} \frac{\langle \phi_{on} | \hat{H}' | \phi_{ok} \rangle \langle \phi_{ok} | \hat{H}' | \phi_{on} \rangle}{E_{on} - E_{ok}}}_{2^{nd} \text{ order}} + \dots$$

$$|\phi_n\rangle = |\phi_{on}\rangle + \underbrace{\sum_{k \neq n} \frac{\langle \phi_{ok} | \hat{H}' | \phi_{on} \rangle}{E_{on} - E_{ok}} |\phi_{ok}\rangle}_{1^{st} \text{ order}} + \dots$$

$\lambda = 1$ above

ex $\hat{H}'(x) =$



Unperturbed system:

$$\phi_{on}(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right)$$

$$E_{on} = \frac{\hbar^2 \pi^2 n^2}{2ma^2}$$

First order perturbed:

$$E_{1n} = \frac{2}{a} \int_{0.4a}^{0.6a} \sin\left(\frac{n\pi x}{a}\right) V' \sin\left(\frac{n\pi x}{a}\right) dx$$

$$\therefore E_{1n} = V' \left(0.2 - \frac{\sin(1.2n\pi) - \sin(0.8n\pi)}{2n\pi}\right)$$

Energy perturbed system (1^{st} order)

$$E_n = E_{on} + E_{1n}$$

- $n=1$, $E_{11} = 0.39V' \rightarrow E_1 = \frac{\hbar^2 \pi^2}{2ma^2} + 0.39V'$

$\bullet\ n=2,\ E_{12} = 0.005V' \rightarrow E_2 = \frac{2\hbar^2\pi^2}{ma^2} + 0.05V'$

Degenerate perturbat° theory

problems will arise if $\rightarrow E_{0n} - E_{0k} < \langle \phi_{0k} | \hat{H}' | \phi_{0n} \rangle$

$\rightarrow$ 2 unperturbed eigenvals are degen

i.e return same energy : $\hat{H}|\phi_{01}\rangle = \hat{H}|\phi_{02}\rangle$

Consider two degenerate states $|\phi_{01}\rangle$ & $|\phi_2\rangle$.

$\downarrow$ TISE

$\hat{H}_0 |\phi_{01}\rangle = E_0 |\phi_{01}\rangle \qquad \hat{H}_0 |\phi_{02}\rangle = E_0 |\phi_{02}\rangle$

Look for solut°s of $(\hat{H}_0 + \hat{H}')|\phi\rangle = E|\phi\rangle$ ①

$|\phi\rangle = a_1 |\phi_{01}\rangle + a_2 |\phi_{02}\rangle$ ②

① → ② = ③ : $(E_0 - E)a_1 |\phi_{01}\rangle + (E_0 - E)a_2 |\phi_{02}\rangle + a_1 \hat{H}' |\phi_{01}\rangle + a_2 \hat{H}' |\phi_{02}\rangle = 0$

$|\phi_{01}\rangle$ & $|\phi_{02}\rangle$ are orthogonal & normalised $\rightarrow \langle \phi_{01} | \phi_{01} \rangle = 1$, $\langle \phi_{01} | \phi_{02} \rangle = 0$

③ $\cdot\ \langle \phi_{01}|\ \&\ \langle \phi_2 |$

$\downarrow$

$(E_0 + H_{11}' - E)a_1 + H_{12}' a_2 = 0$

$H_{21}' a_1 + (E_0 + H_{22}' - E) a_2 = 0$

$H_{\alpha\beta}' = \langle \phi_{0\alpha} | \hat{H}' | \phi_{0\beta} \rangle$

can be expressed in matrix form

$$\begin{pmatrix} (E_0 + H'_{11}) - E & H'_{12} \\ H'_{21} & (E_0 + H'_{22}) - E \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = 0$$

Note: $H'_{21} = (H'_{12})^*$

$\downarrow$

standard matrix eigenval pb

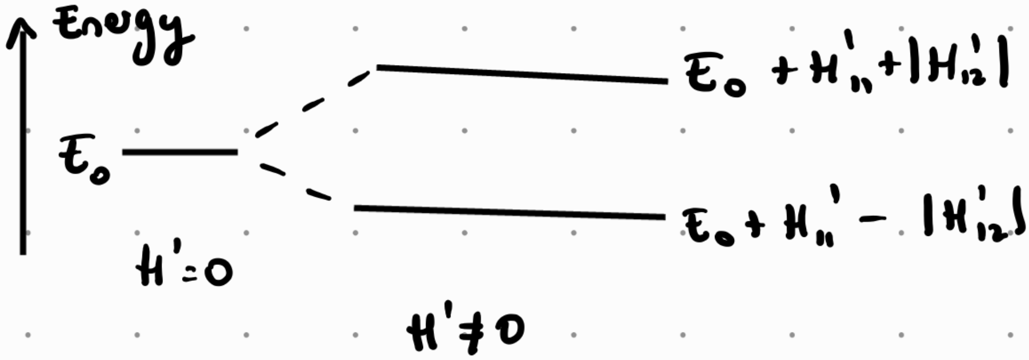
$$\begin{vmatrix} (E_0 + H'_{11}) - E & H'_{12} \\ H'_{21} & (E_0 + H'_{22}) - E \end{vmatrix} = 0$$

If $H'_{11} = H'_{22} \longrightarrow ((E_0 + H'_{11}) - E)^2 - |H'_{12}|^2 = 0$

$$\boxed{\Rightarrow E = E_0 + H'_{11} \pm |H'_{12}|}$$

Perturbat° breaks degeneracy

Two distinct E lvls



M degenerate unperturbed states:

$|\phi\rangle = a_1|\phi_{01}\rangle + a_2|\phi_{02}\rangle$

② → GENERALIZED $\quad |\phi\rangle = \sum_{m=1}^{M} a_m |\phi_{0m}\rangle$

$$\boxed{\begin{vmatrix} H'_{11}-\Delta E & H'_{12} & \cdots & H'_{1M} \\ H'_{21} & H'_{22}-\Delta E & & \\ \vdots & & \ddots & \\ H'_{M1} & \cdots & & H'_{MM}-\Delta E \end{vmatrix} = 0}$$

$$H'_{\alpha\beta} = \langle \phi_{0\alpha}|\hat{H}'|\phi_{0\beta}\rangle$$

$$\Delta E = E - E_0$$

ex One dimensional "solid" of length L $\quad V=0$

Unperturbed states will be free electron states in ⑩ :

$$|\phi_{0k}\rangle = \sqrt{\frac{1}{L}}\,\exp(ikx)$$

example "box" normalised

$$E_{0k} = \frac{\hbar^2 k^2}{2m}$$

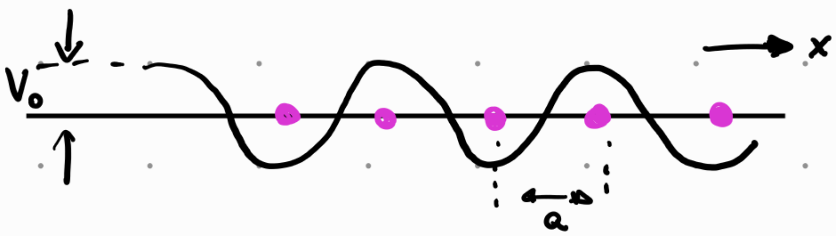
$|\phi_{0k}\rangle$ & $|\phi_{0-k}\rangle$ have same energy ⇒ degen

strength

Perturbat° is a weak periodic potential : $\hat{H}' = V_0 \cos\left(\frac{2\pi x}{a}\right)$

repeat distance

ion core separat°



Eigenvals: $\quad H'_{kk} = H'_{k'k'} = \frac{V_0}{L}\int_0^L \cos\left(\frac{2\pi x}{a}\right)dx = 0$

$$H'_{kk'} = \frac{1}{L}\int_0^L \exp(-ikx)\, V_0 \cos\left(\frac{2\pi x}{a}\right) \exp(ik'x)\, dx$$

$$\boxed{\begin{aligned} &= \frac{V_0}{2} \quad \text{if } k-k' = \pm\frac{2\pi}{a} \\ &= 0 \quad \text{otherwise} \end{aligned}}$$

$$E_{0k} = \frac{\hbar^2 k^2}{2m} \qquad \begin{aligned} k &= \pi/a \\ k' &= -\pi/a \end{aligned}$$

$$k - k' = \frac{2\pi}{a} \quad \text{i.e} \quad H'_{kk'} = H'_{k'k} = \frac{V_0}{2}$$

$$\begin{vmatrix} E_0 - E & V_0/2 \\ V_0/2 & E_0 - E \end{vmatrix} = 0 \quad \xrightarrow{\text{solut}^\circ} \quad \boxed{E = E_0 \pm \frac{V_0}{2}}$$

Perturbat° lifts the degeneracy of electrons with $|k| = \frac{\pi}{a}$

$$k = \frac{\pi}{a} + \delta k \qquad |\phi_{01}\rangle \qquad E_{01} = \frac{\hbar^2}{2m}\left(\left(\frac{\pi}{a}\right)^2 + \delta k^2 + \frac{2\pi\,\delta k}{a}\right)$$

$$k' = -\frac{\pi}{a} + \delta k \qquad |\phi_{02}\rangle \qquad E_{02} = \underbrace{\frac{\hbar^2}{2m}\left(\left(\frac{\pi}{a}\right)^2 + \delta k^2\right.}_{\overline{E_0}}\left. - \frac{2\pi\,\delta k}{a}\right)$$

$$E_{01} = \overline{E_0} + \frac{\hbar^2 \pi\, \delta k}{ma} \qquad E_{02} = \overline{E_0} - \frac{\hbar^2 \pi\, \delta k}{ma}$$

$$H'_{kk} = H'_{k'k'} = 0 \rightarrow H'_{11} = H'_{22} = 0$$

$$H'_{kk'} = H'_{k'k} = \frac{V_0}{2} \rightarrow H'_{12} = H'_{21} = \frac{V_0}{2}$$

$$\begin{vmatrix} (E_{01} + H'_{kk}) - E & H'_{kk'} \\ \dots & \dots \end{vmatrix} = \begin{vmatrix} \frac{\hbar^2 \pi\, \delta k}{ma} - (E - \overline{E_0}) & V_0/2 \\ \dots & \dots \end{vmatrix} = 0$$

$H_{k'k}$ $\quad (E_{0z} + H_{k'k'}) - E \Big| \Big| \quad \frac{V_0}{2} \quad \frac{}{ma} - (E - E_0) \Big|$

$\Downarrow$ solut°

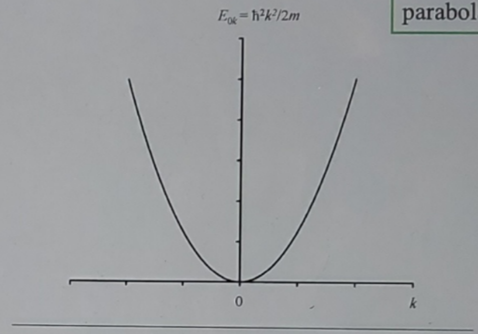
$$\boxed{E = \overline{E_0} \pm \sqrt{\left(\frac{\hbar^2 \pi \delta k}{ma}\right)^2 + \frac{V_0^2}{4}}}$$

The perturbation affects states over a range of δk values where $\frac{\hbar^2 \pi \delta k}{ma}$ is small compared to $\frac{V_0}{2}$ i.e. perturbation has a negligible effect on states that are not close to $k = \pm\frac{\pi}{a}$ - see Rae

When $\delta k = 0$ there is a "band gap" of size V_0

Unperturbed system: -

Free electron parabola



Perturbed system: -

Band gap at Brillouin zone boundary