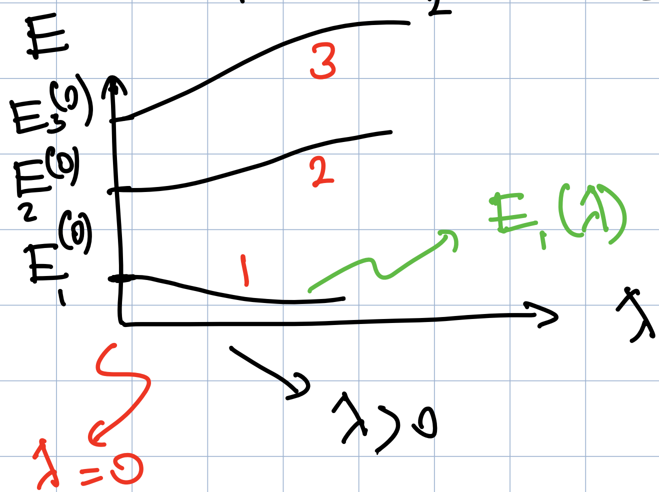
Non-degenerate perturbation theory

$$E_1^{(0)} < E_2^{(0)} < E_3^{(0)} < \cdots$$



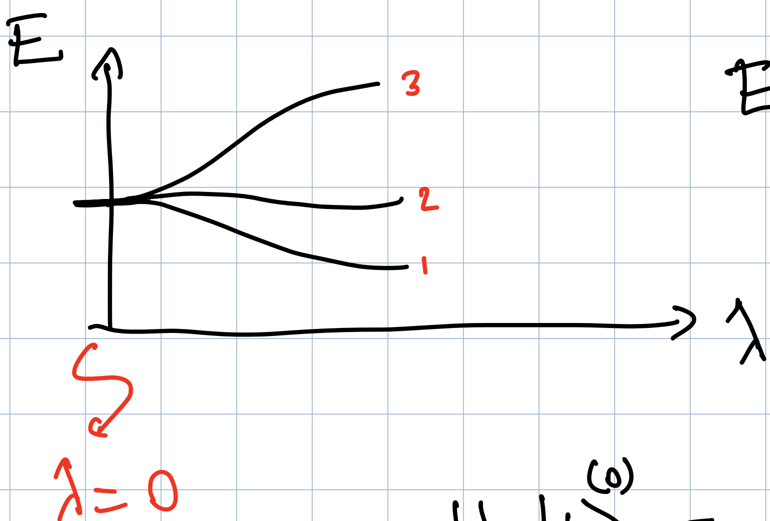
$\lambda \ll 1$

$$E_n^{(1)} = V_{nn} = \langle n | V | n \rangle$$

$$E_n^{(2)} = -\sum_{m \neq n} \frac{|V_{mn}|^2}{E_m^{(0)} - E_n^{(0)}}$$

For some $\underset{\neq m}{n}$: $E_m = E_n$

Degenerate perturbation theory



Energy levels branch out once turning on λ

$$H_0 |1\rangle^{(0)} = E^{(0)} |1\rangle^{(0)}$$

$$H_0 |2\rangle^{(0)} = E^{(0)} |2\rangle^{(0)}$$

Any superposition has the same energy

$$H_0 \frac{1}{\sqrt{2}} \left(|1\rangle^{(0)} + |2\rangle^{(0)} \right) = E^{(0)} \left(\quad \right)$$

Can we determine how these degenerate states branch out once turning on λ?

Our approach:

The problem is stated in a given basis $|n\rangle^{(0)}$.

$$E_1^{(0)} = E_2^{(0)} = \cdots = E_n^{(0)} = \cdots$$

$n = 1, 2, 3, \ldots, n_{max}$

We assume that degeneracy is lifted once $\lambda \neq 0$, and designate these states by $|k\rangle_\lambda$

$$|k\rangle^{(0)} = |k\rangle_{\lambda \to 0}$$

possibly a superposition of $|n\rangle^{(0)}$

We then repeat $\longrightarrow$ perturbation theory

$$|k\rangle_\lambda = |k\rangle^{(0)} + \lambda |k\rangle^{(1)} + \cdots$$

$$E_k(\lambda) = E^{(0)} + \lambda E_k^{(1)} + \cdots$$

We have to solve

$$H(\lambda)|k\rangle_\lambda = E_k(\lambda)|k\rangle_\lambda$$

To the zeroth order,

$$\lambda^0 : \quad \left(H^{(0)} - E^{(0)}\right) |k\rangle^{(0)} = 0$$

To the next order:

$$\left(H^{(0)} - E^{(0)}\right) |k\rangle^{(1)} = \left(E_k^{(1)} - V\right) |k\rangle^{(0)}$$

→ multiply from left by ${}^{(0)}\langle l|$

$${}^{(0)}\langle l| \; H^{(0)} - E^{(0)} \; |k\rangle^{(1)} = {}^{(0)}\langle l| \, E_k^{(1)} - V \, |k\rangle^{(0)}$$

$$E^{(0)} - E^{(0)} = 0 = E_k^{(1)} \delta_{lk} - V_{lk}$$

$$\longrightarrow \quad V_{lk} = E_k^{(1)} \delta_{lk}$$

This means that $\boxed{V \text{ is diagonal in the } k \text{ basis}}$

Recipe: start in any basis spanned by $|n\rangle^{(0)}$

Write down the matrix $V_{mn} = {}^{(0)}\langle m|V|n\rangle^{(0)}$

$$[V] = \begin{pmatrix} V_{11} & V_{12} & \cdots \\ V_{21} & V_{22} & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix}$$

$V \longrightarrow$ $\underbrace{\text{Diagonalize}}$ $\mathcal{V} \longrightarrow$ eigenvectors give you the basis where the degeneracy is lifted

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Back to nearly free electrons:

$$H = H_0 + V$$ periodic

$$H_0 |k\rangle = \varepsilon_k^{(0)} |k\rangle$$ $\frac{\hbar^2 k^2}{2m}$

$$H_0 = \frac{\vec{p}^{\,2}}{2m}$$

1st order perturba. th.

$$\varepsilon_k = \varepsilon_k^{(0)} + \underbrace{\langle \vec{k} | V | \vec{k} \rangle}_{V_0 \text{ : just energy shift}}$$

2nd order " "

$$\varepsilon_k = \varepsilon_k^{(0)} + V_0 + \sum_{k' \neq k} \frac{|\langle k' | V | k \rangle|^2}{\varepsilon_k^{(0)} - \varepsilon_{k'}^{(0)}}$$

Problem! $\begin{cases} k' = k + G \\ \varepsilon_{k'}^{(0)} = \varepsilon_k^{(0)} \end{cases}$

Numerator:

$$\langle k' | V | k \rangle = \frac{1}{vol.} \int dr\, e^{i(\vec{k} - \vec{k}').\vec{r}}\, V(\vec{r})$$

This quantity is nonzero only if

$$\vec{k} - \vec{k}' = \vec{G}$$

is a reciprocal lattice vector.

$$V(\vec{r}) = V(\vec{r} + \vec{b})$$

vector in direct lattice

Ex.

$$V(\vec{r}) = const$$

$$\langle k' | V | k \rangle$$

$$\langle k' | V | k \rangle \propto \int_{-\infty}^{+\infty} d\vec{r}\, e^{i(\vec{k} - \vec{k}').\vec{r}}\, V(\vec{r})$$

$$= \int d\vec{r}\, e^{i(\vec{k} - \vec{k}').(\vec{r} + \vec{b})}\, V(\vec{r} + \vec{b})$$

$$= e^{i(\vec{k} - \vec{k}').\vec{b}} \int d\vec{r}\, e^{i(\vec{k} - \vec{k}').\vec{r}}\, V(\vec{r})$$

$$\langle k' | V | k \rangle = e^{i(\vec{k} - \vec{k}').\vec{b}} \langle k' | V | k \rangle$$

$$\# = e^{i(\ \ )} \quad \#$$

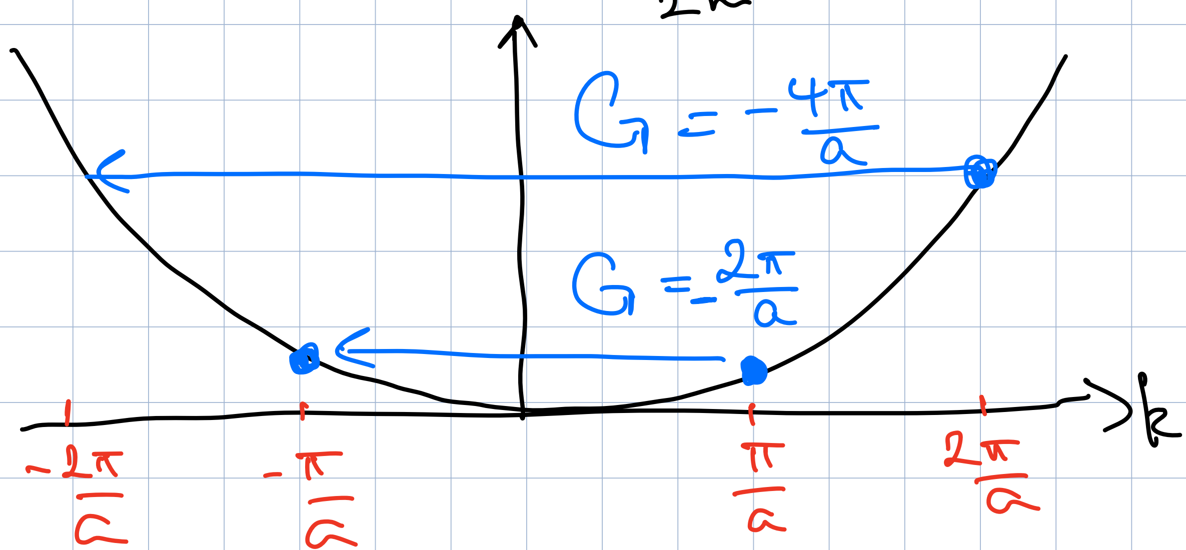
$$e^{i(\vec{k}-\vec{k}')\cdot\vec{b}} = 1 \qquad \forall\, \vec{b}$$

$$\longrightarrow \quad \vec{k} - \vec{k}' = \vec{G} \in \text{Recip. lattice}$$

$$\vec{G}\cdot\vec{b} = n\, 2\pi$$

But we should be careful about the degenerate situation:

$$E = \frac{\hbar^2 k^2}{2m} \qquad \mathcal{E}^{(0)}_{k} = \mathcal{E}^{(0)}_{k+G}$$



In one dimension we take $\boxed{k = \frac{\pi}{a} \quad \& \quad G = -\frac{2\pi}{a}}$.

Look at matrix elements of V

V_{mn} : 2x2 matrix $\quad m, n \in \{k, k+G\}$
$= \{\frac{\pi}{a}, -\frac{\pi}{a}\}$

Find 4 matrix elements:

$$V_{11} = \langle k | V | k \rangle = V_0$$

$$V_{22} = \langle k+G | V | k+G \rangle = V_0$$

$$V_{12} = \langle k | V | k+G \rangle = V_G$$

$$V_{21} = \langle k+G | V | k \rangle = V_G^*$$

$$\longrightarrow [V]_{2\times 2} = \begin{pmatrix} V_0 & V_G \\ V_G^* & V_0 \end{pmatrix}$$

Diagonalize this matrix: Find eigenvalues

$$\text{Eigenvalues} = V_0 \pm |V_G|$$

$$k = \pm \frac{\pi}{a}$$

What happens close to $\pm \frac{\pi}{a}$
(not exactly at)

$$H_0 = \frac{\hbar^2 k^2}{2m} \qquad H = H_0 + V$$

$$V_{mn} \longrightarrow H_{mn}$$

Compute matrix elements of H

$$H_{11} = \langle k | H | k \rangle = V_0 + \mathcal{E}_k^{(0)}$$

$$H_{22} = \langle k+G | H | k+G \rangle = V_0 + \mathcal{E}_{k+G}^{(0)}$$

$$H_{12} = \langle k | H | k+G \rangle = V_G$$

$$H_{21} = \langle k+G | H | k \rangle = V_G^*$$

$$\longrightarrow [H]_{2\times 2} = \begin{pmatrix} \mathcal{E}_k^{(0)} + V_0 & V_G \\ V_G^* & \mathcal{E}_{k+G}^{(0)} + V_0 \end{pmatrix}$$