So far,

Tight-binding model:

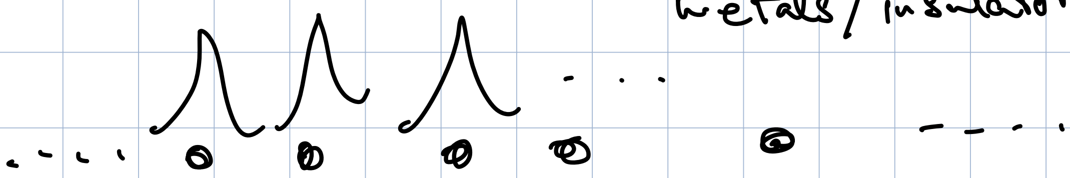
atomic orbitals

+ hopping

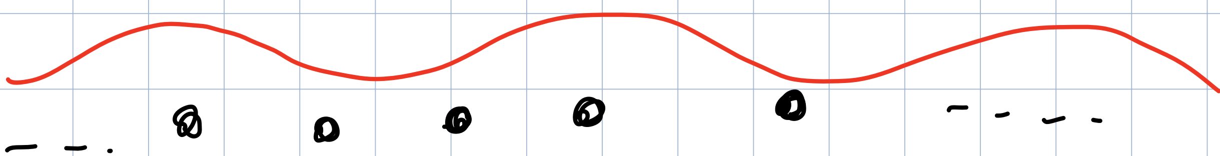
Nearly free electrons:

plane waves + periodic potential

energy Bands / Band gaps / metals / insulators



↳ orbitals: electrons tightly bound to nuclei



$$H = \underbrace{\frac{p^2}{2m}}_{} + V(x)$$

↳ periodic potential: to be treated as a perturbation

Which approach describes materials?

Both!

Nearly free electrons

- we rediscover many of the properties (energy bands, energy gaps, ...) and make contact w/ tight-binding model.
- We put everything on a more solid foundation that is exact and encompasses both limits.

Set-up:

$$H = H_0 + V(\vec{x})$$

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

Free electron : $H_0 |\underset{\sim}{\vec{k}}\rangle = \varepsilon_k^{(0)} |k\rangle$, $\varepsilon_k^{(0)} = \frac{\hbar^2 k^2}{2m}$

Next, we assume weak periodic potential

Q: How do energy and states are modified by introducing periodic potential?

Resort to perturb. th.

$$\varepsilon_k = \varepsilon_k^{(0)} + \underbrace{\langle k | V | k\rangle}_{V_0}$$

$$\langle \vec{k}' | V | \vec{k} \rangle = \frac{1}{L^3} \int d^3\vec{r} \; e^{i(\vec{k} - \vec{k}') \cdot \vec{r}} \; V(\vec{r})$$

$$\langle \vec{r} | \vec{k} \rangle = \frac{1}{\sqrt{L^3}} e^{i\vec{k}\cdot\vec{r}}$$

$$\langle k | V | k \rangle = \frac{1}{L^3} \int d^3\vec{r} \; V(\vec{r}) = V_0$$

V_0 : just energy shift $\longrightarrow$ incosequential

Have to go to higher order of pert. th.

Also, in a special case (BZ boundaries!) we have to do a degenerate pert. th.

Perturbation th. (see QM)

$$\hat{H}(\lambda) = \hat{H}^{(0)} + \lambda \hat{V}$$

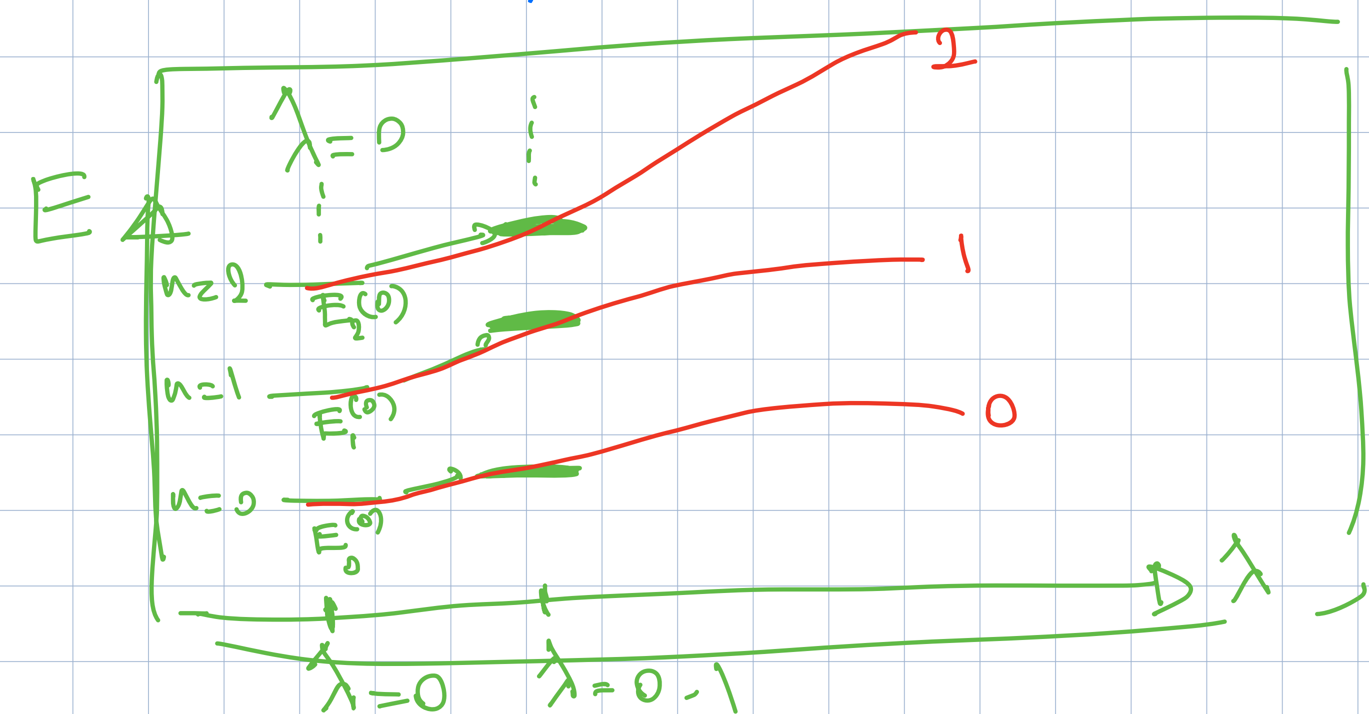
↳ $\lambda \ll 1$

■ Non-degenerate PT

easy → $H^{(0)} |n^{(0)}\rangle = E_n^{(0)} |n^{(0)}\rangle$

$|n^{(0)}\rangle$ is non-degerate $\ldots < E_{n-1}^{(0)} < E_n^{(0)} < E_{n+1}^{(0)} \ldots$

hard → $\boxed{H(\lambda) |n\rangle_\lambda = E_n(\lambda) |n\rangle_\lambda}$



Let's expand everything in λ:

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

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

$$\left(H^{(0)} + \lambda V\right)|n\rangle_\lambda = E_n(\lambda)|n\rangle_\lambda$$

$$\rightarrow \left(H^{(0)} + \lambda V - E_n(\lambda)\right)|n\rangle_\lambda = 0$$

$$\rightarrow \left[\left(H^{(0)} - E_n^{(0)}\right) + \lambda\left(V - E_n^{(1)}\right) - \lambda^2 E_n^{(2)} - \dots\right]$$

$$\cdot \left[|n^{(0)}\rangle + \lambda |n^{(1)}\rangle + \lambda^2 |n^{(2)}\rangle + \dots\right] = 0$$

We can write this as

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

$$\lambda^0 : \left(H^{(0)} - E_n^{(0)}\right)|n^{(0)}\rangle = 0$$

$$(*)\quad \lambda^1 : \left(H^{(0)} - E_n^{(0)}\right)|n^{(1)}\rangle = -\left(V - E_n^{(1)}\right)|n^{(0)}\rangle$$

multiply both sides by $\langle n^{(0)}|$ from the left

$$\langle n^{(0)}|\left(H^{(0)} - E_n^{(0)}\right)|n^{(1)}\rangle = -\langle n^{(0)}|\left(V - E_n^{(1)}\right)|n^{(0)}\rangle$$

$$0 = E_n^{(1)} - \langle n^{(0)}|V|n^{(0)}\rangle$$

$$\longrightarrow \boxed{E_n^{(1)} = \langle n^{(0)}|V|n^{(0)}\rangle}$$

In a similar way, one can show that

$$E_n^{(k)} = \langle n^{(0)}|V|n^{(k-1)}\rangle$$

To obtain the correction to 2nd order in λ

Let's find $|n^{(1)}\rangle$

Take eq. $*$ and multiply that eq by $\langle m^{(0)}|$ from the left $m \neq n$

$$\langle m^{(0)}| H^{(0)} - E_n^{(0)})|n^{(1)}\rangle = \langle m^{(0)}| E_n^{(1)} - V|n^{(0)}\rangle$$

$$(E_m^{(0)} - E_n^{(0)}) \langle m^{(0)}|n^{(1)}\rangle = -\underbrace{\langle m^{(0)}|V|n^{(0)}\rangle}_{V_{mn}}$$

$$\rightarrow \langle m^{(0)}|n^{(1)}\rangle = -\frac{\langle m^{(0)}|V|n^{(0)}\rangle}{E_m^{(0)} - E_n^{(0)}}$$

$$\rightarrow |n^{(1)}\rangle = \sum_m |m^{(0)}\rangle \langle m^{(0)}|n^{(1)}\rangle$$

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

$|n^{(1)}\rangle$ becomes a nontrivial superposition $|m^{(0)}\rangle$.

$$E_n^{(2)} = \langle n^{(0)}|V|n^{(1)}\rangle = -\sum_{m\neq n} \frac{\overbrace{\langle n^{(0)}|V|m^{(0)}\rangle}^{V_{mn}^*} V_{mn}}{E_m^{(0)} - E_n^{(0)}}$$

note: $\langle n^{(0)}|V|m^{(0)}\rangle = V_{nm} = V_{mn}^*$

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