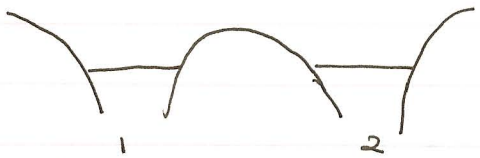
LCAO

Reminder – diatomic molecule.



$H_1|1\rangle = E_0|1\rangle$

$H_2|2\rangle = E_0|2\rangle$.

$\langle 1|2\rangle = 0$ (not quite true).

$H = T + V_1 + V_2$.

Assume $|\psi\rangle = c_1|1\rangle + c_2|2\rangle$.

$\therefore \quad H|\psi\rangle = (T + V_1 + V_2)(c_1|1\rangle + c_2|2\rangle)$

$= c_1 E_0|1\rangle + c_1 V_2|1\rangle + c_2 E_0|2\rangle + c_2 V_1|2\rangle$

$= E_0(c_1|1\rangle + c_2|2\rangle) + c_1 V_2|1\rangle + c_2 V_1|2\rangle$

$(H - E)|\psi\rangle = 0 = (E_0 - E)(\quad) + \quad$ "

$\langle 1|(H-E)|\psi\rangle = (E_0 - E)c_1 + c_1\langle 1|V_2|1\rangle + c_2\langle 1|V_1|2\rangle$

$\langle 2|(H-E)|\psi\rangle = (E_0 - E)c_2 + c_2\langle 2|V_1|2\rangle + c_1\langle 2|V_2|1\rangle$

$$\begin{bmatrix} (\tilde{E}_0 - E) & t \\ t^* & (\tilde{E}_0 - E) \end{bmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0 .$$

$\boxed{t < 0}$ Simplest case

Eigenvalues $(\tilde{E}_0 - E)^2 - |t|^2 = 0 \Rightarrow E = \tilde{E}_0 \pm |t|$.

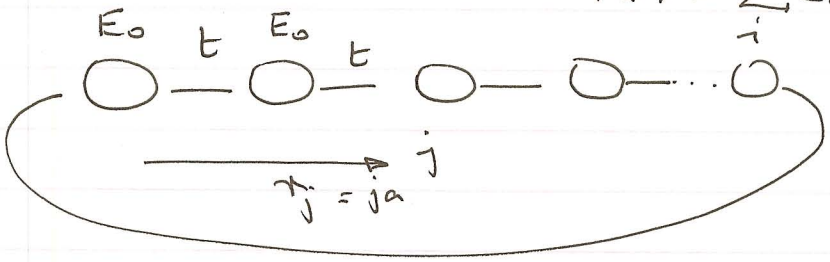
$|\psi\rangle = \frac{1}{\sqrt{2}}\left[|1\rangle \mp |2\rangle\right]$

$\psi_+ \; |1\rangle + |2\rangle \qquad E = \tilde{E}_0 - |t|$

$|1\rangle - |2\rangle \qquad E = \tilde{E}_0 + |t|$.

Ring of N-atoms:

$$|\psi\rangle = \sum_i c_i |i\rangle$$



$$\begin{bmatrix} E_0-E & t & 0 & \cdots & t \\ t & E_0-E & t & & \\ 0 & t & \ddots & & \\ \vdots & & & E_0-E & t \\ t & & & t & E_0-E \end{bmatrix} \begin{bmatrix} C_1 \\ \vdots \\ C_N \end{bmatrix} = 0$$

Solution: m^{th} eigenstate. has $0, 1 \ldots N-1$

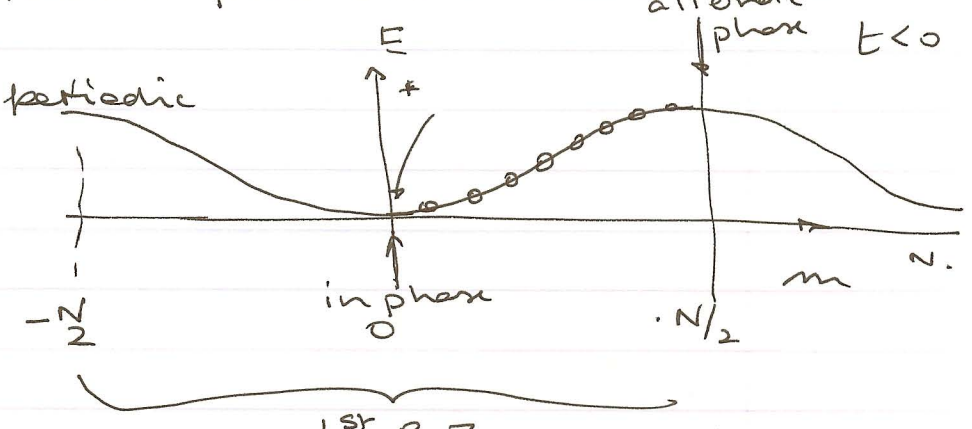
$$c_j^{(m)} = \frac{1}{\sqrt{N}} e^{\frac{2\pi i \, jm}{N}} \qquad E^m = E_0 + 2t\cos\left(\frac{2\pi m}{N}\right)$$

1) $|\psi_j^m|^2 = \frac{1}{N}$ — density uniform.

— phase relation from site to site

2) Energy is periodic

— in a band



3) Rewrite $r_j = ja$

$k = \frac{2\pi m}{Na}$. → Def^n same as for 1D phonon chain.

$e^{\frac{2\pi i \, jm}{N}} \Longrightarrow e^{-i\underline{k}\cdot\underline{r}_j}$

This satisfies a general theorem.

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V(r)$$

$$U(\vec{r}+\vec{R}) = U(\vec{r}) \quad \forall \vec{R}$$ — periodic on lattice.

then the eigenstates have the form.

$$\psi_{nk}(r) = e^{-ik\cdot r}\, u_{nk}(r)$$

where $u(r) = u(r+R) \quad \forall R$ (periodic)

or $$\psi_{nk}(r+R) = e^{ik\cdot R}\,\psi_{nk}(r)$$ equiv.

NB. $k \to k+G$ ψ unchanged $E_{nk} = E_{nk+G}$

1D chain again.

Note that $$\psi_k(r) = \frac{1}{\sqrt{N}}\sum_j e^{ik\cdot R_j}\,\phi(r-R_j)$$

(ϕ: at. wfn.)

$$k = \frac{2\pi m}{Na}\,; \quad R_j = ja.$$

→ No choice about wfn

Evaluate energy

$$E(k) = \langle\psi_k|H|\psi_k\rangle$$

$$= \frac{1}{N}\sum_{j,m} e^{-ik\cdot R_j}\langle j|H|m\rangle e^{ik\cdot R_m}$$

write $R_m = R_j + \rho_n$.

$$E(k) = \frac{1}{N}\sum_{j,n} e^{ik\cdot R_n} \times \underbrace{\langle j|H|j+n\rangle}_{\equiv \langle 0|H|n\rangle}$$

$$= \left(\frac{1}{N}\sum_{j}\right) \sum_{n} e^{i\underline{k}\cdot\underline{R}_n} \langle 0|H|n\rangle .$$

$$= 1$$

$$\tilde{E}_0$$

$$\bigcirc \overset{t}{-} \bigcirc \overset{t}{-} \bigcirc$$

$$-1 \quad 0 \quad 1$$

$$= \langle 0|H|0\rangle + \langle 0|H|1\rangle e^{ika} + \langle 0|H|-1\rangle e^{-ika}.$$

$$= \tilde{E}_0 + 2t\cos(ka).$$

What about the index n?

— more than one orbital / cell

⟶ extra bands (cp. diatomic chain — phonons)

General procedure (will need for graphite).

Bloch state for orbital of type α.

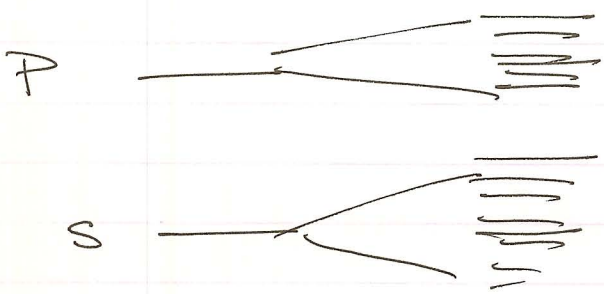
$$\psi_{\alpha k}(r) = \frac{1}{\sqrt{N}} \sum_{j} e^{i\underline{k}\cdot\underline{R}_j} \phi_\alpha(r - R_j)$$

⇒ Then

$$\underline{\psi}_{nk}(r) = \sum_{\alpha} C_\alpha^{(n)}(k)\, \psi_{\alpha k}(r)$$

Remarks

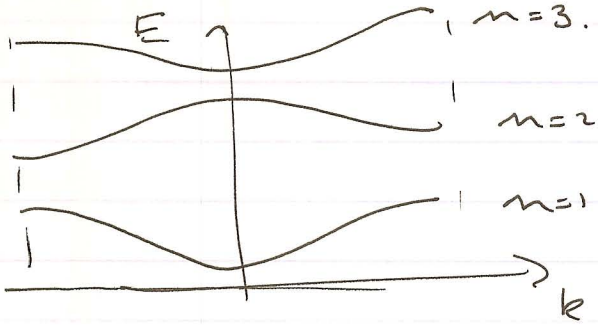
- # of bands ⟺ # of states per atom



should be ∞ ... but just neglect high energies

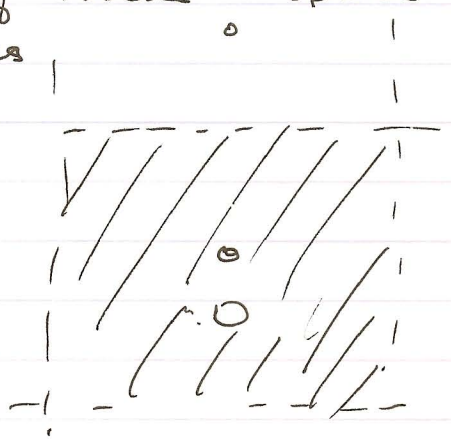
— not so simple because $\langle s_j | H | p_{(j+1)} \rangle \neq 0$
— & all mix.

- Bloch shows this is general.



- $E_n(k+G) = E_n(k)$ — restrict k to 1st B.Z.

— volume of momentum space bounded by BZ planes



- In 1D $\Delta k = \frac{2\pi}{L}$

$\Rightarrow$ 3D $\Delta^3 k = \left(\frac{2\pi}{V}\right)^3$ — as for free el^{n}.

- Vol of B.Z. $= \frac{(2\pi)^3}{\Omega_{cell}}$ — see Qu.

$\therefore$ # of k-points / unit cell.

$$= \frac{(2\pi)^3/\Omega_{cell}}{(2\pi)^3/V} = N_{cell}.$$

- Pauli: each kstate occ by ↑ ↓

- Even # rule.

— ~~diam~~ crystal with n electrons/cell

$\Rightarrow$ n/2 filled bands.

— unless n even, must have

Partially filled band $\Rightarrow$ fermi surface

when $E(k) = E_F$

Na, Al. ....

— if n even, may have insulator

(if bands don't overlap)

e.g. Si, Ge, GaAs, (Cl_2) (O_2)

Mg ? — overlapping bands.