Energy levels of e^- in solid

① Physical picture

discrete atomic levels highly degenerate ⟷ broaden to bands

increasing low P — separation — decreasing high P

can ever get metal-insulator transitions if bands themselves touch

② tight binding ← technically easy

③ solve Schr. eqn ← technically hard

Bloch Thm underlies

must use computer "density functional theory"

but doesn't include details of nuclear potentials "chemistry"

2

Tight binding lattice of sites, e^- can hop between neighbors
$\psi(\ell)$ wave function on site ℓ

Amusing similarity to phonon math

lattice of atoms, springs between neighbors
$x(\ell)$ displacement of atom ℓ

$$H = \begin{pmatrix} E_a & -t & & & \\ -t & E_a & -t & & \\ & -t & E_a & -t & \\ & & & \ddots & \end{pmatrix} \leftarrow d=1$$

E_a = original atomic level

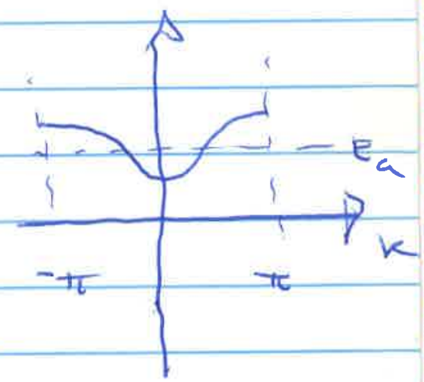
$$H\psi = E\psi$$

$$E_a \psi_\ell - t\psi_{\ell-1} - t\psi_{\ell+1} = E\psi_\ell$$

$$\psi_\ell = \psi_a e^{ik\ell}$$

$$E_a\psi_a + (-2t\cos k)\psi_a = E\psi_a$$

If $\psi_a \neq 0$ $E = E_a - 2t\cos k$



Two types of atoms

$$\begin{matrix} E_a & -t & & \\ -t & E_b & -t & \\ & -t & E_a & -t \\ & & -t & E_b \end{matrix}$$

Method #1 $\quad \psi_\ell = \psi_a e^{ik\ell} \qquad \ell = \text{odd}$

$\qquad\qquad\quad \psi_b e^{ik\ell} \qquad \ell = \text{even}$

$$E_a \psi_a - 2t\cos k\, \psi_b = E\psi_a$$

$$E_b \psi_b - 2t\cos k\, \psi_a = E\psi_b$$

$$\begin{pmatrix} E_a - E & -2t\cos k \\ -2t\cos k & E_b - E \end{pmatrix} \begin{pmatrix} \psi_a \\ \psi_b \end{pmatrix} = 0$$

determinant must vanish

$$(E_a - E)(E_b - E) - (2t\cos k)^2 = 0$$

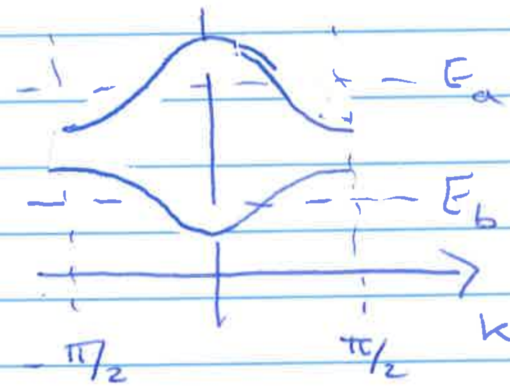
$$E^2 - (E_a + E_b)E + E_a E_b - (2t\cos k)^2 = 0$$

$$E = \frac{E_a + E_b \pm \sqrt{(E_a - E_b)^2 + (2t\cos k)^2}}{2}$$

t small $\quad (E_a - E_b)\left[1 + \left(\frac{2t\cos k}{E_a - E_b}\right)^2\right]^{1/2}$

$$\approx (E_a - E_b)\left[1 + \frac{1}{2}\left(\frac{2t\cos k}{E_a - E_b}\right)^2\right]$$

$$E \approx \begin{cases} E_a + \dfrac{(t\cos k)^2}{E_a - E_b} \\ E_b - \dfrac{(t\cos k)^2}{E_a - E_b} \end{cases}$$



NB $\quad \cos^2 k + \sin^2 k = 1$

$\quad \cos^2 k - \sin^2 k = \cos 2k$

$$\cos^2 k = \frac{1}{2}(1 + \cos 2k)$$

$$E \approx E_a + \frac{t^2}{2(E_a - E_b)} + \frac{t^2}{2(E_a - E_b)}\cos 2k$$

Already hint that $E_a = E_b$ (degenerate) is special. We will see more of this.

2D square

$$\psi(\ell_x, \ell_y) = \psi_a e^{i(k_x \ell_x + k_y \ell_y)}$$

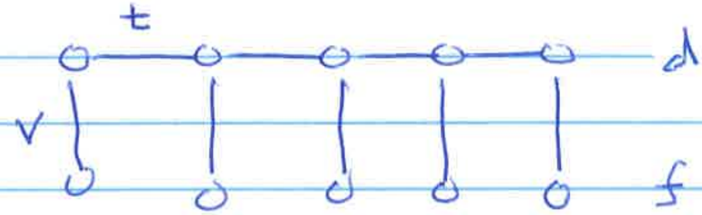
$$E_a \psi(\ell_x, \ell_y) - t\psi(\ell_x+1, \ell_y) - t\psi(\ell_x - 1, \ell_y)$$

$$- t\psi(\ell_x, \ell_y+1) - t\psi(\ell_x, \ell_y - 1) = E\psi(\ell_x, \ell_y)$$

$$E = E_a - 2t\cos k_x - 2t\cos k_y$$

"PAM"

$d = 1$ for simplicity

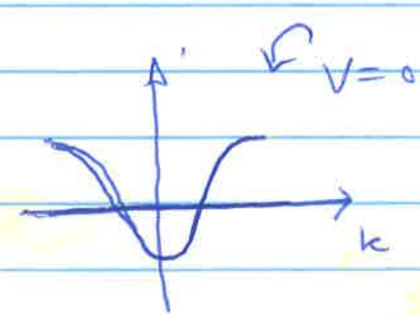


$$E_d \psi_d(\ell) - t\psi_d(\ell+1) - t\psi_d(\ell-1) - V\psi_f(\ell) = E\psi_d(\ell)$$

$$E_f \psi_f(\ell) \qquad - V\psi_d(\ell) = E\psi_f(\ell)$$

$$\begin{pmatrix} E_d - 2t\cos k & -V \\ -V & E_f \end{pmatrix} \begin{pmatrix} \psi_d \\ \psi_f \end{pmatrix} = E \begin{pmatrix} \psi_d \\ \psi_f \end{pmatrix}$$

Consider case $E_d = E_f$
$= 0$
wlog



6.

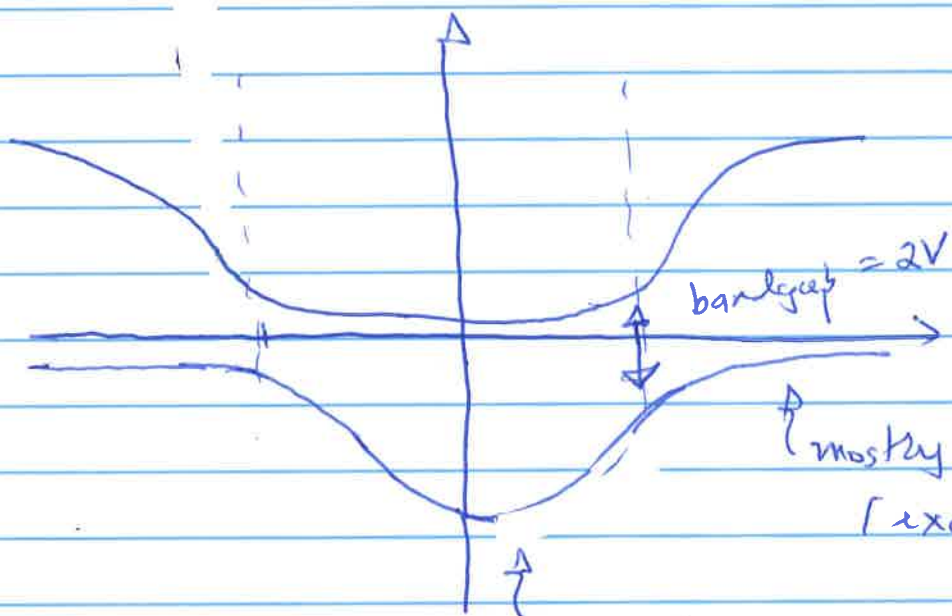
$$(-2t\cos k - E)(-E) - V^2 = 0$$

$$E^2 + E\,2t\cos k - V^2 = 0$$

$$E = \left[-2t\cos k \pm \sqrt{(2t\cos k)^2 + 4V^2}\right] \tfrac{1}{2}$$

If you sketch it:

$k = \pi/2 \quad E = \pm V$



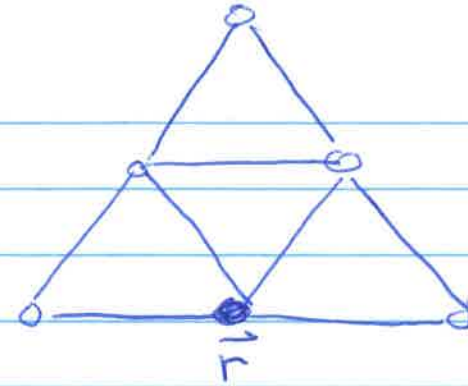
mostly f character
(examine eigenfunctions)

mostly d character
(eigenfunction

Biggest effect of V
is at degenerate
points $k = \pm\pi/2$
where bands touch

Triangular lattice 2D

discrete indices less appropriate



square $\vec{r} = l_x \hat{x} + l_y \hat{y}$

$$E_a \psi(\vec{r}) - t\,\psi(\vec{r} + \hat{x}) - t\,\psi(\vec{r} + \tfrac{1}{2}\hat{x} + \tfrac{\sqrt{3}}{2}\hat{y})$$

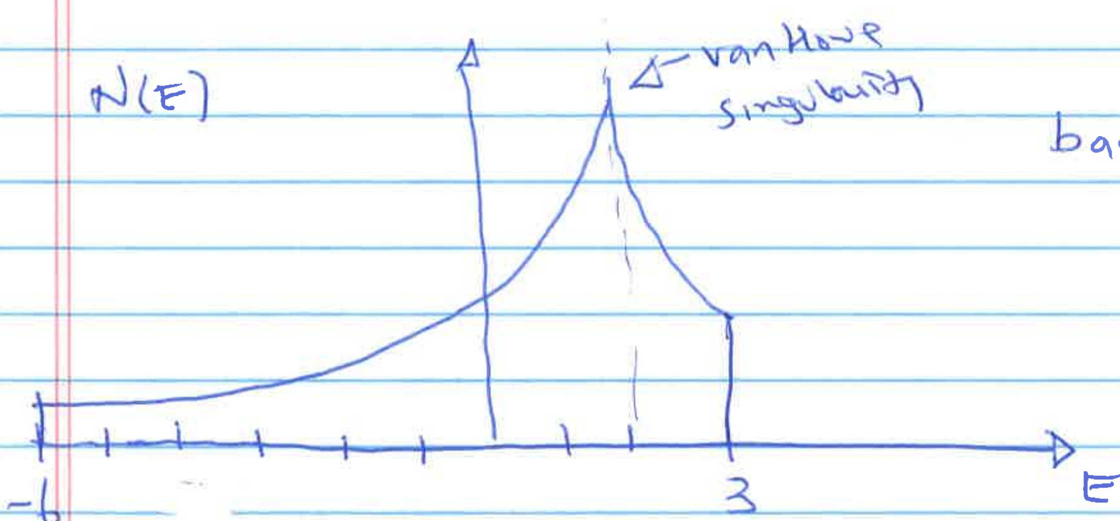
$$- t\,\psi(\vec{r} - \tfrac{1}{2}\hat{x} + \tfrac{\sqrt{3}}{2}\hat{y}) + hc$$

$$= E\psi(\vec{r})$$

$$\psi(\vec{r}) = \psi_a e^{i\vec{k}\cdot\vec{r}}$$

Na_xCoO_2
Sodium cobaltate
Co atoms on triangular lattice

$$E(k_x k_y) = -2t\left[\cos k_x + 2\cos\frac{k_x}{2}\cos\frac{\sqrt{3}}{2}k_y\right]$$



bandwidth $= 9t$

"particle-hole symmetry" $N(E) \neq N(-E)$