

QCMP-2014/15 — Quantum Condensed Matter Physics

Problem sheet 2: Band structure

1. Optical absorption of simple metals

Sketch the typical energy-wavevector dependence, or dispersion relation, of electrons in a one-dimensional periodic potential within nearly free electron theory. In your sketch, include the unperturbed dispersion, the effects of the periodic potential, the Brillouin zone, the relevant reciprocal lattice wavevector, and the folded-back band structure. How can this approach explain the formation of energy gaps in solids?

In the first Brillouin zone of a body centred cubic (BCC) crystal, the shortest distance from the zone centre to the zone boundary is $\sqrt{2}\pi/a$, where a is the width of the conventional cubic unit cell. Demonstrate that the free electron Fermi surface of a monovalent metal with the BCC structure is contained entirely within the first Brillouin zone.

The absorption of photons in metals excites an electron from a filled state at wavevector \mathbf{k} to an empty state at the same wavevector, but in a higher band. In the electronic dispersion diagram drawn up above, indicate the absorption process which requires the minimum, or threshold energy E_0 . For a BCC monovalent material, show that this energy is $E_0 \approx 0.64E_F$.

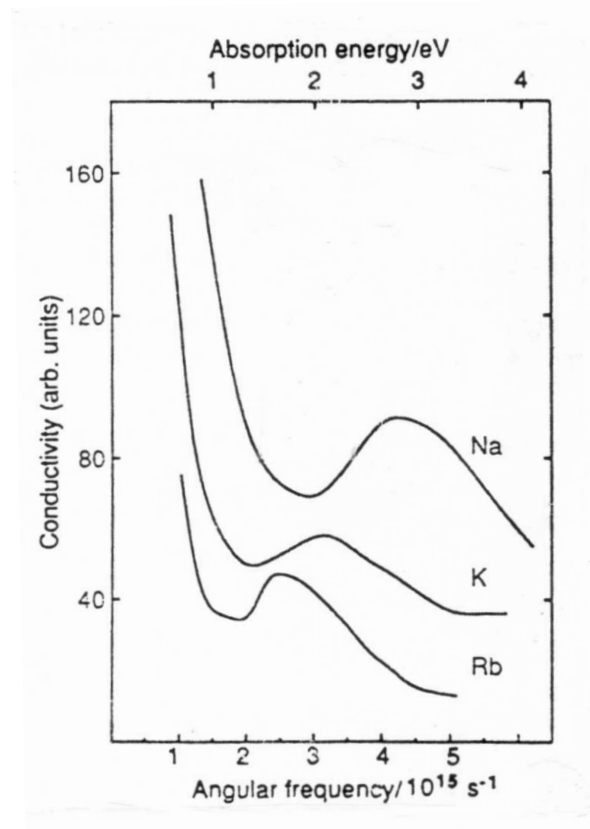
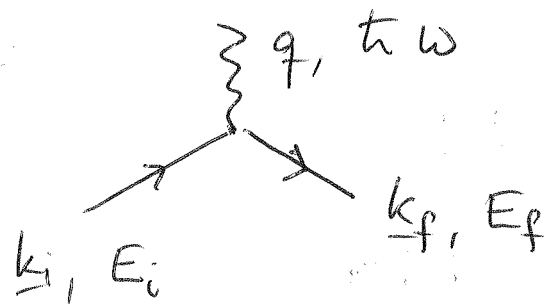


Figure 1: AC-conductivity for three alkaline metals

Alkali metals have a BCC structure. The experimental data on Fig. 1 show the frequency dependence of the conductivity in the alkali metals Na, K, and Rb, which have lattice constants a , respectively, of 0.423 nm, 0.523 nm, and 0.559 nm. The broad peaks at higher frequencies in each curve have been interpreted as arising from interband optical absorption. Is this qualitatively consistent with nearly free electron behaviour?

Solution:



$\hbar k_f = \hbar(k_i + q + \frac{q}{2})$ cons. of crystal mtr.

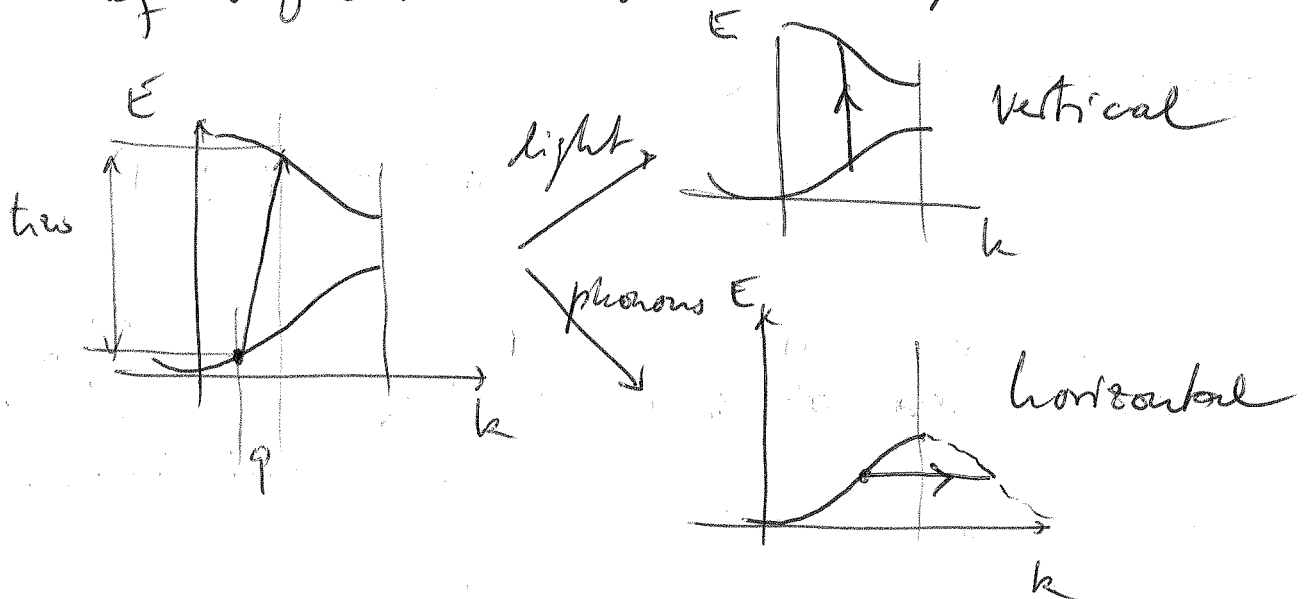
$$E_f = E_i + \hbar\omega = E_i + \hbar\omega q$$

photons: $v = c = 3 \cdot 10^8 \frac{m}{s} \Rightarrow$ energy transfer large

phonons: $v \sim 10^3 \frac{m}{s} \Rightarrow$ energy transfer small

For light, $\lambda \sim 0.5 \mu m \Rightarrow q \ll \frac{2\pi}{a}$

$\Rightarrow k_f$ very close to k_i on scale of BZ.



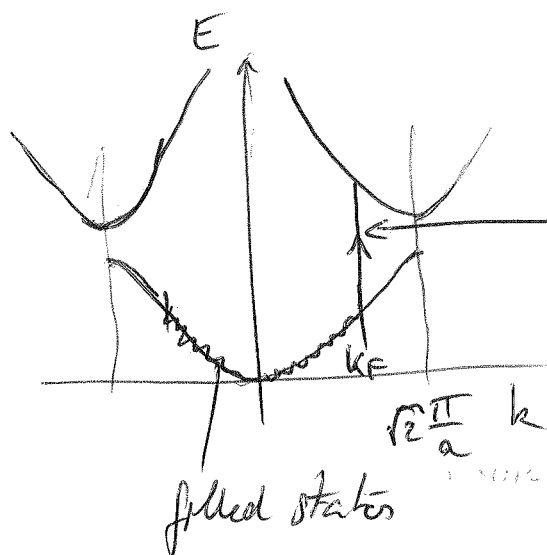
(3)

$$V_{\text{unit cell}} = \frac{a^3}{2} \quad \text{BCC} \xrightarrow{\text{FT}} \text{FCC}$$

$$\text{Shortest } q_B = \sqrt{2} \frac{\pi}{a}$$

$$k_F^3 = 3\pi^2 \frac{1}{V_{u.c.}} = 3\pi^2 \frac{2}{a^3} \Rightarrow k_F = \frac{(6\pi^2)^{1/3}}{a} < \sqrt{2} \frac{\pi}{a}$$

\Rightarrow FS contained inside 1st BZ.



$$\Rightarrow E_0 = \frac{\hbar^2}{2m^*} \left(\left(k_F - 2 \frac{\sqrt{2}\pi}{a} \right)^2 - k_F^2 \right) =$$

$$= \frac{\hbar^2}{2m^*} \left(\frac{8\pi^2}{a^2} - \frac{4\sqrt{2}\pi}{a} k_F \right) =$$

$$= \frac{\hbar^2}{2m^*} k_F^2 \left(\frac{8\pi^2}{(6\pi^2)^{2/3}} - \frac{4\sqrt{2}\pi}{(6\pi^2)^{1/3}} \right) = \underline{0.64 E_F}$$

(3)

	a [Å]	E_F [eV]	$0.64 E_F$ [eV]
Na	4.23	3.14	1.9
K	5.23	2.06	1.3
Rb	5.59	1.8	1.2

↑
onset of absorption

$$\left(\frac{E_F}{\text{eV}} = \frac{\hbar^2}{2m} \left(6\pi^2 \frac{1}{a^3} \right)^{2/3} \frac{1}{1.6 \cdot 10^{-19}} = \left(\frac{a}{\text{Å}} \right)^{-2} \cdot 56.2 \right)$$

(3)

2. The diatomic chain

The lattice potential $U(x)$ of a chain of atoms has Fourier components

$$U_g = \frac{1}{L} \int_{-L/2}^{L/2} e^{-igx} U(x) dx, \quad (1)$$

where $L \rightarrow \infty$ is the length of the chain. Using the NFE approximation valid for momenta near the zone boundary $k \rightarrow \pi/a$, show that the energy eigenvalues are given by

$$E^\pm(\mathbf{k}) = \frac{1}{2} \frac{\hbar^2}{2m} (k^2 + (k - 2\pi/a)^2) \pm \frac{1}{2} \sqrt{\left[\frac{\hbar^2}{2m} (k^2 - (k - 2\pi/a)^2) \right]^2 + 4 |U_{2\pi/a}|^2}. \quad (2)$$

Show that this leads to:

- (a) an energy gap on the zone boundary of magnitude $2|U_{2\pi/a}|$, and
- (b) wavefunctions for $\mathbf{k} \rightarrow \pi/a$ given by $c_k^\pm / c_{k-2\pi/a}^\pm = \pm U_{2\pi/a} / |U_{2\pi/a}|$.

Hence show that the probability density for the electronic states at $k = \pi/a$ take the form

$$\begin{aligned} |\psi^{(1)}(x)|^2 &\propto \cos^2\left(\frac{\pi x}{a} + \frac{\phi}{2}\right) \\ |\psi^{(2)}(x)|^2 &\propto \sin^2\left(\frac{\pi x}{a} + \frac{\phi}{2}\right), \end{aligned} \quad (3)$$

where ϕ is the phase of the complex Fourier component $U_{2\pi/a}$, $\psi^{(1)}$ refers to the higher energy ('anti-bonding') state, and $\psi^{(2)}$ denotes the lower energy ('bonding') state.

Consider a one-dimensional diatomic lattice with lattice constant a (Fig. 2), in which two atoms labelled A (light grey circles) and B (dark grey circles) take positions $R_n^{(A)} = na + (a/4)(1 - \delta)$ and $R_n^{(B)} = na - (a/4)(1 - \delta)$.

Show that $U_{2\pi/a}$ can be written

$$U_{2\pi/a} = \sin\left(\frac{\pi\delta}{2}\right)(U_{2\pi/a}^A + U_{2\pi/a}^B) - i \cos\left(\frac{\pi\delta}{2}\right)(U_{2\pi/a}^A - U_{2\pi/a}^B), \quad (4)$$

where

$$U_{2\pi/a}^{A,B} = \frac{1}{L} \int_{-L/2}^{L/2} dx e^{-i2\pi x/a} \sum_n U^{A,B}(x - na), \quad (5)$$

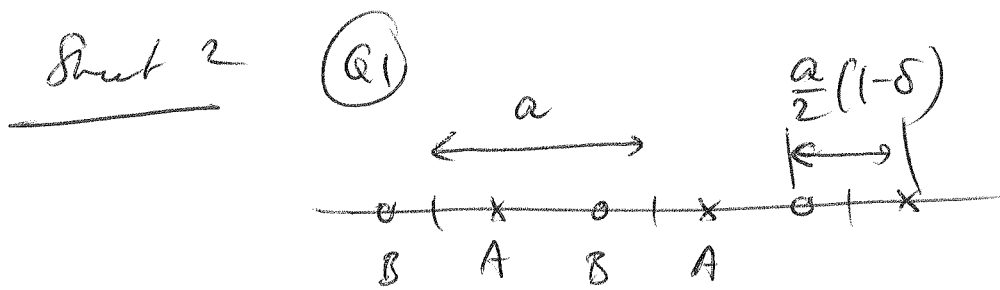
and $U^{A,B}(x)$ is the potential due to a single atom of type A, B centred at $x = 0$.

The system contains an average of one electron per atom, or equivalently two electrons per unit cell. Discuss the values of the energy gaps and plot the charge densities corresponding to the highest filled electron state and the lowest empty electron state in the three cases;

- (a) identical atoms, $U_A = U_B$, and $\delta = 0$;
- (b) different atoms $U_A \neq U_B$, and $\delta = 0$;
- (c) identical atoms, $U_A = U_B$, and $\delta \neq 0$.

Explain how this provides a simple model of either an *ionic* or *covalent* solid.

Solution:



$$u(x) = \sum_n u_A \left(x - \frac{a}{4}(1-\delta) - na \right) + u_B \left(x + \frac{a}{4}(1-\delta) - na \right)$$

$$u_g = \frac{1}{a} \int_{-\frac{a}{2}}^{\frac{a}{2}} u_A \left(x - \frac{a}{4}(1-\delta) \right) e^{-igx} dx + \frac{1}{a} \int_{-\frac{a}{2}}^{\frac{a}{2}} u_B \left(x + \frac{a}{4}(1-\delta) \right) e^{-igx} dx =$$

$$= e^{-ig \frac{a}{4}(1-\delta)} u_g^A + e^{ig \frac{a}{4}(1-\delta)} u_g^B =$$

$$= -i \left(\cos\left(\frac{\pi}{2}\delta\right) + i \sin\left(\frac{\pi}{2}\delta\right) \right) u_g^A + i \left(\cos\left(\frac{\pi}{2}\delta\right) - i \sin\left(\frac{\pi}{2}\delta\right) \right) u_g^B =$$

$$= \sin\left(\frac{\pi}{2}\delta\right) (u_g^A + u_g^B) - i \cos\left(\frac{\pi}{2}\delta\right) (u_g^A - u_g^B)$$

NFE theory: $|\psi\rangle = c_k |k\rangle + c_{k-g} |k-g\rangle$

$$\langle k | H | \psi \rangle = c_k E = c_k E_k^{(0)} + c_{k-g} \langle k | H | k-g \rangle$$

$$\langle k-g | H | \psi \rangle = c_{k-g} E = c_k \langle k-g | H | k \rangle + c_{k-g} E_{k-g}^{(0)}$$

①

$$E_k^{(0)} = \frac{\hbar^2}{2m} k^2 \quad E_{k-g}^{(0)} = \frac{\hbar^2}{2m} (k-g)^2$$

$$\langle k | H | k-g \rangle = \langle g | U \rangle = U_g$$

$$\begin{pmatrix} E_k^{(0)} - E & U_g \\ U_g^* & E_{k-g}^{(0)} - E \end{pmatrix} \begin{pmatrix} c_k \\ c_{k-g} \end{pmatrix} = 0$$

$$\Rightarrow E_{\pm} = \frac{1}{2} (E_k^{(0)} + E_{k-g}^{(0)}) \pm \left(\left(\frac{E_k^{(0)} - E_{k-g}^{(0)}}{2} \right)^2 + |U_g|^2 \right)^{1/2}$$

$$\xrightarrow{k = \frac{\pi}{a}} \frac{\hbar^2}{2m} \left(\frac{\pi}{a} \right)^2 \pm |U_g|$$

a) $\Rightarrow \text{gap size} = 2|U_g|$

b) Write $U_g = |U_g| e^{i\varphi}$. ($\pm |U_g| c_k + U_g c_{k-g} = 0$)

$$c_k = \pm \frac{U_g}{|U_g|} c_{k-g}$$

$$\Rightarrow \begin{matrix} \text{lower en.} \\ \downarrow \\ + c_{\frac{\pi}{a}} + e^{i\varphi} c_{-\frac{\pi}{a}} = 0 \\ \uparrow \\ \text{higher en.} \end{matrix}$$

$$c_{\frac{\pi}{a}} = e^{i\varphi/2}$$

$$c_{-\frac{\pi}{a}} = \begin{matrix} \text{lower en.} \\ \downarrow \\ - e^{-i\varphi/2} \\ \uparrow \\ \text{higher en.} \end{matrix}$$

①

higher en. solution:

$$\psi_1 = e^{i\frac{\varphi}{2}} e^{i\frac{\pi}{a}x} + e^{-i\frac{\varphi}{2}} e^{-i\frac{\pi}{a}x} = \cos\left(\frac{\pi}{a}x + \frac{\varphi}{2}\right)$$

$$|\psi_1|^2 = \cos^2\left(\frac{\pi}{a}x + \frac{\varphi}{2}\right)$$

lower energy solution:

$$\psi_2 = e^{i\frac{\varphi}{2}} e^{i\frac{\pi}{a}x} - e^{-i\frac{\varphi}{2}} e^{-i\frac{\pi}{a}x} = \sin\left(\frac{\pi}{a}x + \frac{\varphi}{2}\right)$$

$$|\psi_2|^2 = \sin^2\left(\frac{\pi}{a}x + \frac{\varphi}{2}\right)$$

q) $U_A = U_B$, $\delta = 0$: $U_g = 0$

no more splitting, because have returned to

monatomic chain:

Doubling the unit cell causes

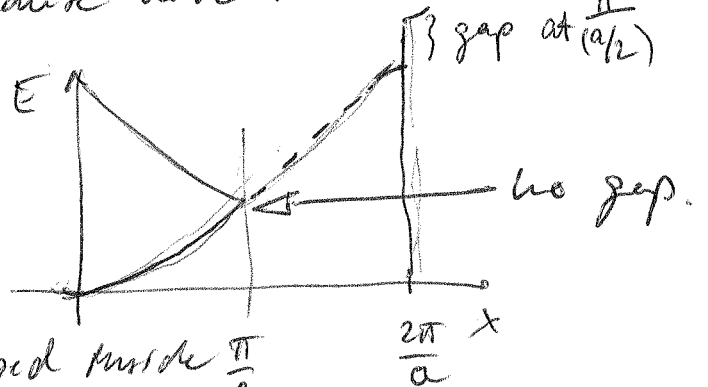
BZ to halve, and the

dashed segment is mapped inside $\frac{\pi}{a}$

the smaller BZ, but there is no

gap at $\frac{\pi}{a}$ unless the lattice pot. has a periodicity

of a (larger unit cell).



①

(b) $U_A \neq U_B, \delta = 0$

take $\{U_A\} > \{U_B\}$, U_A, U_B real
 more negative \Rightarrow B more attractive

$$U_g = -i(U_A - U_B) \quad \varphi = -\frac{\pi}{2}$$

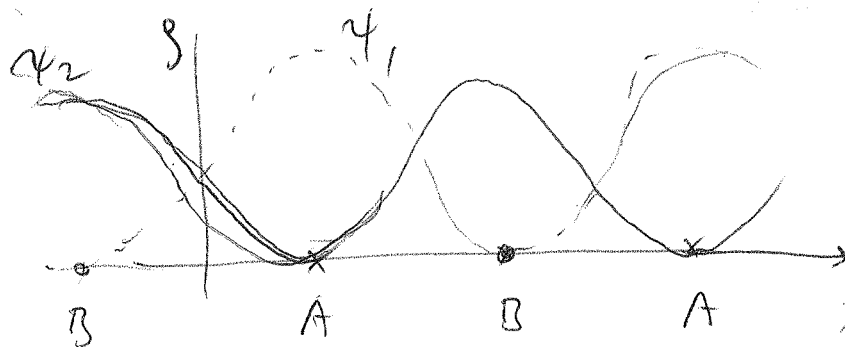
$$\psi_2 = \sin\left(\frac{\pi}{a}x - \frac{\pi}{4}\right)$$

\uparrow
 $\frac{\pi}{a} \cdot \frac{a}{4}$

lower en. solution

$$\psi_1 = \cos\left(\frac{\pi}{a}x - \frac{\pi}{4}\right)$$

higher en. solution



charge shifts to more attractive atoms \Rightarrow ionic character.

charge disproportionation

(c) $U_A = U_B, \delta \neq 0$
 take $\delta > 0$

$$U_g = U_A \cdot 2\sin\left(\frac{\pi\delta}{2}\right) \Rightarrow \varphi = \pi$$

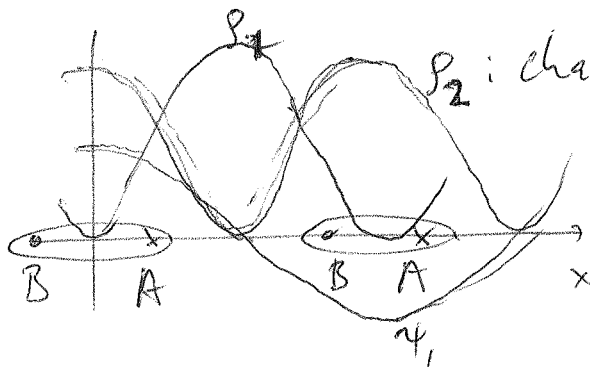
\uparrow
 < 0

higher en.
 $\psi_1 = -\sin\left(\frac{\pi}{a}x\right)$

lower en.
 $\psi_2 = \cos\left(\frac{\pi}{a}x\right)$

$$|\psi_1|^2 = \sin^2\left(\frac{\pi}{a}x\right)$$

$$|\psi_2|^2 = \cos^2\left(\frac{\pi}{a}x\right)$$



P_2 : charge accumulates between pairs of atoms, which have moved together: covalent, dimerisation, Peierls transition.

④

3. Nearly free electron approximation for a square lattice

The potential in a 2-dimensional square crystal of side a is given by

$$V(x, y) = -2V_0 \left[\cos\left(\frac{2\pi x}{a}\right) + \cos\left(\frac{2\pi y}{a}\right) \right] . \quad (6)$$

Use the nearly-free electron approximation to calculate the electron energies at the wave-vectors

$$\mathbf{k}_0 = \frac{2\pi}{a}(0, 0) , \mathbf{k}_1 = \frac{2\pi}{a}\left(\frac{1}{2}, 0\right) , \mathbf{k}_2 = \frac{2\pi}{a}\left(\frac{1}{2}, \frac{1}{2}\right) . \quad (7)$$

(a) Write down the form of the wavefunction within the nearly-free-electron approximation, using 1 plane wave at \mathbf{k}_0 , 2 plane waves at \mathbf{k}_1 , and 4 plane waves at \mathbf{k}_2 .

(b) In each case, substitute these wavefunctions into the Schrödinger equation, and write the resulting equations in matrix form.

(c) Solve the three eigenvalue problems for the energy levels at \mathbf{k}_0 , \mathbf{k}_1 , and \mathbf{k}_2 .

Solution:

Sheet 2 (Q2)

$$V(x, y) = -2 V_0 \left[\cos\left(\frac{2\pi x}{a}\right) + \cos\left(\frac{2\pi y}{a}\right) \right]$$

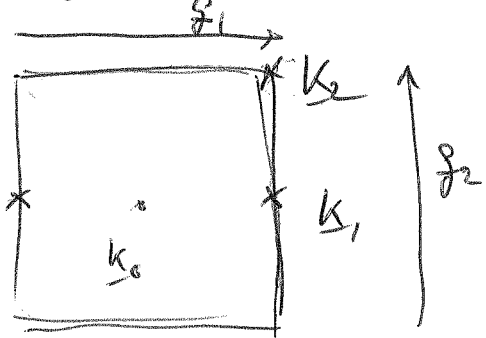
a) i) at $\underline{k}_0 = \frac{2\pi}{a} (0, 0)$ $\psi_{\underline{k}_0}(\underline{r}) = 1$

ii) at $\underline{k}_1 = \frac{2\pi}{a} (\frac{1}{2}, 0)$

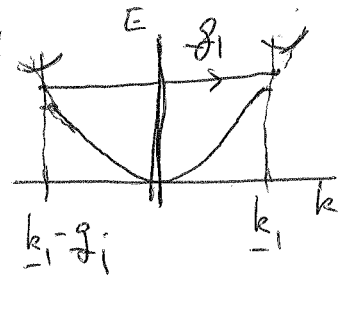
$|\underline{k}_1\rangle$ and $|\underline{k}_1'\rangle$ are

degenerate and linked

by reciprocal lattice vector \underline{g}_1



$$|\psi_{\underline{k}_1}\rangle = \alpha |\underline{k}_1\rangle + \beta |\underline{k}_1'\rangle = \alpha |\underline{k}_1\rangle + \beta |\underline{k}_1 - \underline{g}_1\rangle$$



iii) at \underline{k}_2 : $|\underline{k}_2\rangle, |\underline{k}_2 - \underline{g}_1\rangle, |\underline{k}_2 - \underline{g}_2\rangle, |\underline{k}_2 - \underline{g}_1 - \underline{g}_2\rangle$

are degenerate and linked by rec. latt.

vectors

$$|\psi_{\underline{k}_2}\rangle = \alpha |\underline{k}_2\rangle + \beta |\underline{k}_2 - \underline{g}_1\rangle + \gamma |\underline{k}_2 - \underline{g}_2\rangle + \delta |\underline{k}_2 - \underline{g}_1 - \underline{g}_2\rangle$$

b) i) $H|\psi_{\underline{k}_0}\rangle = E|\psi_{\underline{k}_0}\rangle \Rightarrow \langle \psi_{\underline{k}_0} | : V_0 = E,$

V_0 usually set to 0. $\Rightarrow E = 0$

(2)

$$ii) \text{ For } \langle \underline{k}_1 | \hat{H} | \psi_{\underline{k}_1} \rangle = \alpha E = \alpha E_{\underline{k}_1}^{(0)} + \beta V_{\underline{g}_1}$$

$$\langle \underline{k}_1 - \underline{g}_1 | \hat{H} | \psi_{\underline{k}_1} \rangle = \beta E = \alpha V_{\underline{g}_1}^* + \beta E_{\underline{k}_1 - \underline{g}_1}^{(0)}$$

$$\uparrow \\ = E_{\underline{k}_1}^{(0)}$$

$$\Rightarrow \begin{pmatrix} E_{\underline{k}_1}^{(0)} - E & V_{\underline{g}_1} \\ V_{\underline{g}_1}^* & E_{\underline{k}_1}^{(0)} - E \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = 0$$

$$E = E_{\underline{k}_1}^{(0)} \pm |V_{\underline{g}_1}| = \frac{\hbar^2}{2m} \left(\frac{\pi}{a} \right)^2 \pm |V_{\underline{g}_1}|$$

$$(iii) \langle \underline{k}_2 | \hat{H} | \psi_{\underline{k}_2} \rangle = \alpha E = \alpha E_{\underline{k}_2}^{(0)} + \beta V_{\underline{g}_1} + \gamma V_{\underline{g}_2} + \delta V_{\underline{g}_1 + \underline{g}_2}$$

$$\text{Note } V_{\underline{g}_1 + \underline{g}_2} = -2V_0 \frac{1}{a^2} \int_{-\frac{a}{2}}^{\frac{a}{2}} \int_{-\frac{a}{2}}^{\frac{a}{2}} dx dy e^{-i \frac{2\pi}{a} x} e^{-i \frac{2\pi}{a} y} \left(\cos \frac{2\pi x}{a} + \cos \frac{2\pi y}{a} \right) \\ = 0 \quad \left(\text{because } \int dx \cos\left(\frac{2\pi}{a} x\right) e^{-i \frac{2\pi}{a} x} \int dy e^{-i \frac{2\pi}{a} y} = 0 \right)$$

$$\langle \underline{k}_2 - \underline{g}_1 | \hat{H} | \psi_{\underline{k}_2} \rangle = \beta E = \alpha V_{\underline{g}_1}^* + \beta E_{\underline{k}_2}^{(0)} + \gamma V_{\underline{g}_1 + \underline{g}_2}^* + \delta V_{\underline{g}_2}$$

$$\langle \underline{k}_2 - \underline{g}_2 | \hat{H} | \psi_{\underline{k}_2} \rangle = \gamma E = \alpha V_{\underline{g}_2}^* + \beta V_{\underline{g}_1 + \underline{g}_2}^* + \gamma E_{\underline{k}_2}^{(0)} + \delta V_{\underline{g}_1}$$

$$\langle \underline{k}_2 - \underline{g}_1 - \underline{g}_2 | \hat{H} | \psi_{\underline{k}_2} \rangle = \delta E = \alpha V_{\underline{g}_1 + \underline{g}_2}^* + \beta V_{\underline{g}_2}^* + \gamma V_{\underline{g}_1}^* + \delta E_{\underline{k}_2}^{(0)}$$

$$\text{All } E_0 = E_{\underline{k}_2}^{(0)}, -V_0 = V_{\underline{g}_1} = V_{\underline{g}_2}$$

(2)

②

$$\begin{bmatrix} E_0 - E & -V_0 & -V_0 & 0 \\ -V_0 & E_0 - E & 0 & -V_0 \\ -V_0 & 0 & E_0 - E & -V_0 \\ 0 & -V_0 & -V_0 & E_0 - E \end{bmatrix} \begin{pmatrix} \alpha \\ \beta \\ \gamma \\ \delta \end{pmatrix} = 0$$

Guess 4 e1-vectors from symmetry:

$$\begin{matrix} + & + \\ + & + \end{matrix} = \begin{pmatrix} 1 \\ 1 \\ 1 \\ 1 \end{pmatrix}, \quad \begin{matrix} + & + \\ - & - \end{matrix} = \begin{pmatrix} 1 \\ 1 \\ -1 \\ -1 \end{pmatrix}, \quad \begin{matrix} + & + \\ - & + \end{matrix} = \begin{pmatrix} 1 \\ -1 \\ 1 \\ -1 \end{pmatrix}, \quad \begin{matrix} - & + \\ + & - \end{matrix} = \begin{pmatrix} 1 \\ -1 \\ -1 \\ 1 \end{pmatrix}$$

$$\begin{matrix} + & + \\ + & + \end{matrix}: M \begin{pmatrix} 1 \\ 1 \\ 1 \\ 1 \end{pmatrix} = \begin{pmatrix} 1 \\ 1 \\ 1 \\ 1 \end{pmatrix} \cdot (E_0 - E - 2V_0) \Rightarrow E = E_0 - 2V_0$$

$$\begin{matrix} + & + \\ - & - \end{matrix}: M \begin{pmatrix} 1 \\ 1 \\ -1 \\ -1 \end{pmatrix} = \begin{pmatrix} 1 \\ 1 \\ -1 \\ -1 \end{pmatrix} \cdot (E_0 - E) \Rightarrow E = E_0$$

$$\begin{matrix} + & - \\ + & - \end{matrix}: M \begin{pmatrix} 1 \\ -1 \\ 1 \\ -1 \end{pmatrix} = \begin{pmatrix} 1 \\ -1 \\ 1 \\ -1 \end{pmatrix} \cdot (E_0 - E) \Rightarrow E = E_0$$

$$\begin{matrix} - & + \\ + & - \end{matrix}: M \begin{pmatrix} 1 \\ -1 \\ -1 \\ 1 \end{pmatrix} = \begin{pmatrix} 1 \\ -1 \\ -1 \\ 1 \end{pmatrix} \cdot (E_0 - E + 2V_0) \Rightarrow E = E_0 + 2V_0$$

$$\begin{array}{l} - E_0 + 2V_0 \\ - E_0 \\ - E_0 - 2V_0 \end{array}$$

③

4. Tight binding for BCC and FCC lattices

Show that the tightbinding bandstructure based on a single orbital per site for a body centred cubic lattice (include only the hopping to the eight nearest neighbours) is

$$E(\mathbf{k}) = \epsilon_0 + 8t \cos\left(\frac{1}{2}k_x a\right) \cos\left(\frac{1}{2}k_y a\right) \cos\left(\frac{1}{2}k_z a\right), \quad (8)$$

and for the face centred cubic lattice (twelve nearest neighbours)

$$E(\mathbf{k}) = \epsilon_0 + 4t \left[\cos\left(\frac{1}{2}k_x a\right) \cos\left(\frac{1}{2}k_y a\right) + \cos\left(\frac{1}{2}k_y a\right) \cos\left(\frac{1}{2}k_z a\right) + \cos\left(\frac{1}{2}k_z a\right) \cos\left(\frac{1}{2}k_x a\right) \right]. \quad (9)$$

Solution:

$$|\Psi_k\rangle = \sum_n e^{i\mathbf{k} \cdot \mathbf{R}_n} |n\rangle$$

$$\langle 0 | H | \Psi_k \rangle = E_k = t \sum_{nn'} e^{i\mathbf{k} \cdot \mathbf{R}_{nn'}} + \tilde{E}_0$$

bcc: $\mathbf{R}_n = \pm \frac{a}{2} \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix}, \pm \frac{a}{2} \begin{pmatrix} 1 \\ -1 \\ 1 \end{pmatrix}, \pm \frac{a}{2} \begin{pmatrix} 1 \\ 1 \\ -1 \end{pmatrix},$
 $\pm \frac{a}{2} \begin{pmatrix} -1 \\ 1 \\ 1 \end{pmatrix}$

$$E_k = \tilde{E}_0 + t \sum e^{i(\pm k_x \frac{a}{2} \pm k_y \frac{a}{2} \pm k_z \frac{a}{2})} =$$

8 = 2³ combinations

$$= \tilde{E}_0 + t \left(e^{ik_x \frac{a}{2}} + e^{-ik_x \frac{a}{2}} \right) \left(e^{ik_y \frac{a}{2}} + e^{-ik_y \frac{a}{2}} \right) \left(e^{ik_z \frac{a}{2}} + e^{-ik_z \frac{a}{2}} \right)$$

$$= \tilde{E}_0 + 8t \cos(k_x \frac{a}{2}) \cos(k_y \frac{a}{2}) \cos(k_z \frac{a}{2})$$

fcc: $\mathbf{R}_n = \pm \frac{a}{2} \begin{pmatrix} 1 \\ 1 \\ 0 \end{pmatrix}, \pm \frac{a}{2} \begin{pmatrix} 1 \\ 0 \\ 1 \end{pmatrix}, \pm \frac{a}{2} \begin{pmatrix} 0 \\ 1 \\ 1 \end{pmatrix},$
 $\pm \frac{a}{2} \begin{pmatrix} 1 \\ -1 \\ 0 \end{pmatrix}, \pm \frac{a}{2} \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix}, \pm \frac{a}{2} \begin{pmatrix} 0 \\ 1 \\ -1 \end{pmatrix}$

$$E_k = \tilde{E}_0 + t \sum_{nn'} e^{i(-1)^m k_x \frac{a}{2}} e^{i(-1)^n k_y \frac{a}{2}} + \sum e^{i(-1)^m k_x \frac{a}{2}} e^{i(-1)^n k_z \frac{a}{2}} + \sum e^{ik_y} e^{ik_z}$$

$$= \tilde{E}_0 + 4t \left[\cos(k_x \frac{a}{2}) \cos(k_y \frac{a}{2}) + \cos(k_x \frac{a}{2}) \cos(k_z \frac{a}{2}) + \cos(k_y \frac{a}{2}) \cos(k_z \frac{a}{2}) \right]$$

5. 2D tight binding band

This question is to encourage you to visualise bands in two dimensions (and higher!). Using a simple numerical package to plot representative cases will help.

Consider a two-dimensional band structure on a rectangular lattice

$$E(k) = 2 * t_1 \cos(ak_x) + 2 * t_2 \cos(bk_y) \quad (10)$$

- (a) What is the reciprocal lattice? Draw the first Brillouin zone boundary.
- (b) What is the real space lattice?
- (c) Suppose that $t_1 < 0$, $t_2 < 0$, $|t_1| > |t_2|$, and $a < b$. (Do you expect there to be a relation?) Plot some contours of constant energy. At which momenta do you find the band minima, maxima, and saddle points? What are the effective masses of electrons at these points (keep track of signs)?
- (d) For what range of energies are the energy contours open or closed? Does this bear any relationship to the energies of the saddle points?
- (e) * Make a numerical estimation of the density of states as a function of energy (plot a histogram, say). Can you give an analytic form for the energy- dependence of the density of states near the singular points?

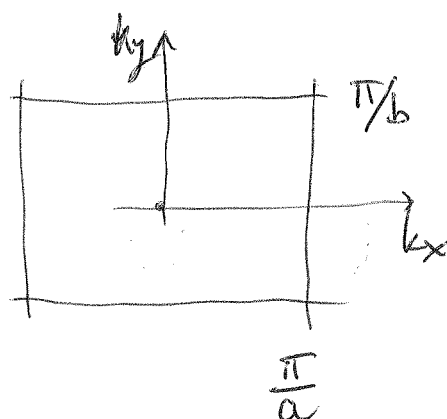
Solution:

Sheet 2 (Q5)

$$E(k) = -2t_1 \cos(ak_x) - 2t_2 \cos(bk_y)$$

a) reciprocal lattice vectors $(\frac{2\pi}{a}, 0)$, $(0, \frac{2\pi}{b})$

b) \Rightarrow real lattice $(a, 0)$, $(0, b)$

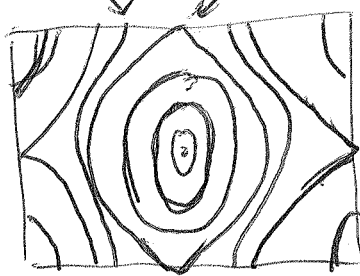


For $a < b$

c) If $a < b$, expect $|t_1| > |t_2|$, because overlap (hopping) integrals are larger if atoms are closer together.

open orbit

saddle



saddle

Dispersion is stronger in k_x -direction \Rightarrow energy contours are more widely spaced in k_y direction

Saddle point = van Hove singularity.

Minima: $k = (0, 0)$

Maxima: $k = (\frac{\pi}{a}, \frac{\pi}{b})$ (and points related by reciprocal lattice vectors)

(5)

Saddle points: $\underline{k} = \left(0, \frac{\pi}{b}\right) + \frac{\pi}{2}$

$$\underline{k} = \left(\frac{\pi}{a}, 0\right) + \frac{\pi}{2}$$

effective mass: mass tensor obtained from

Taylor expansion $E(\underline{k}) = E(\underline{k}_0) + \frac{1}{2} \hbar^2 \partial_{\underline{k}} \underline{m}^{-1} \partial_{\underline{k}}$

$$m_{ij}^{-1} = \partial_i \partial_j \bigg|_{\underline{k}=\underline{k}_0} E(\underline{k}) \cdot \frac{1}{\hbar^2}$$

Here, $\underline{m}^{-1} = \frac{1}{\hbar^2} \begin{pmatrix} 2 \frac{\hbar^2}{a^2} & 0 \\ 0 & 2 \frac{\hbar^2}{b^2} \end{pmatrix} = \begin{pmatrix} m_x^{-1} & 0 \\ 0 & m_y^{-1} \end{pmatrix}$
(at $\underline{k}=0$)

Effective mass m^* defined such that we obtain

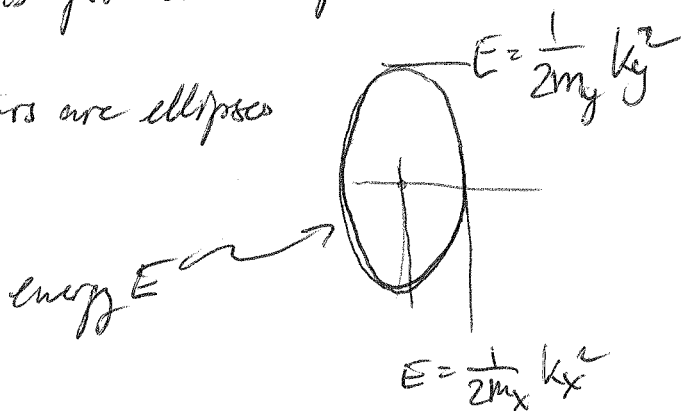
the same $g(E)$ (DOS) as for anisotropic mass

tensor. Here, energy contours are ellipses

Area of ellipse $= \pi k_x k_y =$

$$= \pi (2m_x E)^{1/2} (2m_y E)^{1/2} =$$

$$= 2\pi \sqrt{m_x m_y} E$$



(2)

5

states inside ellipse $N = \frac{V}{(2\pi)^3} 2\pi \sqrt{m_x m_y} E$

$\frac{\partial N}{\partial E}$ gives DOS. For isotropic case, $m_x = m_y = m^*$

\Rightarrow ~~the~~ mapping our problem onto isotropic case

requires $m^* = \sqrt{m_x m_y}$ to obtain same $N(E)$.

At minimum: $m^* = \left(\frac{2}{\hbar^2} \sqrt{t_1 t_2} a \cdot b \right)^{-1}$

At maximum: $m_x, m_y < 0 \Rightarrow m^* < 0$

$$m^* = \left(-\frac{2}{\hbar^2} \sqrt{t_1 t_2} a \cdot b \right)^{-1}$$

At saddle point: ① $\underline{k} = \left(0, \frac{\pi}{b} \right)$: $m_x^{-1} = \frac{2t_1 a^2}{\hbar^2}$

$$m_y^{-1} = -\frac{2t_2 b^2}{\hbar^2}$$

② $\underline{k} = \left(\frac{\pi}{a}, 0 \right)$: $m_x^{-1} = -\frac{2t_1 a^2}{\hbar^2}$

$$m_y^{-1} = \frac{2t_2 b^2}{\hbar^2}$$

m^* not defined near saddle

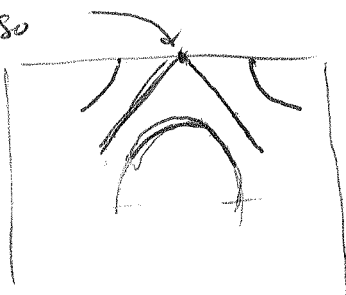
points (van Hove singularities).

3

(5)

d) For analytic expression near van Hove singularity in 2D, consider saddle point at $(0, \frac{\pi}{b})$:

shift energy so that $E=0$ at sing.



Put origin at singular \underline{k} :

$$\underline{q} = \underline{k} - (0, \frac{\pi}{b})$$

$$E = \alpha q_x^2 - \beta q_y^2$$

where $\alpha = t_1 a^2$, $\beta = t_2 b^2$

$$\nabla_{\underline{q}} E = \begin{pmatrix} 2\alpha q_x \\ -2\beta q_y \end{pmatrix} \quad |\nabla_{\underline{q}} E| = 2\sqrt{\alpha^2 q_x^2 + \beta^2 q_y^2}$$

For contour at energy E : $\beta q_y^2 = \alpha q_x^2 - E$

$$g(E) = \frac{A}{(2\pi)^2} \cdot \int_{\text{along contour } E} \frac{1}{|\nabla_{\underline{k}} E|} = \frac{A}{(2\pi)^2} \int dq_x \left| 1, \left(\frac{-E + \alpha q_x^2}{\beta} \right)^{1/2} \cdot \frac{\alpha q_x}{\beta} \right| \cdot \frac{1}{2\sqrt{\alpha^2 q_x^2 + \beta^2 q_y^2}} =$$

$$= \frac{A}{(2\pi)^2} \int dq_x \left(1 + \alpha^2 q_x^2 \beta^{-1} \frac{1}{\alpha q_x^2 - E} \right)^{1/2} \frac{1}{2\sqrt{\alpha^2 q_x^2 + \alpha \beta q_x^2 - \beta E}} =$$

$$= \frac{A}{(2\pi)^2} \int dq_x \frac{1}{\beta} \frac{1}{\alpha q_x^2 - E} \approx \frac{A}{(2\pi)^2} 2 \int_{-\alpha q_0^2}^{\alpha q_c^2} \frac{1}{\alpha \beta} \frac{1}{\sqrt{q^2 + q_0^2}} dq$$

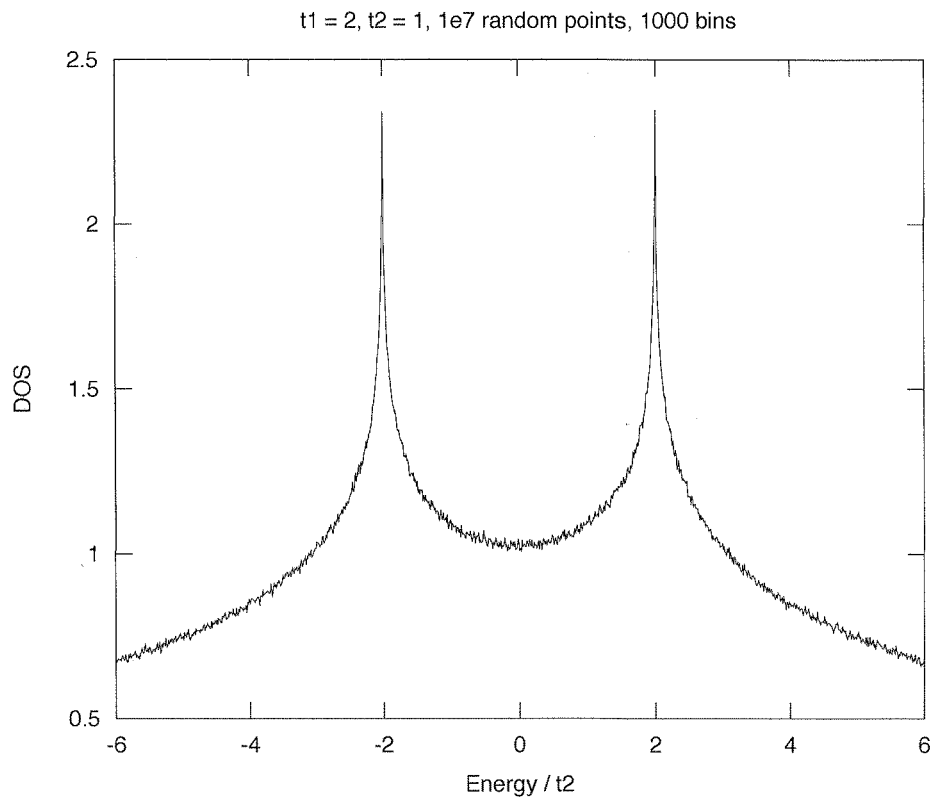
(q_c = cut-off)

$$\approx \frac{A}{(2\pi)^2 \sqrt{\alpha \beta}} \int_{q_0}^{q_c} \frac{1}{q} dq = \frac{A}{(2\pi)^2 \sqrt{\alpha \beta}} \left(\ln \frac{q_c}{q_0} \right) \approx \ln |E|$$

logarithmic divergence with energy approaching sing. (4)

(5) d) chd.

Numerically obtained DOS-vs. energy



(2D rectangular lattice, note logarithmic divergence of DOS at the two van Hove singularities)

Octave (Matlab) code:

```
N=1e7
M=1e3
t1=2; t2=1; a=1; b=2;
kx=pi/a*rand(1,N);
ky=pi/b*rand(1,N);
E=-2*t1*cos(a*kx)-2*t2*cos(b*ky);
[nn,xx]=hist(E,M,M)
plot(xx,nn)
xlabel('Energy / t2')
ylabel('DOS')
title('t1 = 2, t2 = 1, 1e7 random points, 1000 bins')
```

FMG, 1/3/2011

(5)

(5)

e) For $E < E_{\text{saddle}1} = -2(t_1 - t_2)$:
closed orbits (electron pockets)

For $E > E_{\text{saddle}2} = -2(t_2 - t_1)$
closed orbits (hole pockets)

In between, i.e. $-2(t_1 - t_2) < E < -2(t_2 - t_1)$
open orbits.

(6)

6. * Graphite

A single sheet of graphite has two carbon atoms in the unit cell at positions $\mathbf{d}_1 = 0$ and $\mathbf{d}_2 = (a/\sqrt{3})(0, 1, 0)$. The translation vectors for the two-dimensional hexagonal lattice are $\mathbf{t}_1 = (a/2)(1, \sqrt{3}, 0)$ and $\mathbf{t}_2 = (a/2)(-1, \sqrt{3}, 0)$.

The electronic configuration of the carbon atom is $1s^2 2s^2 2p^2$, and ignoring the $1s$ core states, we need to make a band structure from the s , p_x , p_y and p_z orbitals. Because s , p_x and p_y orbitals are even under reflection through the plane, and p_z odd, the two sets do not mix. The first three states hybridise to form σ -bonds with a large gap between the bonding and anti-bonding orbitals. Within this gap lie the π -orbitals arising from the hybridised p_z . The three bonding σ orbitals will accommodate 6 electrons per cell, leaving 2 electrons per unit cell in the π -bands. This question considers the electronic π -bands only.

(a) Construct Bloch states that consist of a linear mixture of the two p_z orbitals in the unit cell, and show how this gives rise to the secular equation to determine the eigenstate energies

$$\begin{vmatrix} E_p - E & tF(\mathbf{k}) \\ tF^*(\mathbf{k}) & E_p - E \end{vmatrix} = 0, \quad (11)$$

where t is the two center hopping matrix element between neighbouring p_z orbitals, and

$$F(\mathbf{k}) = 1 + 2 \cos\left(\frac{k_x a}{2}\right) \exp\left(-i \frac{\sqrt{3} k_y a}{2}\right). \quad (12)$$

(b) Show that the reciprocal lattice is also a hexagonal lattice, at an angle of $\pi/6$ to the real-space lattice. Show that the first Brillouin zone is a hexagon centred at the point $\Gamma = (000)$, whose corners are at the points $P = (2\pi/a)(2/3, 0, 0)$

(c) Determine a formula for the dispersion curves for the two eigenstates, and plot them in the directions ΓP , and ΓQ . (Here $Q = (2\pi/a)(1/2, 1/2\sqrt{3}, 0)$ is at the middle of a zone face.

(d) Where will the π -bands lie in energy relative to the sp^2 σ - orbitals? Is a single layer of graphite a metal or an insulator?

(e) Carbon nanotubes are formed by curling a graphite sheet into a tube, connecting the atoms with periodic boundary conditions. There are many ways to do this, and the different nanotubes can be indexed by the vector $m\mathbf{t}_1 + n\mathbf{t}_2$ that identifies which atoms are connected periodically. Assuming the band-structure is unchanged, show that the allowed k -states now lie on a set of lines whose direction is parallel to the tube. Discuss the situations under which the resulting tube will be semiconducting or metallic.

Solution:

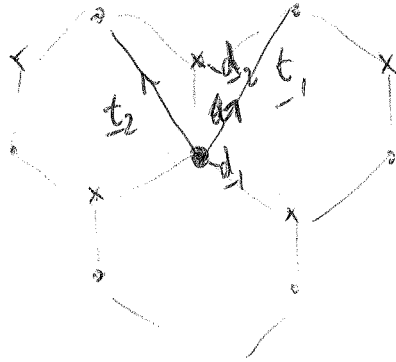
Q6

Graphite

$$\underline{t}_1 = \frac{a}{2} (1, \sqrt{3}, 0)$$

$$\underline{t}_2 = \frac{a}{2} (-1, \sqrt{3}, 0)$$

$$\underline{d}_2 = \frac{a}{\sqrt{3}} (0, 1, 0)$$



$$\langle (s \ p_x \ p_y) | H | p_z \rangle = 0$$

$$\text{because } [H, H] = 0$$

$\Rightarrow H$ maps π -spin onto π -spin with same k -value. $\langle \phi | \psi \rangle =$
 $= \langle \phi | H^{-1} H | \psi \rangle = \langle \phi | H H | \psi \rangle =$

$$2e^- \text{ per unit cell in } \pi\text{-bands} \quad \left| \begin{aligned} \langle (H\phi) | \psi \rangle &= \\ &= \sum_{\vec{r}} \sum_{\vec{r}'} \langle \phi | \psi \rangle \rightarrow 0 \end{aligned} \right.$$

$$\text{Take MO } |u\rangle = \alpha |u_1\rangle + \beta |u_2\rangle$$

$$|\psi_k\rangle = \sum_{\vec{r}} e^{i\vec{k}\cdot\vec{r}} (\alpha |u_1\rangle + \beta |u_2\rangle)$$

$$\langle 0_1 | H | \psi_k \rangle = \alpha E = \alpha E_p + \beta t \left(1 + e^{-i\vec{t}_2 \cdot \vec{k}} + e^{-i\vec{t}_1 \cdot \vec{k}} \right)$$

$$\langle 0_2 | H | \psi_k \rangle = \beta E = \beta E_p + \alpha t^* \left(1 + e^{i\vec{t}_2 \cdot \vec{k}} + e^{i\vec{t}_1 \cdot \vec{k}} \right)$$

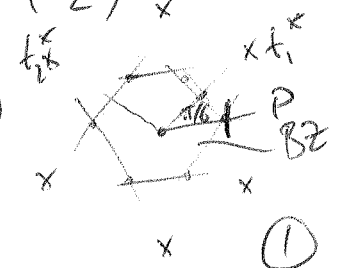
$$\begin{vmatrix} E_p - E & t F(k) \\ t^* F^* & E_p - E \end{vmatrix} = 0$$

$$F(k) = 1 + e^{i\frac{k_x a}{2}} e^{-i\frac{\sqrt{3}}{2} k_y a} + e^{-i\frac{k_x a}{2}} e^{-i\frac{\sqrt{3}}{2} k_y a}$$

$$= 1 + 2 \cos\left(\frac{k_x a}{2}\right) e^{-i\frac{\sqrt{3}}{2} k_y a}$$

$$\underline{t}_1^* = \frac{2\pi}{a} \left(1, \frac{1}{\sqrt{3}}, 0 \right) \quad \underline{t}_2^* = \frac{2\pi}{a} \left(-1, \frac{1}{\sqrt{3}}, 0 \right)$$

$$|\vec{k}| = \frac{2\pi}{a} \sqrt{\frac{4}{3}} \cdot \frac{\frac{1}{2} \cdot \frac{2\pi}{a} \sqrt{\frac{4}{3}}}{\cos 30^\circ} = \frac{2\pi}{a} \cdot \frac{2}{3} \rightarrow \underline{P} = \frac{2\pi}{a} \left(\frac{2}{3}, 0, 0 \right)$$



①

(6)

15/5/09

$$(E - E_p)^2 = t^2 |F|^2$$

$$E = E_p \pm t|F|$$

* For $\underline{k} = k \left(\frac{2\pi}{a} \left(\frac{2}{3}, 0, 0 \right) \right)$ (along $\Gamma - P$)

$$|F| = \left| 1 + 2 \cos \left(k \frac{\pi}{a} \cdot \frac{2}{3} a \right) \right| = \left| 1 + 2 \cos \left(\frac{2\pi}{3} k \right) \right|$$

* For $\underline{k} = k \left(\frac{2\pi}{a} \left(\frac{1}{2}, \frac{1}{2\sqrt{3}}, 0 \right) \right)$ (along $\Gamma - Q$)

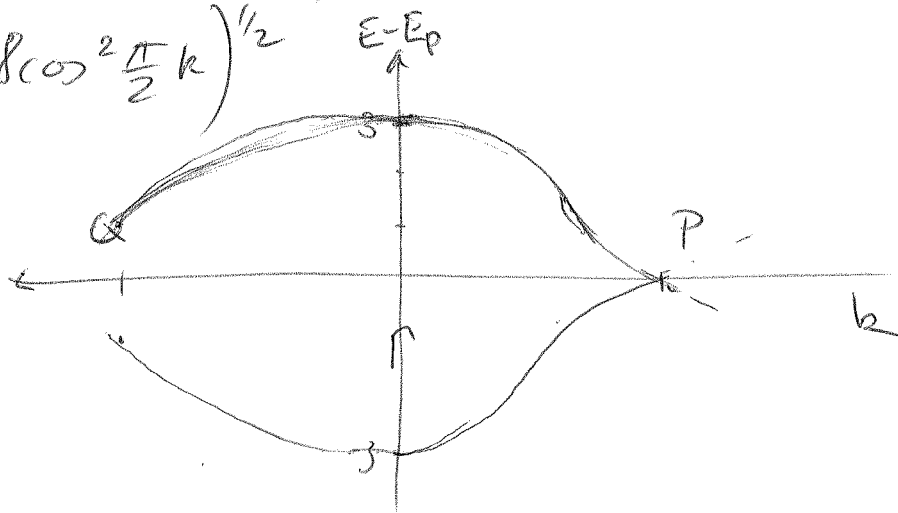
$$|F| = \left| 1 + 2 \cos \left(k \frac{\pi}{a} \frac{a}{2} \right) e^{-i \frac{\sqrt{3}}{2} k \frac{8\pi}{a} \frac{k}{2\sqrt{3}}} \right| =$$

$$= \left| 1 + 2 \cos \left(\frac{\pi}{2} k \right) e^{-i \frac{\pi}{2} k} \right| =$$

$$= \left[\left(1 + 2 \cos \left(\frac{\pi}{2} k \right) e^{-i \frac{\pi}{2} k} \right) \left(1 + 2 \cos \left(\frac{\pi}{2} k \right) e^{i \frac{\pi}{2} k} \right) \right]^{1/2} =$$

$$= \left(1 + 4 \cos \left(\frac{\pi}{2} k \right) \cancel{\cos \left(\frac{\pi}{2} k \right)} + 4 \cos^2 \frac{\pi}{2} k \right)^{1/2} =$$

$$= \left(1 + 8 \cos^2 \frac{\pi}{2} k \right)^{1/2}$$



(2)

(6)

d) lower band full, upper band empty.

Fermi points at P .

e) Nanotubes: connect 0 to $m \underline{t}_1 + n \underline{t}_2 = \underline{w}$

\Rightarrow allowed \underline{k} values s.t. $e^{i \underline{k} \underline{w}} = 1$

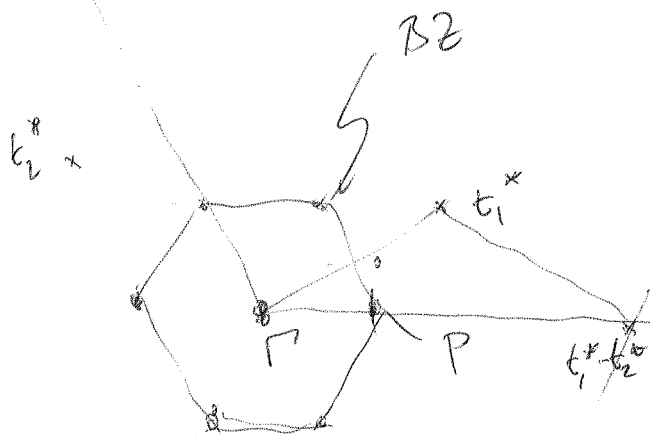
$$\underline{k}_{||} = q \cdot \frac{2\pi}{|\underline{w}|} \cdot \underline{w}$$

\uparrow integer

$\underline{k}_{\perp} \perp \underline{w}$, along tube.

by b.c. on that dirⁿ.

$$\begin{aligned} \underline{k}_{\perp} &= \frac{1}{m} \underline{t}_1^* - \frac{1}{n} \underline{t}_2^* \text{ is } \perp \underline{w} \\ &= (n \underline{t}_1^* - m \underline{t}_2^*) \frac{1}{mn} \end{aligned}$$



$$\underline{k} = q_1 \underline{t}_1^* + q_2 \underline{t}_2^*$$

$$\underline{k} \cdot \underline{w} = 2\pi l = 2\pi (q_1 m + q_2 n)$$

$$\underline{P} = \frac{1}{3} (\underline{t}_1^* - \underline{t}_2^*) = \frac{1}{3} \left(\frac{4\pi}{a}, 0, 0 \right) \quad \left. \begin{array}{l} \text{eqn. of plane } \perp \underline{w} \\ \text{must be integer} = l \end{array} \right\}$$

the ~~other~~ metal, if \underline{P} falls on line defined by

$$\text{Try: } q_1 = \frac{1}{3}, q_2 = -\frac{1}{3} \cdot \frac{1}{3} m - \frac{1}{3} n = l$$

$$\Rightarrow \boxed{m - n = 3l} \quad \text{e.g. } m=1, n=10 \text{ would be metallic.}$$

(3)

7. Band structure of d-band metals

In many transition metals a narrow d -band lies within a broad energy band originating from s -orbitals. This question discusses the band structure using a simple one-dimensional model constructed from a tight-binding Hamiltonian with one s -orbital $\phi_s(r)$ and one d -orbital $\phi_d(r)$ per atom; the atoms are arranged in a linear chain of lattice constant a .

- (a) Write down two Bloch states $\phi_s(k)$ and $\phi_d(k)$ formed from the atomic s - and d - states respectively. The eigenstates must be linear combinations of these.
- (b) Hence show that the one-particle bandstructure $E(k)$ can be found from the determinantal equation

$$\begin{vmatrix} E_s - 2t_{ss}\cos(ka) - E(k) & -2t_{sd}\cos(ka) \\ -2t_{sd}\cos(ka) & E_d - 2t_{dd}\cos(ka) - E(k) \end{vmatrix} = 0 \quad .$$

Identify and explain the parameters appearing in the determinantal equation, and discuss the approximations made that lead to this form.

- (c) Discuss why you would expect that $t_{ss} > |t_{sd}| > t_{dd}$.
- (d) Plot the dispersion of the two bands when $|E_d - E_s| \ll 2|t_{ss}|$, and t_{sd} and t_{dd} are neglected.
- (e) How is the dispersion modified from (d) by the inclusion of small values of t_{sd} and t_{dd} ?
- (f) Discuss the relevance of this model to the electronic bandstructure of Cu metal.

Solution:

* narrow d-band from $|d_n\rangle$

$$(\phi_d(\underline{r}) = \langle \underline{r} | d_0 \rangle, \phi_d(\underline{r} - \underline{R}_n) = \langle \underline{r} | d_n \rangle)$$

* wide s-band from $|s_n\rangle$

$$(\phi_s(\underline{r}) = \langle \underline{r} | s_0 \rangle, \phi_s(\underline{r} - \underline{R}_n) = \langle \underline{r} | s_n \rangle)$$

$$a) |s_{\underline{k}}\rangle = \sum e^{i\underline{k} \cdot \underline{R}_n} |s_n\rangle$$

$$|d_{\underline{k}}\rangle = \sum e^{i\underline{k} \cdot \underline{R}_n} |d_n\rangle$$

$$\begin{aligned} |\psi_{\underline{k}}\rangle &= \alpha_{\underline{k}} |s_{\underline{k}}\rangle + \beta_{\underline{k}} |d_{\underline{k}}\rangle \\ &= \sum e^{i\underline{k} \cdot \underline{R}_n} (\alpha_{\underline{k}} |s_n\rangle + \beta_{\underline{k}} |d_n\rangle) \end{aligned}$$

b) Define matrix elements:

$$E_s = \langle s_0 | H | s_0 \rangle = \langle s_n | H | s_n \rangle$$

$$E_d = \langle d_n | H | d_n \rangle$$

$$\langle s_n | d_m \rangle = 0, \quad \langle s_n | s_m \rangle = \delta_{nm}$$

$$t_{ss} = - \langle s_n | H | s_{n\pm 1} \rangle$$

$$t_{ds} = - \langle s_n | H | d_{n\pm 1} \rangle$$

$$t_{dd} = - \langle d_n | H | d_{n\pm 1} \rangle$$

$$\langle s_n | H | d_n \rangle = 0 \text{ because of symmetry}$$

$$(\text{e.g. for } d_{xy}, d_{xz}, d_{yz} : \text{mirror symm } M|d\rangle = -|d\rangle)$$

$$\begin{aligned} \Rightarrow \langle s_n | H | d_n \rangle &= \langle s_n | H | M M | d_n \rangle = \langle s_n | M H M | d_n \rangle = \\ &= \langle \underbrace{M s_n} | H | \underbrace{M d_n}_{-|d_n\rangle} \rangle = - \langle s_n | H | d_n \rangle \end{aligned}$$

* Apply \hat{H} :

$$H | \psi_k \rangle = E | \psi_k \rangle$$

* left multiply with basis states:

$$\begin{aligned} \langle s_0 | H | \psi_k \rangle &= \alpha_k E = \alpha_k E_s - \alpha_k t_{ss} (e^{ika} + e^{-ika}) \\ &\quad - \beta_k t_{sd} (e^{ika} + e^{-ika}) \approx \end{aligned}$$

$$\begin{aligned} \langle d_0 | H | \psi_k \rangle &= \beta_k E = -\alpha_k t_{sd} 2 \cos ka - \beta_k t_{dd} 2 \cos ka \\ &\quad - \beta_k E_d \end{aligned}$$

\Rightarrow eigenvalue problem:

$$\begin{vmatrix} E_s - 2t_{ss}\cos ka - E & -2t_{sd}\cos ka \\ -2t_{sd}\cos ka & E_d - 2t_{dd}\cos ka - E \end{vmatrix} = 0$$

Note that definition of hopping matrix elts has opposite sign from that used in lectures. There is some ambiguity regarding the sign of t in the literature.

Approx.: Nearest neighbour hopping only, orthogonal basis states $|s_n\rangle, |d_n\rangle$, matrix elt. $\langle s_n | H | d_n \rangle = 0$

c) ~~transition~~ Highest occupied d-orbitals (e.g. 3d)

are spatially more confined than highest occupied s-orbitals (4s), "the d-electrons sit inside a cloud of s-electrons". \Rightarrow orbital overlap

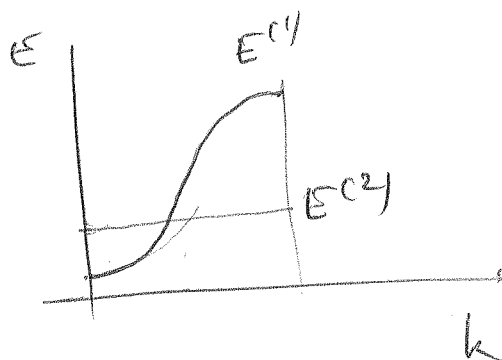
between neighbouring d-orbitals is very small

$$\Rightarrow |t_{dd}| \ll |t_{sd}| \ll |t_{ss}|$$

d) $|E_d - E_s| \ll 2|t_{ss}|, \quad t_{sd} = t_{dd} = 0$

$\Rightarrow E_k^{(1)} = E_s - 2t_{ss} \cos ka$

$E_k^{(2)} = E_d$

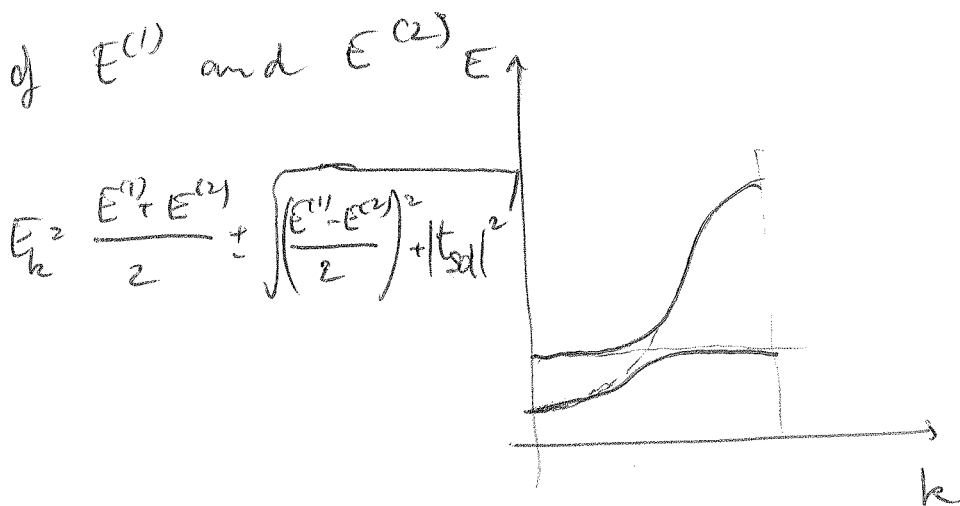


e) $t_{da} \neq 0 \Rightarrow$ dispersion in $E_k^{(2)}$



$t_{sd} \neq 0 \Rightarrow$ hybridization, anti-crossing

of $E^{(1)}$ and $E^{(2)}$

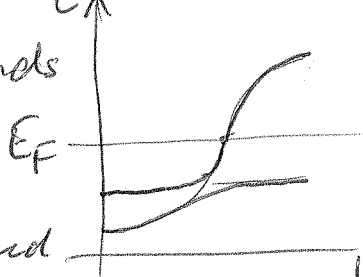


f) Electronic conf. of Cu $3d^{10} 4s^1 \Rightarrow E_F$

lies above full d-bands

like free electron

band crossing E_F is found



$\Rightarrow v_F = \frac{1}{\hbar} \frac{dE}{dk}$

theory, because

from s-states

* FS of Cu almost spherical, because effectively the same as alkaline metal, but slight distortion due to s-d hybridization.

* reddish colour caused by optical transitions from d-band in the visible range.

Note: Starred questions are challenge problems; they will do you good, but they go beyond the minimum requirements of the course.

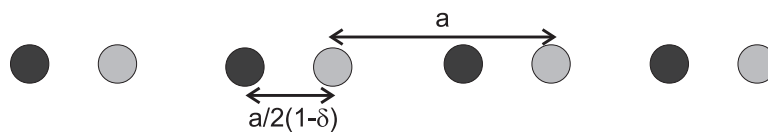


Figure 2: Diatomic chain of atoms. Note that if the potentials on the two atoms are identical, and $\delta = 0$, the chain converts to a monatomic chain of period $a/2$

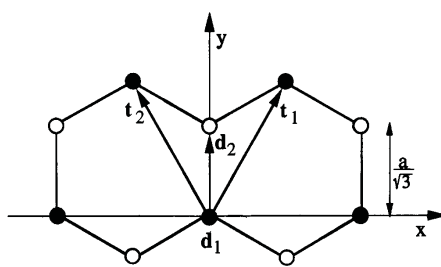


Figure 3: Two dimensional structure of graphite