Question 12

Consider $T_R^{+} |\psi\rangle = e^{i\hat{P}.\hat{R}/\hbar} |\psi\rangle$ (1)

T_R commutes with H.

[Proof $T_R H(r)\psi(r) = H(r+R)\psi(r+R)$ def^{n}.

$= H(r)\psi(r+R)$ since $H(r+R) = H(r)$

$= H(r)T_R\,\psi(r)$.

This is true for any function $\psi(r)$

Hence $T_R H = H T_R$ ⌋

Thus $|\psi\rangle$ can be separately an eigenf^{n} of both H and T_R.

So choose $T_R^{+}|\psi\rangle = C_R|\psi\rangle$ (2)

where C_R is the eigenvalue.

Now left multiply by $\langle k|$, an eigenfunction of momentum

From (1) $\langle k|T_R^{+}|\psi\rangle = \langle k|e^{i\hat{P}.\hat{R}/\hbar}|\psi\rangle = e^{i\underline{k}.\underline{R}}\langle k|\psi\rangle$.

From (2) $\langle k|T_R^{+}|\psi\rangle = C_R\langle k|\psi\rangle$.

Hence. $C_R = e^{i\underline{k}.\underline{R}}$.

Question 13
L

Basic formula for tight-binding bands with one ~~electron~~ orbital / unit cell

$$E(\underline{k}) = \varepsilon_0 + t\sum_{\underline{\rho}} e^{-i\underline{k}\cdot\underline{\rho}} + \underbrace{t_2\sum_{\rho_2} e^{-i\underline{k}\cdot\rho_2}}_{2^{nd}\text{ nearest neighbours}} + \cdots\cdots$$

ε_0: atomic energy with crystal field corrections

$\underline{\rho}$: sum over nearest neighbours.

In BCC there are eight nearest neighbours at the points. $\frac{a}{2}(111)$, $(11\bar{1})$, $(1\bar{1}1)$, $(\bar{1},11)$ + inversions.

In FCC there are 12 neighbours at

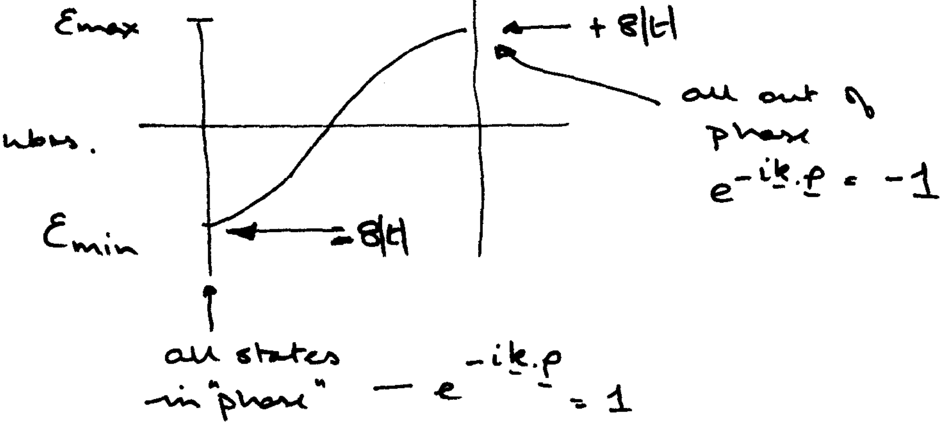
$\frac{a}{2}(0,1,1)$, (101) (110) etc.

→ just algebra. ~~[illegible]~~

Note that for BCC the total bandwidth is

16|t|.

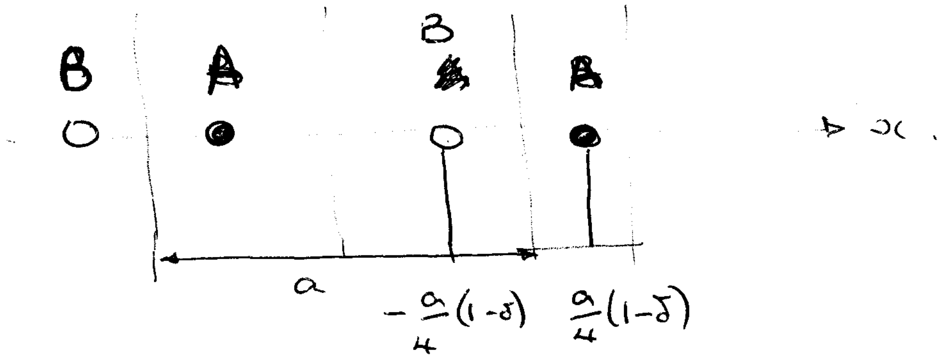
= 2 × # of nearest nbrs. × t.



In FCC, the minimum of the band is at −12|t|

— the <u>maximum</u> is not at +12|t|, because it is not possible to arrange all of the $e^{-i\underline{k}\cdot\underline{\rho}}$ to be simultaneously −1. FCC is a "frustrated" lattice because of the existence of equilateral Δ of neighbours.

Question 14



NFE approx near 1st B.Z. boundary $k \simeq \frac{\pi}{a}$

Write
$$\Psi_k(x) = C_0(k)\, e^{ikx} + C_1(k)\, e^{i(k-\frac{2\pi}{a})x}$$
+ other terms neglected

Then the usual procedure [substitute & take matrix elements with plane waves] gives

$$\begin{bmatrix} k^2 - E & U_0 \\ U_0^* & (k-\frac{2\pi}{a})^2 - E \end{bmatrix} \begin{bmatrix} C_0 \\ C_1 \end{bmatrix} = 0 \qquad (1)$$

Eigenstates
$$\left\| \begin{matrix} (k^2-E) & U_0 \\ U_0^* & (k-\frac{2\pi}{a})^2 - E \end{matrix} \right\| = 0$$

$$E = \frac{1}{2}\left[k^2 + (k-\tfrac{2\pi}{a})^2\right] \pm \frac{1}{2}\sqrt{\left\{\left[k^2 - (k-\tfrac{2\pi}{a})^2\right]^2 + 4|U_0|^2\right\}} \qquad ②$$

At $k = \pi/a$.

$$E^{\pm} = k^2 \pm |U_0| \qquad ③$$

Subst ③ → ① to determine eigenfunctions at Z.B.

$$\mp|U_0|C_0 + U_0 C_1 = 0 \Rightarrow \frac{C_0}{C_1} = \frac{\pm|U_0|}{U_0} = \pm e^{i\phi} \qquad ④$$

Then
$$\begin{matrix}\psi^+ \\ \psi^-\end{matrix} = \frac{1}{\sqrt{2}}\left[e^{i\left[\frac{\pi x}{a} + \frac{\phi}{2}\right]} \pm e^{-i\left[\frac{\pi x}{a} + \frac{\phi}{2}\right]}\right] \times \text{arbitrary phase factor}$$

$$\Rightarrow \left.\begin{matrix} |\psi^+|^2 \propto \cos^2\left(\frac{\pi x}{a} + \frac{\phi}{2}\right) \\ |\psi^-|^2 \propto \sin^2\left(\frac{\pi x}{a} + \frac{\phi}{2}\right) \end{matrix}\right\} \quad (6.17)$$

The potential U_0 is

$$U_0 = \langle k | U(x) | k - \tfrac{2\pi}{a} \rangle = \int dx\, e^{-ikx}\, U(x)\, e^{i(k - \frac{2\pi}{a})x}$$

$$= \int dx\, U(x)\, e^{-\frac{2\pi x}{a} i} \quad \times (\text{Normalisation})$$

Now
$$U(x) = \sum_n \Big[U_A\big(x - na - \tfrac{a}{4}(1-\delta)\big) + U_B\big(x - na + \tfrac{a}{4}(1-\delta)\big) \Big]$$

Notice that the sum over n gives N identical terms (change variables $x' = x - na$) which then cancels the normalisation factor.

Thus
$$U_0 = \int dx\, e^{-i\frac{2\pi x}{a}} \Big\{ U_A\big(x - \tfrac{a}{4}(1-\delta)\big) + U_B\big(x + \tfrac{a}{4}(1-\delta)\big) \Big\}.$$

$$= e^{-i\frac{\pi}{2}(1-\delta)} \int dx\, U_A(x)\, e^{-i\frac{2\pi x}{a}} + e^{i\frac{\pi}{2}(1-\delta)} \int dx\, U_B(x)\, e^{-i\frac{2\pi x}{a}}$$

$$\left.\begin{aligned} &= \sin\left(\tfrac{\pi\delta}{2}\right)\big(U_A(q) + U_B(q)\big) \\ &\quad - i\cos\left(\tfrac{\pi\delta}{2}\right)\big(U_A(q) - U_B(q)\big) \end{aligned}\right\} (6.18)$$

Notice that U_0 is in general complex

Case (a) $U_A = U_B$, $\delta = 0$.

Then $U_G = 0 \Rightarrow$ No gap.

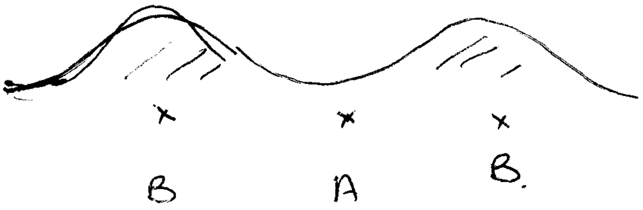
Should have expected this, because with identical, evenly spaced atoms, the lattice constant is actually $a/2$, and the ~~first~~ BZ. boundary at $k = 2\pi/a$. .

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

Then $U_G = -i(U_A - U_B)$ $\Rightarrow \phi = \pi/2$
(if $U_A > U_B$)

Charge piles up on more electronegative atom

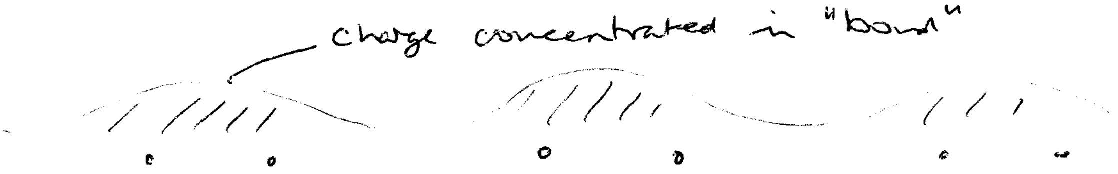
$|\psi^+|^2$



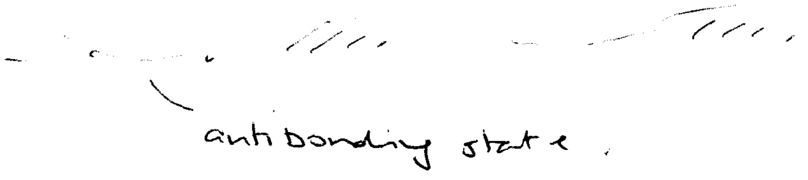
$|\psi^-|^2$

Case (c) $U_A = U_B$, $\delta \neq 0$ $\phi = 0$ (or π) $\rightarrow$ depends on sign of δ

$|\psi_-|^2$



$|\psi_+|^2$



Question 15

(1) Nearly-free electron approximation in 2-dimensions

$$\left[-\frac{\hbar^2}{2m}\left(\frac{d^2}{dx^2}+\frac{d^2}{dy^2}\right)+V\right]\Psi = E\Psi$$

where
$$V(x,y) = -V_o\left[e^{i2\pi x/a}+e^{-i2\pi x/a}+e^{i2\pi y/a}+e^{-i2\pi y/a}\right] .$$

At $k_0 = (0,0)\frac{2\pi}{a}$

$$\Psi = A \quad , \quad E = 0$$

At $k_1 = (\frac{1}{2},0)\frac{2\pi}{a}$

$$\Psi = Ae^{i\pi x/a}+Be^{-i\pi x/a}$$

Substitute into the Schrödinger equation:
$$\left[\frac{\hbar^2\pi^2}{2ma^2}+V\right]\left[Ae^{i\pi x/a}+Be^{-i\pi x/a}\right] = E\left[Ae^{i\pi x/a}+Be^{-i\pi x/a}\right]$$

Compare coefficients of $e^{i\pi x/a}$ and $e^{-i\pi x/a}$. Neglect all other terms:

$$e^{i\pi x/a} : \quad \frac{\hbar^2\pi^2}{2ma^2}A - V_oB = EA \quad ,$$
$$e^{-i\pi x/a} : \quad \frac{\hbar^2\pi^2}{2ma^2}B - V_oA = EB \quad .$$

Write in matrix form:
$$\begin{bmatrix} \frac{\hbar^2\pi^2}{2ma^2}-E & -V_o \\ -V_o & \frac{\hbar^2\pi^2}{2ma^2}-E \end{bmatrix}\begin{bmatrix} A \\ B \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix} .$$

Set the determinant equal to zero and solve for the two eigenvalues, which are

$$E = \frac{\hbar^2\pi^2}{2ma^2} \pm V_o \quad .$$

At $k_2 = \left(\frac{1}{2},\frac{1}{2}\right)\frac{2\pi}{a}$

$$\Psi = Ae^{i(x+y)\pi/a} + Be^{i(x-y)\pi/a} + Ce^{i(-x+y)\pi/a} + De^{i(-x-y)\pi/a} \quad .$$

Substitute into the Schrödinger equation:

$$\left[\frac{\hbar^2\pi^2}{ma^2} + V\right]\left[Ae^{i(x+y)\pi/a} + Be^{i(x-y)\pi/a} + Ce^{i(-x+y)\pi/a} + De^{i(-x-y)\pi/a}\right]$$
$$= E\left[Ae^{i(x+y)\pi/a} + Be^{i(x-y)\pi/a} + Ce^{i(-x+y)\pi/a} + De^{i(-x-y)\pi/a}\right]$$

Compare coefficients of $e^{i(x+y)\pi/a}$, $e^{i(x-y)\pi/a}$, $e^{i(-x+y)\pi/a}$ and $e^{i(-x-y)\pi/a}$. Neglect all other terms.

$$e^{i(x+y)\pi/a} \quad : \quad \frac{\hbar^2\pi^2}{ma^2}A - V_oB - V_oC = EA$$
$$e^{i(x-y)\pi/a} \quad : -V_oA + \frac{\hbar^2\pi^2}{ma^2}B - V_oD = EB$$
$$e^{i(-x+y)\pi/a} \quad : -V_oA + \frac{\hbar^2\pi^2}{ma^2}C - V_oD = EC$$
$$e^{i(-x-y)\pi/a} \quad : -V_oB - V_oC + \frac{\hbar^2\pi^2}{ma^2}D = ED$$

Write in matrix form and set the determinant equal to zero:

$$\begin{vmatrix} \frac{\hbar^2\pi^2}{ma^2} - E & -V_o & -V_o & 0 \\ -V_o & \frac{\hbar^2\pi^2}{ma^2} - E & 0 & -V_o \\ -V_o & 0 & \frac{\hbar^2\pi^2}{ma^2} - E & -V_o \\ 0 & -V_o & -V_o & \frac{\hbar^2\pi^2}{ma^2} - E \end{vmatrix} = 0$$

This equation is a little more complicated, but it is not too hard to show that the eigenvalues are:

$$E_1 = \frac{\hbar^2\pi^2}{ma^2} + 2V_o \quad , \quad E_2 = \frac{\hbar^2\pi^2}{ma^2} - 2V_o \quad , \quad E_3 = E_4 = \frac{\hbar^2\pi^2}{ma^2} \quad .$$

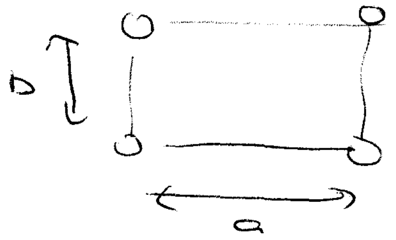
Note that at this level of approximation the lowest band gaps at k_1 and k_2 are both equal to $2V_o$.

Question 16

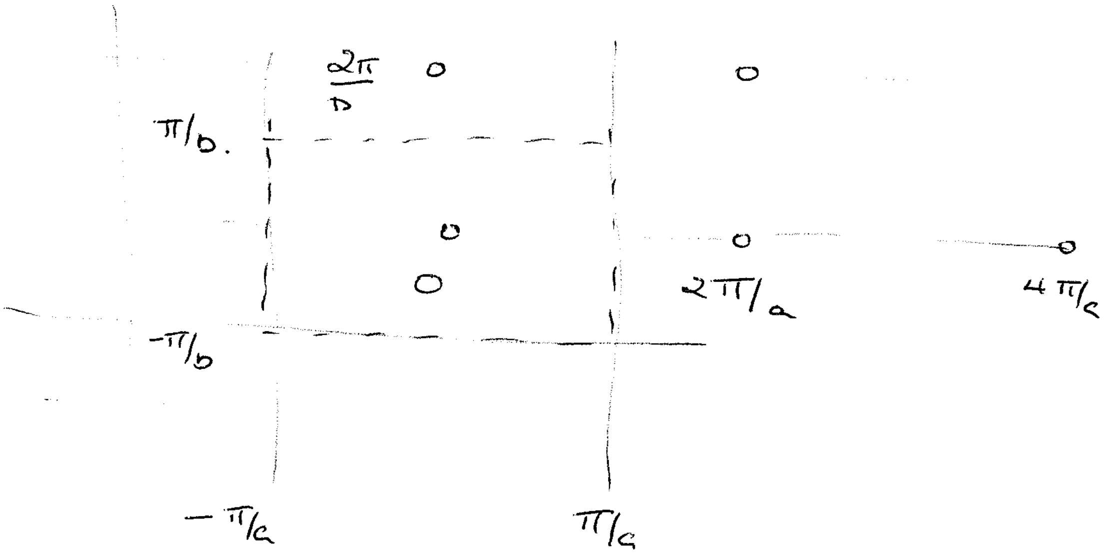
$$E(k) = -2t_1 \cos(k_x a) + 2t_2 \cos(k_y a)$$

(a) Real space lattice

— rectangular



(b) Reciprocal lattice



(c) If $a < b$, expect hopping matrix element $t_1 > t_2$. (closer — more overlap).

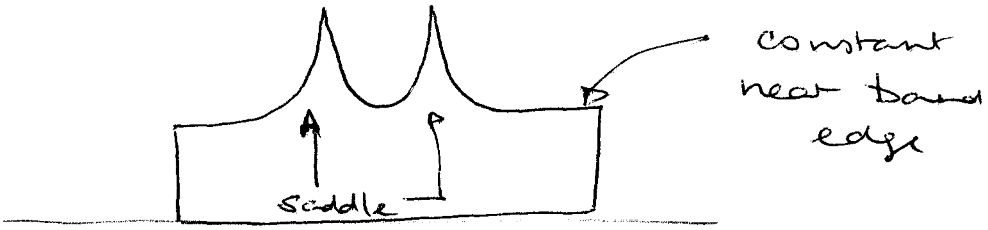
See plots on next page.

NB. Min — at $(0,0)$

Max — at $(\pi/a, \pi/b)$

Saddles — at $(\pi/a, 0)$ & $(0, \pi/b)$

Generic DOS — in 2D

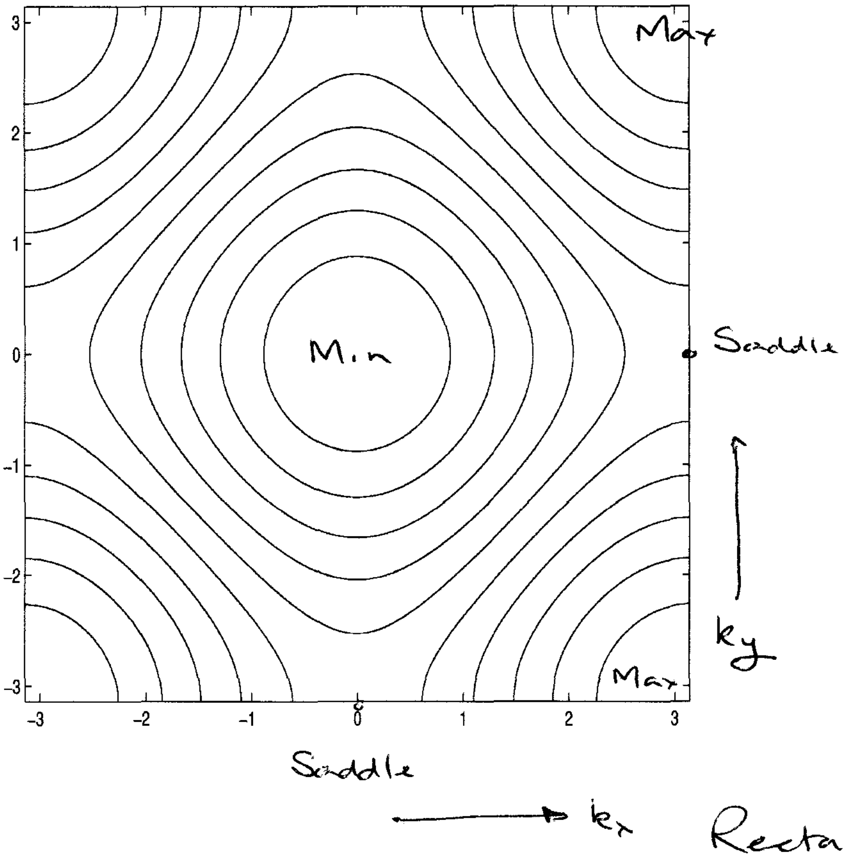


Question 16 - 2

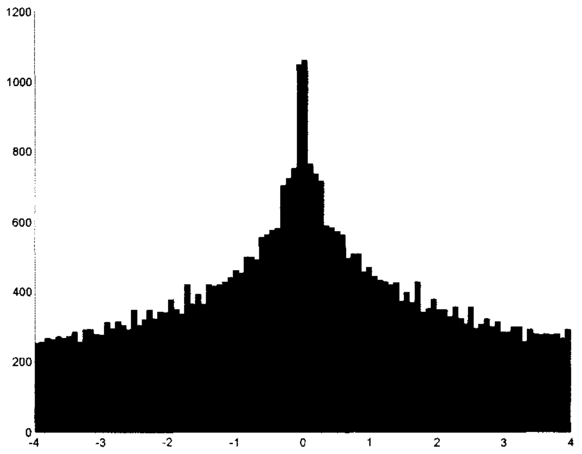
$a=1, b=1$

$t_1 = t_2 = 1$

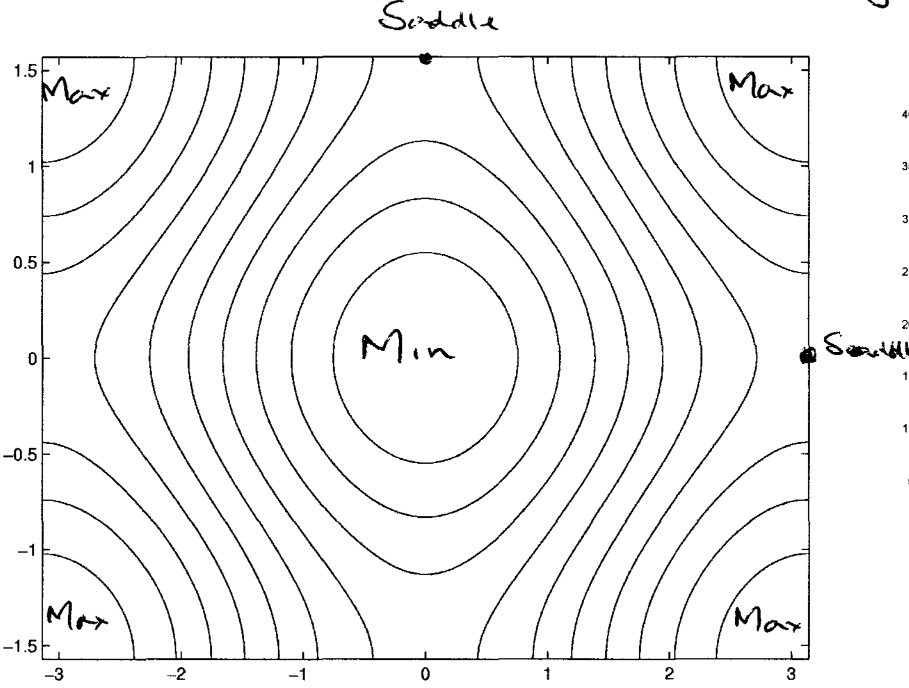
Square lattice



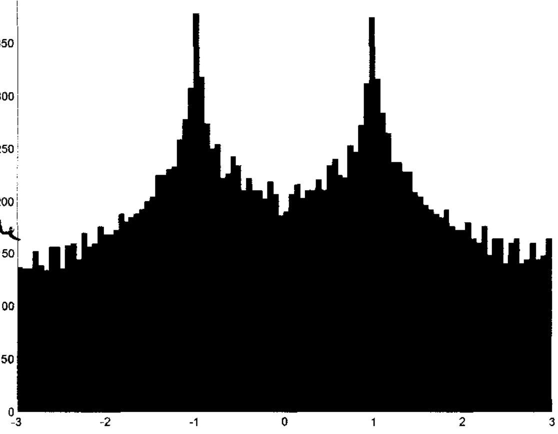
Density of states



Rectangular lattice



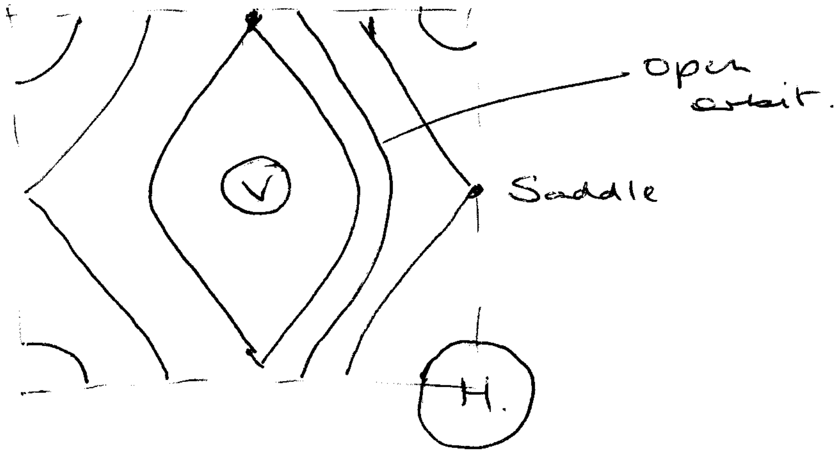
Density of states.



$a=1, b=2, t_1=1, t_2=1/2$

d). — See figures for plots.

e) — Notice that for lowest energy
→ electron orbits (valley)
Highest energy → "hole" orbits (hills)
In between saddle points, orbits are open
— run from one BZ into the nex



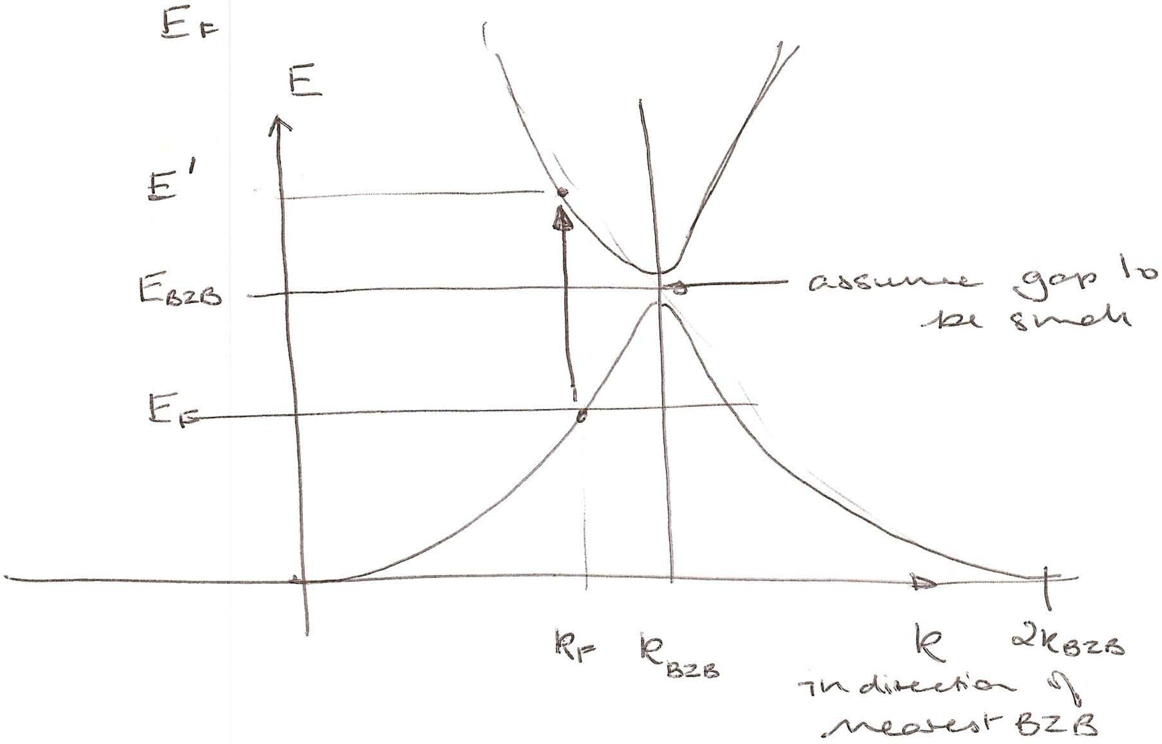
Question 17

$$k_F = \left(\frac{3\pi^2 N}{V}\right)^{1/3} = \left(\frac{3\pi^2 2}{a^3}\right)^{1/3}$$

$$\therefore E_F = \frac{\hbar^2 k_F^2}{2m} = \frac{\hbar^2}{2ma^2}\left(6\pi^2\right)^{2/3}$$ (a^3 = cubic unit cell. volume)

$$E_{BZB} = \frac{\hbar^2}{2ma^2}\left(\sqrt{2}\pi\right)^2$$

$$\therefore \frac{E_{BZB}}{E_F} \simeq 1.3$$



Threshold energy

$$= E' - E_F = \frac{\hbar^2}{2m}\left[2k_{BZB} - k_F\right]^2 - \frac{\hbar^2}{2m}k_F^2$$

$$= E_F\left\{\left(\frac{2k_{BZB}}{k_F} - 1\right)^2 - 1\right\} \simeq 0.64\, E_F$$

[N.B. – if the eigenstates were <u>really</u> single plane waves, there would be no absorption because

$$\langle e^{i\underline{k}_F\cdot\underline{r}} \,|\, \underset{\substack{\uparrow\\ \text{light}\\ q\sim 0}}{e^{i\underline{q}\cdot\underline{r}}} \,|\, e^{i(2k_{BZB}-k_F)\cdot r} \rangle \equiv 0.$$

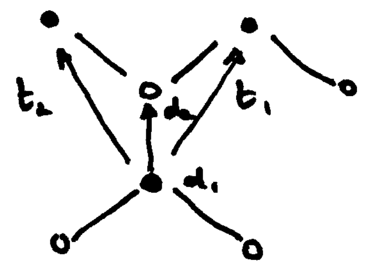
– but exists because of wide mixing of Fourier components with correct reciprocal lattice vector]

Question 17 - 2

	Na	K	Rb	
E_F	3.2	2.1	1.9.	(eV)
onset of absorption	1.9	1.3	1.2.	(eV).

— reasonable agreement with factor of 0.64

(a)



2 atoms / cell.

Tight binding basis

$$\phi_{1k}(r) = \frac{1}{\sqrt{N}} \sum_{t_m} e^{i\underline{k}.\underline{t}_m} \phi_z(\underline{r} - \underline{d}_1 - \underline{t}_m)$$

$$\phi_{2k}(r) = \frac{1}{\sqrt{N}} \sum_{t_m} e^{i\underline{k}.\underline{t}_m} \phi_z(\underline{r} - \underline{d}_2 - \underline{t}_m)$$

P_z orbital centered at point $\underline{r} = \underline{d}_2 + \underline{t}_m$

General solution in the form

$$\psi_k(r) = \alpha_k \phi_{1k}(r) + \beta_k \phi_{2k}(r)$$

Construct $\langle \psi_k | H | \psi_k \rangle$

$$= (\alpha_k \quad \beta_k) \begin{pmatrix} \langle \phi_{1k}|H|\phi_{1k}\rangle & \langle \phi_{1k}|H|\phi_{2k}\rangle \\ \langle \phi_{2k}|H|\phi_{1k}\rangle & \langle \phi_{2k}|H|\phi_{2k}\rangle \end{pmatrix} \begin{pmatrix} \alpha_k \\ \beta_k \end{pmatrix}$$

Including only onsite and nearest neighbour terms

$$\langle \phi_{1k}|H|\phi_{1k}\rangle \simeq E_p = \langle \phi_{2k}|H|\phi_{2k}\rangle$$

— no k-dependence because there is no nearest neighbour of • in the same unit cell (or of o in the same unit cell).

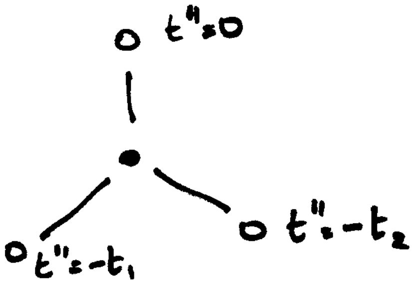
$$\langle \phi_{1k} | H | \phi_{2k} \rangle = \frac{1}{N}\sum_{t t'} e^{-i\underline{k}\cdot(\underline{t}-\underline{t}')} \langle \phi_z(r-d_1-t)|H|\phi_z(r-d_2-t')\rangle$$

let $t - t' = -t''$

$$= \frac{1}{N}\sum_{t t''} e^{i\underline{k}\cdot\underline{t}''} \langle \phi_z(r-d_1-t)|H|\phi_z(r-d_2-t-t'')\rangle$$

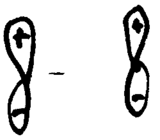
$$= \sum_{t''} e^{i\underline{k}\cdot\underline{t}''} \langle \phi_z(r-d_1)|H|\phi_z(r-d_2-t'')\rangle$$

three terms contribute.



$$= V(pp\pi)\left[1 + e^{-i\underline{k}\cdot\underline{t}_1} + e^{-i\underline{k}\cdot\underline{t}_2}\right]$$

means "π"-overlap

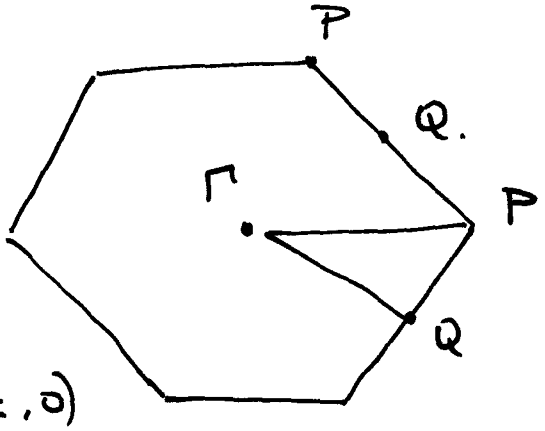


$$= V(pp\pi)\left[1 + 2\cos\frac{k_x a}{2}\, e^{-ik_y\frac{a\sqrt{3}}{2}}\right] = V(pp\pi)F(k)$$

Hence eigenvalues follow from

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

(b)



$\Gamma = (0,0)$

$P = \frac{2\pi}{a}\left(\frac{2}{3}, 0\right)$

$Q = \frac{2\pi}{a}\left(\frac{1}{2}, \frac{1}{2\sqrt{3}}\right)$

R.L. Vectors are

$b_1 = \frac{2\pi}{a}\left(1, \frac{1}{\sqrt{3}}, 0\right)$

$b_2 = \frac{2\pi}{a}\left(-1, \frac{1}{\sqrt{3}}, 0\right)$

$|\Gamma P| = \frac{2\pi}{a} \cdot \frac{2}{3}$

$|\Gamma Q| = \frac{2\pi}{a} \cdot \frac{1}{\sqrt{3}}$

Bands are

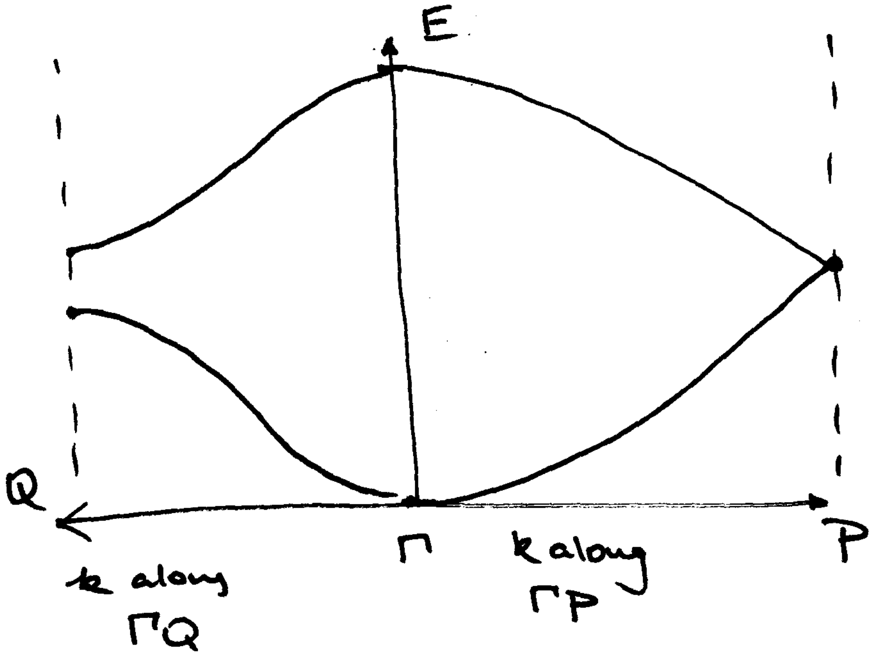
$$E(k) = E_p \pm V(pp\pi)\,|F(k)|.$$

Along ΓP. , $k_y = 0$

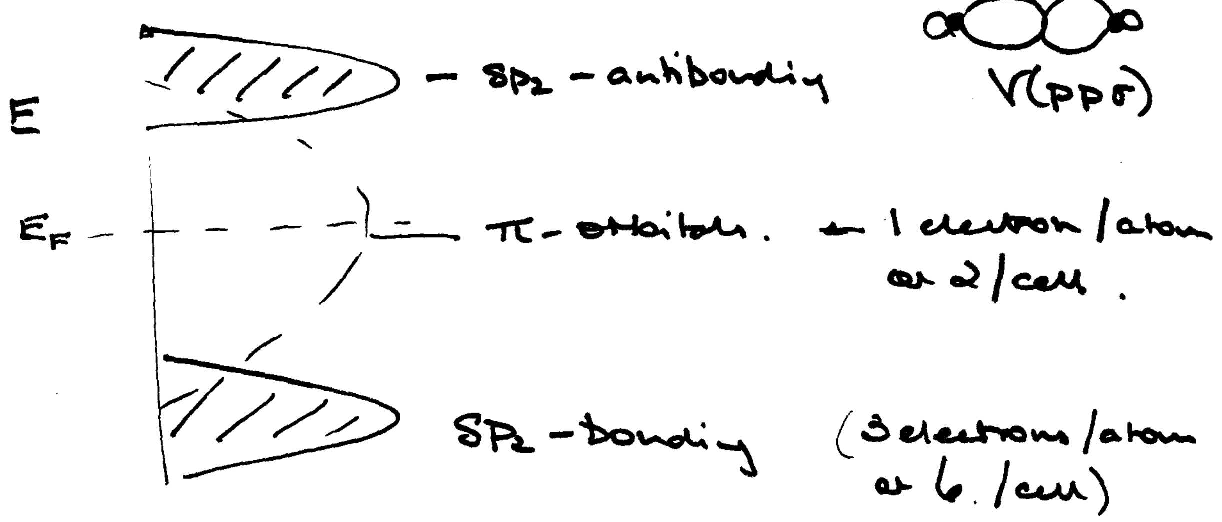
$$F(k) = 1 + 2\cos\left(\frac{k_x a}{2}\right) \Rightarrow 0 \text{ at } P$$

Along ΓQ , $k_y = 1/\sqrt{3}\, k_x$

$$F(k) = \sqrt{\left[1 + 8\cos^2\left(\frac{k_x a}{2}\right)\right]} \Rightarrow 1 \text{ at } Q$$



(c) SP$_2$ orbitals are widely split by large SP$_2$ - SP$_2$ hybridization



Hence 1st BZ of π orbitals ~~are~~ filled

— normally this gives an insulator but in graphite the gap is zero at the six points P on the zone face

→ graphite is a semimetal.

(d) Periodicity will require that the allowed $\underline{k}$-values satisfy. $e^{i\underline{k}\cdot(m\underline{t}_1+n\underline{t}_2)}=1$

If we write $\underline{k} = x_1\underline{b}_1 + x_2\underline{b}_2$ ($\underline{b}_1, \underline{b}_1$ are recip. latt. vectors) then we must have

$$x_1 m + x_2 n = l$$ where l is an integer.

— this defines a set of equally spaced lines

Notice the points P are all 1/3 of the way to a reciprocal lattice vector. (eg. $\frac{2\pi}{a}\left(\frac{2}{3},0\right) = \frac{1}{3}(\underline{b}_1-\underline{b}_2)$)

∴ P is an allowed k-point if

$$\frac{m}{3}-\frac{n}{3}=l \quad \text{or} \quad m-n=3l.$$

∴ $m=10, n=1$ metal ; others insulating.

Bloch states:

$$\underline{\Phi}_{sk}(\underline{r}) = \sum_{\underline{R}_i} e^{i\underline{k}\cdot\underline{R}_i}\,\phi_s\underbrace{(\underline{r}-\underline{R}_i)}\ \text{atomic s-f}^n$$

$$\underline{\Phi}_{dk}(\underline{r}) = \sum_{R_j} e^{i\underline{k}\cdot\underline{R}_j}\,\phi_d\underbrace{(\underline{r}-\underline{R}_j)}\ \text{atomic d-f}^{\underline{n}}.$$

$R_j = ja$: a = latt. const.

Assume.

$$\underline{\Phi}_{nk}(r) = \alpha_k\underline{\Phi}_{sk} + \beta_k\underline{\Phi}_{dk}$$

$\langle\underline{\Phi}_{nk}|H|\underline{\Phi}_{nk}\rangle$.

$$\Rightarrow.\ \begin{vmatrix} \langle sk|H|sk\rangle & \langle sk|H|dk\rangle \\ \langle dk|H|sk\rangle & \langle dk|H|dk\rangle. \end{vmatrix}.$$

If we neglect overlaps between neighbours

ie $\langle\phi_s(r-R)|\phi_s(r-R')\rangle$ etc.

and include only nearest neighbour matrix elements of H.

$$\Rightarrow\ \langle sk|H|sk\rangle = E_s - \sum_{\rho=n.n} t_{ss}e^{i\underline{k}\cdot\underline{\rho}}$$

$$= E_s - 2t_{ss}\cos(ka)$$

where $t_{ss} = -\langle\phi_s(r)|H|\phi_s(r-a)\rangle \quad > 0.$

Similarly $\langle sk|H|dk\rangle = -2t_{sd}\cos(ka)$

($N.B\ \langle\phi_s(r)|H|\phi_d(r)\rangle = 0$ by symmetry if we use a real d-f$^{\underline{n}}$).

$\langle dk|H|dk\rangle = -2t_{dd}\cos(ka)$

Again, expect $t_{sd} \ngtr 0$, $t_{dd} \ngtr 0$.

Also. $t_{ss} > t_{sd} > t_{dd}$

because d-wavefunction is more localised about atomic site than the (relevant) s-state.

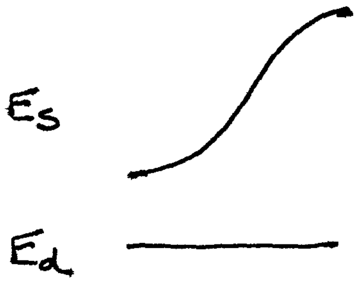
[Aside: In atom 4s states filled before 3d but 4s is more extended than 3d.

Why? 4s orthogonal to 1s, 2s, 3s etc ⇒ nodes in wavefn — weak pseudopotential.

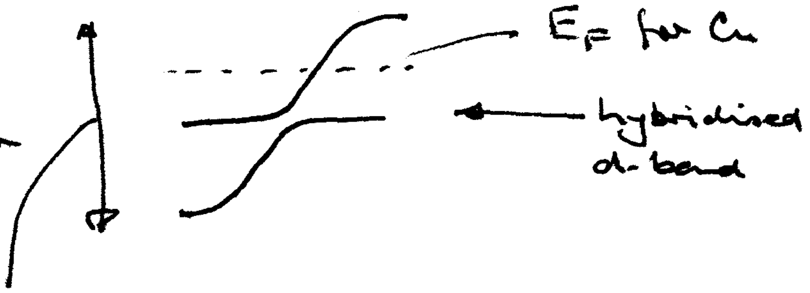
3d ~~sees~~ has no "core" states to orthogonalise to — sees the "full" atomic charge Z.

4s states lower in energy than 3d (in atom) because more extended ⇒ less Coulomb energy.]

If you neglect the d-dispersion entirely ($t_{dd} = 0$) you get in the two cases either



or



In Cu, the fermi energy is in the s-band, but the change in dispersion is just enough to produce the famous open dispersion of the F.S.

The reddish colour of Cu is due to optical transitions from d-p in the visible range.