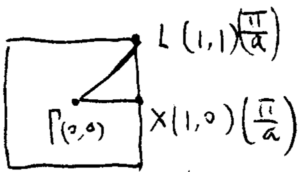
1.

(a). $E(\vec{k}) = \frac{\hbar^2}{2m}\cdot(\vec{k}+\vec{G})^2$, where $\vec{G}$ is reciprocal Lattic vector;

for a 2-D square lattice with lattice constant a,

$$E(\vec{k}) = \frac{\hbar^2}{2m}\cdot\left[(k_x+G_x)^2+(k_y+G_y)^2\right], \quad \begin{cases} G_x = \frac{2\pi}{a}\cdot(1,0)\cdot n \\ G_y = \frac{2\pi}{a}\cdot(0,1)\cdot m \end{cases} \quad m, n = 0, \pm1, \pm2, \cdots$$

(b). Along $\Gamma \to X$: $\vec{k} = (k_x, 0)$,



$$E(\vec{k}) = \frac{\hbar^2}{2m}\cdot\left[(k_x+G_x)^2+G_y^2\right], \quad \text{for X and } \Gamma:$$

$\vec{G}$	$E(\vec{k})$	$E^{\Gamma}(\vec{k})$	$E^{X}(\vec{k})$
$\left(\frac{2\pi}{a}\right)\cdot(0,0)$	$\frac{\hbar^2}{2m}\cdot k_x^2$	0	$\frac{\hbar^2}{2m}\cdot\left(\frac{\pi}{a}\right)^2\cdot 1$
$\left(\frac{2\pi}{a}\right)\cdot(1,0)$	$\frac{\hbar^2}{2m}\cdot\left(k_x+\frac{2\pi}{a}\right)^2$	$\frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2\cdot 4$	$\frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2\cdot 9$
$\frac{2\pi}{a}\cdot(\bar{1},0)$	$\frac{\hbar^2}{2m}\cdot\left(k_x-\frac{2\pi}{a}\right)^2$	$\frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2\cdot 4$	$\frac{\hbar^2}{2m}\cdot\left(\frac{\pi}{a}\right)^2\cdot 1$
$\frac{2\pi}{a}\cdot(0,1)$	$\frac{\hbar^2}{2m}\cdot\left[k_x^2+\left(\frac{2\pi}{a}\right)^2\right]$	$\frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2\cdot 4$	$\frac{\hbar^2}{2m}\cdot\left(\frac{\pi}{a}\right)^2\cdot 5$
$\frac{2\pi}{a}\cdot(0,\bar{1})$	$\frac{\hbar^2}{2m}\cdot\left[k_x^2+\left(\frac{2\pi}{a}\right)^2\right]$	$\frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2\cdot 4$	$\frac{\hbar^2}{2m}\cdot\left(\frac{\pi}{a}\right)^2\cdot 5$
$\frac{2\pi}{a}\cdot(1,1)$	$\frac{\hbar^2}{2m}\cdot\left[\left(k_x+\frac{2\pi}{a}\right)^2+\left(\frac{2\pi}{a}\right)^2\right]$	$\frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2\cdot 8$	$\frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2\cdot 13$
$\frac{2\pi}{a}\cdot(\bar{1},1)$	$\frac{\hbar^2}{2m}\cdot\left[\left(k_x-\frac{2\pi}{a}\right)^2+\left(\frac{2\pi}{a}\right)^2\right]$	$\frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2\cdot 8$	$\frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2\cdot 5$
$\frac{2\pi}{a}\cdot(1,\bar{1})$	$\frac{\hbar^2}{2m}\cdot\left[\left(k_x+\frac{2\pi}{a}\right)^2+\left(\frac{2\pi}{a}\right)^2\right]$	$\frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2\cdot 8$	$\frac{\hbar^2}{2m}\cdot\left(\frac{\pi}{a}\right)^2\cdot 13$
$\frac{2\pi}{a}\cdot(\bar{1},\bar{1})$	$\frac{\hbar^2}{2m}\cdot\left[\left(k_x-\frac{2\pi}{a}\right)^2+\left(\frac{2\pi}{a}\right)^2\right]$	$\frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2\cdot 8$	$\frac{\hbar^2}{2m}\cdot\left(\frac{\pi}{a}\right)^2\cdot 5$
$\frac{2\pi}{a}\cdot(\bar{2},0)$	$\frac{\hbar^2}{2m}\cdot\left(k_x-\frac{4\pi}{a}\right)^2$	$\frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2\cdot 16$	$\frac{\hbar^2}{2m}\cdot\left(\frac{\pi}{a}\right)^2\cdot 9$

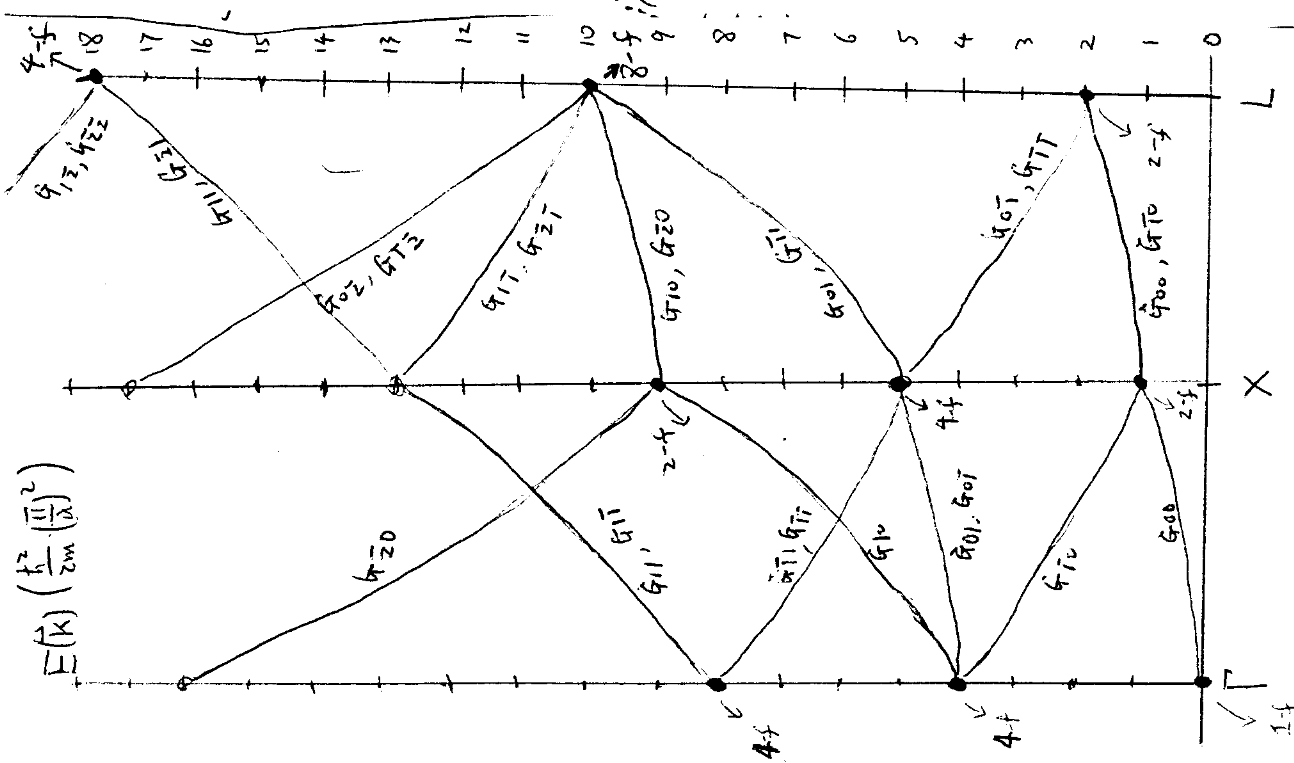
See Part (c);

(c). Along X − L direction : $\vec{k} = (\pi/a, k_y)$

$$E(\vec{k}) = \frac{\hbar^2}{2m} \cdot \left[\left(\frac{\pi}{a} + G_x\right)^2 + \left(G_y + k_y\right)^2 \right],$$

$\vec{G}$	$E(\vec{k})$	$E(\vec{k})$ at X	$E(\vec{k})$ at L
$\frac{2\pi}{a}\cdot(0,0)$	$\frac{\hbar^2}{2m}\left[\left(\frac{\pi}{a}\right)^2 + k_y^2\right]$	$\frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2\cdot 1$	$\frac{\hbar^2}{2m}\cdot\left(\frac{\pi}{a}\right)^2\cdot 2$
$\frac{2\pi}{a}\cdot(\bar{1},0)$	$\frac{\hbar^2}{2m}\left[\left(\frac{\pi}{a}\right)^2 + k_y^2\right]$	$\frac{\hbar^2}{2m}\cdot\left(\frac{\pi}{a}\right)^2\cdot 1$	$\frac{\hbar^2}{2m}\cdot\left(\frac{\pi}{a}\right)^2\cdot 2$
$\frac{2\pi}{a}\cdot(0,1)$	$\frac{\hbar^2}{2m}\cdot\left[\left(\frac{\pi}{a}\right)^2 + \left(k_y + \frac{2\pi}{a}\right)^2\right]$	$\frac{\hbar^2}{2m}\cdot\left(\frac{\pi}{a}\right)^2\cdot 5$	$\frac{\hbar^2}{2m}\cdot\left(\frac{\pi}{a}\right)^2\cdot 10$
$\frac{2\pi}{a}\cdot(0,\bar{1})$	$\frac{\hbar^2}{2m}\cdot\left[\left(\frac{\pi}{a}\right)^2 + \left(k_y - \frac{2\pi}{a}\right)^2\right]$	$\frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2\cdot 5$	$\frac{\hbar^2}{2m}\cdot\left(\frac{\pi}{a}\right)^2\cdot 2$
$\frac{2\pi}{a}\cdot(1,0)$	$\frac{\hbar^2}{2m}\cdot\left[9\cdot\left(\frac{\pi}{a}\right)^2 + k_y^2\right]$	$\frac{\hbar^2}{2m}\cdot\left(\frac{\pi}{a}\right)^2\cdot 9$	$\frac{\hbar^2}{2m}\cdot\left(\frac{\pi}{a}\right)^2\cdot 10$
$\frac{2\pi}{a}\cdot(\bar{2},0)$	$\frac{\hbar^2}{2m}\cdot\left[9\cdot\left(\frac{\pi}{a}\right)^2 + k_y^2\right]$	$\frac{\hbar^2}{2m}\cdot\left(\frac{\pi}{a}\right)^2\cdot 9$	$\frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2\cdot 10$
$\frac{2\pi}{a}\cdot(\bar{1},1)$	$\frac{\hbar^2}{2m}\cdot\left[\left(\frac{\pi}{a}\right)^2 + \left(\frac{2\pi}{a} + k_y\right)^2\right]$	$\frac{\hbar^2}{2m}\cdot\left(\frac{\pi}{a}\right)^2\cdot 5$	$\sim\cdot 10$
$\frac{2\pi}{a}\cdot(\bar{1},\bar{1})$	$\frac{\hbar^2}{2m}\cdot\left[\left(\frac{\pi}{a}\right)^2 + \left(-\frac{2\pi}{a} + k_y\right)^2\right]$	$\cdots 5$	2
$\frac{2\pi}{a}\cdot(0,\bar{2})$	$\frac{\hbar^2}{2m}\cdot\left[\left(\frac{\pi}{a}\right)^2 + \left(k_y - \frac{4\pi}{a}\right)^2\right]$	17	10
$\frac{2\pi}{a}\cdot(1,\bar{1})$	$\frac{\hbar^2}{2m}\cdot\left[9\cdot\left(\frac{\pi}{a}\right)^2 + \left(k_y - \frac{2\pi}{a}\right)^2\right]$	13	10
$\frac{2\pi}{a}\cdot(\bar{1},\bar{2})$	$\frac{\hbar^2}{2m}\cdot\left[\left(\frac{\pi}{a}\right)^2 + \left(k_y - \frac{4\pi}{a}\right)^2\right]$	17	10

$\vec{G}$	$E(\vec{k})$	$E^X(\vec{k})$	$E^L(\vec{k})$
$\frac{2\pi}{a}\cdot(\bar{2},\bar{1})$	$\frac{\hbar^2}{2m}\cdot\left[9\left(\frac{\pi}{a}\right)^2+\left(k_y-\frac{2\pi}{a}\right)^2\right]$	13	10
$\frac{2\pi}{a}\cdot(1,1)$	$\frac{\hbar^2}{2m}\cdot\left[9\cdot\left(\frac{\pi}{a}\right)^2+\left(k_y+\frac{2\pi}{a}\right)^2\right]$	13	18
$\frac{2\pi}{a}\cdot(1,\bar{2})$	$\frac{\hbar^2}{2m}\cdot\left[9\cdot\left(\frac{\pi}{a}\right)^2+\left(k_y-\frac{4\pi}{a}\right)^2\right]$	25	18
$\frac{2\pi}{a}\cdot(\bar{2},1)$	$\frac{\hbar^2}{2m}\cdot\left[9\cdot\left(\frac{\pi}{a}\right)^2+\left(k_y+\frac{2\pi}{a}\right)^2\right]$	13	18
$\frac{2\pi}{a}\cdot(\bar{1},\bar{2})$	$\frac{\hbar^2}{2m}\cdot\left[9\cdot\left(\frac{\pi}{a}\right)^2+\left(k_y-\frac{4\pi}{a}\right)^2\right]$	25	18



(d). Since the "slope" of $E(\vec{k})$ at the Γ point is the same in both $\hat{x}$ and $\hat{y}$ directions, this pocket will be a circle and there will be only one; at X-point, ($4/2 = 2$ equivalent pockets), the pockets are eliptical shape, at L-point, pockets will be circle ($4/4 = 1$),

d) Wave functions for 3 lowest X-point levels:

Bloch's Theorem: $\psi_k(r) = e^{i\bar{k}\bar{r}} \cdot u_k(r)$

$u_k(r)$ has the periodicity of the lattice, therefore

$$u_k(r) = \sum_{\{G_i\}} u_{G_i}\, e^{-i\bar{G}_i \cdot \bar{r}}$$ $\bar{G}_i$ – reciprocal lattice vectors

$$\psi_k(r) = \sum_{\{G_i\}} u_{G_i}\, e^{+i(\bar{k}-\bar{G}_i)\bar{r}}$$

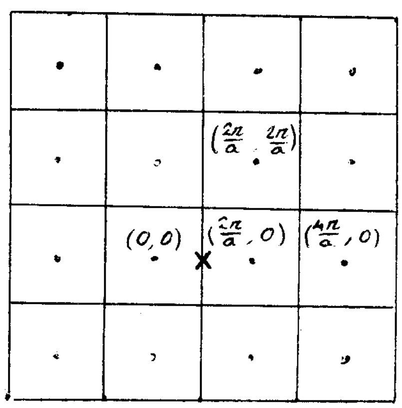
Since $V=0$, eigenfunctions are obtained for $\left\{ u_{G_i} = \frac{1}{\sqrt{A}},\ u_{G_{j \neq i}} = 0 \right\}$

$\Downarrow$

$$\psi_{k,G_i}(r) = \frac{1}{\sqrt{A}} e^{i(\bar{k}-\bar{G}_i)\bar{r}}$$

$$\psi_{X,G_i}(r) = \frac{1}{\sqrt{A}} e^{i(\frac{\pi}{a}\hat{x}-\bar{G}_i)\bar{r}} \qquad E_{X,G_i} = \frac{\hbar^2}{2m}\left|\frac{\pi}{a}\hat{x}-\bar{G}_i\right|^2$$

$$\left\{ \begin{aligned} \psi_{X,(0,0)}(r) &= \frac{1}{\sqrt{A}} e^{i\frac{\pi}{a}x} \\ \psi_{X,(\frac{2\pi}{a},0)}(r) &= \frac{1}{\sqrt{A}} e^{-i\frac{\pi}{a}x} \end{aligned} \right. \qquad E = \frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2$$



$$\left\{ \begin{aligned} \psi_{X,(0,\frac{2\pi}{a})}(r) &= \frac{1}{\sqrt{A}} e^{i\frac{\pi}{a}(x-2y)} \\ \psi_{X,(0,-\frac{2\pi}{a})}(r) &= \frac{1}{\sqrt{A}} e^{i\frac{\pi}{a}(x+2y)} \\ \psi_{X,(\frac{2\pi}{a},\frac{2\pi}{a})}(r) &= \frac{1}{\sqrt{A}} e^{i\frac{\pi}{a}(-x-2y)} \\ \psi_{X,(\frac{2\pi}{a},-\frac{2\pi}{a})}(r) &= \frac{1}{\sqrt{A}} e^{i\frac{\pi}{a}(-x+2y)} \end{aligned} \right. \qquad E = \frac{5\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2$$

$$\left\{ \begin{aligned} \psi_{X,(\frac{4\pi}{a},0)}(r) &= \frac{1}{\sqrt{A}} e^{-i\frac{3\pi}{a}x} \\ \psi_{X,(-\frac{2\pi}{a},0)}(r) &= \frac{1}{\sqrt{A}} e^{i\frac{3\pi}{a}x} \end{aligned} \right. \qquad E = \frac{9\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2$$

e. According to Degenerate Perturbation Theory we need to solve the determinant: $\left| \underline{\underline{H}} - E\underline{\underline{I}} \right| = 0$

$$H_{i,j} = \langle \Psi_j | \hat{H} | \Psi_i \rangle = \langle \Psi_j | H_0 + V | \Psi_i \rangle$$

$$I_{i,j} = \delta_{i,j} \quad \text{(identity matrix)}$$

According to part (d) we have 2 sets of doubly degenerate levels and 1 set of degeneracy of 4.

Degeneracy = 2

$H_{11} = E_0 + V_0 \quad \leftarrow E_0$ from part (d), $V_0 = \int \frac{1}{A} V(r)\,d\bar{r} = \int_{\text{unit cell}} V(r)\,d\bar{r}$

$H_{22} = E_0 + V_0$

$H_{12} = H_{21}^* = V_1 = \langle \Psi_2 | V | \Psi_1 \rangle$

$$\left| \underline{\underline{H}} - E\underline{\underline{I}} \right| = (E_0 + V_0 - E)^2 - |V_1|^2 = E^2 - 2E(E_0+V_0) + (E_0+V_0)^2 - |V_1|^2 = 0$$

$$E = \frac{1}{2}\left[2(E_0+V_0) \pm \sqrt{4(E_0+V_0)^2 - 4(E_0+V_0)^2 + 4|V_1|^2} \right] = E_0 + V_0 \pm |V_1|$$

So the degeneracy is lifted if $V_1 \neq 0$

$$V_1 = \int \Psi_2^* V \Psi_1 \, d\bar{r} = \frac{1}{A} \int e^{-i(\frac{\pi}{a}\hat{x} - \bar{G}_2)\bar{r}} \cdot V \cdot e^{i(\frac{\pi}{a}\hat{x} - \bar{G}_1)\bar{r}} \, d\bar{r}$$

$$= \frac{1}{A} \int V \cdot e^{-i(\bar{G}_1 - \bar{G}_2)\bar{r}} \, d\bar{r}$$

Therefore the degeneracy is lifted only if $V(\bar{r})$ has a Fourier component corresponding to the vector difference $(\bar{G}_1 - \bar{G}_2)$

For $\Psi_{X,(0,0)}$ & $\Psi_{X,(\frac{2\pi}{a},0)}$ $\quad V \propto \cos(\frac{2\pi}{a}x)$ will create a splitting

For $\Psi_{X,(\frac{4\pi}{a},0)}$ & $\Psi_{X(-\frac{2\pi}{a},0)}$ $\quad V \propto \cos(\frac{6\pi}{a}x)$ will create a splitting

Degeneracy = 4

Same treatment on a 4-by-4 determinant:

$$\begin{vmatrix} E_0+V_0-E & V_{12} & V_{13} & V_{14} \\ V_{12}^* & E_0+V_0-E & V_{23} & V_{24} \\ V_{13}^* & V_{23}^* & E_0+V_0-E & V_{34} \\ V_{14}^* & V_{24}^* & V_{34}^* & E_0+V_0-E \end{vmatrix} = 0$$

$$E_0 = \frac{5\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2$$

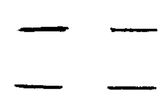
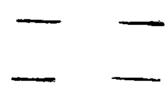
$$V_{ij} = \langle \psi_j | V | \psi_i \rangle$$

$$V_0 = \int_{\substack{\text{unit}\\ \text{cell}}} V(r)\, d\bar{r}$$

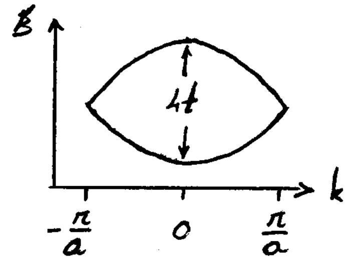
From the form of our 4 wavefunctions we conclude that:

$V_{34} = V_{12}$; $V_{24} = V_{13}$;

Solving the determinant is difficult, but even so we can conclude that only 4 Fourier components of the potential $V(r)$ affect this 4-level system, and those correspond to the following k-space vectors and result in the following splittings (assuming the other components are zero)

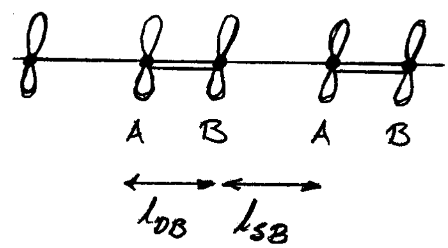
$\bar{k}$	$\frac{4\pi}{a}\hat{y}$ $(V_{12}\neq 0)$	$\frac{2\pi}{a}\hat{x}$ $(V_{13}\neq 0)$	$\frac{2\pi}{a}\hat{x} - \frac{4\pi}{a}\hat{y}$ $(V_{14}\neq 0)$	$\frac{2\pi}{a}\hat{x} + \frac{4\pi}{a}\hat{y}$ $(V_{23}\neq 0)$
splitting				

(2) (a) Using the derivation in the classnotes, Eq. 1.86 (p. 18) with $s=0$, gives $E_\pm(k) = E_{2p} \pm 2t \cos\left(\frac{ka}{2}\right)$



(b) Carbon ($2s^2 2p^2$) needs 4 covalent bonds to reach a full shell configuration (8 electrons). However, each carbon atom in polyacetylene has only 3 neighboring atoms (2 carbons, 1 hydrogen). Thus one of the bonds to an <u>adjacent carbon</u> has to be a <u>double bond</u>.

Now $t_1 = \langle \phi_A(r-R) | H | \phi_B(r-R-l_{DB}) \rangle$
and $t_2 = \langle \phi_A(r-R) | H | \phi_B(r-R+l_{SB}) \rangle$
are not equal to each other!



We have to recalculate the off-diagonal elements

$$H_{AB} = \frac{1}{N} \langle \sum_{R_A} e^{ikR_A} \phi(r-R_A) | H | \sum_{R_B} e^{ikR_B} \phi(r-R_B) \rangle$$

Considering nearest neighbors only:

$$H_{AB} \simeq \frac{1}{N} \sum_{R_A} \langle e^{ikR_A} \phi(r-R_A) | H | e^{ik(R_A+l_{DB})} \phi(r-R_A-l_{DB}) \rangle +$$

$$+ \frac{1}{N} \sum_{R_A} \langle e^{ikR_A} \phi(r-R_A) | H | e^{ik(R_A-l_{SB})} \phi(r-R_A+l_{SD}) \rangle$$

$$H_{AB} \cong e^{ikl_{DB}} \cdot t_1 + e^{-ikl_{SB}} \cdot t_2$$

Similarly,

$$S_{AB} \cong e^{ikl_{DB}} \cdot s_1 + e^{ikl_{SB}} \cdot s_2$$

For simplicity, however, we will assume $S_1 = S_2 = 0$.

Setting the determinant:

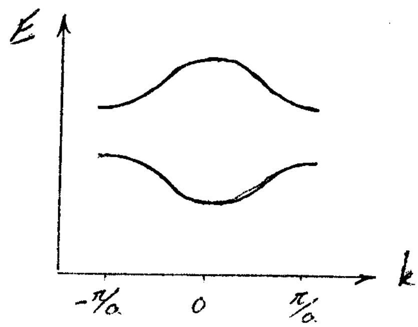
$$\begin{vmatrix} E_{2p} - E & e^{ikl_{DB}} \cdot t_1 + e^{-ikl_{SB}} \cdot t_2 \\ e^{-ikl_{DB}} \cdot t_1 + e^{ikl_{SB}} \cdot t_2 & E_{2p} - E \end{vmatrix} = 0$$

$$(E_{2p} - E)^2 - t_1^2 - t_2^2 - t_1 t_2 \left(e^{ik(l_{DB} + l_{SB})} + e^{-ik(l_{DB} + l_{SB})} \right) = 0$$

$$(E_{2p} - E)^2 = t_1^2 + t_2^2 + 2 t_1 t_2 \cos ka$$

$$E = E_{2p} \pm \sqrt{t_1^2 + t_2^2 + 2 t_1 t_2 \cos ka}$$

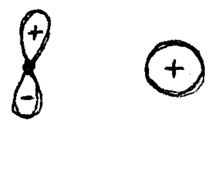
The most prominent effect on the electronic dispersion is the introduction of a band gap of magnitude $\Delta E = 2(t_1 - t_2)$ at the edge of the Brillouin zone.



Another important change is the flattening of the bands particularly at the edges of the Brillouin zone.

(c) Energetics: The $1s^1$ electron in hydrogen is lower in energy compared to the chain p_z orbitals. The perturbation is small.

Symmetry: The overlap integral $\langle \psi_{p_z} \text{ on } C \mid \psi_s \text{ on } H \rangle = 0$



4.

(a). The lower $3 \times 3 = 9$ bands are (three 3-fold degenerate at Γ-point) p-bands associated with the oxygen;
The upper 5 bands are d-bands associated with the Re;

(b).(c). There are 4 atoms in each unit cell: 1 Re and 3 O;
Re: $4f^{14}5d^5 6s^2$; O: $2s^2 2p^4$;
$\Rightarrow 3 \times 4 + 7 = 19$ electrons. $2 \times 9 = 18$ electrons will fill the oxygen p-bands and 1 electron left will fill part of the lower d-bands. So ReO_3 is metal;

(d). As in (a), upper 5 bands are d bands associated with Re;
Oxygen d-bands are much higher;

(e). At Γ-Point, 3 Carrier pockets with different effective masses due to different curvatures;
(Notice the "open surface" in the Γ-X direction due to flat energy band).

(f). 1 electron;

(g).

FERMI SURFACE OF ReO_3

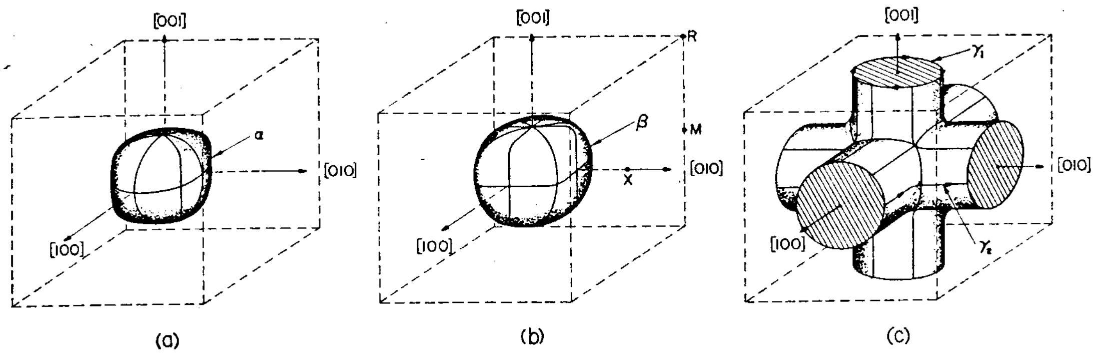


FIG. 6. Three-dimensional sketch of the α(a), β(b), and γ(c) sheets of the ReO_3 Fermi surface.

(h). Lowest energy optical transition is at Σ-point, ($\sim 0.05 Ry$); Not strong transition due to small joint density of states