Homework #2 PHYS732.

(1) $$\varepsilon_2(\omega) = \left(\frac{2\pi e}{m\omega}\right)^2 \sum_k |P_{vc}|^2 \delta(\varepsilon_c(k) - \varepsilon_v(k) - \hbar\omega)$$

Since we are considering a "forbidden" direct gap, $P_{vc}(k) \sim k$, $\varepsilon_c(k) - \varepsilon_v(k) = (\varepsilon_g - \hbar\omega + (\frac{\hbar^2}{2m_c} + \frac{\hbar^2}{2m_v})k^2)$.

So, $\varepsilon_2(\omega) \sim \sum_k k^2 \delta(\varepsilon_g - \hbar\omega + \frac{\hbar^2}{2}(\frac{1}{m_c} + \frac{1}{m_v})k^2) \sim$

$\sim \int d\varepsilon \cdot \sqrt{\varepsilon}\ \delta(\varepsilon_g - \hbar\omega + \varepsilon) \cdot \varepsilon \sim (\hbar\omega - \varepsilon_g)^{3/2}$

(2) a). According to Eq. (19.38)

$\mu = \mu_i - k_B T \sinh^{-1} \frac{N_d - N_a}{2n_i}$ and according to (19.26a) $n_i = \sqrt{N_c N_v}\, e^{-\beta\varepsilon_g/2}$.

At very low T, n_i becomes very small. If $N_a > N_d$, then if the argument of the inverse sinh is negative, and becomes $\mu \approx \mu_i - kT \ln\left(\frac{N_d - N_a}{2\sqrt{N_c N_v}} e^{\beta\varepsilon_g/2}\right) =$

$= \mu_i - \varepsilon_g/2 +$ terms that vanish as $T \to 0 = \varepsilon_v$

So when $\exp[\beta\varepsilon_g/2](N_d - N_a)/\sqrt{N_c N_v} \gg 1$ the donors and acceptors are no longer completely ionized. This critirean makes more precise the entropy argument on the top of p. 532. The chemical potential then moves towards one band edge of the other, depending on whether donors or acceptors dominate.

(B) Everything is the same except that one has

$$\mu = \mu_i + E_g/2 = \varepsilon_c .$$

Criterion $\mu \sim \varepsilon_c$ ($\mu \sim \varepsilon_v$) can be used to find estimate for T (from eq. 19.38), when μ is far from center of the gap.

(3) a). $h(\varepsilon) = \int_{\varepsilon_c}^{\varepsilon} d\varepsilon' g(\varepsilon') \rightarrow g(\varepsilon) = dh(\varepsilon)/d\varepsilon$

b). $h(\varepsilon) = \int_{\varepsilon_v}^{\varepsilon} d\varepsilon\, g_h(\varepsilon) \rightarrow g_h(\varepsilon) = dh(\varepsilon)/d\varepsilon \leftarrow d\varepsilon < 0$

c). $\varepsilon = \varepsilon_{c,v} \pm \frac{\hbar^2}{2}\left(k_1^2/m_1 + k_2^2/m_2 + k_3^2/m_3\right) \rightarrow h(\varepsilon) = \frac{\Omega}{4\pi^3} \cdot \frac{4\pi}{3} \frac{\sqrt{m_1 m_2 m_3}}{\hbar^3} 2^{3/2} |\varepsilon - \varepsilon_{c,v}|^{3/2} \rightarrow$

$$\rightarrow g(\varepsilon) = \sqrt{2|\varepsilon - \varepsilon_{c,v}|}\, \frac{(m_{c,v}^*)^{3/2}}{\pi^2 \hbar^3} \cdot \Omega, \quad m_{c,v}^* = (m_1 m_2 m_3)^{1/3}$$

$$g(\varepsilon) = \pm\, dh(\varepsilon)/d\varepsilon \begin{bmatrix} + \text{electrons} \\ - \text{holes} \end{bmatrix}$$

(4) a. I will take hints from AEM, problem 10.2

(i) From AEM (10.30) and (10.12) we have the general form

$$\left| (\varepsilon(k) - \varepsilon_p)\delta_{ij} + \beta_{ij} + \tilde{\gamma}_{ij}(k) \right| = 0 \qquad (1)$$

where

$$\tilde{\gamma}_{ij} = \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} \gamma_{ij}(\vec{R}) \qquad (2)$$

OVERLAP $\gamma_{ij}(\vec{R}) = -\int d\vec{r}\, \psi_i^*(\vec{r})\psi_j(\vec{r}-\vec{R})\Delta U(\vec{r})$ (3)

$\beta_{ij} = \gamma_{ij}(\vec{R}=0)$ (4)

Equation (1) is still exact but for a small term (the 1st on the right of (10.12)) that we have omitted. The first approximation is to take only p orbitals which have the form:

$$p_x = x\,\phi(|r|)$$
$$p_y = y\,\phi(|r|) \quad (5)$$
$$p_z = z\,\phi(|r|)$$

As they have the same form essentially, the energies E_p are all the same (1) reduces to a 3×3 determinant. Now what are some of the properties of $\Delta U(r)$ and the $\gamma_{ij}(\vec{R}^\eta)$ $(i,j,\eta = \{x,y,z\})$ $(\vec{R}^x = a\hat{x}, \vec{R}^y = a\hat{y}, \vec{R}^z = a\hat{z})$

$\Delta U(r_x, r_y, r_z)$ must have cubic symmetry, and thus

$\Delta U(r_x, r_y, r_z) = \Delta U(\pm r_x, \pm r_y, \pm r_z)$ (P.1) (property 1)

as well as being the same under permutation of the three components of $\vec{r}$ => (P.2)

$$\Delta U(r_x, r_y, r_z) = \Delta U(P(r_x, r_y, r_z)),$$

where P denotes all possible permutations

(isn't cubic symmetry great!)

Now let's look at $\gamma_{ij}(-\vec{R})$:

$$\gamma_{ij}(-\vec{R}) = -\int d\vec{r}\, \psi_i^*(\vec{r})\, \psi_j(\vec{r}+\vec{R})\, \Delta U(\vec{r})$$

If we take $\vec{r} \to -\vec{r}$ and use the fact that p-orbitals have the property $\psi(-\vec{r}) = -\psi(r)$ and $\Delta U(-\vec{r}) = \Delta U(\vec{r})$

$$\gamma_{ij}(-\vec{R}) = \gamma_{ij}(\vec{R}) \quad \text{(P. 3)}$$

Let's look at the $\{\beta_{ij}\}$

$$\beta_{ij} = -\int d\vec{r}\, x_i\, x_j\, |\varphi(r)|^2 \Delta U(\vec{r}) = \beta \delta_{ij} \quad (6)$$

This property can be found by noting that the is odd in x_i & x_j if $i \neq j$; and thus off-diagonal elements are zero. By the cubic symmetry

$$\beta_{xx} = \beta_{yy} = \beta_{zz} = \beta.$$

To solve the determinant (1) we need the $\tilde{\gamma}_{ij}(k)$. We find $\tilde{\gamma}_{jj}(\vec{k}) = \sum_{\vec{R}} \gamma_{jj}(\vec{R})\, e^{i\vec{k}\vec{R}}$, (7)

where the sum is over nearest neighbors. Thus

$$\tilde{\gamma}_{jj}(\vec{k}) = 2\gamma_0 \cos(k_j a) + 2\gamma_1 \cos(k_\ell a) + 2\gamma_1 \cos(k_m a)$$

$$(j \neq \ell \neq m) \quad (8)$$

The determinant becomes: (9)

$$((\varepsilon(\vec{k}) - \varepsilon_p) + \beta + \tilde{\gamma}_{xx}(k))(\varepsilon(k) - \varepsilon_p + \beta + \tilde{\gamma}_{yy}(k))(\varepsilon(k) - \varepsilon_p + \beta + \tilde{\gamma}_{zx}(k)) = 0$$

But at the Γ point ($\vec{k}=0$) all the $\tilde{\gamma}_{ij}$ become the one, namely:

$$\tilde{\gamma}_{ij} = 2\gamma_0 + 4\gamma_1 \qquad (10)$$

and the determinantal equation (9) becomes:

$$((\varepsilon(k) - \varepsilon_p) + \beta + 2\gamma_0 + 4\gamma_1)^3 = 0 \qquad (11)$$

and so there are three degenerate roots, and no splitting at the Γ point!

(ii) Is the result that only two γ's are needed for p-bands a general one?

Let's take the example of a f.c.c. crystal. The 12 nearest neighbors are at the basis vectors:

$$\vec{R} = a(\pm\tfrac{1}{2}, \pm\tfrac{1}{2}, 0),\ a(\pm\tfrac{1}{2}, 0, \pm\tfrac{1}{2}),\ a(0, \pm\tfrac{1}{2}, \pm\tfrac{1}{2})$$

Let's start with off-diagonal elements:

$$\gamma_{xy}(\vec{R})/\vec{R} = a(\tfrac{1}{2}, \tfrac{1}{2}, 0) \Rightarrow$$

$$\Rightarrow \gamma_{xy}(\vec{k}) = -\int dx\, x(y - \tfrac{1}{2}a)\varphi(r)\phi\left(\sqrt{(x-\tfrac{1}{2}a)^2 + (y-\tfrac{1}{2}a)^2 + z^2}\right)\Delta u/r,$$

For the other basis vectors we get:

$\vec{R} = a(\frac{1}{2}, -\frac{1}{2}, 0)$ $\quad -\int dr\, x(y+\frac{1}{2}a)\varphi\varphi(\vec{r}-\vec{R})\Delta u$

$\vec{R} = a(\frac{1}{2}, 0, \frac{1}{2})$ $\quad -\int dr\, xy\varphi(r)\varphi(\vec{r}-\vec{R})\Delta u$ [$=0$!]

If we continue the analysis, we find:

$$\tilde{\gamma}_{xy}(k) = \gamma_1 e^{i(k_x\frac{a}{2}+k_y\frac{a}{2})} - \gamma_1 e^{i(k_x\frac{a}{2}-k_y\frac{a}{2})} +$$

$$+ \gamma_1 e^{i(-k_x\frac{a}{2}-k_y\frac{a}{2})} - \gamma_1 e^{-ik_x a/2 + ik_y a/2} = 2\gamma_1 \cos(\frac{k_x a}{2}+\frac{k_y a}{2}) -$$

$$- 2\gamma_1 \cos(\frac{k_x a}{2}-\frac{k_y a}{2}) = -4\gamma_1 \sin\frac{1}{2}k_x a \cdot \sin\frac{1}{2}k_y a$$

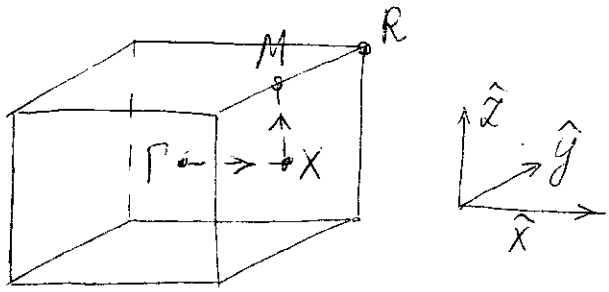
Thus besides the obvious misprint in γ_1 relating to $[y-\frac{1}{2}a^2 \to (y-\frac{1}{2}a)^2]$, there is a second misprint namely: (and not $x-\frac{1}{2}a)(y-\frac{1}{2}a)$!

$$\gamma_1 = -\int d\vec{r}\; x(y-\tfrac{1}{2}a)\varphi(r)\varphi(\sqrt{(x-\tfrac{1}{2}a)^2+(y-\tfrac{1}{2}a)^2+z^2})\Delta u(\vec{r}),$$

If we continue the long and tedious analysis, we find that γ_2 and γ_0 are ok.

The three γ's are clearly independent, we have a counter example, and thus the result of only two γ's is not generalizable to all cubic lattices.

(iii) The points ΓXMR are



There are three bands:

$$x: \varepsilon_x(\vec{k}) = \varepsilon_p - \beta - 2[\gamma_0 \cos(k_x a) + \gamma_1(\cos(k_y a) + \cos(k_z a))] \quad (12)$$

$$y: \varepsilon_y(\vec{k}) = \varepsilon_p - \beta - 2[\gamma_0 \cos(k_y a) + \gamma_1(\cos(k_x a) + \cos(k_z a))]$$

$$z: \varepsilon_z(\vec{k}) = \varepsilon_p - \beta - 2[\gamma_0 \cos(k_z a) + \gamma_1(\cos(k_x a) + \cos(k_y a))]$$

ΓX: k_x goes $0 \to \pi/a$ $\quad 0 \le |k| \le \pi/a$

$k_y = 0$

$k_z = 0$

$$\varepsilon_x(\vec{k}) = \varepsilon_p - \beta - 2\gamma_0 \cos k_x a - 4\gamma_1$$

$$\varepsilon_y(\vec{k}) = \varepsilon_p - \beta - 2(\gamma_0 + \gamma_1) - 2\gamma_1 \cos k_x a \quad (13)$$

$\varepsilon_z(k) = \varepsilon_y(k) \Rightarrow$ <u>doubly degenerate</u>

XII: $k_x = \pi/a$ $\quad \pi/a \le k \le \sqrt{2}\,\pi/a$ $\quad k_y = 0$

$0 \le k_z \le \pi/a$

$$\varepsilon_x(\vec{k}) = \varepsilon_p - \beta + 2\gamma_0 - 2\gamma_1 \cos k_z a - 2\gamma_1 \quad (14)$$

$$\varepsilon_y(\vec{k}) = \varepsilon_p - \beta - 2\gamma_0 - 2\gamma_1 \cos k_z a + 2\gamma_1$$

$$\varepsilon_z(\vec{k}) = \varepsilon_p - \beta - 2\gamma_0 \cos(k_z a) - 2\gamma_1 + 2\gamma_1 = \varepsilon_p - \beta - 2\gamma_0 \cos(k_z a)$$

<u>not degenerate</u>

MR: $k_x = \pi/a$

$0 \le k_y \le \pi/a$

$k_z = \pi/a$

$\sqrt{2}\,\pi/a \le k \le \sqrt{3}\,\pi/a$

(15)

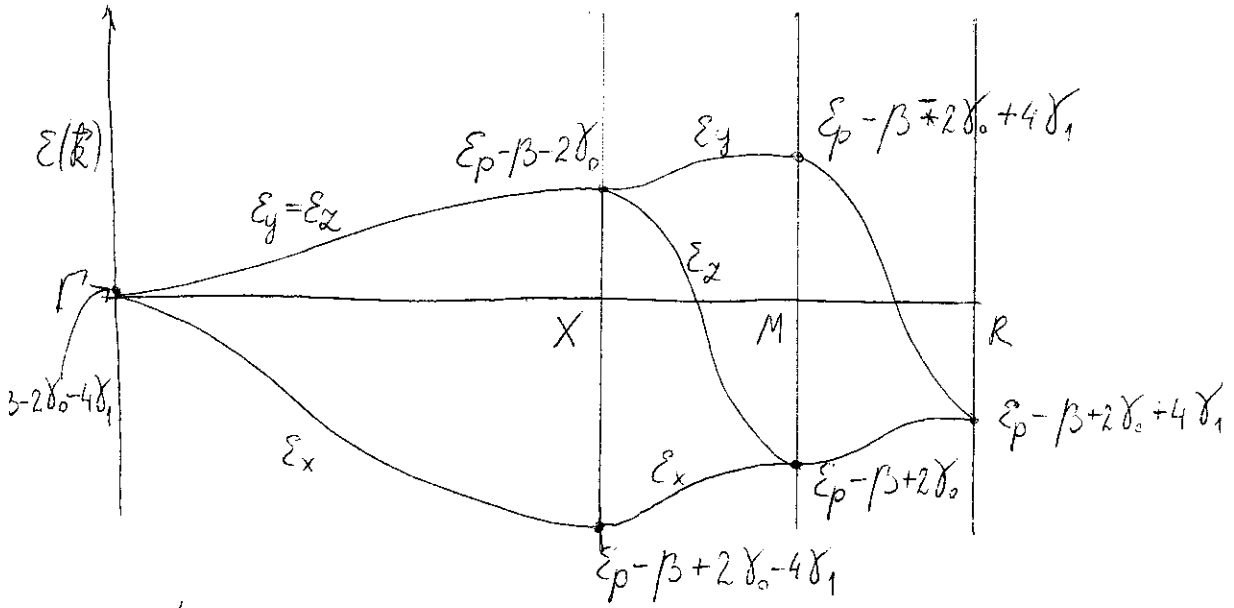
$$\varepsilon_x(\vec{k}) = \varepsilon_p - \beta + 2\gamma_0 + 2\gamma_1 - 2\gamma_1 \cos(k_y a)$$

$$\varepsilon_y(\vec{k}) = \varepsilon_p - \beta - 2\gamma_0 \cos(k_y a) + 4\gamma_1$$

$$\varepsilon_z(\vec{k}) = \varepsilon_p - \beta + 2\gamma_0 + 2\gamma_1 - 2\gamma_1 \cos(k_y a) = \varepsilon_x(\vec{k}) \Rightarrow$$

$\Rightarrow$ doubly degenerate

$\gamma_0 < 0,\ \gamma_1 > 0$



The band width is the difference between the highest point in the band (at M) and the lowest point (at X):

$$(\varepsilon_p - \beta - 2\gamma_0 + 4\gamma_1) - (\varepsilon_p - \beta + 2\gamma_0 - 4\gamma_1) \Rightarrow$$

$\Rightarrow$ band width $= -4\gamma_0 + 8\gamma_1$

3(b) If we add s-orbital, the determinant (1) becomes the determinant of a 4×4 matrix (we need to calculate the elements γ_{ss} and γ_{sp_x}, γ_{sp_y}, γ_{sp_z}, β_{sp_z} etc.

For s-orbitals: $\varphi_s(\vec{r}) = \varphi_s(r)$, and thus, and all terms $\beta_{sp_i} = \int dr\, r_i \varphi_s(r) \rho(r) \Delta u(r) = 0$

$$\beta_{ss} = -\int d\vec{r}\, |\varphi_s(r)|^2 \Delta u(r) \neq 0 \quad (16)$$

$$\gamma_{ss}(\vec{R}) = -\int d\vec{r}\, \varphi_s^*(r)\, \varphi_s(|\vec{r}-\vec{R}|)\, \Delta u(r) \quad (17)$$

It is easy to show, using methods from 3(a) that

$$\gamma_{ss}(\vec{R}) = \gamma_s \text{ for all } \vec{R} \quad (18)$$

Now for the off-diagonal or "mixing" elements

Using the symmetry of the s and p states under inversion of the r_i argument:

$$\gamma_{sp_i}(\vec{R}^n) = 0 \text{ if } i \neq n \quad (19)$$

But for $i = n$:

$$\gamma_{sp_i}(\vec{R}^n) = \gamma_{sp} \neq 0 \text{ if } i = n$$
$$\gamma_{sp_i}(-\vec{R}^n) = -\gamma_{sp} \neq 0 \quad (20)$$

Following the same procedure for the $\gamma_{p_i s}$ we find:

$$\gamma_{p_i s}(\vec{R}^n) = 0 \text{ if } i \neq n$$
$$\gamma_{p_i s}(\vec{R}^n) = -\gamma_{p_i s}(-\vec{R}^n) = \gamma_{p_i s} \text{ if } i = n \quad (21)$$

Now writing out $\tilde{\gamma}_{sp_i}(\vec{k})$ we find:

$$\tilde{\gamma}_{ss}(\vec{k}) = 2\gamma_s[\cos(k_x a) + \cos(k_y a) + \cos(k_z a)] \quad (22)$$

$$\tilde{\gamma}_{sp_x}(\vec{k}) = \gamma_{sp}(e^{ik_x a} - e^{-ik_x a}) = 2i\gamma_{sp}\sin(k_x a) \quad (23)$$

$$\tilde{\gamma}_{sp_y}(\vec{k}) = 2i\gamma_{sp}\sin(k_y a) \quad (24)$$

$$\tilde{\gamma}_{sp_z}(\vec{k}) = 2i\gamma_{sp}\sin(k_z a) \quad (25)$$

$$\tilde{\gamma}_{p_x s}(\vec{k}) = 2i\gamma_{ps}\sin(k_x a) \quad (26)$$

$$\tilde{\gamma}_{p_y s}(\vec{k}) = 2i\gamma_{ps}\sin(k_y a) \quad (27)$$

$$\tilde{\gamma}_{p_z s}(\vec{k}) = 2i\gamma_{ps}\sin(k_z a) \quad (28)$$

Now along ΓX $k_y, k_z = 0 \Rightarrow \tilde{\gamma}_{sp_y}, \tilde{\gamma}_{sp_z}, \tilde{\gamma}_{p_y s}\ \tilde{\gamma}_{p_z s} = 0$ and our determinant takes the form:

$$(29)\quad \begin{vmatrix} \varepsilon(\vec{k}) - \varepsilon_s + \beta_s + \tilde{\gamma}_{ss}(\vec{k}) & \tilde{\gamma}_{sp_x}(\vec{k}) & 0 & 0 \\ \tilde{\gamma}_{p_x s}(\vec{k}) & \varepsilon(\vec{k}) - \varepsilon_p + \beta_p + \tilde{\gamma}_{xx}(\vec{k}) & 0 & 0 \\ 0 & 0 & \varepsilon(\vec{k}) - \varepsilon_p + \beta_p + \tilde{\gamma}_{yy}(\vec{k}) & 0 \\ 0 & 0 & 0 & \varepsilon(\vec{k}) - \varepsilon_p + \beta_p + \tilde{\gamma}_{zz}(\vec{k}) \end{vmatrix}$$

which is block diagonal, so two p bands are independent, and only the p_x-orbital is affected by s-orbitals.

The two remaining bands can be found by solving the upper determinant in (29):

$$[\varepsilon(\vec{k}) - \varepsilon_s) + \beta_s + 2\gamma_s(\cos k_x a + 2)][(\varepsilon(\vec{k}) - \varepsilon_p) + \beta_p + 2\gamma_0 \cos k_x a + 4\gamma_1] -$$
$$-(2i\gamma_{ps}\sin k_x a)(2i\gamma_{sp}\sin k_x a) = 0 \quad (30)$$

We set $\varepsilon_s = \varepsilon_p = 0$, and define:

$$\beta_s + 2\gamma_s(\cos k_x a + 2) = A(k) \text{ ("s" energy)} \quad (31)$$

$$\beta_p + 2\gamma_0 \cos k_x a + 4\gamma_1 = B(k) \text{ ("p" energy)} \quad (32)$$

$$4\gamma_{ps}\gamma_{sp}\sin^2(k_x a) = C(k) \text{ ("mixing" energy)} \quad (33)$$

Thus:

$$\varepsilon(k) = \frac{-A(k) + B(k) \pm \sqrt{(A(k) - B(k))^2 + 4C(k)}}{2}$$

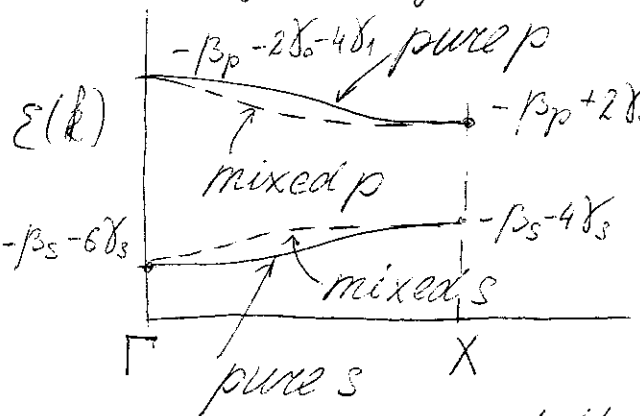
so $\Delta = A(k) - B(k)\big|_{k=0}$ difference between s & p energies at $k = 0$

At Γ-point we have:

$\varepsilon(\vec{k}) = -A(\vec{k}) = -\beta_s - 6\gamma_s$ s-state

and $\varepsilon(\vec{k}') = -B(\vec{k}) = -\beta_p - 2\gamma_0 - 4\gamma_1$ p-state

As we go along the ΓX line we find roughly:



no mixing at X ($C(k) \sim \sin^2\frac{ka}{2} = 0$)

For small mixing ($\gamma_{ps}\gamma_{sp}$), we find that the p-band is slightly pulled down, and the s-band is slightly pulled up. As it gets bigger, the two states will overlap finally