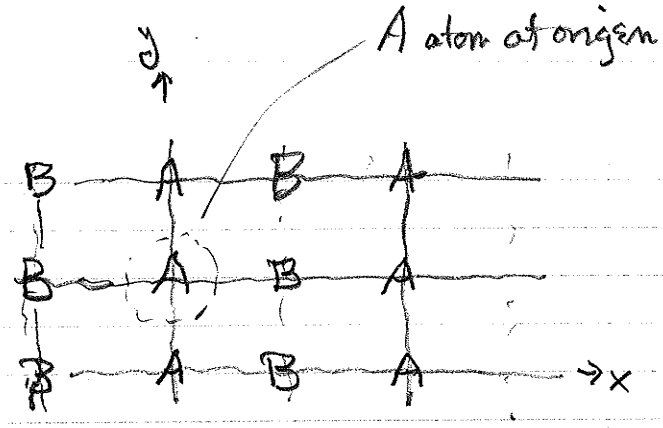
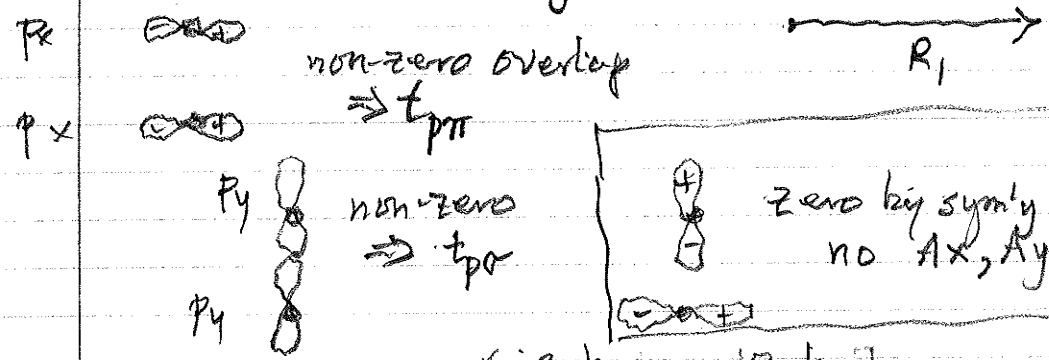
1. Tight Binding.



H_{AA} matrix elements neighbors at $\pm R_2$, each in a different unit cell, so

BUT 2 orbitals $\Rightarrow A_x, A_y$.



$$H_{A_x,A_x} = \varepsilon_{A_x} + t_{p\pi}\left[e^{iR_2\cdot k} + e^{-iR_2\cdot k}\right] = 2t_{p\pi}\cos k_y a$$

$$H_{A_y,A_y} = \varepsilon_{A_y} + t_{p\sigma}\left[\ " \ + \ " \ \right] = 2t_{p\sigma}\cos k_y a \quad \text{by analogy}$$

also $$H_{B,B} = \varepsilon_B + t_s\left[\ " \ + \ " \ \right] = 2t_s\cos k_y a$$

$$H_{A_x,A_y} = 0 \text{ from } (*) \text{ above}$$

$H_{A_y,B}$: by sym'y is zero

$$t_{A_x,B} = t_{ps\sigma}\left[1 + e^{ik\cdot R_1}\right] = t_{sp}\left[1 + e^{-i2k_x a}\right], \quad \leftarrow (-2a, 0)$$

These are all

H	A_x	A_y	B
A_x	$\varepsilon_{A_x} + 2t_{p\pi}\cos k_y a$	0	$t_{sp}\left[1+e^{-i2k_x a}\right]$
A_y	0	$\varepsilon_{A_y} + 2t_{p\sigma}\cos k_y a$	0
B	$t_{sp}\left[1+e^{+i2k_x a}\right]$	0	$\varepsilon_B + 2t_s\cos k_y a$

2. 1D lattice (constant a) of free electrons.

Per spin,

$$g(\varepsilon) = \frac{1}{N}\sum_k \delta(\varepsilon - \varepsilon_k) = \frac{a}{2\pi}\int_{-\pi/a}^{\pi/a} dk\ \delta(\varepsilon - \varepsilon_k)$$

$$= \frac{a}{2\pi}\int_{-\pi/a}^{\pi/a} dk \frac{1}{|\nabla_k \varepsilon_k|_{k=k(\varepsilon)}} \delta(k - k(\varepsilon))$$

Here $\varepsilon = \frac{\hbar^2 k^2(\varepsilon)}{2m}$ so $|k(\varepsilon)| = [2m\varepsilon/\hbar^2]^{1/2}$ $\left\{\text{or } k(\varepsilon) = \pm\sqrt{\frac{2m\varepsilon}{\hbar^2}}\right\}$

$$\nabla_k \varepsilon_k|_{k(\varepsilon)} = \frac{\hbar^2}{m} k(\varepsilon)$$

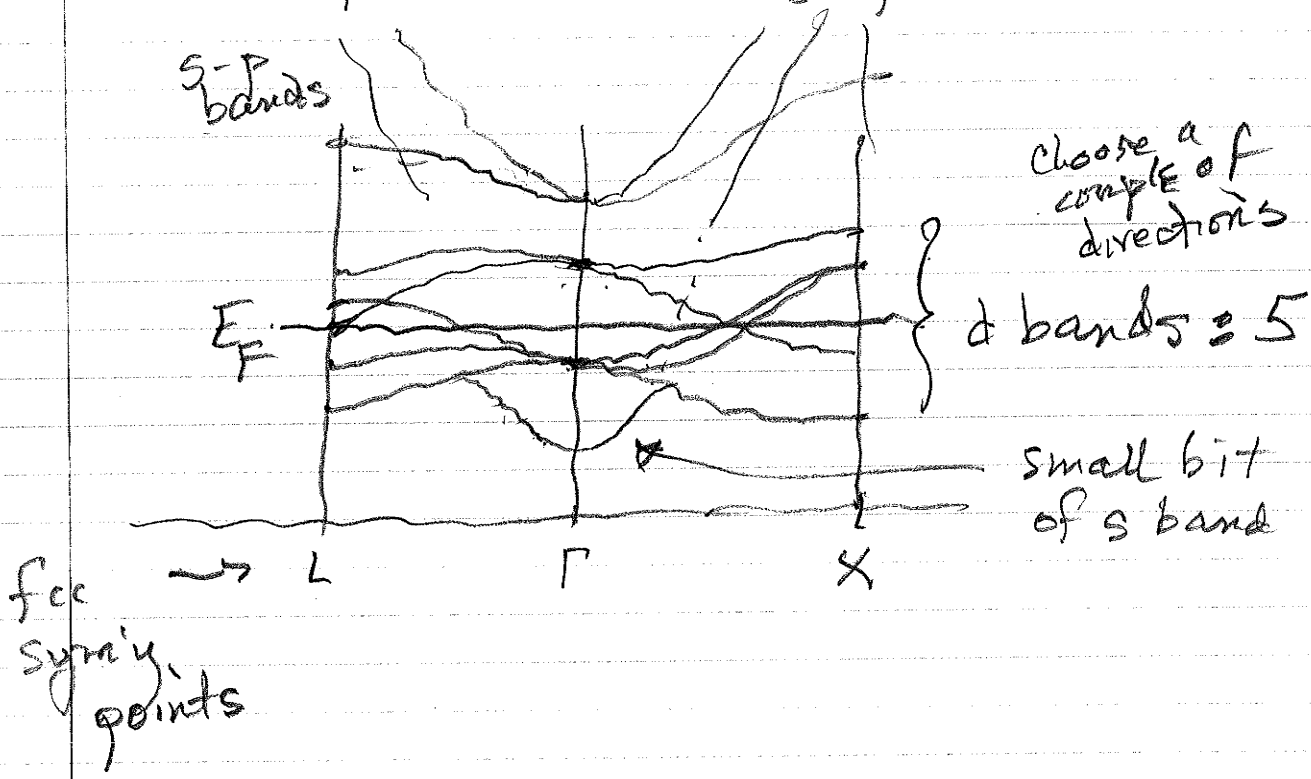
Then $g(\varepsilon) = \frac{a}{2\pi} \times \frac{m}{\hbar^2}\frac{1}{k(\varepsilon)} \times 2$ ← δ-fn satisfied at 2 points $= \frac{a}{\pi}\frac{m}{\hbar^2}\left(\frac{\hbar^2}{2m\varepsilon}\right)^{1/2}$

or $\frac{g(\varepsilon)}{a} = \left(\frac{1}{\pi^2}\frac{m^2}{\hbar^4}\frac{\hbar^2}{2m}\right)^{1/2} \varepsilon^{-1/2} = \frac{1}{\pi\hbar}\sqrt{\frac{m}{2\varepsilon}}$

↑ DOS per unit cell length

3 Band str. of fcc Rh

- items
  - fcc BZ ⇒ high sym'y points Γ, X, K, L, W
  - 5 somewhat narrow d bands
  - E_F roughly in middle of d bands
  - bit of a s band below; s-p bands above.



4.

$$f(\varepsilon-\mu) = \left\{ e^{(\varepsilon-\mu)/kT} + 1 \right\}^{-1} \qquad (k \equiv k_B)$$

$$\frac{\partial f}{\partial \varepsilon}(\varepsilon-\mu) = -\left\{ e^{(\varepsilon-\mu)/kT} + 1 \right\}^{-2} e^{(\varepsilon-\mu)/kT} \left(\frac{1}{kT}\right)$$

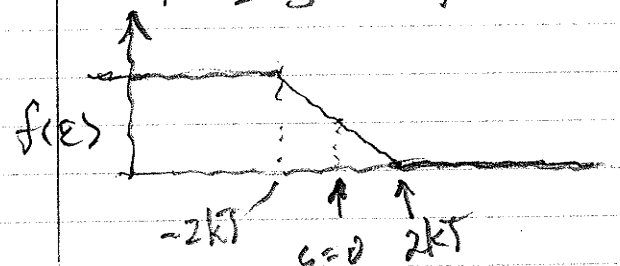
$$\left.\frac{\partial f}{\partial \varepsilon}(\varepsilon-\mu)\right|_{\varepsilon=\mu} = -\frac{1}{kT} 2^{-2} \cdot 1 = -\frac{1}{4kT}$$

So $f(\varepsilon-\mu) = f(\mu) + \left.\frac{\partial f}{\partial \varepsilon}\right|_{\varepsilon=\mu} (\varepsilon-\mu)$, when this is in $[0,1]$.

Setting it equal to 1: $\frac{1}{2} - \frac{1}{4kT}(\varepsilon_{lo}-\mu) = 1 \Rightarrow \varepsilon_{lo} - \mu = -2kT$

setting it " " 0: $\varepsilon_{hi} - \mu = +2kT$

Simplify by setting ε scale relative to μ: $\underline{\mu = 0}$.



$$\text{So } P(T) \approx \int_{-2kT}^{2kT} d\varepsilon \left\{ P(0) + \varepsilon P'(0) + \frac{1}{2} P''(0) \varepsilon^2 + \ldots \right\} \left(-\frac{\varepsilon}{4kT}\right) + \text{const}$$

1st non-zero term $\longrightarrow$ $\int_{-2kT}^{2kT} d\varepsilon\, \varepsilon P'(0) \left(-\frac{\varepsilon}{4kT}\right) = -\frac{1}{4kT} \frac{\varepsilon^3}{3} \Big|_{-2kT}^{2kT} P'(0)$

$$= -\frac{1}{4kT} \frac{1}{3} 2 \left(8 k^3 T^3\right) P'(0) = \underline{-\frac{4}{3} k^2 T^2 P'(0)}$$ is the linear in T term

Sommerfeld value: $-\frac{\pi^2}{6} k^2 T^2 P'(0)$

$\pi^2/6 \approx 1.64$

5. Zero energy states

$-\frac{\hbar^2}{2m}\nabla^2\psi(r) = \varepsilon\,\psi(r)$ for $\varepsilon = 0$.

For $\varepsilon > 0$, there are states $e^{i\vec{k}\cdot\vec{r}}$ w/ $\varepsilon_k = \frac{\hbar^2|k|^2}{2m}$

For $\varepsilon = 0$, this reduces to one state,

$\psi(r) = \text{constant} = \frac{1}{\sqrt{V}}$ (normalized to vol. V)

What about a solution is a spherical representation?
The lowest energy state would be s-type, spherical,
so neglect θ, ϕ parts of ∇^2.

Let's look at radial part $\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) = 0$.
Use primes. Multiply by r^2.

$(r^2\psi')' = 2r\psi' + r^2\psi'' = 0$. Notation: $\phi = \psi'$, $\phi' = \psi''$

Then

$$\phi' = -\frac{2}{r}\phi \quad \text{or} \quad \frac{1}{\phi}\phi' = -\frac{2}{r}$$

Then $(\log\phi)' = -\frac{2}{r}$ so $\log\phi = -2\log r$

or $\phi(r) = \frac{1}{r^2}$. The $\psi(r) = \int\phi(r')dr' = \int\frac{dr'}{r'^2}$.

This last step provides a conundrum: we want $\psi(r)$ for arbitrary r in $(0,\infty)$ so the lower limit should be zero. However, $\int_{\infty}^{r}\frac{dr'}{r'^2}$ is divergent. Hence not a real solution.

[One could say this as $-\int_{r}^{\infty}\frac{dr'}{r'^2}$ gives $\psi(r) = \frac{1}{r}$. This is not normalizable: $\int|\psi(r)|^2dr$ is divergent.]

6. Hartree-Fock

(a) H-F is approximating a solution (wavefn + energy) by assuming a single determinant (per spin) form for the many-body wavefn.

(b) Must get all of the $3! = 6$ permutations right

$$\Psi(r_1, r_2, r_3) = \psi_1(1)\left[\psi_2(2)\psi_3(3) - \psi_2(3)\psi_3(2)\right] + \psi_1(2)\left[\psi_2(3)\psi_3(1) - \psi_2(1)\psi_3(3)\right] + \psi_1(3)\left[\psi_2(1)\psi_3(2) - \psi_2(2)\psi_3(1)\right]$$

$\psi_1\psi_2\psi_3$ in fixed order, permute the coordinates.

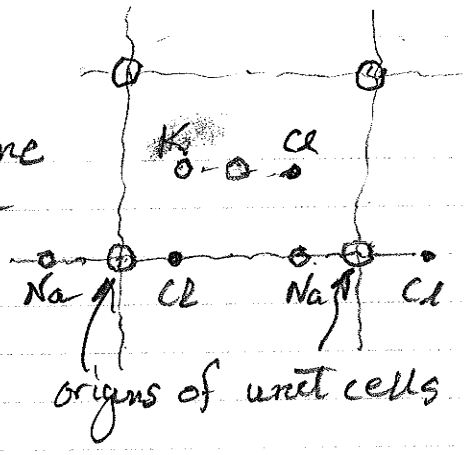
(c) Particles 1 & 2 have spin up. # 3 has spin down

$$\Psi = \left[\psi_1(1)\psi_2(2) - \psi_1(2)\psi_2(1)\right]_{\uparrow}\ \psi_3(3)_{\downarrow}$$

Simple!

7. fcc KCl,

$\vec{b}_1, \vec{b}_2, \vec{b}_3$ are given



$$S_{\underset{\sim}{G}} = \frac{1}{N} \sum_{\text{atoms}} f_a e^{i \underset{\sim}{G} \cdot (\underset{\sim}{R}_a + \underset{\sim}{\tau}_a)}$$

$\underset{\sim}{R}_a$ = direct lattice vector

$\underset{\sim}{\tau}_a$ = position inside cell

Since it is a (fcc) lattice, each atom is inside each cell

$$S_{\underset{\sim}{G}} = \frac{1}{N} \sum_{\underset{\sim}{R}} e^{i \underset{\sim}{G} \cdot \underset{\sim}{R}} \sum_{a=1}^{2} f_a e^{i \underline{G} \cdot \underline{\tau}_a} \qquad \{\vec{G}\} = \{ \sum_i n_i \vec{b}_i \}.$$

$$= \underbrace{\frac{1}{N} \sum_{n_1 n_2 n_3} e^{i 2\pi (n_1 + n_2 + n_3)} \left[(\bar{f} + \delta f) e^{i \underline{G} \cdot \underline{\tau}_K} + (\bar{f} - \delta f) e^{i \underline{G} \cdot \underline{\tau}_{Cl}} \right]}_{\text{unity}}$$

Let $\vec{G} = m_1 \vec{b}_1 + m_2 \vec{b}_2 + m_3 \vec{b}_3 = (m_1, m_2, m_3) \frac{2\pi}{a}$

then

$$\underline{G} \cdot \underline{\tau}_K = (m_1, m_2, m_3) \frac{2\pi}{a} \cdot \left(-\frac{a}{4}, 0, 0\right) = -m_1 \pi/2$$

$$\underline{G} \cdot \underline{\tau}_{Cl} = \qquad\qquad = +m_1 \pi/2$$

So $S_G = 2\bar{f} \cos(m_1 \pi/2) + 2i\, \delta f \sin(m_1 \frac{\pi}{2})$.

Effect of δf: if $\delta f \neq 0$, then $S_G \neq$ for all G.

However, if $\delta f = 0$, then $S_G = 0$ when the cosine term is zero: $\cos(m_1 \frac{\pi}{2}) = 0 \Rightarrow m_1 =$ odd.

So $\delta f \neq 0$ (different atoms) introduces new reflections.