

# Materials 218/UCSB: Assignment V

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1. In class, we examined the band structure of a square lattice of  $s$  orbitals. Sketch out the band structure of a *rectangular* lattice of  $s$  orbitals with  $a$  and  $b$  as the lattice parameters and  $a < b$ . Remember that  $X(0, \frac{\pi}{a})$  and  $Y(\frac{\pi}{b}, 0)$  will not be degenerate. Sketch the DOS alongside.
2. Sketch the band structure of a square lattice of  $p_x$  and  $p_y$  orbitals, with the DOS alongside. For what number of electrons per orbital would distortion of such a lattice (to a rectangle) result in a lowering of energy. Could such a distortion be accompanied by a metal-insulator transition ?
3. The Cyrot-Lackmann theorem:

Sometimes, it is convenient to be able to guess the form of the density of states at some *local* site in a structure. Françoise Cyrot-Lackmann [*J. Phys. Chem. Solids* **29** (1968) 1235] has suggested a theorem (the Moments Theorem) that allows one to do this.

The theorem states:

The  $n^{th}$  moment of the local density of states on an atom  $i$  is the sum of all paths of length  $n$  hops starting and ending on site  $i$ .

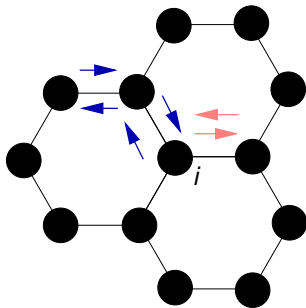
The  $n^{th}$  moment  $\mu_i^{(n)}$  of the local DOS at site  $i$  is defined:

$$\mu_i^{(n)} = \int_{\text{whole band}} (E - \alpha)^n D_i(E) dE$$

where  $\alpha$  is the center of gravity of the local DOS, and  $D_i(E)$  is the local DOS at site  $i$ .

As for any normalized distribution, the zeroth moment is 1 (the area under the DOS curve), the first moment is the mean or the center of gravity  $\alpha$ , the second moment is the width (like the standard deviation) of the DOS, and the higher moments describe the shape (skewness, kurtosis *etc.*).

How are the hops calculated ? This is illustrated for the graphite lattice for the atom at site  $i$ :



The pink arrows indicate hops of length 2. There are three such hops possible.<sup>1</sup> Each of these hops contributes  $\beta^2$  to  $\mu^{(2)}$ .  $\beta$  is the strength of the interaction between ions, and is related to covalency (more covalent  $\Rightarrow$  larger  $\beta$ ). There are no hops of length 3, so  $\mu^{(3)} = 0$ .<sup>2</sup>

The blue arrows indicate hops of length 4. Each of these contributes  $\beta^4$  to  $\mu^{(4)}$  and there are 6 such hops. In addition, one can hop from site  $i$  to a neighbor and back *twice*. This provides an additional  $3 \times \beta^4$  (since there are three neighbors).

So we have:

$$\mu^{(0)} = 1; \mu^{(1)} = \alpha; \mu^{(2)} = 3\beta^2; \mu^{(3)} = 0; \mu^{(4)} = 9\beta^4$$

<sup>1</sup>One can only hop along a bond.

<sup>2</sup> $\mu^{(3)} = 0$  means the DOS is symmetric about its center of gravity. In other words, it is not skewed.  $\mu^{(3)} < 0$  means the distribution is skewed towards higher energies with a long tail at lower energies.  $\mu^{(3)} > 0$  means the opposite.

It is known that for the moments of a distribution, the dimensionless quantity  $s$  given by:

$$s = \frac{\mu^{(4)}\mu^{(2)} - (\mu^{(2)})^3 - (\mu^{(3)})^2}{(\mu^{(2)})^3}$$

is indicative of whether the distribution is unimodal ( $s \geq 1$ ) or bimodal ( $s < 1$ ).

- (a) Calculate  $s$  for the site  $i$  in the graphite lattice and use this to describe the nature of the local DOS at site  $i$ .
- (b) Calculate  $s$  for an atom in the middle of a 1D chain and for an atom at the end of the chain. Are the DOS unimodal or bimodal at these sites ?
- (c) Note that by calculating the first four moments and changing the filling of electrons, one can actually discern why some metals are bcc whilst others are fcc.

#### 4. Effects of dimensionality:

- (a) Show from considerations of  $\mu^{(2)}$  that on going from 1D to 2D, (a chain to a square lattice) the DOS broadens significantly ( $\mu^{(2)}$  is larger). Suggest how this might influence metallicity.