Materials 218/Chemistry 277: Assignment 4

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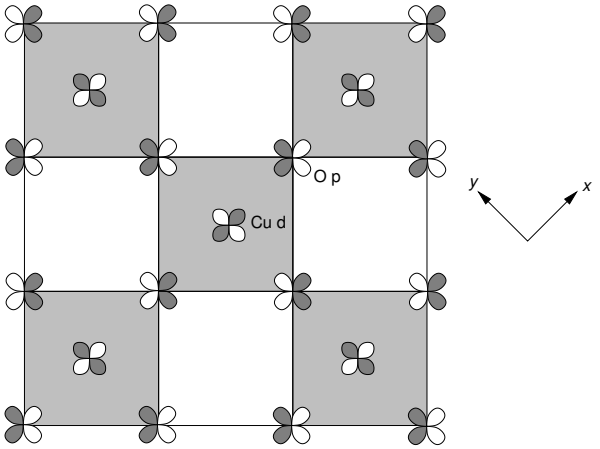
1. In class, we examined the band structure of a square lattice of s orbitals. Sketch out the band structure of a *rectangular* lattice of s orbitals with a and b as the lattice parameters and $a < b$. Remember that $X(0, \frac{\pi}{a})$ and $Y(\frac{\pi}{b}, 0)$ will not be degenerate. Sketch the DOS alongside.

2. Sketch the band structure of square lattice of p_x and p_y orbitals, with the DOS alongside.

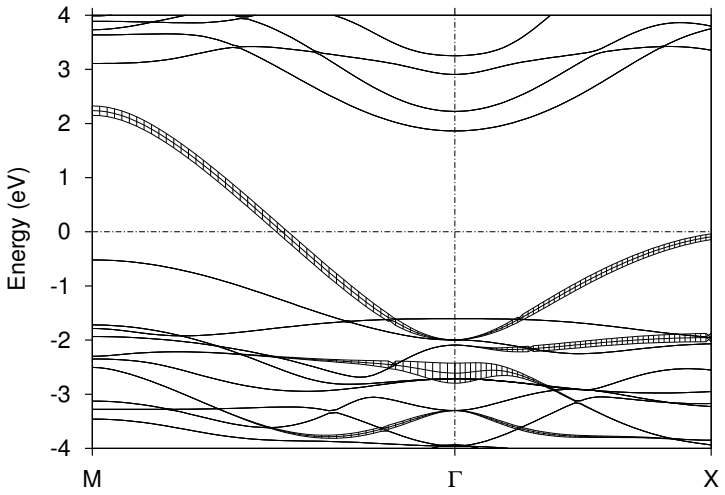
3. The Physics of High-T_C superconductors:

   The essential electronic structural features of High-T_C copper oxide superconductors are summarized in the sketch below, with perovskite CuO_2 planes represented by a chessboard. The black tiles on the chessboard have a copper atom with a $d_{x^2-y^2}$ orbital at the center. At the corner of every tile is an oxygen atom with a p_x and a p_y orbital.



   Sketch out the band structure of such a 2D lattice, concentrating on the band formed through the metal-oxygen-metal network (nearest neighbors). Suggest why similar compounds formed from *early* transition metals such as Ti or V would not have bands that are as disperse.[1].

   Compare your band structure with a DFT calculation on La_2CuO_4, the parent compound of all High-T_C superconductors. Focus on the striped band. The 0 on the energy axis is the Fermi energy:



[1] Think of the filling of electrons into d orbitals in a square-planar crystal field. Highly disperse bands are considered to be very important for High-T_C

4. 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.

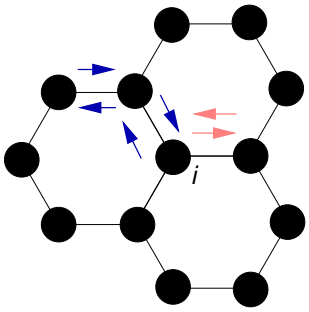
   The n^{th} moment $\mu_i^{(n)}$ of the local DOS at site i is defined:

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

   where α 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 α, 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.[2] Each of these hops contributes β^2 to $\mu^{(2)}$. β is the strength of the interaction between ions, and is related to covalency (more covalent $\Rightarrow$ larger β). There are no hops of length 3, so $\mu^{(3)} = 0$.[3]

   The blue arrows indicate hops of length 4. Each of these contributes β^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:

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

   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 ?

5. Effects of dimensionality:

   (a) Show from considerations of $\mu^{(2)}$ that on going from 2D to 3D, (a square lattice to a simple cubic lattice) the DOS broaden significantly ($\mu^{(2)}$ is larger).

   (b) Is the DOS skewed or symmetric in the above two cases ?

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[2] One can only hop along a bond.

[3] $\mu^{(3)} = 0$ 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.