MATRL 218/CHEM 227: 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 \( X(0, \frac{a}{2}) \) and \( Y(\frac{b}{2}, 0) \) 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. Sketch the most bonding and the most antibonding crystal orbitals formed from \( sp^2 \) orbitals on carbon in graphite. Do the same for \( p_z \) orbitals.

4. Sketch the most antibonding \( sp^3 \) crystal orbital for (a few) Si atoms within the unit cell of diamond Si. Why is molten Si a metallic, while crystalline Si is insulating.

5. \( \text{FeS}_2 \) (fool’s gold) has the pyrite structure (octahedral Fe) and because of a bond between the two S atoms (characterized by a short S-S distance), it can be formulated \( \text{Fe}^{2+}[\text{S}_2]^{2-} \). Magnetic measurements suggest that the compound is non-magnetic.
   
   (a) Sketch out the crystal field (showing \( t_{2g} \) and \( e_g \) levels) and fill them with the correct number of electrons.
   
   (b) Sketch out schematic densities of states showing Fe \( d \) states and S \( p \) states. Do you expect a metal or an insulator ?
   
   (c) What do you expect the situation in Co\( \text{S}_2 \) to be ? It has the same crystal structure.

6. \( \text{TiS}_2 \) has the layered \( \text{CdI}_2 \) structure, and there are no short S-S distances.
   
   (a) What is the oxidation state of Ti ?
   
   (b) Sketch out schematic DOS showing Ti \( d \) states and S \( p \) states. Do you expect an metal or an insulator ?
   
   (c) \( \text{TiS}_2 \) shows metallic conductivity. Suggest a possible origin ?