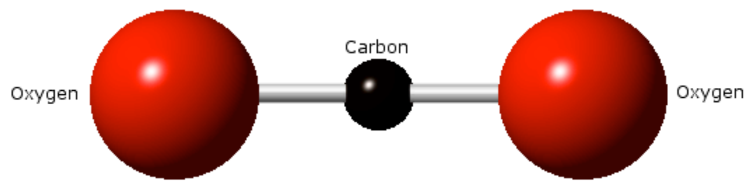
PH575: Introduction to Solid State Physics SPRING 2019
Homework #2 DUE Friday 19, April 2019, in class

1. Based on Sutton, problem #9 p.240. This problem explores the more realistic case where the atomic orbitals $|1\rangle$ and $|2\rangle$ used in the diatomic molecule basis are *not* orthogonal. That is, $\langle 1|2\rangle = S \neq 0$, although they are normalized $\langle 1|1\rangle = \langle 2|2\rangle = 1$. Expand the molecular state $|\Psi\rangle = c_1|1\rangle + c_2|2\rangle$. Let the Hamiltonian matrix have on-site energy $\langle 1|H|1\rangle = \langle 2|H|2\rangle = E_0$ and hopping energy $\langle 1|H|2\rangle = \langle 2|H|1\rangle = \beta$.
   (a) Calculate the energies E_b and E_a and the corresponding normalized state vectors $|\Psi\rangle_b$ and $|\Psi\rangle_a$ of the bonding and antibonding states.
   (b) Discuss the results you obtain for the molecular energy levels and for the molecular orbitals that correspond to them, comparing your results to the $S = 0$ case. Include a plot E_a and E_b as a function of S.

2. Carbon dioxide (CO_2) is a symmetric linear molecule that looks like this:



   A very simplified LCAO approach is to let $|O_1\rangle$, $|C\rangle$ and $|O_2\rangle$ be mutually orthogonal atomic states associated with the respective oxygen and carbon atoms. Let E_O and E_C be, respectively, the on-site energies of electrons on the isolated oxygen and carbon atoms, and let β be the near-neighbor hopping matrix element. (This is too simple because there is only one orbital assumed for each atom, but some basic concepts are illustrated.)
   (a) Following the procedure used in class, write the Hamiltonian matrix, find the energy eigenvalues of this molecule.
   (b) Identify the energies of the bonding and antibonding states. Is there a non-bonding state?

3. Discuss qualitatively the bonding between 2 atoms in the following cases:
   (a) sigma bonding between two equivalent p_z orbitals
   (b) pi bonding between two equivalent p_z orbitals
   (c) sigma bonding between two equivalent d_{z2} orbitals
   (d) pi bonding between two equivalent d_{yz} orbitals
   In each case, sketch qualitatively the approximate electron distribution on the isolated atoms and then the distributions corresponding to the molecular orbitals $|\Psi\rangle = |1\rangle + |2\rangle$ and to $|\Psi\rangle = |1\rangle - |2\rangle$ and say which is the bonding combination, which the antibonding and why.
   (e) What is delta bonding? Sketch an example.

4. In class, we showed that the form of the Hammiltonian matrix for the hydrogen molecule ion was
   $H \doteq \begin{pmatrix} E_0 & \beta \\ \beta & E_0 \end{pmatrix}$ with β<0, using just the 1s atomic orbitals for the two hydrogen atoms as a basis.
   Now imagine **three** hydrogen atoms arranged at the vertices of an equilateral triangle.

(a) What is the form of the Hamiltonian matrix in this case?
(b) Explain why it has this form.
(c) What are the energy eigenvalues and corresponding eigenstates?
(d) Why do the symmetries and degeneracy make sense?
(d) Try to sketch an approximate electron distribution

5. In preparation to use the band structure computation programs, find the crystal structure of Si. The crystal structure of Si is based on a cubic arrangement of atoms.

   (a) Where, exactly, are these atoms located, in units of the lattice parameter? What are the Si-Si bond lengths and angles?

   (b) Draw a sketch of a few unit cells. (It will be very helpful to find a program that does this for you. There are several available online.)
   What is the lattice parameter of Si?
   What is the space group of Si?

   (c) How many atoms in the conventional unit cell?

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6. Optional question for those who want to explore a bit more.

Use a 4-atomic-orbital basis ($|1,1s\rangle, |2,1s\rangle, |1,2s\rangle, |2,2s\rangle$) to describe the ground state of the H_2^+ ion, where now the 2s orbitals could contribute, too. If these are the matrix elements:

$\langle 1,1s|H|1,1s\rangle = -14eV$

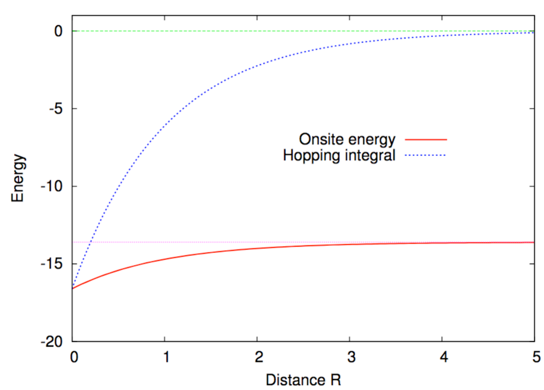
$\langle 1,1s|H|2,1s\rangle = -4eV$

$\langle 1,1s|H|1,2s\rangle = 0$

$\langle 1,1s|H|2,2s\rangle = +2eV$

$\langle 1,2s|H|1,2s\rangle = -4eV$

(find others by symmetry)



Write the energy eigenvalue equation in matrix form and find the ground state energy and c_1, c_2, c_3 and c_4 for the ground state $|\Psi_{ground}\rangle = c_1|1,1s\rangle + c_2|2,1s\rangle + c_3|1,2s\rangle + c_4|2,2s\rangle$. You can use Mathematica or Wolfram Alpha or similar eigenvalue calculator.

Image credit Keivan Esfarjani, UVa http://faculty.virginia.edu/esfarjani/UVA/Teaching_files/tb.pdf

7. Also optional for some more exploration.
The heteronuclear diatomic molecule: Fill in the algebra that leads to Sutton Eq. 2.45 and Eq. 2.46 (explain the physics as you go along) and make a plot like Fig 2.4 based on your results (Sutton's Fig 2.4 is slightly inaccurate). Do a little research to find some parameters for NaCl that indicate where NaCl falls on this plot, *i.e*. the degree of ionicity of the bond indicated by Eq. 2.48.