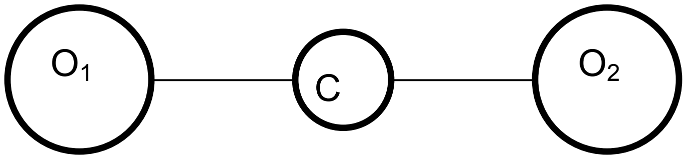
PH575: Introduction to Solid State Physics SPRING 2017
Homework #2 DUE Wednesday 19, April 2017, in class

1. Sutton, problem #9. This question addresses the affect of the non-zero overlap integral, $\langle L|R\rangle$, that arises when analyzing a diatomic molecule. Write two paragraphs that interpret the results you obtain for the molecular energy levels and for the molecular orbitals that correspond to them. Also 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:



Let $|O_1\rangle$, $|C\rangle$ and $|O_2\rangle$ be atomic states (we'll assume they are mutually orthogonal) 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. Assume only near neighbor interactions.
(i) Following the procedure used in class, obtain the secular equation (the one that involves the determinant) and solve for the energy eigenvalues of this molecule. Identify the energies of the bonding and anti-bonding states.

3. Consider bonding between 2 atoms in the following four situations:

(i) sigma bonding between two equivalent p_z orbitals
(ii) pi bonding between two equivalent p_z orbitals
(iii) sigma bonding between two equivalent d_{z2} orbitals
(iv) pi bonding between two equivalent d_{yz} orbitals

For 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 $|\Psi\rangle = |1\rangle - |2\rangle$. Which is the bonding combination, which the anti-bonding combination and why?

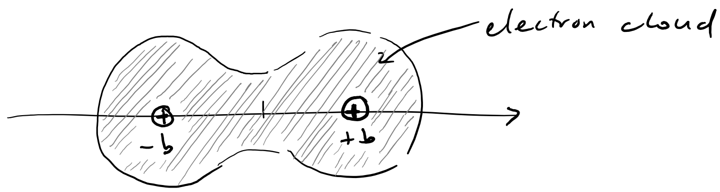
4. The heteronuclear diatomic molecule: Fill in the algebra that leads to Sutton Eq. 2.45 and Eq. 2.46 (explain the physics as you go along) and make a plot like Fig 2.4 based on your results (Sutton's Fig 2.4 is slightly inaccurate). Do a little research to find some parameters for NaCl that indicate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

5. Bonus question. See next page.

HW2 bonus question

Friday, April 14, 2017 10:07 AM

Consider the ground state of the H_2^+ molecule



We will try describing the ground state wavefunction using four basis states (instead of two basis states as was done in class)

$$\Psi(\vec{r}) = \underbrace{c_1 \Psi_{100}(\vec{r}+b\hat{x})}_{|L,1s\rangle} + \underbrace{c_2 \Psi_{100}(\vec{r}-b\hat{x})}_{|R,1s\rangle} + \underbrace{c_3 \Psi_{200}(\vec{r}+b\hat{x})}_{|L,2s\rangle} + \underbrace{c_4 \Psi_{200}(\vec{r}-b\hat{x})}_{|R,2s\rangle}$$

Let

$$\langle L,1s|\hat{H}|L,1s\rangle = -14\,\text{eV}$$
$$\langle L,1s|\hat{H}|R,1s\rangle = -4\,\text{eV}$$
$$\langle L,1s|\hat{H}|L,2s\rangle = 0$$
$$\langle L,1s|\hat{H}|R,2s\rangle = -5\,\text{eV}$$
$$\langle L,2s|\hat{H}|L,2s\rangle = -4\,\text{eV}$$

(Other matrix elements can be found by symmetry)

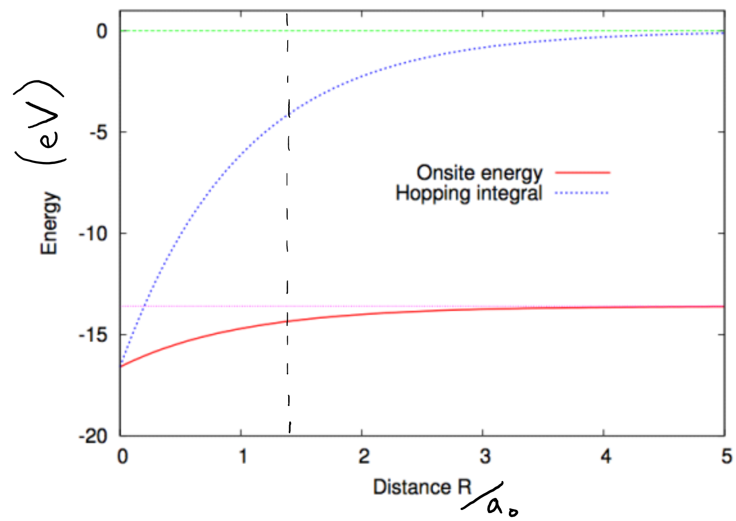


Figure credit: Keivan Esfarjani, Univ. of Virginia

Write the S. Eqn in matrix form using this 4-dimensional basis and find c_1 c_2 c_3 & c_4 for the ground state (we expect that c_3 & c_4 will be negligible). You may use Mathematica or similiar program to help find eigenvectors of the matrix.