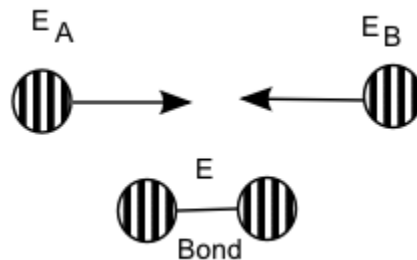


Topic 1-1: Covalent Bonding  
Kittel Pages: 67, 68, 56-58

**Summary:** We begin by introducing covalent bonding in terms of quantum mechanics. Using the time independent Schrodinger equation we are able to describe the energy of covalent bonding as well as an antibonding state in terms of the state of our atoms, the Hamiltonian of our system and weighing coefficients. We then introduce the molecular orbital approach to covalent bonding as well as the concept of hybridization and the effect of this concept on structure of molecules.

- Interested in properties of solids
  - Start with structure
- Begin with gas to make things easier to understand
- $H_2^+$  molecule has two protons and one electron
- Invoke Born-Oppenheimer approximation which says that the nuclei are fixed in space leaving only the electron free to move



- Bring nuclei together, develop an expression for energy of each then observe the change in  $E$  when bond forms
- Start with time independent Schrodinger equation
- $\hat{H}|\psi\rangle = E|\psi\rangle$ , where  $\psi$  is our wavefunction,  $\hat{H}$  is the Hamiltonian of the system and  $E$  is the energy of the system
- our wavefunction is the sum of the states of our system times some weighting coefficient

$$|\psi\rangle = \sum_n c_n |\varphi_n\rangle \quad [1]$$

- The states of our system are the states of each of each individual atom contained within the system
  - Examples of the state of the system include ground state, first excited state and so on
- This will give us valuable information that allows us to obtain the energy of our system through the time independent Schrodinger equation

- Our specific wavefunction is:

$$|\psi\rangle = c_A|\varphi_A\rangle + c_B|\varphi_B\rangle \quad [2]$$

- In the above equation  $|\varphi_A\rangle$  and  $|\varphi_B\rangle$  represent the states of the hydrogen atoms we are bringing together
- After putting the TISE and psi together we get

$$c_A\hat{H}|\varphi_A\rangle + c_B\hat{H}|\varphi_B\rangle = c_A E|\varphi_A\rangle + c_B E|\varphi_B\rangle \quad [3]$$

- Next, we take the inner product of the above equation with  $\langle\varphi_A|$  and  $\langle\varphi_B|$  to get the following secular equations

$$c_A\langle\varphi_A|\hat{H}|\varphi_A\rangle + c_B\langle\varphi_A|\hat{H}|\varphi_B\rangle = c_A E + c_B E\langle\varphi_A|\varphi_B\rangle \quad [4]$$

$$c_A\langle\varphi_B|\hat{H}|\varphi_A\rangle + c_B\langle\varphi_B|\hat{H}|\varphi_B\rangle = c_B E + c_A E\langle\varphi_A|\varphi_B\rangle \quad [5]$$

- We want to solve for energy in terms of  $\hat{H}$ ,  $|\varphi_A\rangle$  and  $|\varphi_B\rangle$  so we need to deal with the weighting coefficients
- The easiest way to do this is to convert to matrix form as seen below

$$\begin{bmatrix} \sim & \sim \\ \sim & \sim \end{bmatrix} \begin{bmatrix} c_A \\ c_B \end{bmatrix} = \text{something} \quad [6]$$

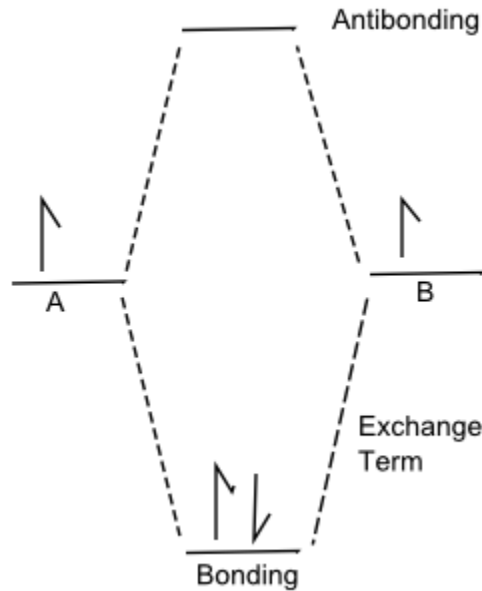
- Setting this equal to zero gives the trivial solution because it gives a null wavefunction
- Get the nontrivial solution by setting the determinant of the first matrix equal to zero and solving
- If we solve this determinant for E we get

$$\frac{\langle\varphi_A|\hat{H}|\varphi_A\rangle \pm \langle\varphi_A|\hat{H}|\varphi_B\rangle}{1 \pm \langle\varphi_A|\varphi_B\rangle} \quad [7]$$

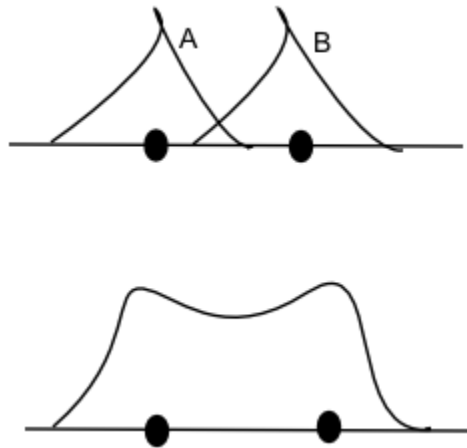
- If we assume that  $|\varphi_A\rangle$  and  $|\varphi_B\rangle$  are orthogonal then  $\langle\varphi_A|\varphi_B\rangle$  is zero and the term in the denominator goes to one

- This leaves  $E = \langle \varphi_A | \hat{H} | \varphi_A \rangle \pm \langle \varphi_A | \hat{H} | \varphi_B \rangle$  which is the onsite interaction plus or minus the exchange term
- The exchange term is critical in that it describes the atomic interactions via the Hamiltonian of the system as seen in the integral below

$$\int dr \varphi_A^* H \varphi_B \quad [8]$$



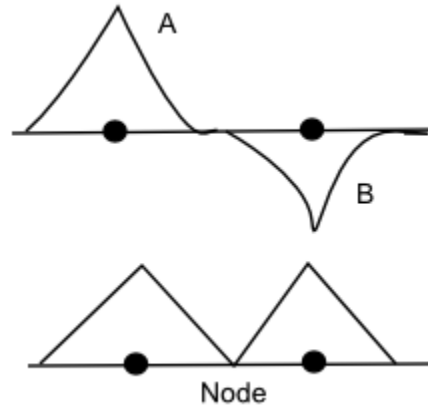
Wavefunction for bonding



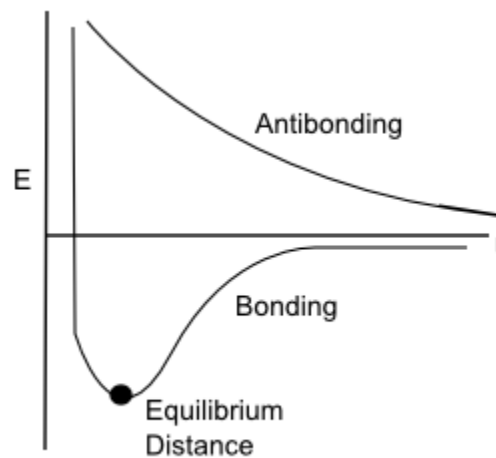
- The bottom graph depicts the probability density or  $\psi^* \psi$
- There is a charge buildup between the two atoms, meaning the probability of finding the electron here is high

- Since charge builds up between atoms this is a covalent bond

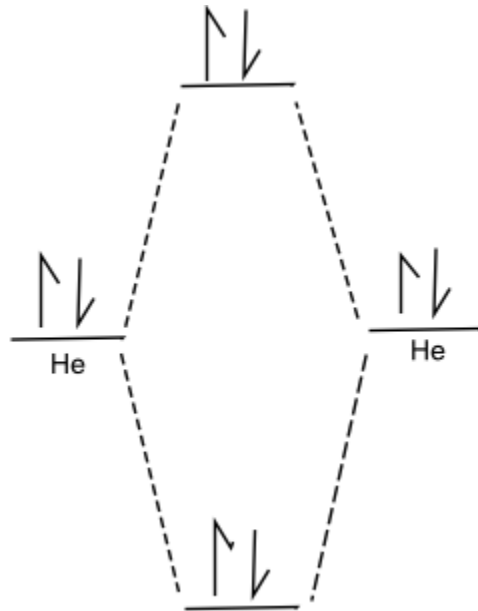
Wavefunctions for antibonding



Energy versus distance

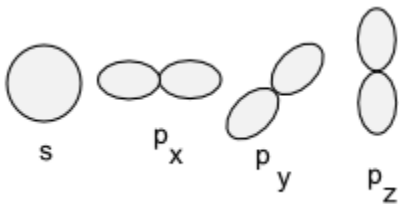


- Rises sharply at the left because as you push the atoms closer than their equilibrium distance they feel a strong coulombic repulsion
- When atoms have core states the Pauli exclusion principle becomes important (i.e. not H or He)
- Pauli exclusion principle: no two electrons can occupy the same state
- Leads to repulsion between overlapping core states
- What about  $\text{He}_2$ ?



- Populates both bonding and antibonding states, effectively no bonding

### Carbon



- Would seem like carbon has 6 nearest neighbors but we know carbon has the diamond structure which is a 4 coordinate structure

### Hybridization

- Started with isolated atoms in a vacuum
  - Atom in a solid is different
- In a solid, hybridization causes the atomic orbitals to reconstitute themselves into new orbitals
- Table for  $sp^3$  orbitals

$$\begin{bmatrix} \phi_1 \\ \phi_2 \\ \phi_3 \\ \phi_4 \end{bmatrix} = \frac{1}{2} \begin{bmatrix} 1 & 1 & 1 & 1 \\ 1 & 1 & -1 & -1 \\ 1 & -1 & 1 & -1 \\ 1 & -1 & -1 & 1 \end{bmatrix} \begin{bmatrix} \psi_s \\ \psi_{p_x} \\ \psi_{p_y} \\ \psi_{p_z} \end{bmatrix}$$

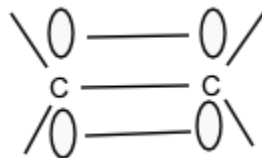
- Values in the above table are just weighting factors for s and p orbitals as show by the following equations

$$\begin{aligned} \phi_1 &= \frac{1}{2}(\psi_s + \psi_{p_x} + \psi_{p_y} + \psi_{p_z}) \\ \phi_2 &= \frac{1}{2}(\psi_s + \psi_{p_x} - \psi_{p_y} - \psi_{p_z}) \\ \phi_3 &= \frac{1}{2}(\psi_s - \psi_{p_x} + \psi_{p_y} - \psi_{p_z}) \\ \phi_4 &= \frac{1}{2}(\psi_s - \psi_{p_x} - \psi_{p_y} + \psi_{p_z}) \end{aligned}$$

- The 4  $sp^3$  orbitals in carbon form a tetrahedral



- A  $sp^3$  hybrid orbital looks like
- Bringing two carbon tetrahedras together causes one of the lobes of each to overlap and puts two electrons in each lobe instead of one
- This creates a covalent bond as well as the diamond structure
- Graphine is another nice hybrid structure



- Has a  $3sp^2+p_z$  structure where the  $p_z$  orbitals (aka the ovals) are sticking out of the page and they also form bonds in addition to those in the xy plane
  - These  $p_z$  bonds are known as pi bonds

Questions to ponder

1. What would bonding in GaAs look like and how do you know?
2. In a real solid would you expect the electron wavefunctions to be localized or extended throughout the material?
3. What type of geometry would result in sp hybridization?