

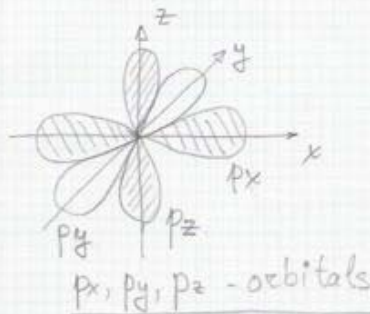
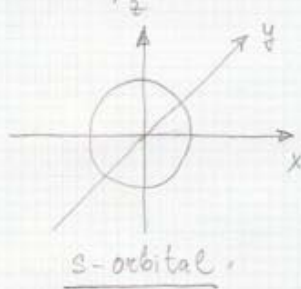
3-3 Covalent crystals

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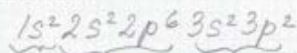
- To understand covalent bond, which is nothing more but a classical electron pair or a homopolar bond of chemistry, and represents a very strong bond, we start from the description of isolated Hydrogen atom, then go into a description of Hydrogen molecule, which will then bring us to tetrahedrally-coordinated semiconductors such as Si, Ge or GaAs, etc.
- Recall that for isolated Hydrogen atom, the total wavefunction is represented as a product of a radial function and spherical harmonics, i.e.

$$\psi_{nlm}(\vec{r}) = R_{nl}(r) Y_l^m(\theta, \varphi)$$

- When $l=0$, we have the s-orbital, which is spherically symmetric and has no directional properties.
- When $l=1$ we have the p-orbitals that have maximum probability along the principal axes of a Cartesian coordinate system.
- When $l=2$, we have the d-orbitals, slightly more complicated in shape, etc.



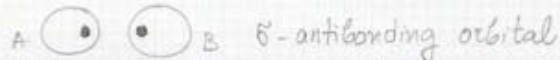
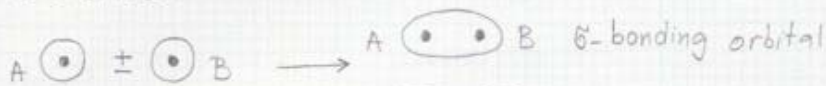
- Now, let us for a moment make a digression and consider a Si-atom with atomic number 14, in which the electrons occupy the following states:



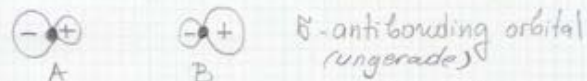
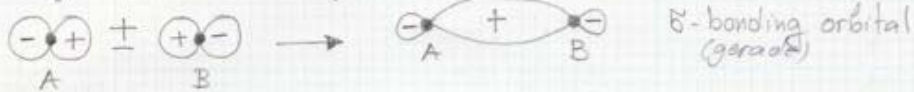
completely filled shells partially-filled shell

The last four electrons, called valence electrons, occupy partially-filled shells, and participate in the formation of a covalent bond. As a result, what we would like to consider is the overlap of the s and p - states wavefunctions.

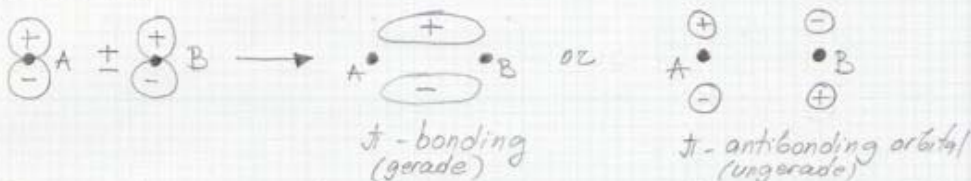
(a) overlap of two s-orbitals to forming bonding and antibonding σ -orbitals (10)



(b) overlap of two p_x -orbitals along the x-axis to forming bonding and antibonding σ -orbitals



(c) Overlap of two p_z -orbitals to form bonding and antibonding π -orbitals:



(d) There is also an overlap between the s-orbitals and p-orbitals.

With the above definitions, the various matrix elements which describe how the interaction mixes the states of the system, are given by:

$$\begin{aligned} \langle s | H | s \rangle &= V_{ss\sigma} & \langle s | H | p_x \rangle &= V_{sp\sigma} \\ \langle p_x | H | p_x \rangle &= V_{pp\sigma} & \langle p_z | H | p_z \rangle &= V_{pp\pi} \end{aligned}$$

- Now, let us go back into the description of a Hydrogen atom and see how the energy states of an H_2 -molecule are changed by the interaction, in this particular case of a type $V_{ss\sigma}$, since the electron occupies 1s state in an H-atom. Let denote the composite wavefunctions for an H_2 molecule as:

$$\psi = u_1 |d_1\rangle + u_2 |d_2\rangle$$

Then, the energy expectation value is

$$E = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{[\langle d_1 | u_1^* + \langle d_2 | u_2^*] H [u_1 | d_1\rangle + u_2 | d_2\rangle]}{[\langle d_1 | u_1^* + \langle d_2 | u_2^*] [u_1 | d_1\rangle + u_2 | d_2\rangle]}$$

$$E = \frac{\langle \psi_1 | H | \psi_1 \rangle U_1^* U_1 + \langle \psi_2 | H | \psi_1 \rangle U_2^* U_1 + \langle \psi_1 | H | \psi_2 \rangle U_1^* U_2 + \langle \psi_2 | H | \psi_2 \rangle U_2^* U_2}{\langle \psi_1 | \psi_1 \rangle U_1^* U_1 + \langle \psi_2 | \psi_1 \rangle U_2^* U_1 + \langle \psi_1 | \psi_2 \rangle U_1^* U_2 + \langle \psi_2 | \psi_2 \rangle U_2^* U_2} \quad (11)$$

$$E = \frac{E_1 U_1^* U_1 + V_{12} U_2^* U_1 + V_{21} U_1^* U_2 + E_2 U_2^* U_2}{U_1^* U_1 + U_2^* U_2}$$

The above expression can also be written in the following form:

$$U_1^* U_1 E_1 + U_1 U_2^* V_{12} + U_1^* U_2 V_{21} + U_2^* U_2 E_2 = E (U_1^* U_1 + U_2^* U_2)$$

We now want to find the minimum of the function $f(U_1, U_2, U_1^*, U_2^*) = 0$ by finding derivatives with respect to U_1^* and U_2^* . This gives:

$$\left. \begin{aligned} E_1 U_1 + V_{21} U_2 &= E U_1 &\Rightarrow (E - E_1) U_1 - V_{21} U_2 &= 0 \\ V_{12} U_1 + U_2 E_2 &= E U_2 &\Rightarrow (E - E_2) U_2 - V_{12} U_1 &= 0 \end{aligned} \right\}$$

In a matrix form, we thus have:

$$\begin{bmatrix} E - E_1 & -V_{21} \\ -V_{12} & E - E_2 \end{bmatrix} \begin{bmatrix} U_1 \\ U_2 \end{bmatrix} = 0 \quad \Rightarrow \underline{A} \underline{U} = 0$$

For the case of obtaining a non-trivial solution, $\det(\underline{A}) = 0$, i.e.

$$(E - E_1)(E - E_2) - \underbrace{V_{12} V_{21}}_{|V_{12}|^2} = 0 \Rightarrow E^2 - (E_1 + E_2)E + E_1 E_2 - |V_{12}|^2 = 0$$

$$E = \frac{1}{2}(E_1 + E_2) \pm \frac{1}{2} \sqrt{(E_1 + E_2)^2 + 4[|V_{12}|^2 - E_1 E_2]}$$

or:

$$E = \frac{E_1 + E_2}{2} \pm \sqrt{\left(\frac{E_1 - E_2}{2}\right)^2 + \frac{4|V_{12}|^2}{4}}$$

$$\begin{aligned} &E_1^2 + E_2^2 + 2E_1 E_2 + 4|V_{12}|^2 - 4E_1 E_2 \\ &= E_1^2 - 2E_1 E_2 + E_2^2 + 4|V_{12}|^2 \\ &= (E_1 - E_2)^2 + 4|V_{12}|^2 \end{aligned}$$

To summarize:

$$E = \frac{E_1 + E_2}{2} \pm \sqrt{\left(\frac{E_1 - E_2}{2}\right)^2 + |V_{12}|^2}$$

Let us now denote the matrix element V_{12} as a COVALENT ENERGY, and the lower-lying energy state as a bonding and the upper as an antibonding state. To proceed with a discussion here, we must distinguish between:

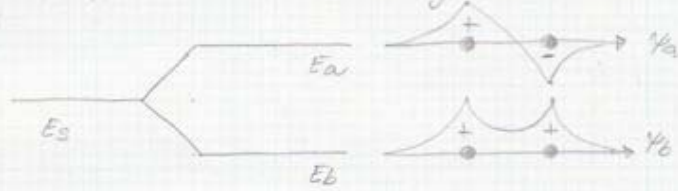
- homopolar diatomic molecule
- heteropolar diatomic molecule

(a) homopolar diatomic molecule

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In this particular case $E_1 = E_2 = E_s$ and the bonding and the antibonding states are

$$\begin{cases} E_b = E_s - |V_{12}| \\ E_a = E_s + |V_{12}| \end{cases}$$



$$\begin{cases} \psi_b = \frac{1}{\sqrt{2}} (|d_1\rangle + |d_2\rangle) \\ \psi_a = \frac{1}{\sqrt{2}} (|d_1\rangle - |d_2\rangle) \end{cases}$$

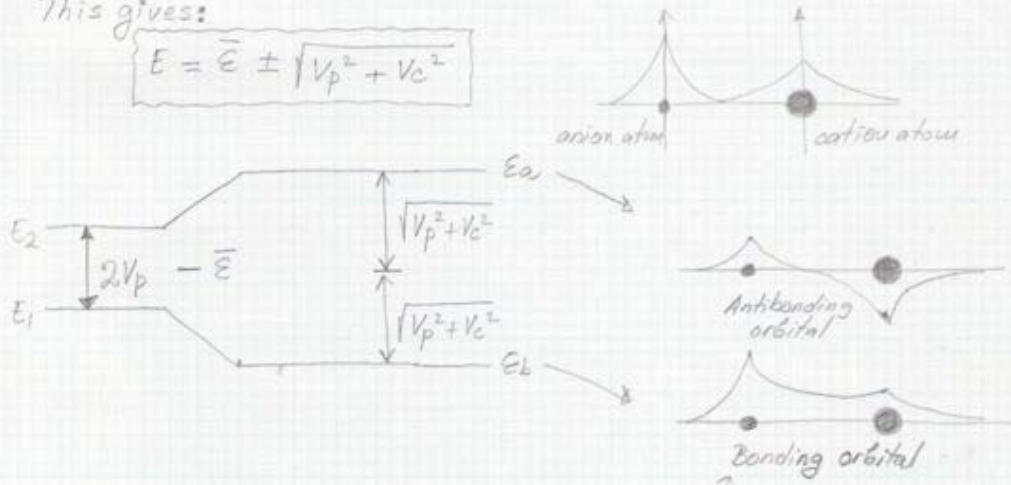
(b) heteropolar diatomic molecule

In this case $E_1 \neq E_2$ and one needs to define a POLAR ENERGY as being equal to the one half of the cation-anion difference. Then

$$V_p = \frac{E_1 - E_2}{2}; \quad V_c = |V_{12}| \quad \text{and} \quad \bar{E} = \frac{E_1 + E_2}{2}$$

This gives:

$$E = \bar{E} \pm \sqrt{V_p^2 + V_c^2}$$



charge density shifts to the low energy side (anion side). As a result of this, the molecule has an electric dipole, i.e. it is said to have a polar bond that leads to polar optical phonon scattering.

The probability that the electron will appear on atom 1 is $(1+dp)/2$, and the probability that it will appear on atom 2 is $(1-dp)/2$, where the polarity dp is defined as:

$$dp = \frac{V_p}{\sqrt{V_p^2 + V_c^2}} \rightarrow \text{The dipole of the bond is proportional to } dp = u_1^2 - u_2^2$$

• After the discussion of an H_2 molecule, from which it followed that the electronic states of a diatomic molecule can be written as a linear combination of the atomic orbitals, we go into the bond orbitals description of Si atoms that leads to tetrahedral crystalline structure. (B)

→ A note here is that bond orbitals and atomic orbitals are equivalent representations, but thinking in terms of bond and antibonding orbitals as representing occupied and empty states of covalent solid is better from the standpoint of making approximations.

→ In the rest of this section, we will first discuss the construction of the sp^3 hybrids and then go on and discuss the construction of bond orbitals.

(a) CONSTRUCTION OF THE sp^3 HYBRIDS

→ A linear combination of two p-orbitals is another p-orbital.

→ A linear combination of a p-orbital and an s-orbital leads to a sp hybrid. This leads to unsymmetric charge distribution; i.e. in the direction of the p-orbital.

The sp^3 hybrids, where 3 indicates that there is three times as much probability of finding an electron in a p-state as of finding it in an s-state, are:

$$|h_1\rangle = \frac{1}{2} [|s\rangle + |p_x\rangle + |p_y\rangle + |p_z\rangle] \quad \rightarrow [111] \text{-orientation}$$

$$|h_2\rangle = \frac{1}{2} [|s\rangle + |p_x\rangle - |p_y\rangle - |p_z\rangle] \quad \rightarrow [1\bar{1}\bar{1}] \text{-orientation}$$

$$|h_3\rangle = \frac{1}{2} [|s\rangle - |p_x\rangle + |p_y\rangle - |p_z\rangle] \quad \rightarrow [\bar{1}1\bar{1}] \text{-orientation}$$

$$|h_4\rangle = \frac{1}{2} [|s\rangle - |p_x\rangle - |p_y\rangle + |p_z\rangle] \quad \rightarrow [\bar{1}\bar{1}1] \text{-orientation}$$

→ We would like to note here that the hybrids are not energy eigenstates, the expectation value of the energy is only an average energy called HYBRID ENERGY, i.e.

$$E_H = \frac{1}{4} (E_s + 3E_p)$$

where we have used the following short-hand notation:

$$E_s = \langle s | H | s \rangle \text{ and } E_p = \langle p_x | H | p_x \rangle = \langle p_y | H | p_y \rangle = \langle p_z | H | p_z \rangle.$$

→ When we deal with polar covalent solids, the sp^3 hybrids can be constructed on each atom type and oriented towards the nearest neighbors. Typically, the hybrid energies will be different and, as before, we can define a polar energy:

$$V_p^h = \frac{1}{2} (E_H^2 - E_H')$$

→ Since the hybrids are not energy eigenstates, the matrix elements between hybrids have nonzero value, and one can show, for example, that:

$$\begin{aligned} \langle h_1 | H | h_2 \rangle &= \frac{1}{4} [\langle s| + \langle p_x| + \langle p_y| + \langle p_z|] H [|s\rangle + |p_x\rangle - |p_y\rangle - |p_z\rangle] \\ &= \frac{1}{4} [E_s + E_p - E_p - E_p] = \frac{1}{4} [E_s - E_p] = -V_1 = -V_H \end{aligned}$$

This matrix element, denoted as $V_1 = V_H$ is called a METALLIC energy.

→ Another very important matrix element is that between hybrids pointed at each other, called HYBRID COVALENT ENERGY,

$$V_2^* = -\langle h^1 | H | h^2 \rangle = (-V_{ss\sigma} + 2\sqrt{3}V_{sp\sigma} + 3V_{pp\sigma})/4 \rightarrow 4.37 \text{ eV/mol}^2$$

(b) CONSTRUCTION OF BOND ORBITALS

→ In here, we switch from consideration of pairs of hybrid orbitals to bonding and antibonding combinations in each bond. This is done in a similar manner as for the case of an H_2 molecule. Therefore, the total wavefunction is written as a linear combination between the two hybrids, i.e.

$$|\Psi\rangle = u_1 |h^1\rangle + u_2 |h^2\rangle$$

→ When constructing the hybrids, it will be assumed that $\langle h^1 | h^2 \rangle = 0$. This can be accomplished via a redefinition of the covalent and polar energies, and in the contribution to the overlap interaction between atoms. Let us now state the final results when performing the previously outlined procedure:

(1) Average hybrid energy: $\bar{E} = \frac{1}{2} (E_{h^1} + E_{h^2})$

(2) Covalent energy: $V_C = \langle h^1 | H | h^2 \rangle$

(3) Bonding and antibonding energy:

$$E_{b,a} = \bar{E} \mp \sqrt{V_C^2 + V_P^2}$$

(4) Bond polarity: $d_p = \frac{V_P}{\sqrt{V_C^2 + V_P^2}}$

(5) Bonding and antibonding wavefunctions:
$$\begin{cases} \psi_1^b = \sqrt{\frac{1+d_p}{2}} |h^1\rangle + \sqrt{\frac{1-d_p}{2}} |h^2\rangle \\ \psi_1^a = \sqrt{\frac{1-d_p}{2}} |h^1\rangle - \sqrt{\frac{1+d_p}{2}} |h^2\rangle \end{cases}$$