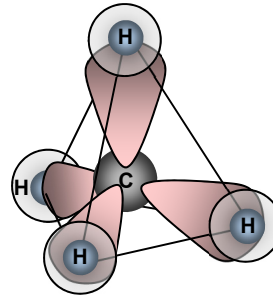


Handout 8

Linear Combination of Atomic Orbitals (LCAO)

In this lecture you will learn:

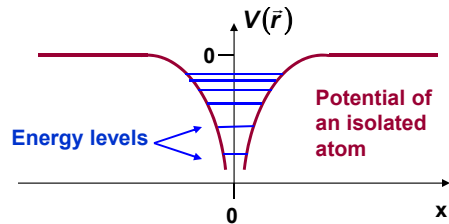
- An approach to energy states in molecules based on the linear combination of atomic orbitals



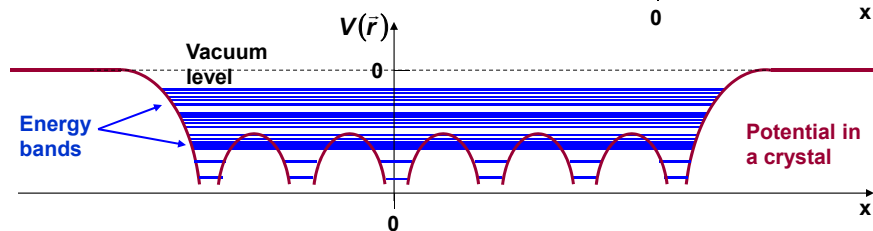
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Energy Bands and Atomic Potentials in Crystals

The potential energy of an electron due to a single isolated atom looks like:



In a crystal, the potential energy due to all the atoms in the lattice looks like:

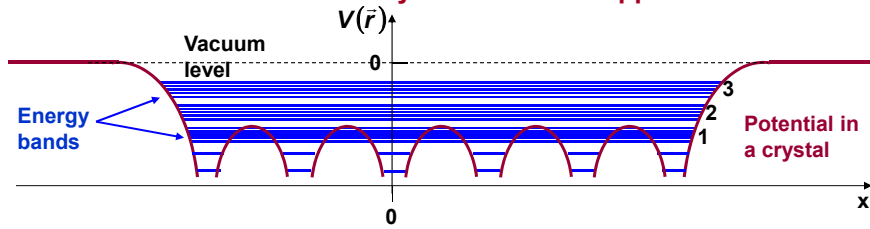


The lowest energy levels and wavefunctions of electrons remain unchanged when going from an isolated atom to a crystal

The higher energy levels (usually corresponding to the outermost atomic shell) get modified, and the corresponding wavefunctions are no longer localized at individual atoms but become spread over the entire crystal

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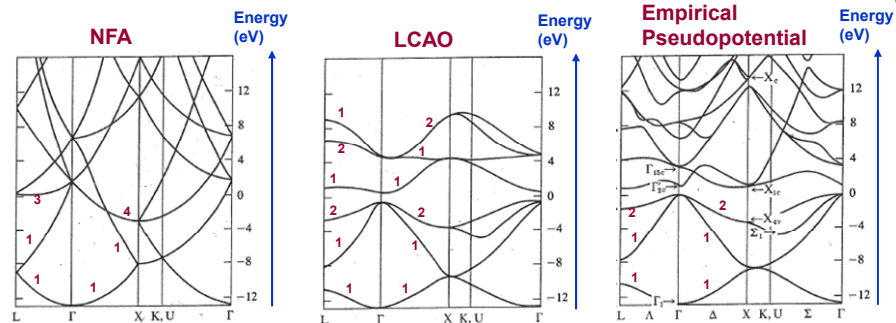
Failure of the Nearly-Free-Electron Approach



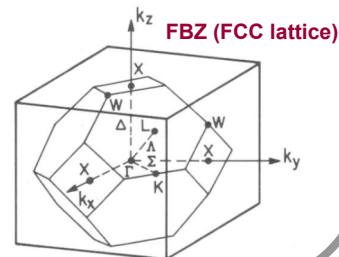
- For energy bands that are higher in energy (e.g. 2 & 3 in the figure above) the periodic potential of the atoms can be taken as a small perturbation
 - ⇒ For higher energy bands, the nearly-free-electron approach works well and gives almost the correct results
- For energy bands that are lower in energy (e.g. 1 in the figure above) the periodic potential of the atoms is a strong perturbation
 - ⇒ For lower energy bands, the nearly-free-electron approach does not usually work very well

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Nearly-Free-Electron Approach Vs LCAO for Germanium



- For most semiconductors, the nearly-free-electron approach does not work very well
- LCAO (or tight binding) works much better and provides additional insights



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LCAO: From Hydrogen Atom to Hydrogen Molecule

Consider a Hydrogen atom with one electron in the 1s orbital:

One can solve the Schrodinger equation:

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(\vec{r}) + V(\vec{r})\psi(\vec{r}) = E \psi(\vec{r})$$

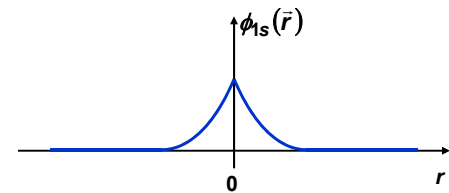
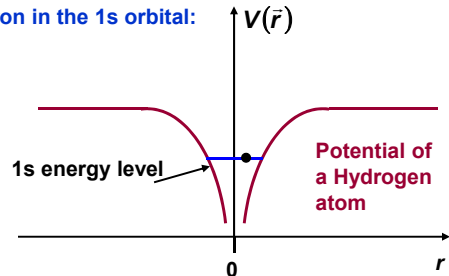
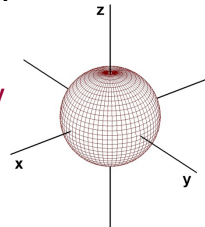
and find the energy of the 1s orbital and its wavefunction

$$\hat{H}_0 |\phi_{1s}(\vec{r})\rangle = E_{1s} |\phi_{1s}(\vec{r})\rangle$$

where:

$$\hat{H}_0 = -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r})$$

Angular probability distribution for the 1s orbital



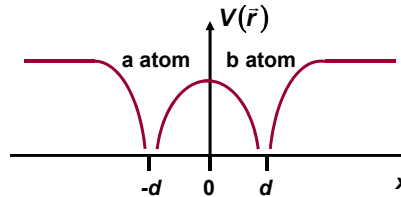
$$\phi_{1s}(\vec{r}) = \frac{1}{\sqrt{\pi} a_0^3} e^{-r/a_0}$$

Radial amplitude for the 1s orbital

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Linear Combination of Atomic Orbitals (LCAO)

Now consider a Hydrogen molecule made up of two covalently bonded Hydrogen atoms sitting at a distance of $2d$ from each other, as shown:



Hamiltonian for an electron is:

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r} - d\hat{x}) + V(\vec{r} + d\hat{x})$$

The basic idea behind LCAO approach is to construct a trial variational solution in which the wavefunction is made up of a linear combination (or superposition) of orbitals of isolated atoms:

$$|\psi(\vec{r})\rangle = c_a |\phi_{1s}(\vec{r} - d\hat{x})\rangle + c_b |\phi_{1s}(\vec{r} + d\hat{x})\rangle$$

And then plugging the trial solution into the Schrodinger equation to find the coefficients c_a and c_b and the new eigenenergies:

$$\hat{H} |\psi(\vec{r})\rangle = E |\psi(\vec{r})\rangle$$

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LCAO: From Hydrogen Atom to Hydrogen Molecule

Plug the LCAO solution: $|\psi(\vec{r})\rangle = c_a |\phi_{1s}(\vec{r} - d\hat{x})\rangle + c_b |\phi_{1s}(\vec{r} + d\hat{x})\rangle$

into: $\hat{H}|\psi(\vec{r})\rangle = E|\psi(\vec{r})\rangle$ $\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r} - d\hat{x}) + V(\vec{r} + d\hat{x})$

STEP 1: take the bra of the equation first with $\langle \phi_{1s}(\vec{r} - d\hat{x}) |$ to get:

$$\begin{aligned} \langle \phi_{1s}(\vec{r} - d\hat{x}) | \hat{H} [c_a |\phi_{1s}(\vec{r} - d\hat{x})\rangle + c_b |\phi_{1s}(\vec{r} + d\hat{x})\rangle] \\ = E \langle \phi_{1s}(\vec{r} - d\hat{x}) | [c_a |\phi_{1s}(\vec{r} - d\hat{x})\rangle + c_b |\phi_{1s}(\vec{r} + d\hat{x})\rangle] \end{aligned}$$

Note that:

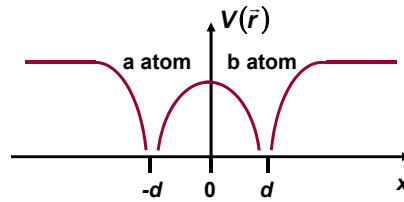
$$\langle \phi_{1s}(\vec{r} - d\hat{x}) | \hat{H} | \phi_{1s}(\vec{r} - d\hat{x}) \rangle \approx E_{1s}$$

Let:

$$\langle \phi_{1s}(\vec{r} - d\hat{x}) | \hat{H} | \phi_{1s}(\vec{r} + d\hat{x}) \rangle \approx -V_{ss\sigma}$$

$$\langle \phi_{1s}(\vec{r} - d\hat{x}) | \phi_{1s}(\vec{r} + d\hat{x}) \rangle \approx 0$$

↳ Not exactly zero – but we will assume so for simplicity



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LCAO: From Hydrogen Atom to Hydrogen Molecule

So we get finally:

$$E_{1s} c_a - V_{ss\sigma} c_b = E c_a$$

STEP 2: take the bra of the equation now with $\langle \phi_{1s}(\vec{r} + d\hat{x}) |$ to get:

$$E_{1s} c_b - V_{ss\sigma} c_a = E c_b$$

Write the two equations obtained in matrix form:

$$\begin{bmatrix} E_{1s} & -V_{ss\sigma} \\ -V_{ss\sigma} & E_{1s} \end{bmatrix} \begin{bmatrix} c_a \\ c_b \end{bmatrix} = E \begin{bmatrix} c_a \\ c_b \end{bmatrix}$$

This is now an eigenvalue equation and the two solutions are:

$$E = E_{1s} \pm V_{ss\sigma}$$

$$\begin{bmatrix} c_a \\ c_b \end{bmatrix}_+ = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ 1 \end{bmatrix} \quad \begin{bmatrix} c_a \\ c_b \end{bmatrix}_- = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ -1 \end{bmatrix}$$

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Bonding and Anti-Bonding Orbitals

For the lower energy solution we have:

$$E_B = E_{1s} - V_{ss\sigma}$$

$$|\psi_B(\vec{r})\rangle = \frac{1}{\sqrt{2}} [|\phi_{1s}(\vec{r} - d\hat{x})\rangle + |\phi_{1s}(\vec{r} + d\hat{x})\rangle]$$

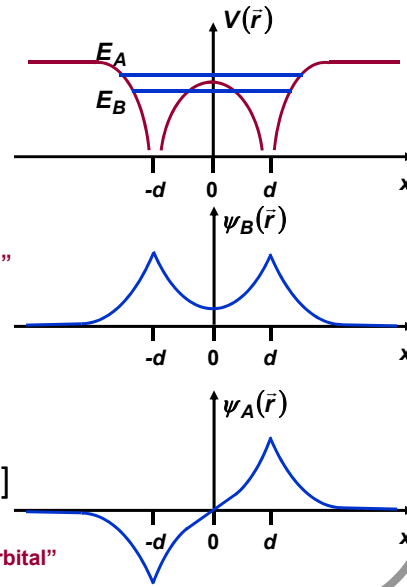
This is called the "Bonding molecular orbital"

For the higher energy solution we have:

$$E_A = E_{1s} + V_{ss\sigma}$$

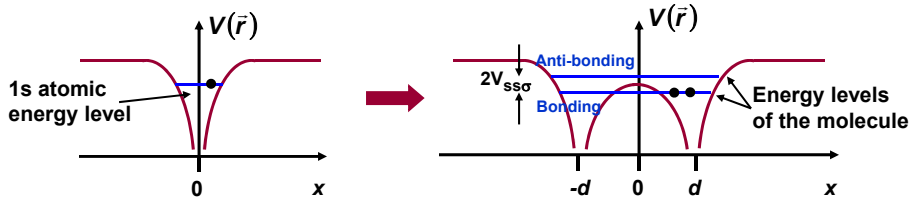
$$|\psi_A(\vec{r})\rangle = \frac{1}{\sqrt{2}} [|\phi_{1s}(\vec{r} - d\hat{x})\rangle - |\phi_{1s}(\vec{r} + d\hat{x})\rangle]$$

This is called the "Anti-bonding molecular orbital"

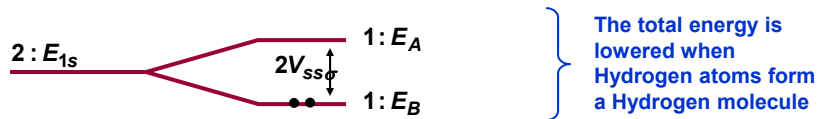


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LCAO: Energy Level Splitting and the Energy Matrix Element



Energy level diagram going from two isolated atoms to the molecule:



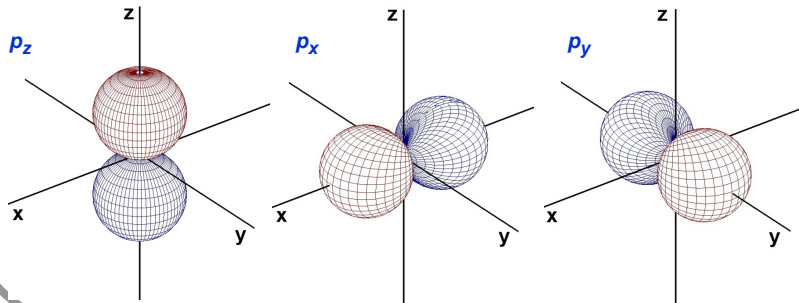
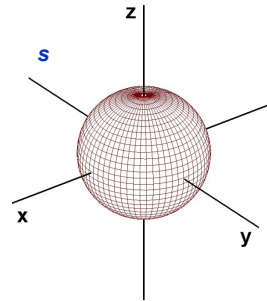
The two 1s orbitals on each Hydrogen atom combine to generate two molecular orbitals – the bonding orbital and the anti-bonding orbital – with energy splitting related to the energy matrix element:

$$\langle \phi_{1s}(\vec{r} - d\hat{x}) | \hat{H} | \phi_{1s}(\vec{r} + d\hat{x}) \rangle \approx -V_{ss\sigma}$$

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Atomic Orbitals

- Wavefunction amplitudes of the atomic s and p orbitals in the angular directions are plotted
- The s-orbital is spherically symmetric
- The p-orbitals have +ve and -ve lobes and are oriented along x-axis, y-axis, and z-axis

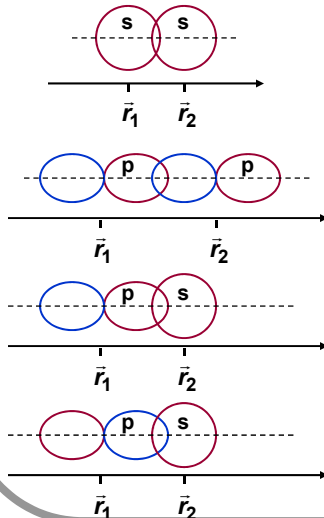


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Orbitals and Bonding

There are two main types of co-valent bonds: sigma bonds (or σ -bonds) and pi-bonds (or π -bonds)

(1) Sigma bonds (or σ -bonds):



s-s σ -bond

(Example: Hydrogen molecule, semiconductors)

$$\langle \phi_s(\vec{r} - \vec{r}_1) | \hat{H} | \phi_s(\vec{r} - \vec{r}_2) \rangle \approx -V_{ss\sigma}$$

p-p σ -bond

(Example: Semiconductors)

$$\langle \phi_p(\vec{r} - \vec{r}_1) | \hat{H} | \phi_p(\vec{r} - \vec{r}_2) \rangle \approx V_{pp\sigma}$$

s-p σ -bond

(Example: Semiconductors)

$$\langle \phi_p(\vec{r} - \vec{r}_1) | \hat{H} | \phi_s(\vec{r} - \vec{r}_2) \rangle \approx -V_{sp\sigma}$$

s-p σ -bond

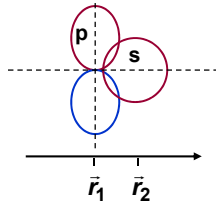
(Example: Semiconductors)

$$\langle \phi_p(\vec{r} - \vec{r}_1) | \hat{H} | \phi_s(\vec{r} - \vec{r}_2) \rangle \approx V_{sp\sigma}$$

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Orbitals and Bonding

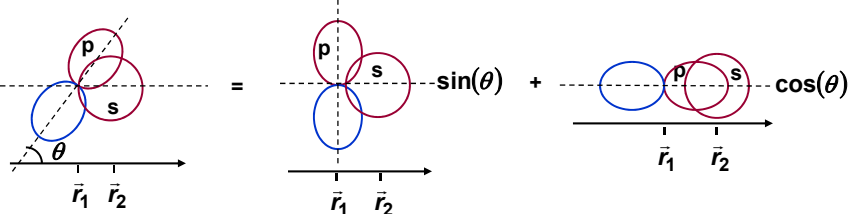
What about this situation?



$$\langle \phi_p(\vec{r} - \vec{r}_1) | \hat{H} | \phi_s(\vec{r} - \vec{r}_2) \rangle \approx 0$$

The Hamiltonian is up-down symmetric
 The s-orbital is up-down symmetric
 The p-orbital is up-down anti-symmetric
 \Rightarrow The matrix element is zero! No bonding possible

What about this situation? What should be the matrix element?

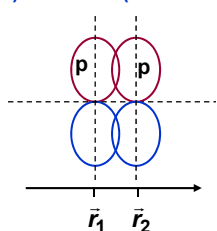


$$\begin{aligned} \langle \phi_p(\vec{r} - \vec{r}_1) | \hat{H} | \phi_s(\vec{r} - \vec{r}_2) \rangle &\approx 0 \cdot \sin(\theta) + (-V_{sp\sigma}) \cdot \cos(\theta) \\ &= -V_{sp\sigma} \cos(\theta) \end{aligned}$$

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Orbitals and Bonding

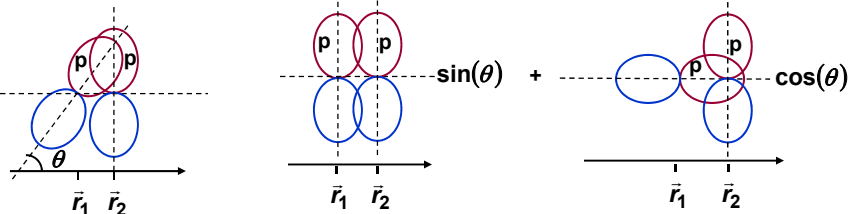
(2) Pi bonds (or π -bonds):



p-p π -bond
 (Example: graphene, carbon nanotubes, conjugated conducting molecules)

$$\langle \phi_p(\vec{r} - \vec{r}_1) | \hat{H} | \phi_p(\vec{r} - \vec{r}_2) \rangle \approx -V_{pp\pi}$$

What about this situation? What should be the matrix element?



$$\begin{aligned} \langle \phi_p(\vec{r} - \vec{r}_1) | \hat{H} | \phi_p(\vec{r} - \vec{r}_2) \rangle &\approx (-V_{pp\pi}) \cdot \sin(\theta) + 0 \cdot \cos(\theta) \\ &= -V_{pp\pi} \sin(\theta) \end{aligned}$$

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LCAO: Methane Molecule

A methane molecule consists of one carbon atom covalently bonded to 4 hydrogen atoms in a tetrahedral configuration:

Carbon:

Atomic number: 6

Electron Configuration: $1s^2 2s^2 2p^2$

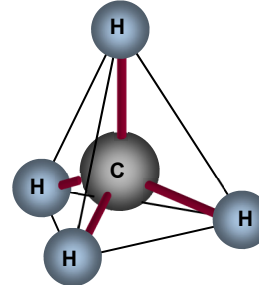
Number of electrons in the outermost shell: 4

Hydrogen:

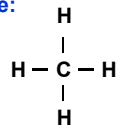
Atomic number: 1

Electron Configuration: $1s^1$

Number of electrons in the outermost shell: 1



Methane:



The four electrons from the outermost shell of the carbon atom and the four electrons from the four hydrogen atoms take part in covalent bonding

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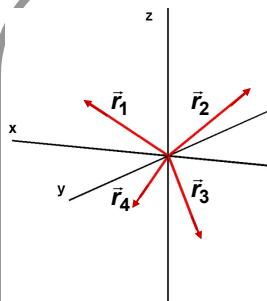
LCAO: Methane Molecule

- The carbon atom is sitting at the origin

- The position vectors of the four hydrogen atoms are:

$$\vec{r}_1 = \frac{d}{\sqrt{3}}(1,1,1) \quad \vec{r}_2 = \frac{d}{\sqrt{3}}(-1,-1,1) \quad \vec{r}_3 = \frac{d}{\sqrt{3}}(-1,1,-1)$$

$$\vec{r}_4 = \frac{d}{\sqrt{3}}(1,-1,-1) \quad \longrightarrow \text{Tetrahedral configuration}$$



- The carbon atom has one 2s orbital and three 2p orbitals
- Each hydrogen atom has one 1s orbital
- One can write the solution for the methane molecule as a linear combination of all available orbitals

$$|\psi(\vec{r})\rangle = \sum_{j=1}^4 c_j |\phi_{1s}(\vec{r} - \vec{r}_j)\rangle + c_5 |\phi_{2s}(\vec{r})\rangle + c_6 |\phi_{2px}(\vec{r})\rangle + c_7 |\phi_{2py}(\vec{r})\rangle + c_8 |\phi_{2pz}(\vec{r})\rangle$$

But we will pursue a different, and simpler, approach

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LCAO: Methane Molecule – sp_3 Hybridization

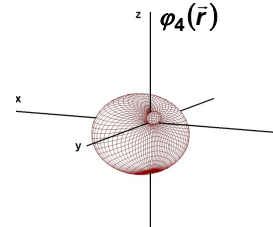
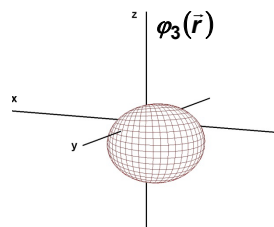
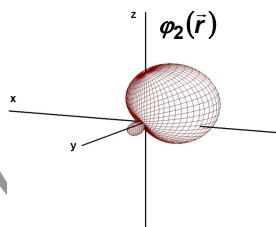
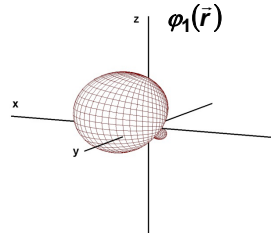
For the carbon atom, do a change of basis and define 4 new sp_3 atomic orbitals from the 4 existing (one 2s and three 2p) atomic orbitals

$$|\varphi_1(\vec{r})\rangle = \frac{1}{2} [|\phi_{2s}(\vec{r})\rangle + |\phi_{2p_x}(\vec{r})\rangle + |\phi_{2p_y}(\vec{r})\rangle + |\phi_{2p_z}(\vec{r})\rangle]$$

$$|\varphi_2(\vec{r})\rangle = \frac{1}{2} [|\phi_{2s}(\vec{r})\rangle - |\phi_{2p_x}(\vec{r})\rangle - |\phi_{2p_y}(\vec{r})\rangle + |\phi_{2p_z}(\vec{r})\rangle]$$

$$|\varphi_3(\vec{r})\rangle = \frac{1}{2} [|\phi_{2s}(\vec{r})\rangle - |\phi_{2p_x}(\vec{r})\rangle + |\phi_{2p_y}(\vec{r})\rangle - |\phi_{2p_z}(\vec{r})\rangle]$$

$$|\varphi_4(\vec{r})\rangle = \frac{1}{2} [|\phi_{2s}(\vec{r})\rangle + |\phi_{2p_x}(\vec{r})\rangle - |\phi_{2p_y}(\vec{r})\rangle - |\phi_{2p_z}(\vec{r})\rangle]$$



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LCAO: Methane Molecule – sp_3 Hybridization

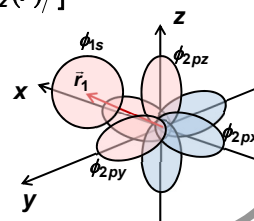
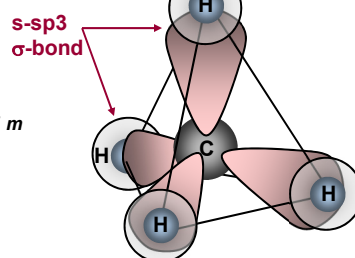
• Each carbon sp_3 orbital forms a s- sp_3 σ -bond with the 1s orbital of the hydrogen atoms towards which it is pointing:

Average energy of the sp_3 orbital:

$$\Rightarrow \langle \varphi_j(\vec{r}) | \hat{H} | \varphi_m(\vec{r}) \rangle = E_{sp_3} \delta_{j m} = \frac{E_{2s} + 3E_{2p}}{4} \delta_{j m}$$

Important matrix element for the s- sp_3 bond:

$$\begin{aligned} & \langle \phi_{1s}(\vec{r} - \vec{r}_1) | \hat{H} | \varphi_1(\vec{r}) \rangle \\ &= \langle \phi_{1s}(\vec{r} - \vec{r}_1) | \hat{H} \frac{1}{2} [|\phi_{2s}(\vec{r})\rangle + |\phi_{2p_x}(\vec{r})\rangle + |\phi_{2p_y}(\vec{r})\rangle + |\phi_{2p_z}(\vec{r})\rangle] \\ &= -\frac{1}{2} V_{ss\sigma} - \frac{1}{2} \frac{V_{sp\sigma}}{\sqrt{3}} - \frac{1}{2} \frac{V_{sp\sigma}}{\sqrt{3}} - \frac{1}{2} \frac{V_{sp\sigma}}{\sqrt{3}} \\ &= -\left(\frac{V_{ss\sigma} + \sqrt{3}V_{sp\sigma}}{2} \right) = -\eta \end{aligned}$$



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LCAO: Methane Molecule – sp_3 Hybridization

- Matrix elements for all s-sp3 σ -bonds are the same

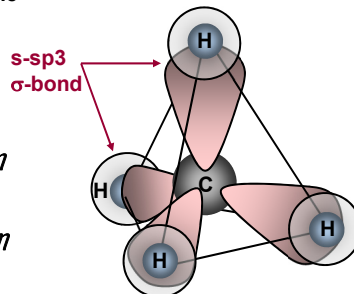
Important matrix elements:

$$\langle \phi_{1s}(\vec{r} - \vec{r}_1) | \hat{H} | \phi_1(\vec{r}) \rangle = -\left(\frac{V_{ss\sigma} + \sqrt{3}V_{sp\sigma}}{2} \right) = -\eta$$

$$\langle \phi_{1s}(\vec{r} - \vec{r}_2) | \hat{H} | \phi_2(\vec{r}) \rangle = -\left(\frac{V_{ss\sigma} + \sqrt{3}V_{sp\sigma}}{2} \right) = -\eta$$

$$\langle \phi_{1s}(\vec{r} - \vec{r}_3) | \hat{H} | \phi_3(\vec{r}) \rangle = -\left(\frac{V_{ss\sigma} + \sqrt{3}V_{sp\sigma}}{2} \right) = -\eta$$

$$\langle \phi_{1s}(\vec{r} - \vec{r}_4) | \hat{H} | \phi_4(\vec{r}) \rangle = -\left(\frac{V_{ss\sigma} + \sqrt{3}V_{sp\sigma}}{2} \right) = -\eta$$



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LCAO: Methane Molecule – sp_3 Hybridization

Write the solution for the methane molecule using the sp_3 orbitals of the carbon atom:

$$|\psi(\vec{r})\rangle = \sum_{j=1}^4 c_j |\phi_{1s}(\vec{r} - \vec{r}_j)\rangle + c_5 |\phi_1(\vec{r})\rangle + c_6 |\phi_2(\vec{r})\rangle + c_7 |\phi_3(\vec{r})\rangle + c_8 |\phi_4(\vec{r})\rangle$$

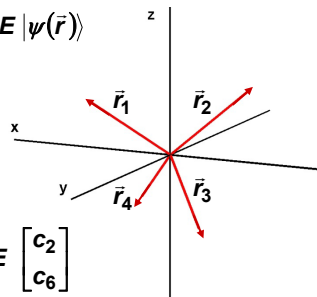
And plug it into the Schrodinger equation: $\hat{H}|\psi(\vec{r})\rangle = E|\psi(\vec{r})\rangle$

To a first approximation, $1s$ orbital on each Hydrogen atom has a large matrix element only with the sp_3 orbital pointing towards it, so instead of one giant 8×8 matrix equation one gets a set of four 2×2 matrix equations:

$$\begin{bmatrix} E_{1s} & -\eta \\ -\eta & E_{sp3} \end{bmatrix} \begin{bmatrix} c_1 \\ c_5 \end{bmatrix} = E \begin{bmatrix} c_1 \\ c_5 \end{bmatrix} \quad \begin{bmatrix} E_{1s} & -\eta \\ -\eta & E_{sp3} \end{bmatrix} \begin{bmatrix} c_2 \\ c_6 \end{bmatrix} = E \begin{bmatrix} c_2 \\ c_6 \end{bmatrix}$$

$$\begin{bmatrix} E_{1s} & -\eta \\ -\eta & E_{sp3} \end{bmatrix} \begin{bmatrix} c_3 \\ c_7 \end{bmatrix} = E \begin{bmatrix} c_3 \\ c_7 \end{bmatrix} \quad \begin{bmatrix} E_{1s} & -\eta \\ -\eta & E_{sp3} \end{bmatrix} \begin{bmatrix} c_4 \\ c_8 \end{bmatrix} = E \begin{bmatrix} c_4 \\ c_8 \end{bmatrix}$$

$$\text{Where: } \eta = \left(\frac{V_{ss\sigma} + \sqrt{3}V_{sp\sigma}}{2} \right) = -\langle \phi_{1s}(\vec{r} - \vec{r}_1) | \hat{H} | \phi_1(\vec{r}) \rangle$$



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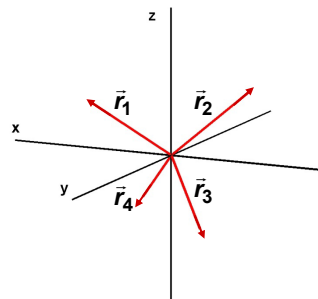
LCAO: Methane Molecule – sp_3 Hybridization

$$\begin{bmatrix} E_{1s} & -\eta \\ -\eta & E_{sp3} \end{bmatrix} \begin{bmatrix} c_1 \\ c_5 \end{bmatrix} = E \begin{bmatrix} c_1 \\ c_5 \end{bmatrix}$$

The energy eigenvalues of any one of these four 2x2 equations are:

$$E_A = \left(\frac{E_{1s} + E_{sp3}}{2} \right) + \sqrt{\left(\frac{E_{1s} - E_{sp3}}{2} \right)^2 + \eta^2}$$

$$E_B = \left(\frac{E_{1s} + E_{sp3}}{2} \right) - \sqrt{\left(\frac{E_{1s} - E_{sp3}}{2} \right)^2 + \eta^2}$$



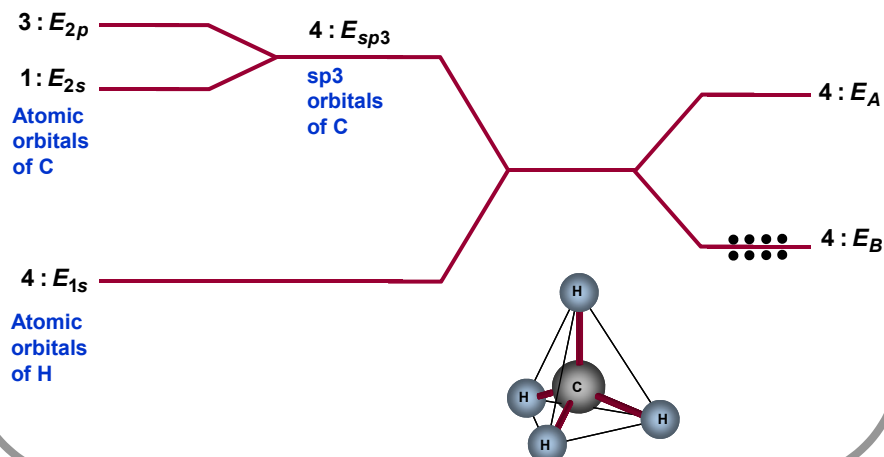
- The higher energy corresponds to the **anti-bonding state** and the lower energy corresponds to the **bonding state**.

- In this case, the bonding and anti-bonding states are made up of a linear combination of the hydrogen 1s state and one of the carbon sp_3 state.

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LCAO: Methane Molecule – sp_3 Hybridization

Energy level diagram going from isolated hydrogen and carbon atoms to the orbitals of the methane molecule is:



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LCAO: Boron Trifluoride Molecule

A BF_3 molecule consists of one boron atom covalently bonded to 3 fluorine atoms and all atoms lie in the same plane

Boron:

Atomic number: 5

Electron Configuration: $1s^2 2s^2 2p^1$

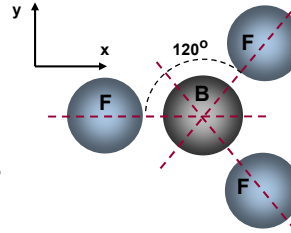
Number of electrons in the outermost shell: 3

Fluorine:

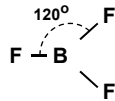
Atomic number: 9

Electron Configuration: $1s^2 2s^2 2p^5$

Number of electrons in the outermost shell: 7



BF_3 :



All three electrons from the outermost shell of the boron atom and only one of the 7 electrons from each fluorine atom take part in covalent bonding

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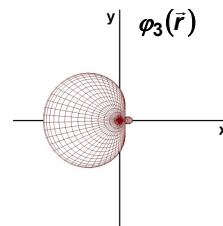
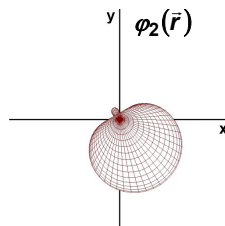
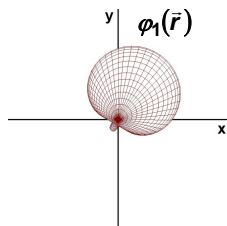
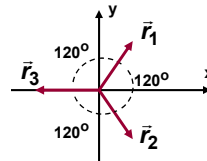
LCAO: BF_3 Molecule – sp_2 Hybridization

For the boron atom, do a change of basis and define 3 new sp_2 atomic orbitals from the 3 existing (one $2s$ and two $2p$) atomic orbitals

$$|\varphi_1(\vec{r})\rangle = \frac{1}{\sqrt{3}} |\phi_{2s}(\vec{r})\rangle + \frac{1}{\sqrt{6}} |\phi_{2px}(\vec{r})\rangle + \frac{1}{\sqrt{2}} |\phi_{2py}(\vec{r})\rangle$$

$$|\varphi_2(\vec{r})\rangle = \frac{1}{\sqrt{3}} |\phi_{2s}(\vec{r})\rangle + \frac{1}{\sqrt{6}} |\phi_{2px}(\vec{r})\rangle - \frac{1}{\sqrt{2}} |\phi_{2py}(\vec{r})\rangle$$

$$|\varphi_3(\vec{r})\rangle = \frac{1}{\sqrt{3}} |\phi_{2s}(\vec{r})\rangle - \sqrt{\frac{2}{3}} |\phi_{2px}(\vec{r})\rangle$$



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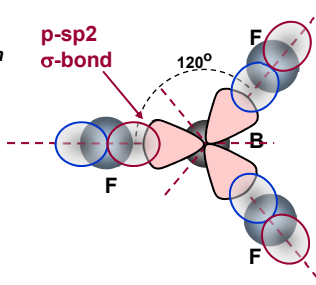
LCAO: BF₃ Molecule – sp₂ Hybridization

• In the fluorine atom, the 2s orbital and the two 2p orbitals that are perpendicular to the line joining the fluorine atom to the boron atom are all filled with 2 electrons each and do not participate in bonding

• The remaining p-orbital in fluorine that is pointing towards the boron atom, and contains one electron, forms a σ-bond with the sp₂ orbital pointing towards it

Average energy of the sp₂ orbital:

$$\Rightarrow \langle \phi_j(\vec{r}) | \hat{H} | \phi_m(\vec{r}) \rangle = E_{sp2} \delta_{j m} = \frac{E_{2s} + 2E_{2p}}{3} \delta_{j m}$$



Important matrix elements:

$$\begin{aligned} \langle \phi_{2p}(\vec{r} - \vec{r}_1) | \hat{H} | \phi_1(\vec{r}) \rangle &= \left(\frac{V_{sp\sigma} + \sqrt{2}V_{pp\sigma}}{\sqrt{3}} \right) = \eta \\ \langle \phi_{2p}(\vec{r} - \vec{r}_2) | \hat{H} | \phi_2(\vec{r}) \rangle &= \left(\frac{V_{sp\sigma} + \sqrt{2}V_{pp\sigma}}{\sqrt{3}} \right) = \eta \\ \langle \phi_{2p}(\vec{r} - \vec{r}_3) | \hat{H} | \phi_3(\vec{r}) \rangle &= - \left(\frac{V_{sp\sigma} + \sqrt{2}V_{pp\sigma}}{\sqrt{3}} \right) = -\eta \end{aligned}$$

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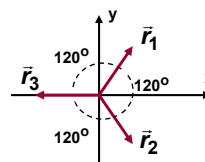
LCAO: BF₃ Molecule – sp₂ Hybridization

Write the solution for the BF₃ molecule using the sp₂ orbitals of the boron atom:

$$|\psi(\vec{r})\rangle = \sum_{j=1}^3 c_j |\phi_{2p}(\vec{r} - \vec{r}_j)\rangle + c_4 |\phi_1(\vec{r})\rangle + c_5 |\phi_2(\vec{r})\rangle + c_6 |\phi_3(\vec{r})\rangle$$

And plug it into the Schrodinger equation: $\hat{H}|\psi(\vec{r})\rangle = E|\psi(\vec{r})\rangle$

To a first approximation, the 2p orbital on each fluorine atom has a large matrix element only with the sp₂ orbital pointing towards it, so instead of one giant 6x6 matrix equation one gets a set of three 2x2 matrix equations:



$$\begin{bmatrix} E_{2p} & \eta \\ \eta & E_{sp2} \end{bmatrix} \begin{bmatrix} c_1 \\ c_4 \end{bmatrix} = E \begin{bmatrix} c_1 \\ c_4 \end{bmatrix} \quad \begin{bmatrix} E_{2p} & \eta \\ \eta & E_{sp2} \end{bmatrix} \begin{bmatrix} c_2 \\ c_5 \end{bmatrix} = E \begin{bmatrix} c_2 \\ c_5 \end{bmatrix}$$

$$\begin{bmatrix} E_{2p} & -\eta \\ -\eta & E_{sp2} \end{bmatrix} \begin{bmatrix} c_3 \\ c_6 \end{bmatrix} = E \begin{bmatrix} c_3 \\ c_6 \end{bmatrix}$$

Where:

$$\eta = \left(\frac{V_{sp\sigma} + \sqrt{2}V_{pp\sigma}}{\sqrt{3}} \right) = \langle \phi_{2p}(\vec{r} - \vec{r}_1) | \hat{H} | \phi_1(\vec{r}) \rangle$$

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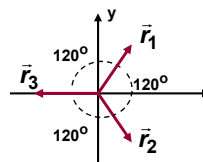
LCAO: BF₃ Molecule – sp₂ Hybridization

$$\begin{bmatrix} E_{2p} & \eta \\ \eta & E_{sp2} \end{bmatrix} \begin{bmatrix} c_1 \\ c_4 \end{bmatrix} = E \begin{bmatrix} c_1 \\ c_4 \end{bmatrix}$$

The energy eigenvalues of any one of these three 2x2 equations are:

$$E_A = \left(\frac{E_{2p} + E_{sp2}}{2} \right) + \sqrt{\left(\frac{E_{2p} - E_{sp2}}{2} \right)^2 + \eta^2}$$

$$E_B = \left(\frac{E_{2p} + E_{sp2}}{2} \right) - \sqrt{\left(\frac{E_{2p} - E_{sp2}}{2} \right)^2 + \eta^2}$$



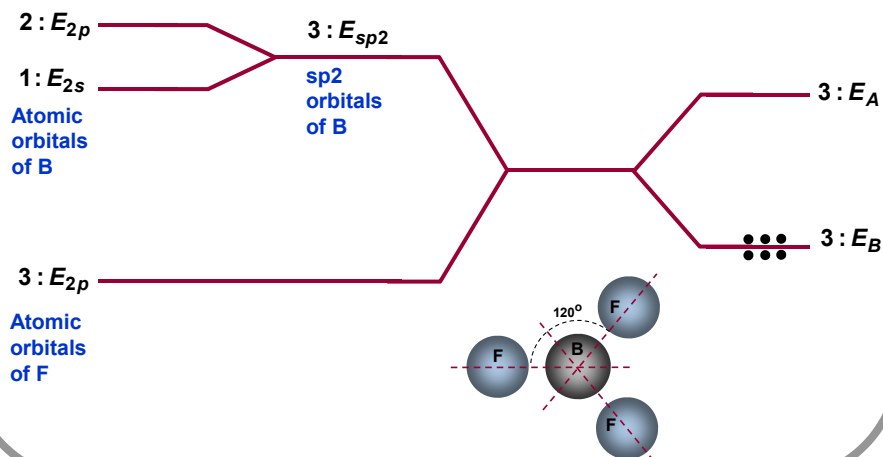
- The higher energy corresponds to the **anti-bonding state** and the lower energy corresponds to the **bonding state**.

- In this case, the bonding and anti-bonding states are made up of a linear combination of the fluorine 2p state and one of the carbon sp₂ state.

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LCAO: BF₃ Molecule – sp₂ Hybridization

Energy level diagram going from isolated fluorine and carbon atoms to the orbitals of the BF₃ molecule is:



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