

Time-Independent Perturbation Theory

$$\text{Hamiltonian: } \mathbf{H} = \mathbf{H}_0 + \mathbf{V}$$

The known exact solution of the equation

$$\mathbf{H}_0 \Psi_m^{(0)}(\mathbf{q}) = \mathbf{E}_m^{(0)} \Psi_m^{(0)}(\mathbf{q})$$

We seek for an approximate solution for

$$(\mathbf{H}_0 + \mathbf{V}) \Psi(\mathbf{q}) = \mathbf{E} \Psi(\mathbf{q})$$

Nondegenerate case: $\mathbf{E}_m^{(0)} \neq \mathbf{E}_{m'}^{(0)}$

1. The unknown wavefunction $\Psi(\mathbf{q})$ can be expanded over the orthogonal set $\Psi_m^{(0)}(\mathbf{q})$
2. This expansion is substituted to the full-Hamiltonian Schrödinger equation
3. The obtained expression is multiplied by $\Psi_n^{(0)}(\mathbf{q})$ and then integrated over all \mathbf{q} .
4. The obtained expression is solved giving an approximate values of the energy \mathbf{E} and the coefficients c_m .

$$\Psi(\mathbf{q}) = \sum_m c_m \Psi_m^{(0)}(\mathbf{q})$$

Non-Degenerate Case: Solution

First correction to the energy level n

$$E_n \approx E_n^{(0)} + \int \Psi_n^{(0)*}(q) V \Psi_n^{(0)}(q) dq = \langle n | V | n \rangle$$

First correction to the wavefunction Ψ_n

$$\Psi_n(q) \approx \Psi_n^{(0)}(q) + \sum_k' \frac{\langle k | V | n \rangle}{E_n^{(0)} - E_k^{(0)}} \Psi_k^{(0)}(q)$$

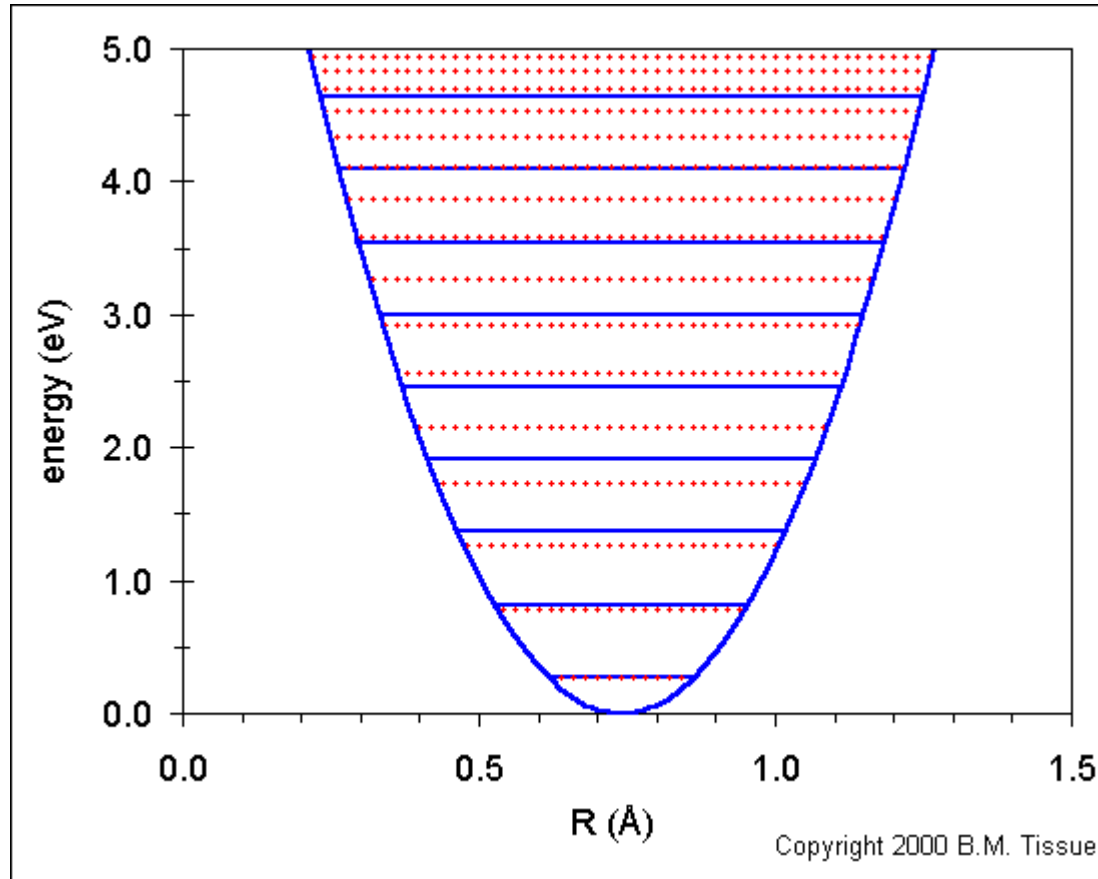
Second correction to the energy level n

$$E_n \approx E_n^{(0)} + E_n^{(1)} + \sum_k' \frac{|\langle k | V | n \rangle|^2}{E_n^{(0)} - E_k^{(0)}}$$

Example: Harmonic Oscillator

$$H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{kx^2}{2}$$

$$E_v = (v + \frac{1}{2}) \nu_e$$



$$H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{kx^2}{2} + \alpha x^3 + \beta x^4 \quad E_v = (v + \frac{1}{2})\nu_e - (v + \frac{1}{2})^2 \nu_e x_e + (v + \frac{1}{2})^3 \nu_e y_e$$

Chemical Bonds

Time-Independent Perturbation Theory

$$\text{Hamiltonian: } \mathbf{H} = \mathbf{H}_0 + \mathbf{V}$$

The known exact solution of the equation

$$\mathbf{H}_0 \psi_n^{(0)} = \mathbf{E}^{(0)} \psi_n^{(0)}$$

We seek for an approximate solution for

$$(\mathbf{H}_0 + \mathbf{V}) \psi = \mathbf{E} \psi$$

Degenerate case: $E_n^{(0)} = E_{n'}^{(0)}$

1. The zero-approximation wavefunction $\Psi^{(0)}(q)$ can be written as superposition of the set $\Psi_n^{(0)}(q)$
2. This expansion is substituted to the full-Hamiltonian Schrödinger equation
3. The obtained expression is multiplied by $\Psi_{n'}^{(0)}(q)$ and then integrated over all q .
4. The obtained set of algebraic equations is solved giving values of the energies E_n and the coefficients $c_n^{(0)}$.

$$\Psi^{(0)}(q) = \sum_n c_n^{(0)} \Psi_n^{(0)}(q)$$

Degenerate Case: Solution

A set of N linear homogeneous equations over the coefficients $c_n^{(0)}$ and energies E_n

$$\sum_{n'} \left(\langle n | V | n' \rangle - \delta_{n,n'} E_n \right) c_{n'}^{(0)} = 0$$

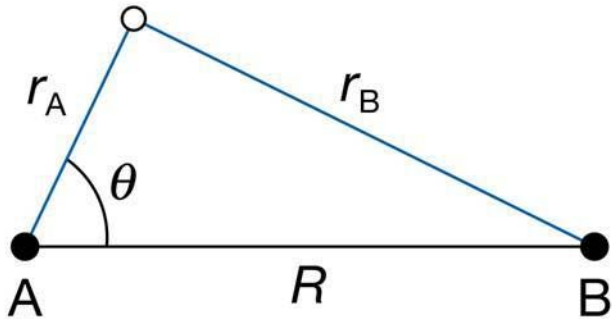
The determinant must be equal to zero. It is equivalent to the linear algebraic equation of the N -th order, which is known as the **Secular Equation**

$$\begin{vmatrix} V_{11} - E & V_{12} & \cdots & V_{1N} \\ V_{21} & V_{22} - E & \cdots & V_{2N} \\ \cdots & \cdots & \cdots & \cdots \\ V_{N1} & V_{N2} & \cdots & V_{NN} - E \end{vmatrix} = 0$$

Time-Independent Perturbation Theory

Degenerate Case: H_2^+ ion

Coordinate system



Schrödinger equation: $H\Psi = E\Psi$

Hamiltonian: $\hat{H} = \hat{H}_0 + \hat{V}$

$$\hat{H}_0 = -\frac{\hbar^2}{2m_e} \Delta \quad \hat{V} = -\frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_A} + \frac{1}{r_B} - \frac{1}{R} \right)$$

Secular equation:

$$\begin{vmatrix} \alpha - E & \beta - ES \\ \beta - ES & \alpha - E \end{vmatrix} = 0$$

$$\alpha = \langle \Psi_A | H | \Psi_A \rangle = \langle \Psi_B | H | \Psi_B \rangle \quad \text{Coulomb Integral}$$

$$\beta = \langle \Psi_A | H | \Psi_B \rangle = \langle \Psi_B | H | \Psi_A \rangle \quad \text{Resonance Integral}$$

$$S = \langle \Psi_A | \Psi_B \rangle \quad \text{Exchange Integral} \quad \text{Chemical Bonds}$$

Zero-order wavefunctions

$$\Psi_A = \frac{e^{-r_A/a_0}}{(\pi a_0^3)^{1/2}} \quad \Psi_B = \frac{e^{-r_B/a_0}}{(\pi a_0^3)^{1/2}}$$

Molecular wavefunction

$$\Psi = c_A \Psi_A + c_B \Psi_B$$

H₂⁺ ion: Solutions

Energies

$$\alpha < 0$$

$$\beta \leq 0$$

$$E_1 = \frac{\alpha + \beta}{1 + S}$$

$$E_2 = \frac{\alpha - \beta}{1 - S}$$

Wavefunctions: σ molecular orbitals

$$\Psi_+ = N [\Psi_A(r_A) + \Psi_B(r_B)]$$

$$\Psi_- = N [\Psi_A(r_A) - \Psi_B(r_B)]$$

Bonding Molecular Orbital

Antibonding Molecular Orbital

$$\Psi_A = \frac{e^{-r_A/a_0}}{(\pi a_0^3)^{1/2}}$$

$$\Psi_B = \frac{e^{-r_B/a_0}}{(\pi a_0^3)^{1/2}}$$

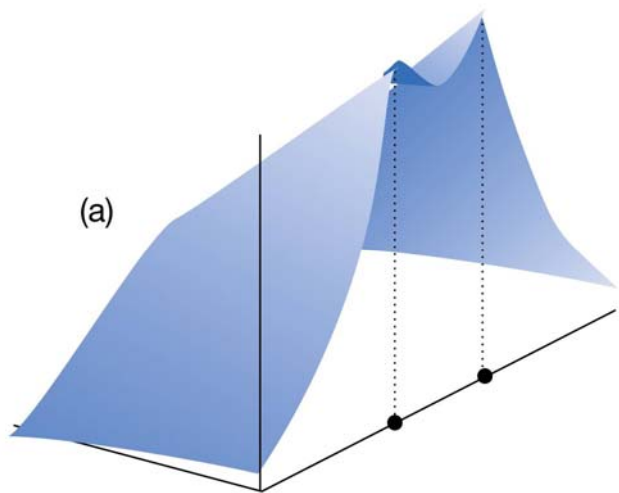
$$N = \frac{1}{[2(1 + S)]^{1/2}}$$

Normalization Factor

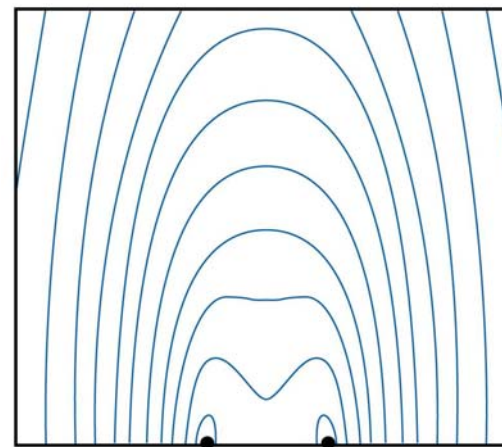
H₂⁺ ion

Bonding σ orbital:

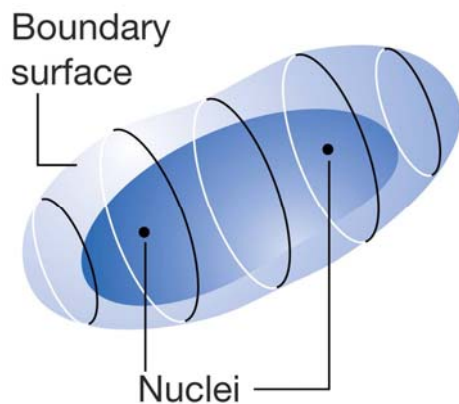
$$\Psi_+ = N [\Psi_A(r_A) + \Psi_B(r_B)]$$



Amplitude representation



Contour plot representation

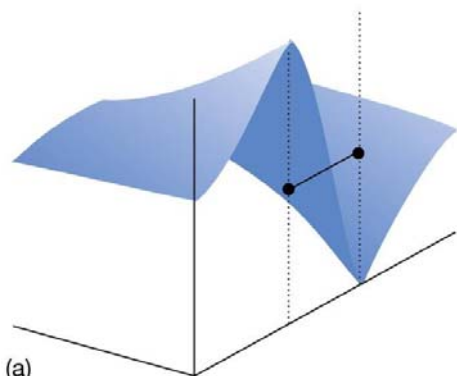


Chemical Bonds

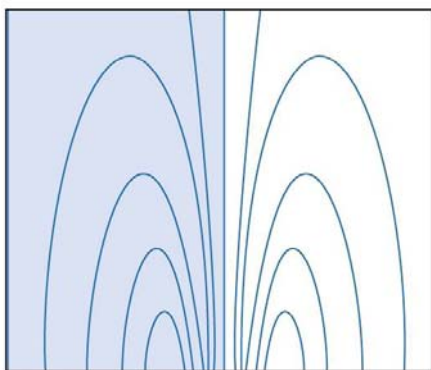
H₂⁺ ion

Antibonding σ^* orbital:

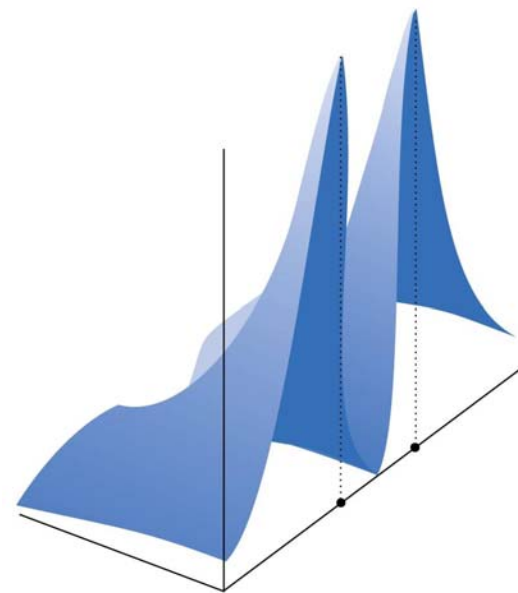
$$\Psi_- = N [\Psi_A(r_{A1}) - \Psi_B(r_{B1})]$$



Amplitude representation

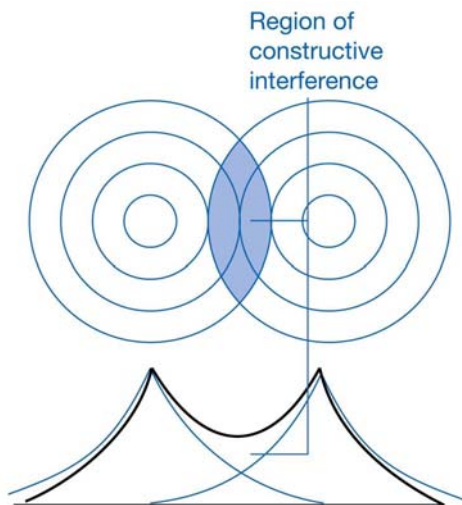


Contour plot representation



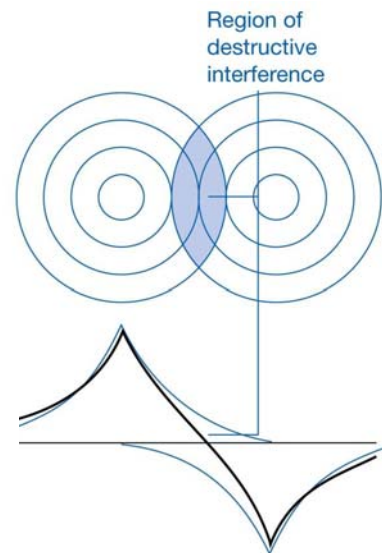
Electron density: $|\Psi_-|^2$

H₂⁺ ion



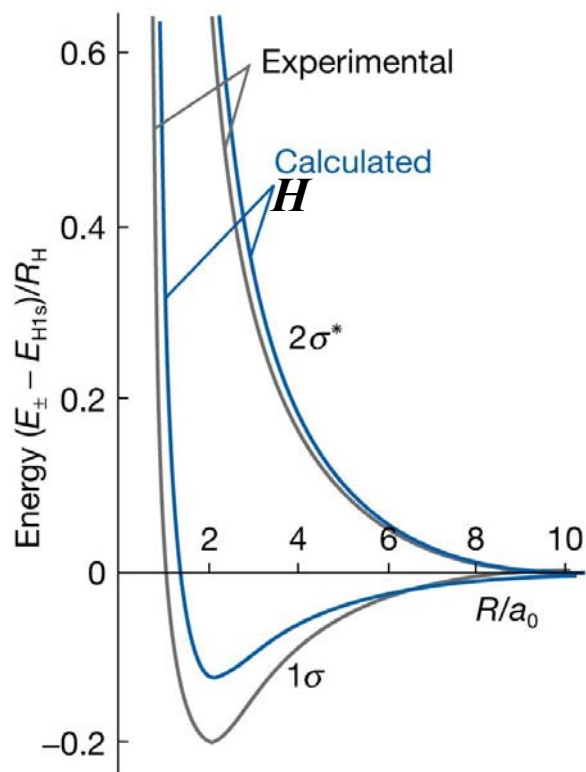
1σ_g orbital

$$E_g = (\alpha + \beta) / (1 + S)$$



2σ_u* orbital

$$E_u = (\alpha - \beta) / (1 - S)$$



Chemical Bonds

Time-Dependent Perturbation Theory

Hamiltonian: $\mathbf{H} = \mathbf{H}_0 + \mathbf{V}(t)$

The known exact solution of the equation

$$i\hbar \frac{\partial}{\partial t} \psi_k^{(0)}(\mathbf{q}, t) = \mathbf{H}_0 \psi_k^{(0)}(\mathbf{q}, t)$$

We seek for an approximate solution for

$$i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{q}, t) = (\mathbf{H}_0 + \mathbf{V}(t)) \Psi(\mathbf{q}, t)$$

1. The unknown wavefunction $\Psi(\mathbf{q}, t)$ can be expanded over the orthogonal set $\Psi_k^{(0)}(\mathbf{q}, t)$
2. This expansion is substituted to the full-Hamiltonian Schrödinger equation
3. The obtained expression is multiplied by $\Psi_n^{(0)}(\mathbf{q}, t)$ and then integrated over all coordinates \mathbf{q} .
4. The obtained equation is solved giving an approximate values of the expansion coefficients $a_k(t)$.

$$\Psi(\mathbf{q}, t) = \sum_k a_k(t) \Psi_k^{(0)}(\mathbf{q}, t)$$

Time-Dependent Perturbation Theory: Solution

$$\text{Hamiltonian: } \mathbf{H} = \mathbf{H}_0 + \mathbf{V}(t)$$

The known exact solution of the equation

$$i\hbar \frac{\partial}{\partial t} \Psi_k^{(0)}(q,t) = \mathbf{H}_0 \Psi_k^{(0)}(q,t)$$

We seek for an approximate solution for

$$i\hbar \frac{\partial}{\partial t} \Psi(q,t) = (\mathbf{H}_0 + \mathbf{V}(t)) \Psi(q,t)$$

$$\Psi(q,t) = \sum_k a_k(t) \Psi_k^{(0)}(q,t)$$

$$i\hbar \frac{\partial a_k^{(1)}}{\partial t} = \langle k | \mathbf{V} | 0 \rangle e^{i\omega_k t}$$



$$a_k^{(1)}(t) = -\frac{i}{\hbar} \int_0^t \langle k | \mathbf{V} | 0 \rangle e^{i\omega_k \tau} d\tau$$

The population rate of the state $|k\rangle$

$$W_{k \leftarrow 0} = \frac{d|a_k^{(1)}(t)|^2}{dt} \propto |\langle k | \mathbf{V} | 0 \rangle|^2$$

Important particular case:

$$V = -\boldsymbol{\mu} \cdot \mathbf{E} \cos(\omega t) = -\mu_z E_z \cos(\omega t)$$

$$W_{k \leftarrow 0} \propto |\langle k | \mu_z | 0 \rangle|^2 E_z^2$$

The Variation Method

Schrödinger equation to be solved:

$$H\Psi(q) = E\Psi(q)$$

Multiplying from the left by $\Psi^*(q)$ and integrating over q we get:

$$E = \frac{\int \Psi^*(q) \hat{H} \Psi(q) dq}{\int \Psi^*(q) \Psi(q) dq}$$

But we do not know $\Psi(q)$!

Using a probe function $\Psi_{pr}(q)$ obeying the same boundary conditions as $\Psi(q)$ and integrating over q we get:

$$\langle \hat{H} \rangle = \frac{\int \Psi_{pr}^*(q) \hat{H} \Psi_{pr}(q) dq}{\int \Psi_{pr}^*(q) \Psi_{pr}(q) dq}$$

Variation Theorem

$$\langle \hat{H} \rangle \geq E_{gr} \quad \Rightarrow \quad \delta \langle \hat{H} \rangle = 0$$

Gives the upper limit for the ground state energy of the system E_{gr}

Linear Combination of Atomic Orbitals (LCAO): Homonuclear Diatomic Molecules

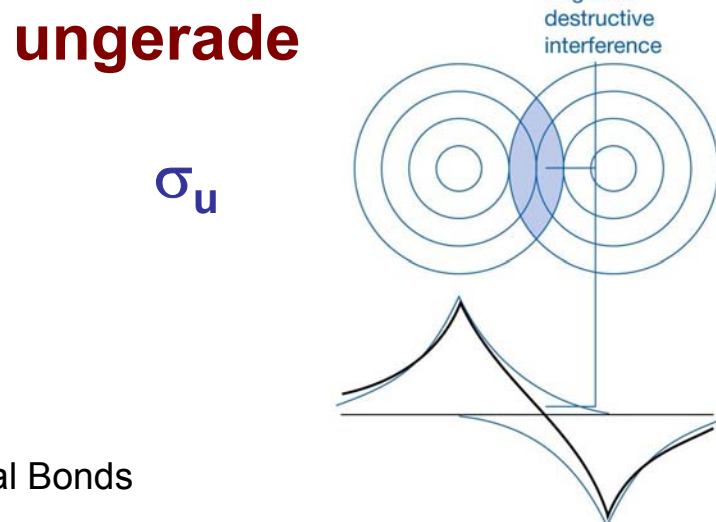
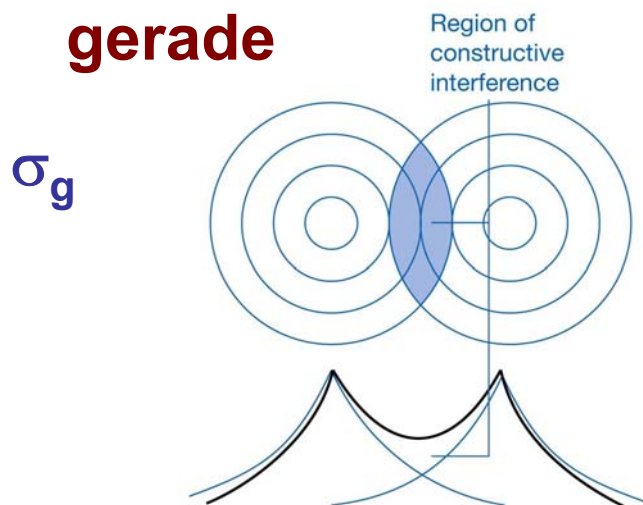
$$\Psi(q) = \sum_i c_i \phi_i(q)$$

All atomic orbitals of an appropriate symmetry can contribute to a molecular orbital

Symmetry of one-electron molecular orbitals

1. Electron axial angular momentum: $I_z = \pm \lambda \hbar$ $\lambda = 0, 1, 2, 3, \dots$
Orbital $\sigma, \pi, \delta, \phi, \dots$

2. Inversion of the electron wave function in the molecular center of symmetry:



Chemical Bonds

Wolfgang Ernst Pauli

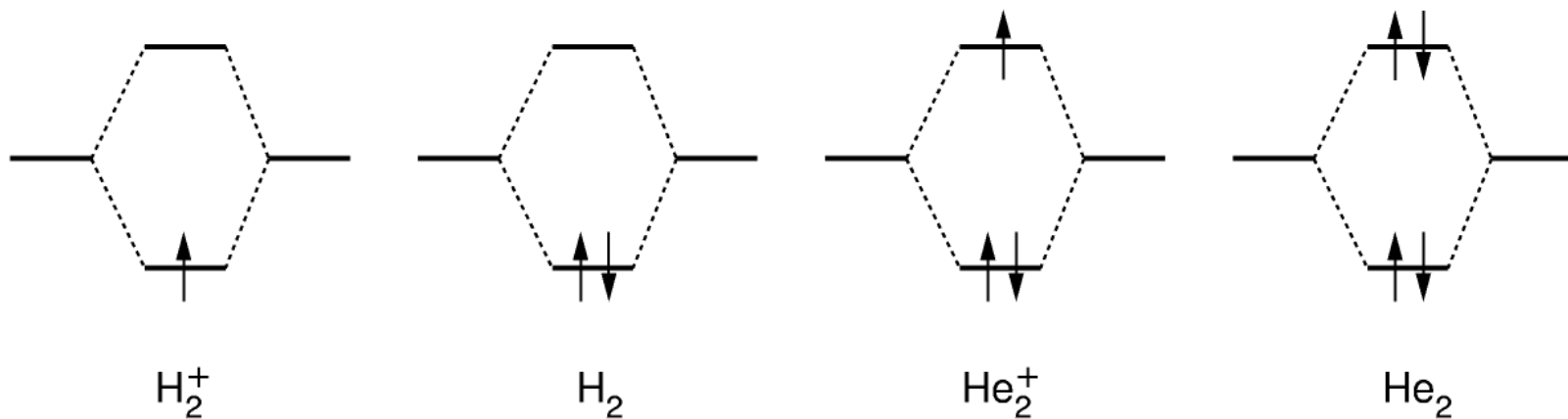


Nobelpreis 1945



* 25. April 1900 in Wien
+ 15. Dez. 1958 in Zürich

Orbital Energy Level Diagrams for Period 1 Diatomic Molecules



H_2^+

H_2

He_2^+

He_2

Configuration:

$1\sigma_g$

$1\sigma_g^2$

$1\sigma_g^2 1\sigma_u^*$

$1\sigma_g^2 1\sigma_u^{*2}$

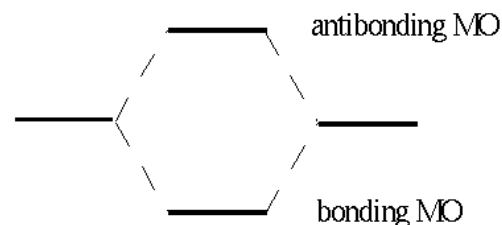
$$\sigma_g = N_g (\Phi_A + \Phi_B) \quad \sigma_u^* = N_u (\Phi_A - \Phi_B)$$

where Φ_A, Φ_B are atomic 1s orbitals

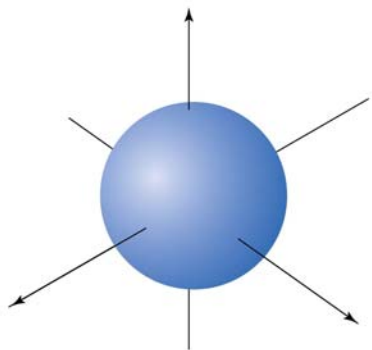
$$H_2: \Psi_g \approx \sigma_g(1) \sigma_g(2)$$

$$He_2: \Psi_g \approx \sigma_g(1) \sigma_g(2) \sigma_u^*(3) \sigma_u^*(4)$$

Chemical Bonds

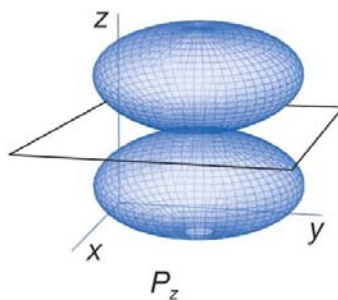


Hydrogen atom wavefunctions: angular part

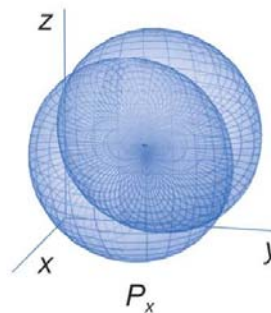


s orbital
 $l=0, m=0$

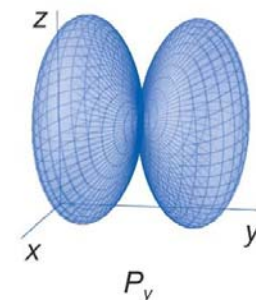
p_z orbital
 $l=1, m=0$



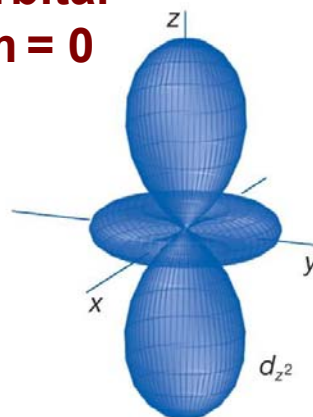
p_x orbital
 $l=1, m=\pm 1$



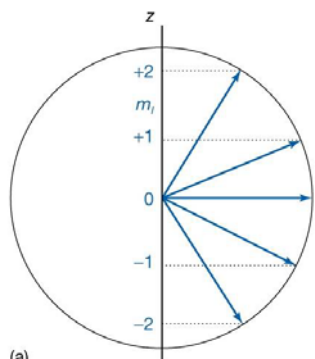
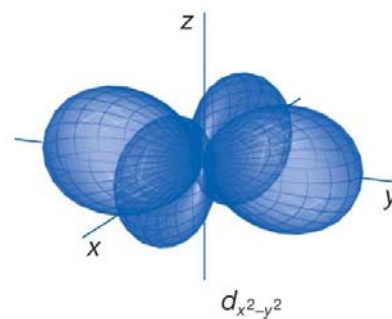
p_y orbital
 $l=1, m=\pm 1$



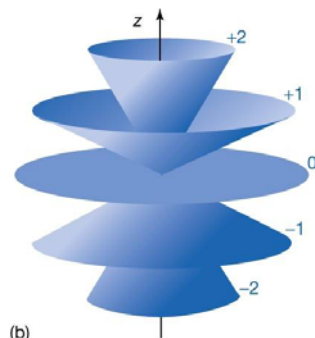
d_{z^2} orbital
 $l=2, m=0$



$d_{x^2-y^2}$ orbital
 $l=2$

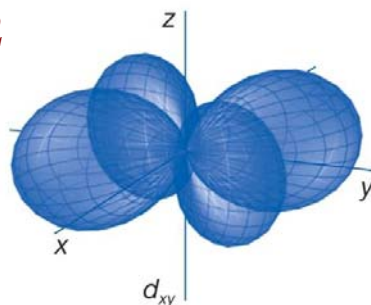


$l=2$ (a)

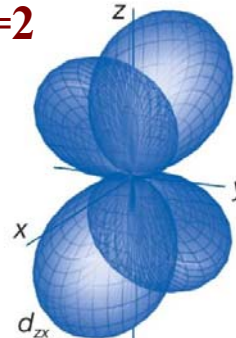


(b)

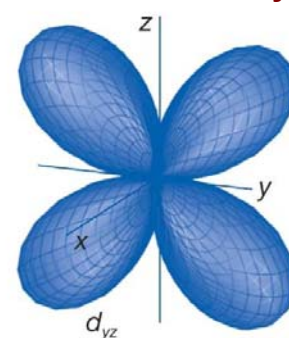
d_{xy} orbital
 $l=2$



d_{zx} orbital
 $l=2$



d_{yz} orbital
 $l=2$



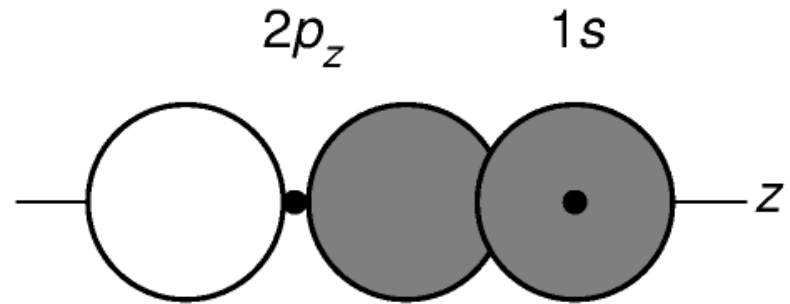
Period 2 Diatomic Molecules:

$\text{Li}_2, \text{Be}_2, \text{B}_2, \text{C}_2, \text{N}_2, \text{O}_2, \text{F}_2, \text{Ne}_2$

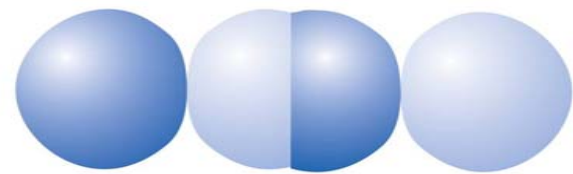
These atomic orbitals have **the same** symmetry and **can** interact with each other

$s + s$

$p_z + s$



$p_z + p_z$



$4\sigma^*$



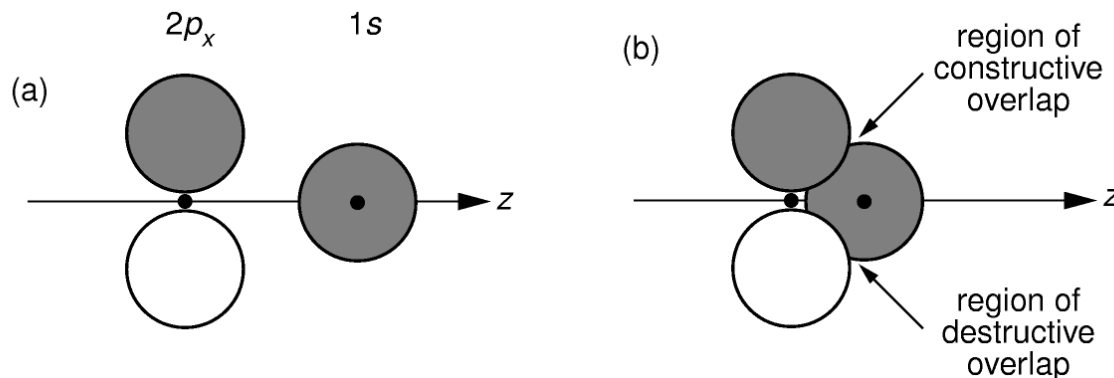
3σ

Chemical Bonds

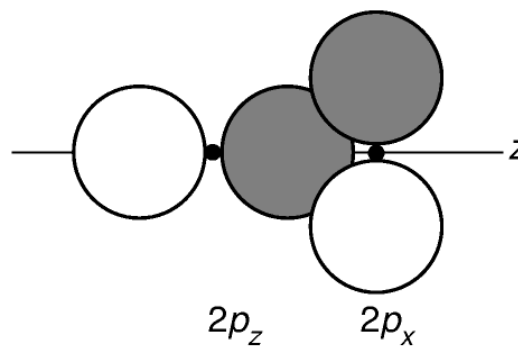
Period 2 Diatomic Molecules: σ orbitals

These atomic orbitals have **different** symmetry and **cannot** interact with each other

$s + p_x$



$p_z + p_x$



Chemical Bonds

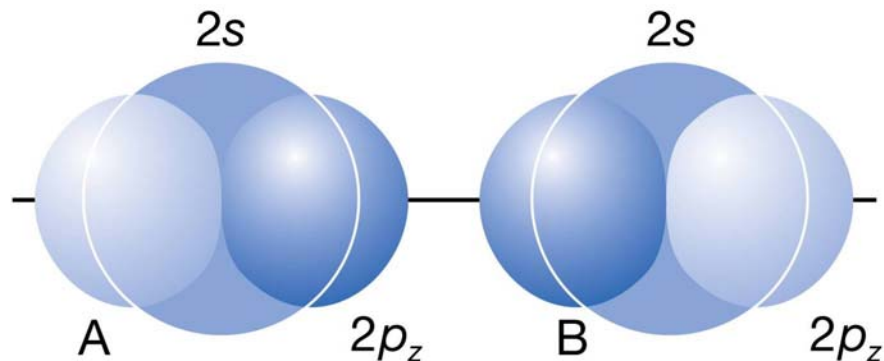
Period 2 Diatomic Molecules

σ orbitals

In general:
$$\Psi_{\sigma} = C_{A2s} \Phi_{A2s} + C_{B2s} \Phi_{B2s} + C_{A2pz} \Phi_{A2pz} + C_{B2pz} \Phi_{B2pz}$$

Let us assume that **Z** axis is parallel to the internuclear axis **R**

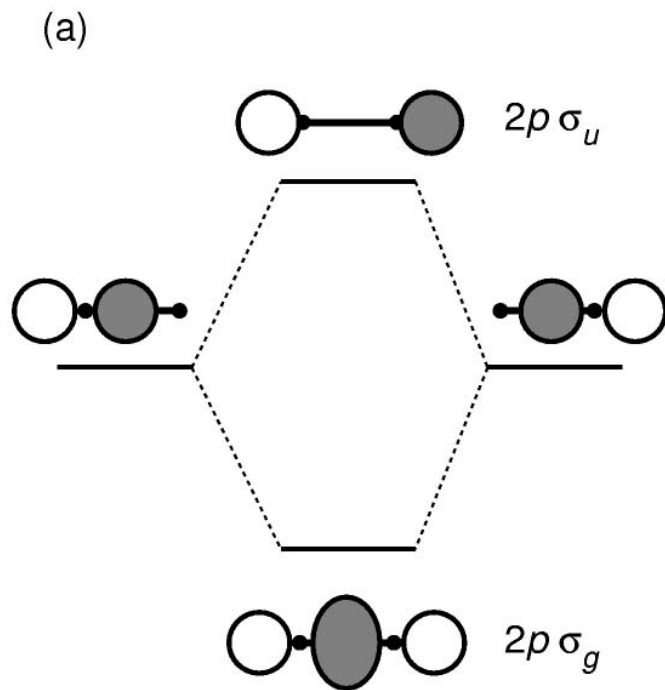
Only 2s and 2p_z atomic orbitals can interact producing molecular σ orbitals.



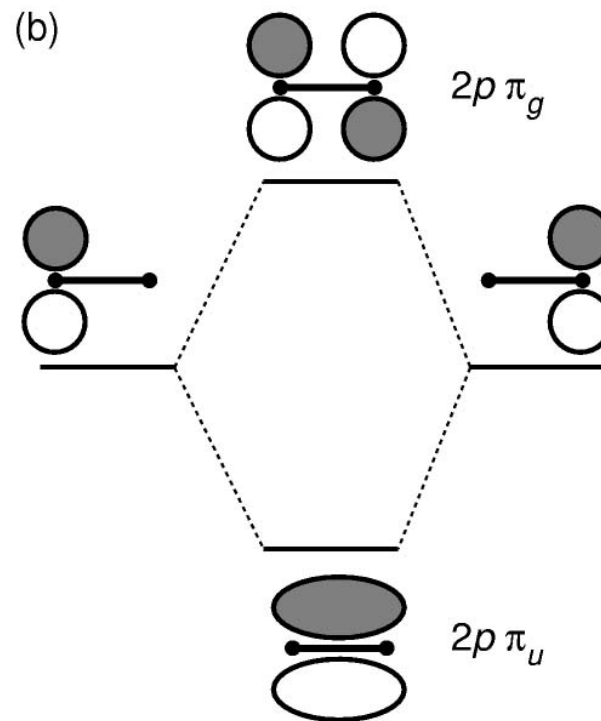
Sometimes, the 2s and 2p_z orbitals can be treated separately, as they distinctly different energies. Then, two 2s orbitals of the two atoms overlap with each other giving a pair of σ_g and σ_u^* molecular orbitals and two 2p_z orbitals overlap with each other giving another pair of σ_g and σ_u^* molecular orbitals.

Period 2 Diatomic Molecules: π orbitals

$2p_x$ and $2p_y$ orbitals of both atoms oriented to the same side can produce bonding π_u and antibonding π_g^* molecular orbitals. The $\pi 2p_x$ and $\pi 2p_y$ orbitals have the same energy, thus π_u and π_g^* orbitals can be populated by the maximum four electrons.

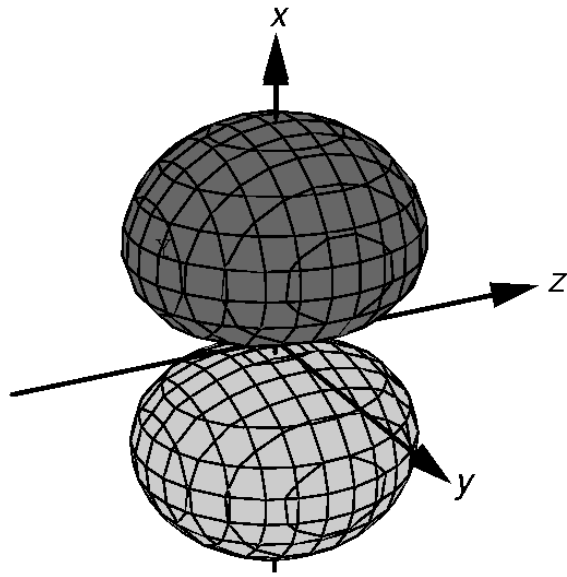


σ orbitals

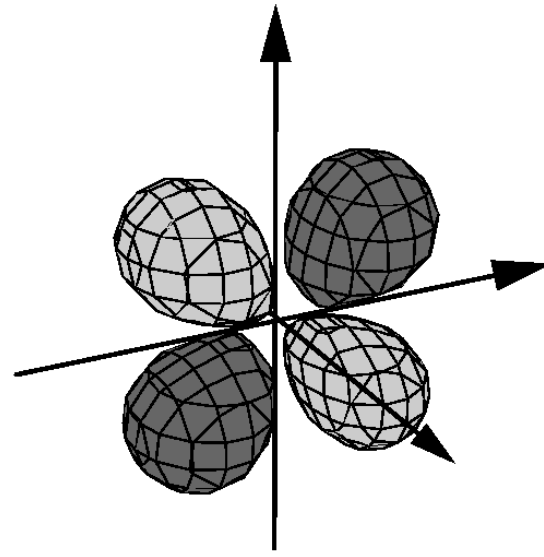


π orbitals

Period 2 Diatomic Molecules: Inversion of π orbitals

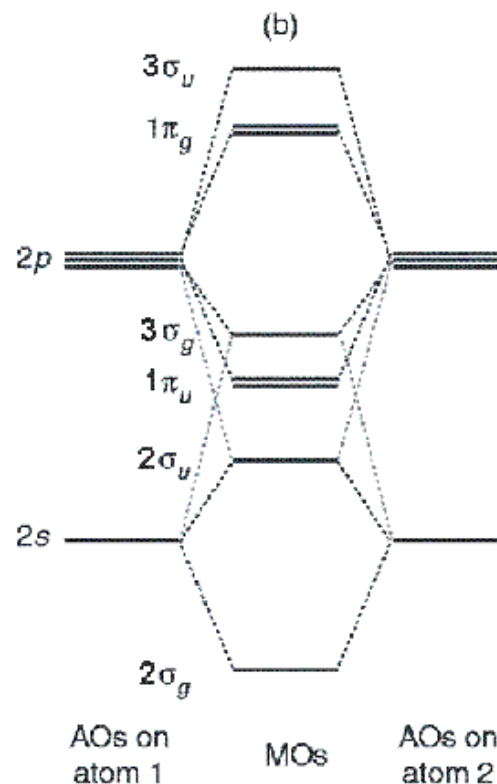
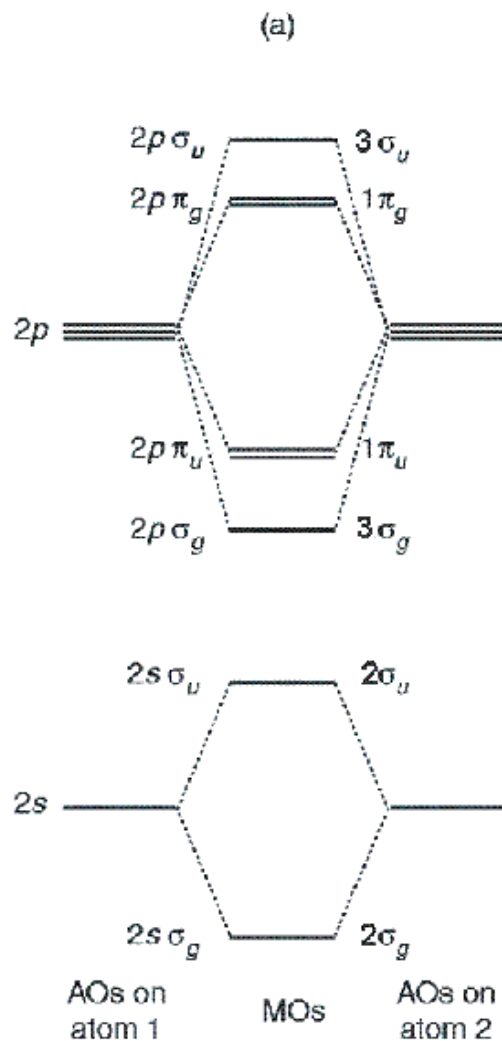


$2p \pi_u$ bonding MO



$2p \pi_g$ anti-bonding MO

Schematic Diagram for the Energy Orbitals of Homonuclear Period 2 Diatomic Molecules

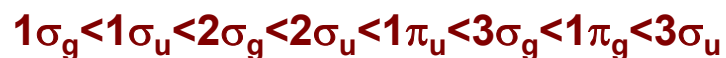


Orbital configuration valid for O_2 and F_2



Chemical Bonds

Orbital configuration valid from Li_2 till N_2



Aufbau Principles

With the orbitals established, we can deduce the ground configuration of the molecules by adding the appropriate number of electrons to the orbitals and following the **Aufbau principles**:

- **Electron occupy different orbitals approximately in the order of their energies**
- **Only two electrons can occupy any non-degenerate orbital**
- **An atom, or a molecule in its ground state adopts a configuration with the greatest number of unpaired electrons (Hund's maximum multiplicity rule)**

Bonding Order

A measure of the net bonding in a diatomic molecule is its **bond order, b** :

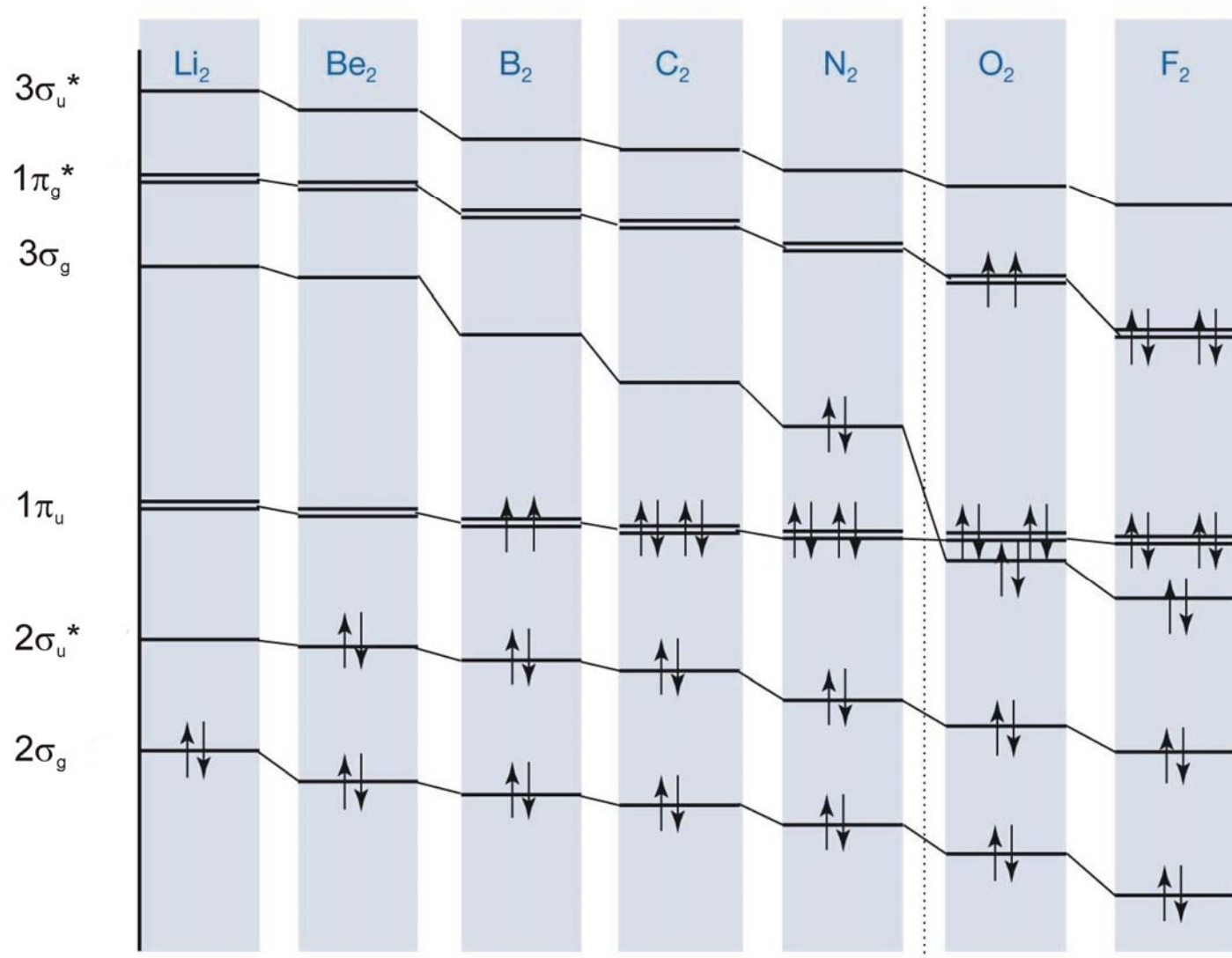
$$b = \frac{1}{2}(n - n^*)$$

where n is the number of electrons in bonding orbitals and n^* is the number of electrons in antibonding orbitals.

Examples:

- H_2 $b = 1$, corresponding to a single bond $\text{H} - \text{H}$,
- He_2 $b = 0$, corresponding to no bond at all.

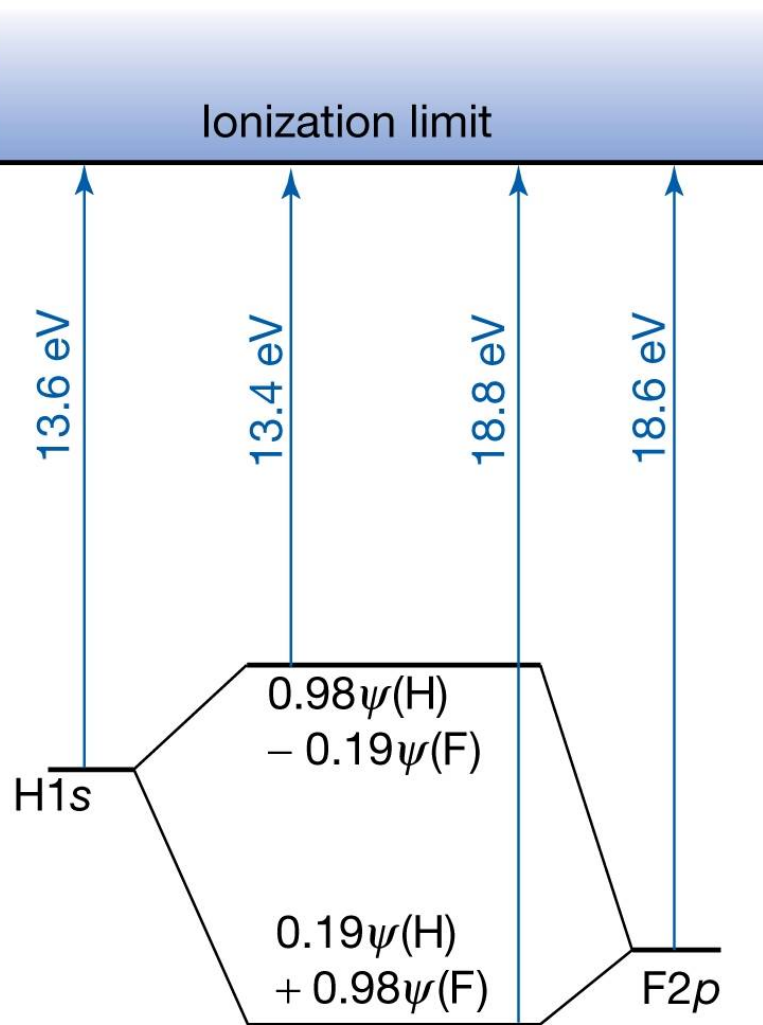
Electron Structure of the Period 2 Homonuclear Diatomic Molecules



Chemical Bonds

Heteronuclear Diatomic Molecules: Polar Bonds

Molecular Orbital Energy Levels of HF (simplified)



If only two atomic orbitals are involved, the one-electron molecular orbital can be written as LCAO:

$$\Psi = c_H \Phi_H + c_F \Phi_F$$

The general Principles

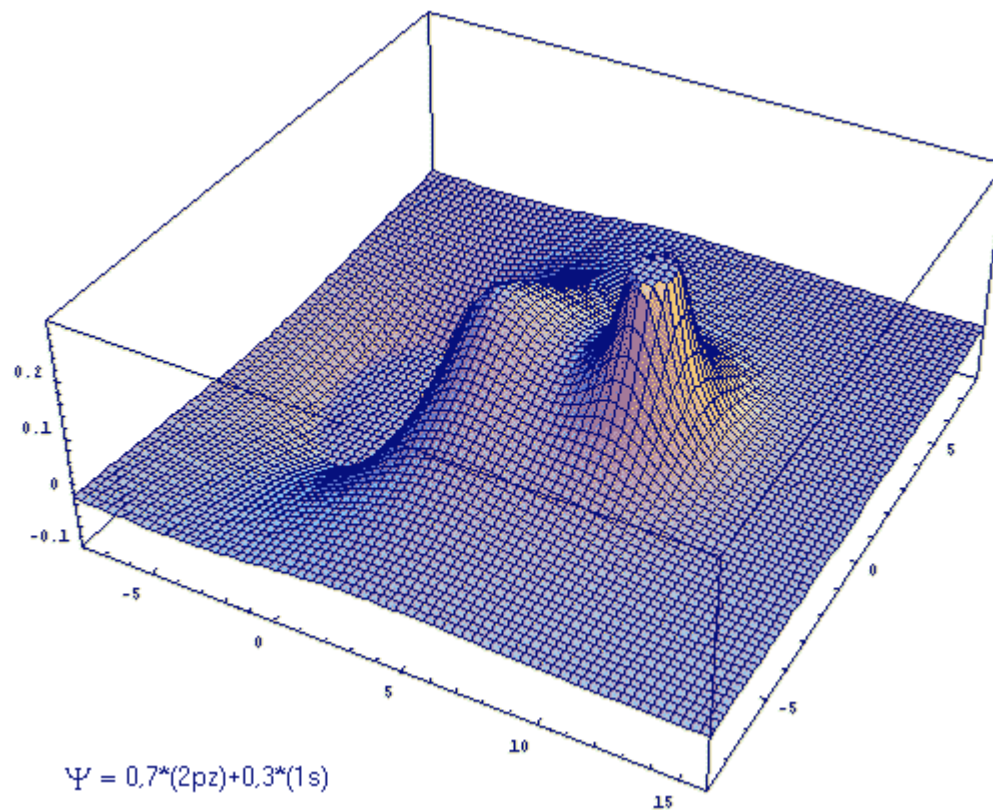
1. The energy levels of the atomic orbitals Φ_H and Φ_F cannot differ too much
2. The symmetry of the atomic orbitals must be the same
3. The overlap of the orbitals Φ_H and Φ_F must be high.

The most likely: $|c_H|^2 < |c_F|^2$

which is called **Polar Bond** and gives the molecule the **Electric Dipole Moment**

Heteronuclear Diatomic Molecules: HF

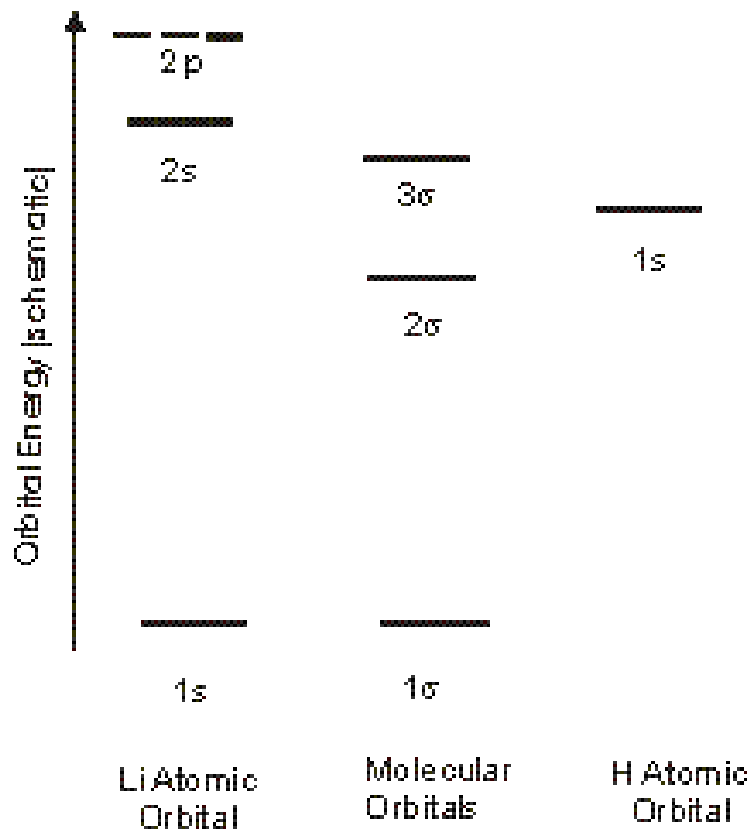
Three-dimensional plot of a one-electron bonding orbital



Chemical Bonds

Hybridization of Atomic Orbitals: LiH

Correlation Diagram for Lithium Hydride Molecule



“True” molecular orbitals:

$$|1\sigma\rangle \approx |1s\text{ Li}\rangle$$

$$|2\sigma\rangle \approx 0.33|2s\text{ Li}\rangle - 0.21|2p_z\text{ Li}\rangle - 0.70|1s\text{ H}\rangle$$

Approximate Molecular orbitals:

$$|1\sigma\rangle \approx |1s\text{ Li}\rangle$$

$$|2\sigma\rangle \approx -0.47|sp^1\text{ Li}\rangle - 0.88|1s\text{ H}\rangle$$

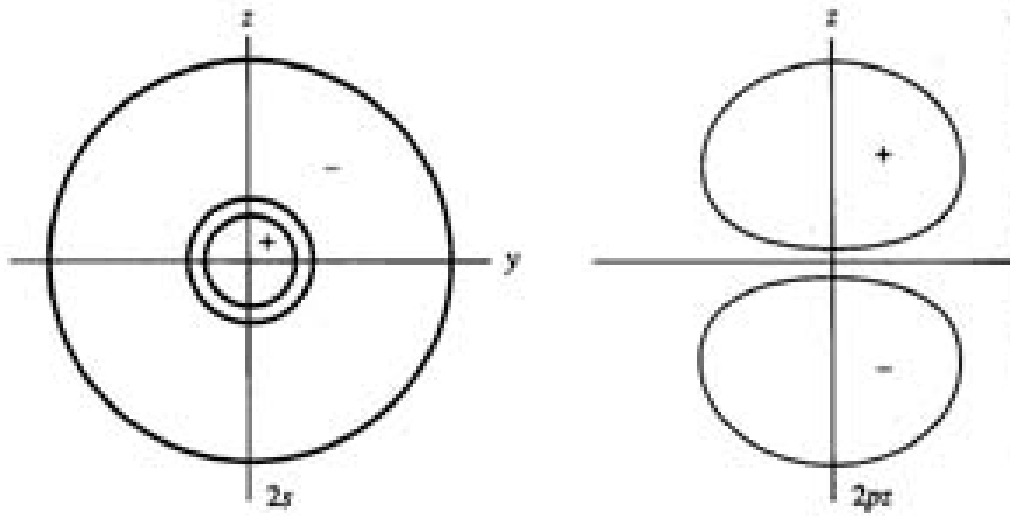
where

$$|sp^1\text{ Li}\rangle = 2^{-1/2}(-|2s\text{ Li}\rangle + |2p_z\text{ Li}\rangle)$$

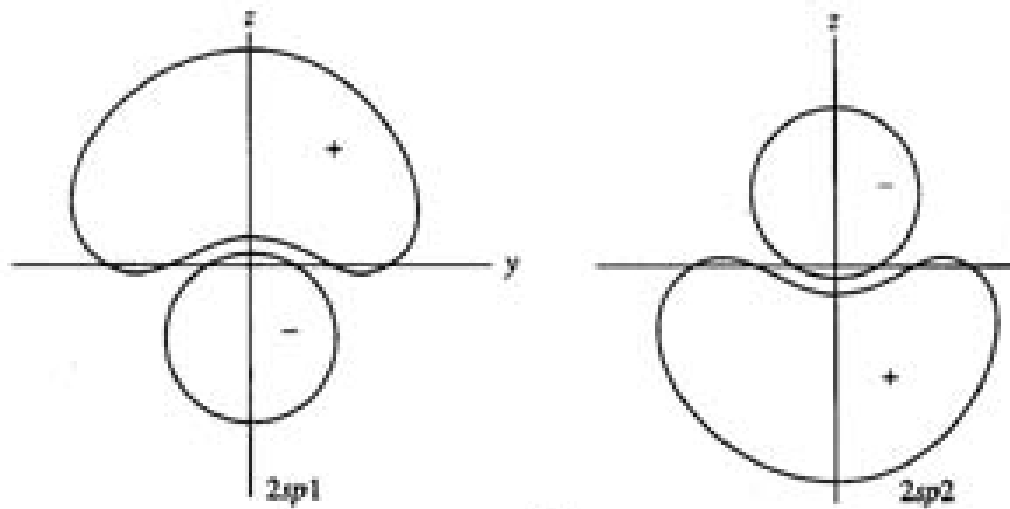
$$|sp^2\text{ Li}\rangle = 2^{-1/2}(-|2s\text{ Li}\rangle - |2p_z\text{ Li}\rangle)$$

The orbitals $|sp^1\text{ Li}\rangle$ and $|sp^2\text{ Li}\rangle$ are called **sp hybrid atomic orbitals**

sp Hybridization of Atomic Orbitals



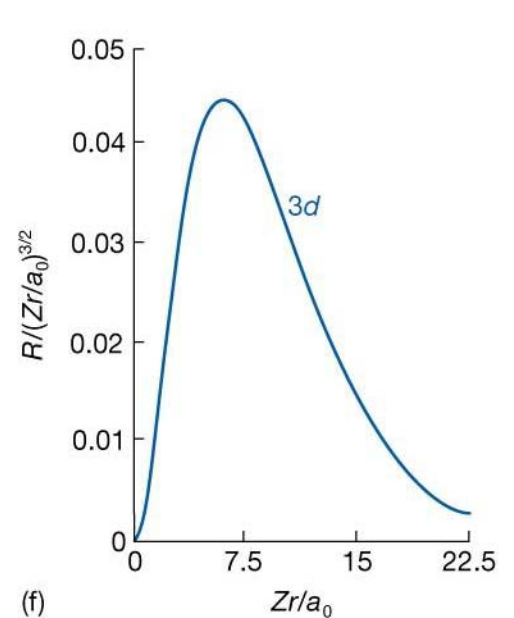
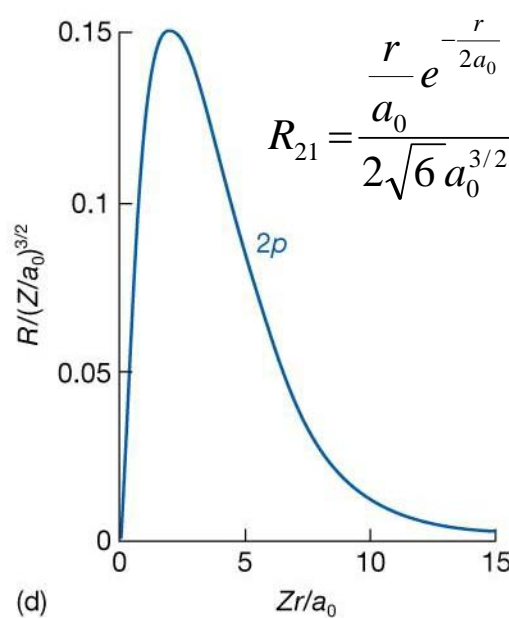
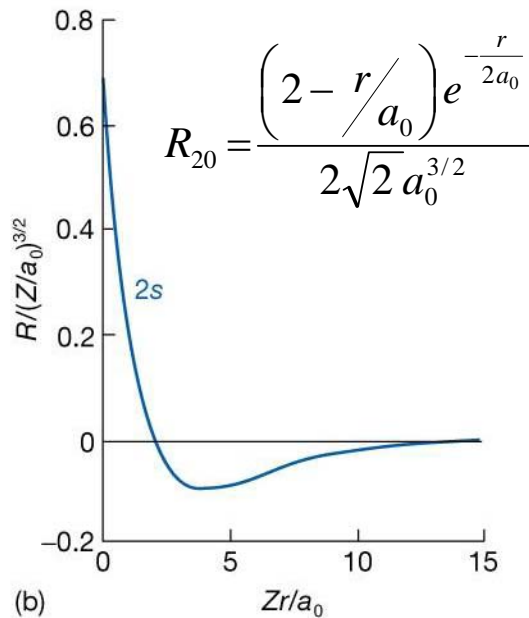
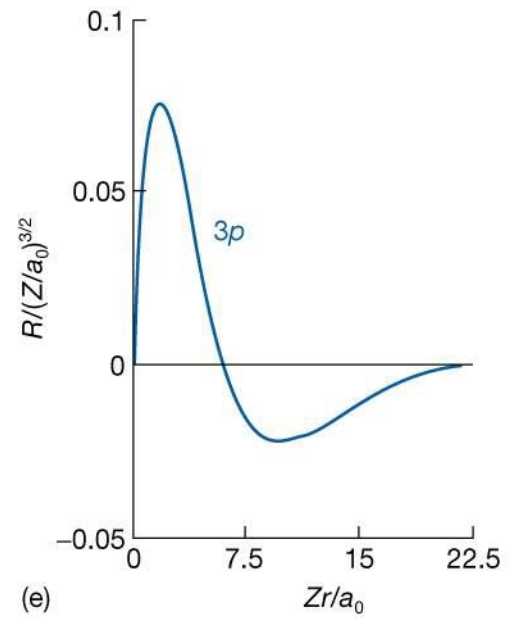
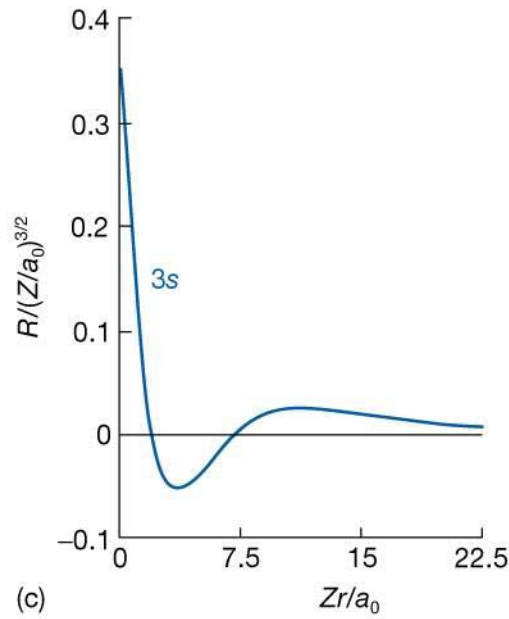
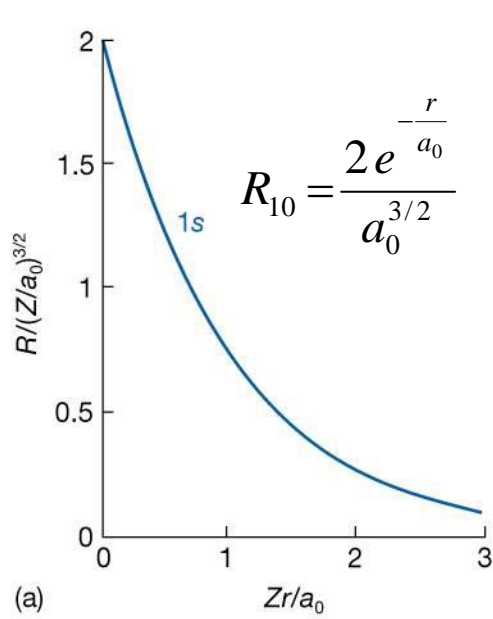
(a)



(b)

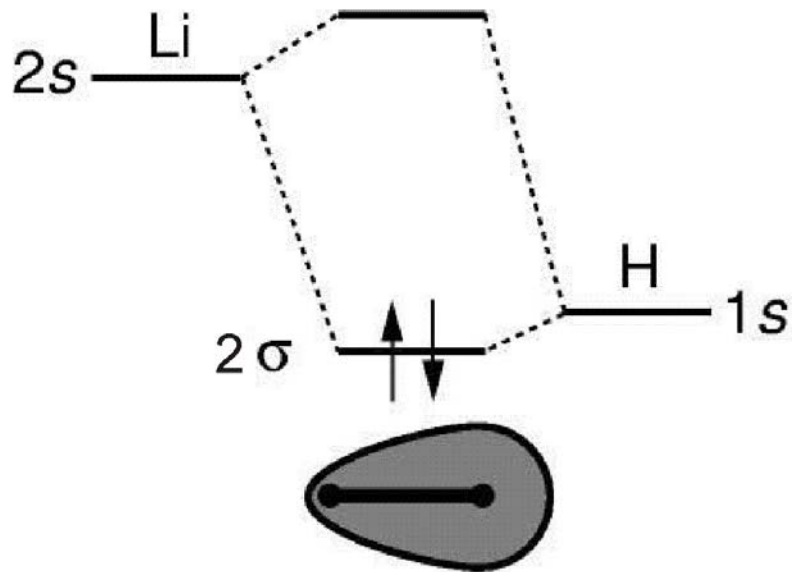
Chemical Bonds

Hydrogen Atom Wavefunctions: Radial Part

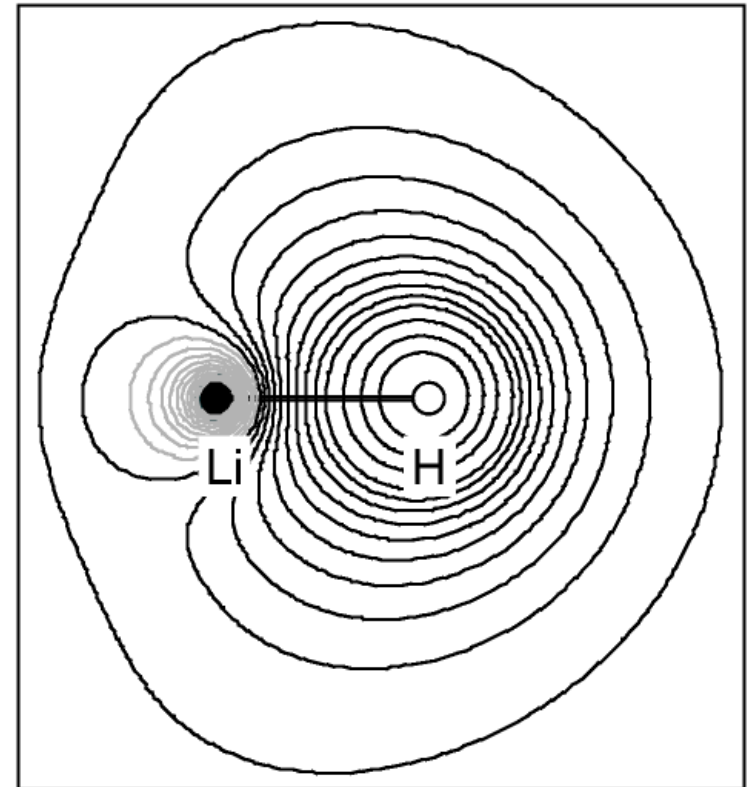


Heteronuclear Diatomic Molecules: LiH

Molecular Orbital Energy Levels



Wavefunction Contour plot

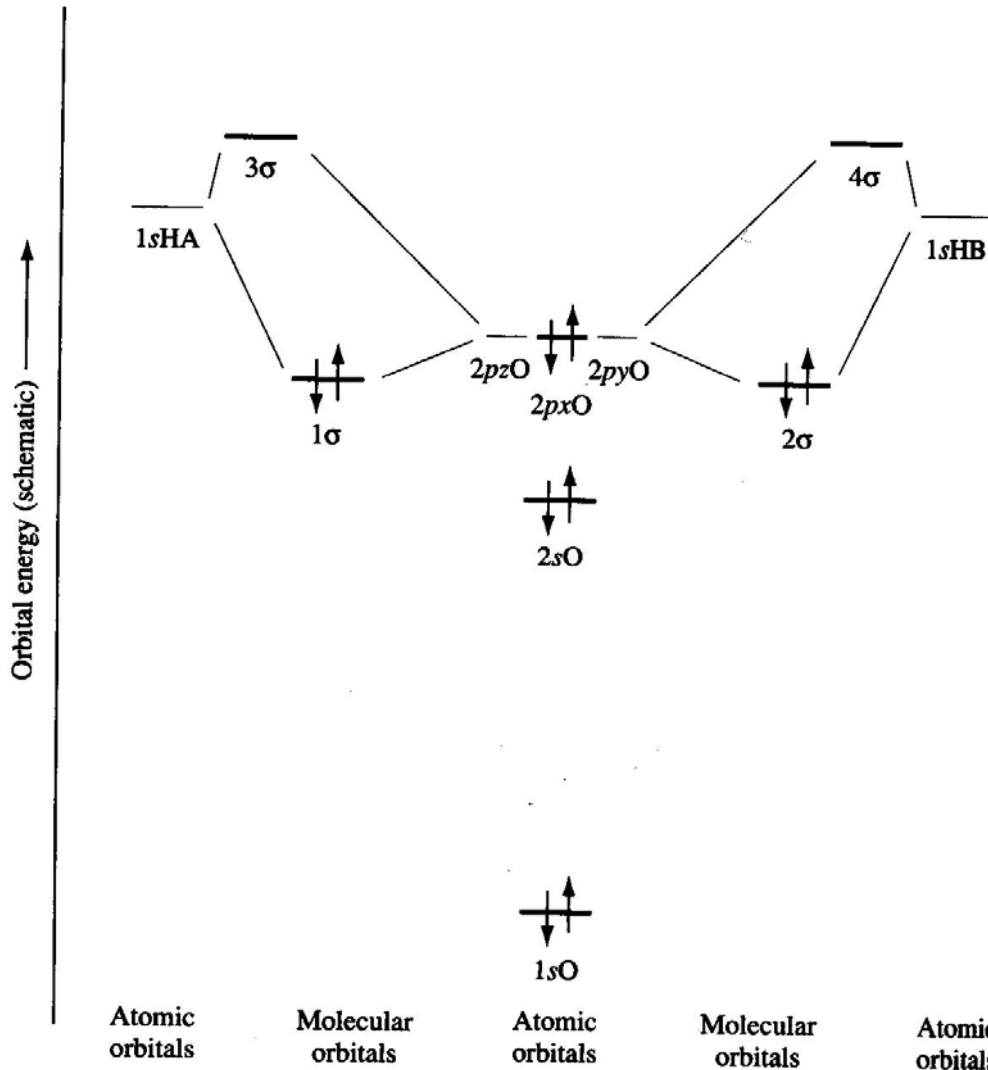


Approximate Molecular orbitals:

$$|1\sigma\rangle \approx |1s \text{ Li}\rangle$$

$$|2\sigma\rangle \approx -0,47 |sp^1 \text{ Li}\rangle - 0,88 |1s \text{ H}\rangle$$

Correlation Diagram for the Water Molecule: Unmodified Atomic Orbitals



Bonding orbitals

$$|1\sigma\rangle = c_O|2p_zO\rangle + c_H|1sH_A\rangle$$

$$|2\sigma\rangle = c_O|2p_yO\rangle + c_H|1sH_B\rangle$$

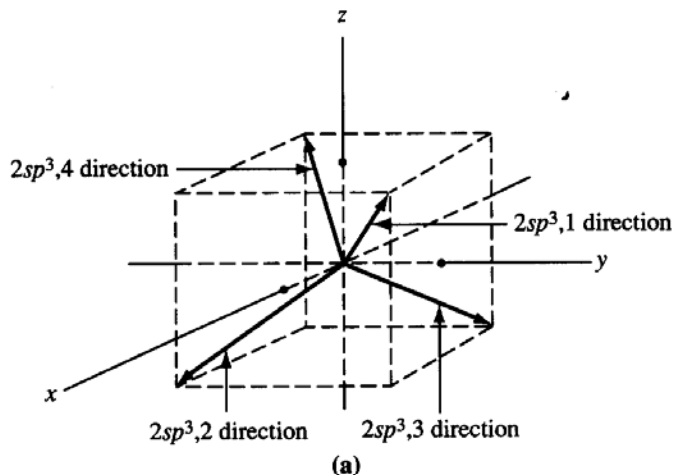
Ground state configuration

$$(1sO)^2(2sO)^2(2p_xO)^2(1\sigma)^2(2\sigma)^2$$

However, these results disagree with the experimental value of the bond angle of 104.5° and with the known fact that the H-atoms in H_2O molecule are equivalent!

sp³ Hybridization of Atomic Orbitals

Tetrahedral hybrid orbitals

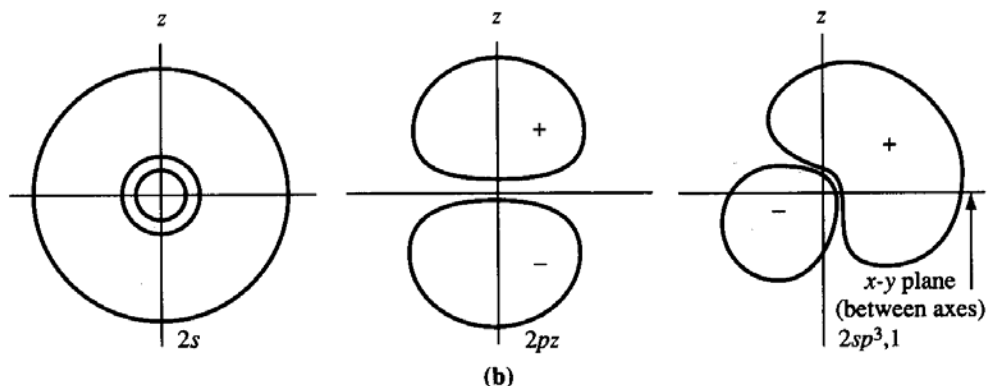


$$|2sp^3_1\rangle = \frac{1}{2}(-|2s\rangle + |2p_x\rangle + |2p_y\rangle + |2p_z\rangle)$$

$$|2sp^3_2\rangle = \frac{1}{2}(-|2s\rangle + |2p_x\rangle - |2p_y\rangle - |2p_z\rangle)$$

$$|2sp^3_3\rangle = \frac{1}{2}(-|2s\rangle - |2p_x\rangle + |2p_y\rangle - |2p_z\rangle)$$

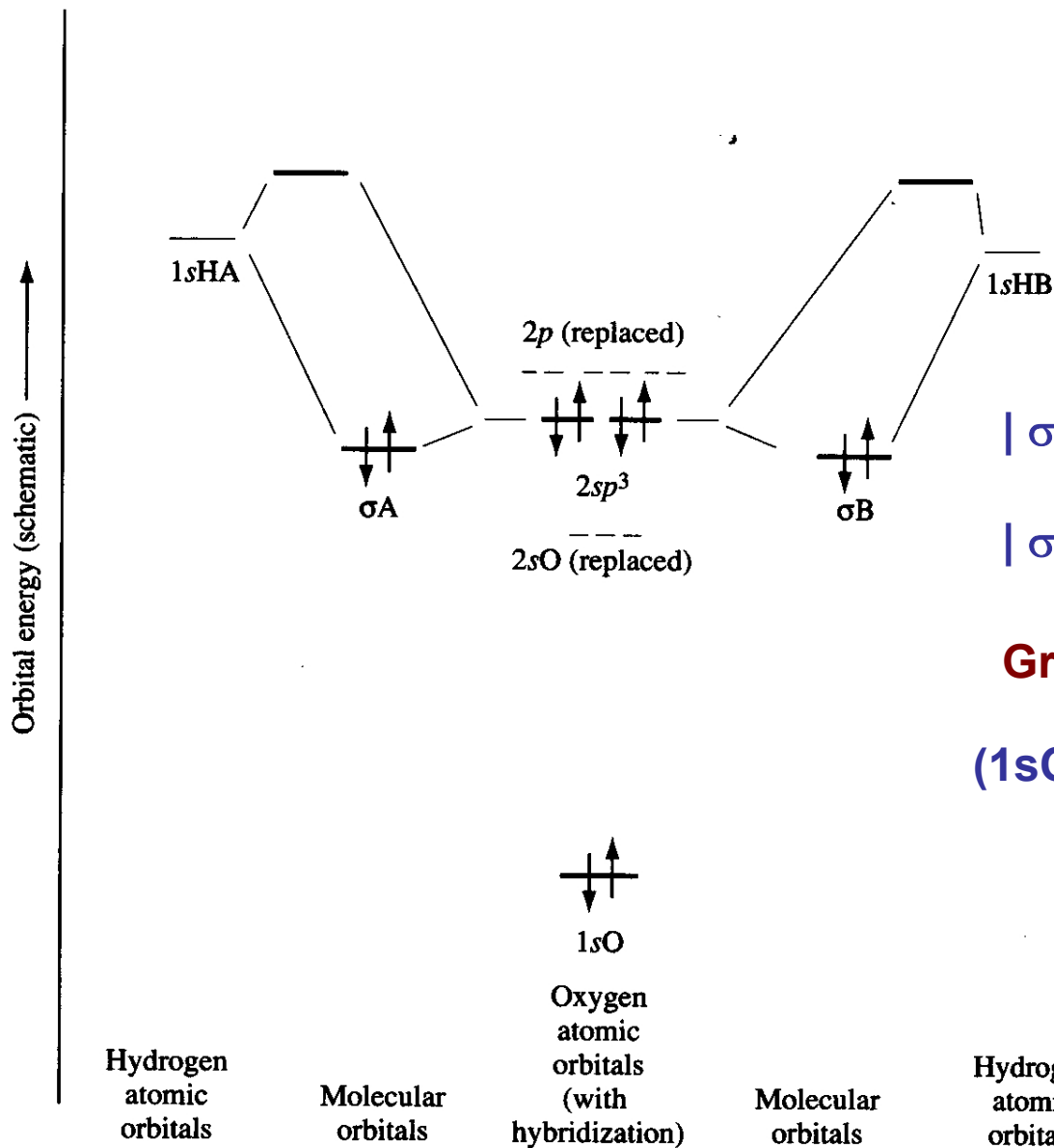
$$|2sp^3_4\rangle = \frac{1}{2}(-|2s\rangle - |2p_x\rangle - |2p_y\rangle + |2p_z\rangle)$$



The angle between any two of the axes shown is called the **tetrahedral angle** and approximately equal to 109 degrees

Connecting the four alternative corners of a cube with line segments constructs a regular **tetrahedron**

Correlation Diagram for the Water Molecule: 2sp³ Hybrid Orbitals



Bonding orbitals

$$|\sigma_A\rangle = c_O |2sp^3_2\rangle + c_H |1sH_A\rangle$$

$$|\sigma_B\rangle = c_O |2sp^3_3\rangle + c_H |1sH_B\rangle$$

Ground state configuration

$$(1sO)^2(2sp^3_1)^2(2sp^3_4)^2(\sigma_A)^2(\sigma_B)^2$$

Electron Pair-Bond Approach

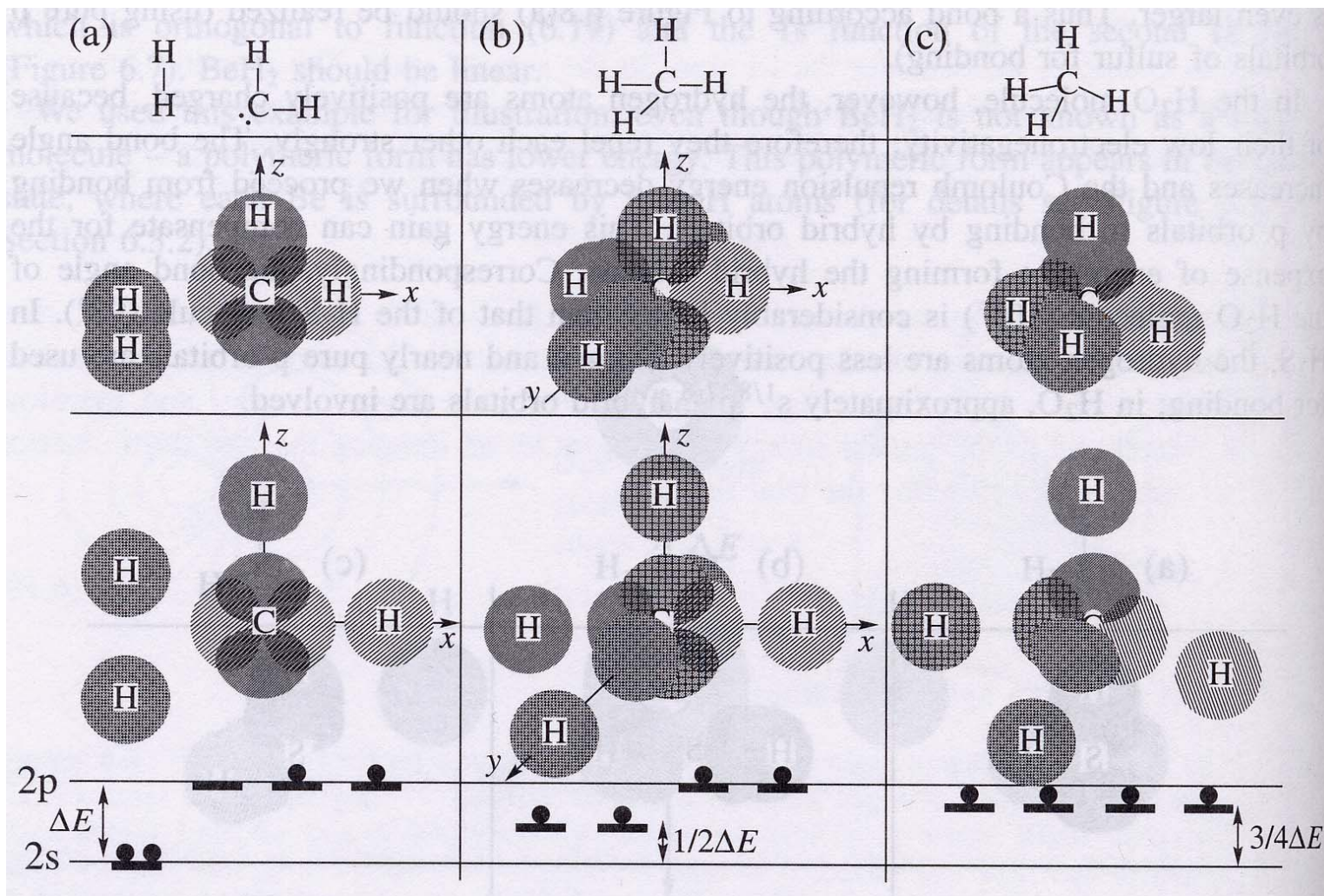
Conditions

- Both partners provide one suitable orbital each for building the molecular bond.
- Two electrons are needed for the bond: each partner can contribute one electron, or both electrons can be contributed by one partner.

The **electron pair bond approach** is closely related to the **valence-bond theory** which was the first quantum mechanical theory of bonding. Although this theory has undergone less much computational development than the **molecular orbital theory** we explained above, it is very useful for qualitative explanation and widely used throughout chemistry.

2sp³ Hybrid Orbitals: methane molecule (CH₄)

Electron pair-bond approach



Bonding through
two 2p orbitals

Bonding through
two sp hybrid
orbitals

Bonding through
sp³ hybrid orbitals

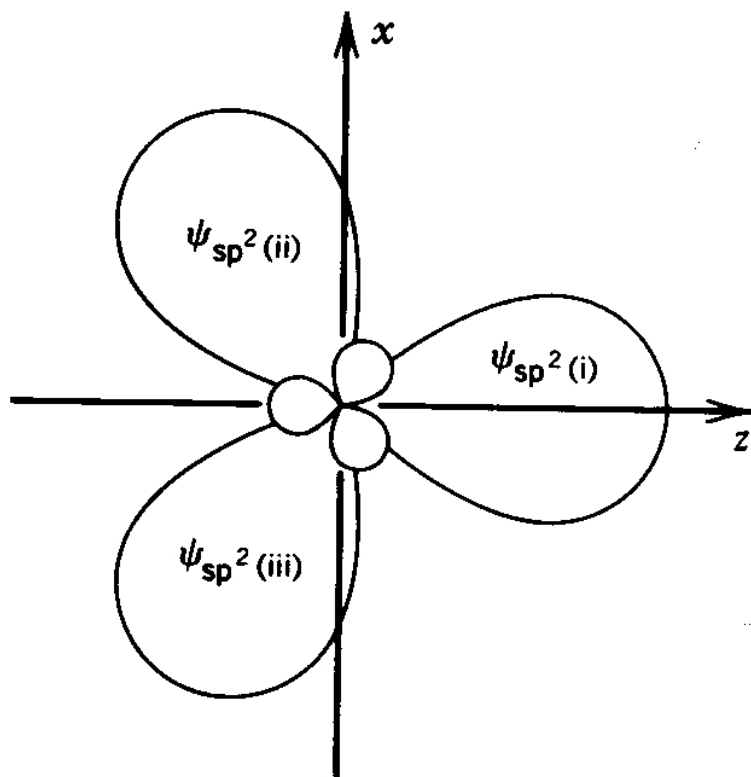
sp² Hybridization of Atomic Orbitals

Trigonal planar hybrid orbitals

$$|2sp^2_1\rangle = 1/\sqrt{3}(-|2s\rangle + \sqrt{2}|2p_z\rangle)$$

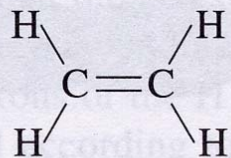
$$|2sp^2_2\rangle = 1/\sqrt{3}(-|2s\rangle - 1/\sqrt{2}|2p_z\rangle + \sqrt{3}/\sqrt{2}|2p_x\rangle)$$

$$|2sp^2_3\rangle = 1/\sqrt{3}(-|2s\rangle - 1/\sqrt{2}|2p_z\rangle - \sqrt{3}/\sqrt{2}|2p_x\rangle)$$

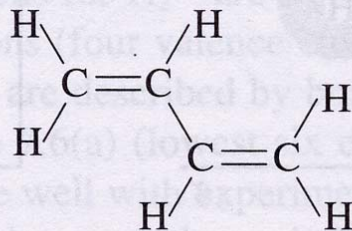


Three hybrid orbitals lie in a plane and point toward the corners of an equivalent triangle. The third 2p orbital, (2p_y) is not included in the hybridization: its axis is perpendicular to the plane where the hybrids lie. The **trigonal hybrid orbitals** are important in describing the structure of planar molecules.

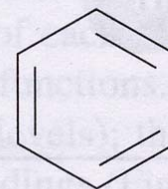
Molecules with π Electron Systems: Double and Triple Bonds



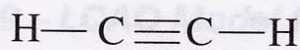
Ethene



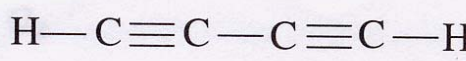
Butadiene



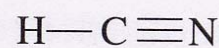
Benzene



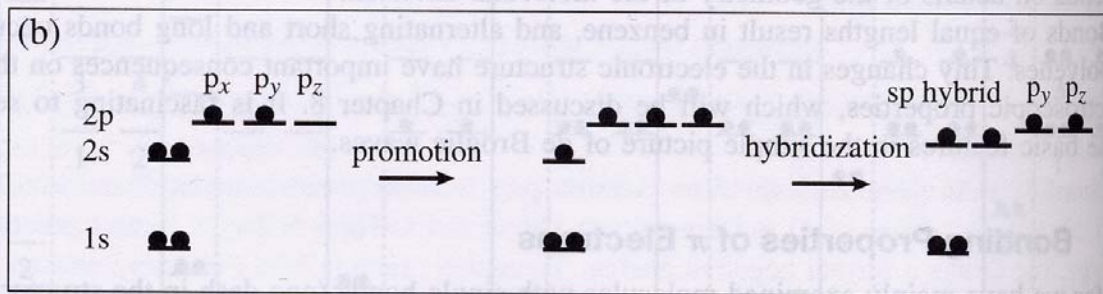
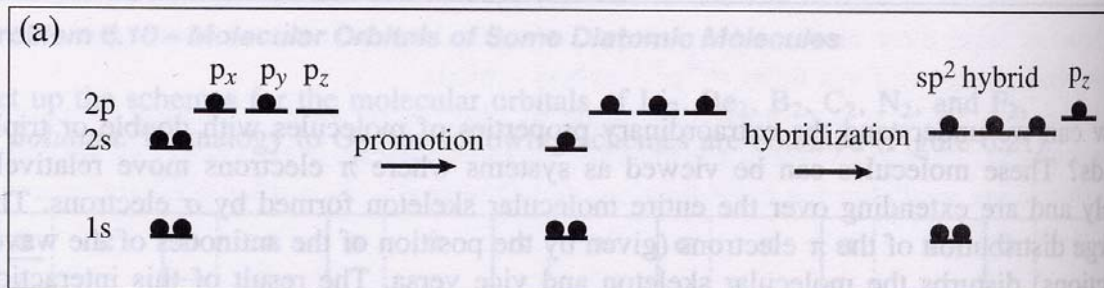
Ethyne



Diethyne



Hydrogen cyanide



π -Orbitals in ethene (C_2H_4)

For planar molecules the σ bonds are **nodeless** with respect to the molecular plane and the π bonds **have a node** in the molecular plane.

The hybrid orbitals which can fit the symmetry of the C_2H_4 molecule is the trigonal sp^2 orbital described above.

The frontier orbitals can be calculated using the Hückel approximations:

- Only the frontier π orbitals are calculated, while the lower energy σ orbitals are assumed to form a rigid framework that determines the general shape of the molecule.
- All the C atoms are treated identically, so all Coulomb integrals α for the atomic orbitals which contribute to the π orbitals are set equal.
- All overlap integrals S are set equal to zero.
- Only the resonance integrals between the neighbor C atoms are set nonzero and all equal to β .

π -Orbitals in ethene C_2H_4

The two π orbitals in C_2H_4 can be expressed as LCAO of two $C2p_z$ orbitals, Φ_A and Φ_B which are perpendicular to the molecular plane:

$$\Psi = c_A \Phi_A + c_B \Phi_B$$

For obtaining the expansion coefficients c_A and c_B and the energies we have to solve the second-order secular determinant:

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0$$

where the exchange integral is assumed to be zero, $S = 0$.

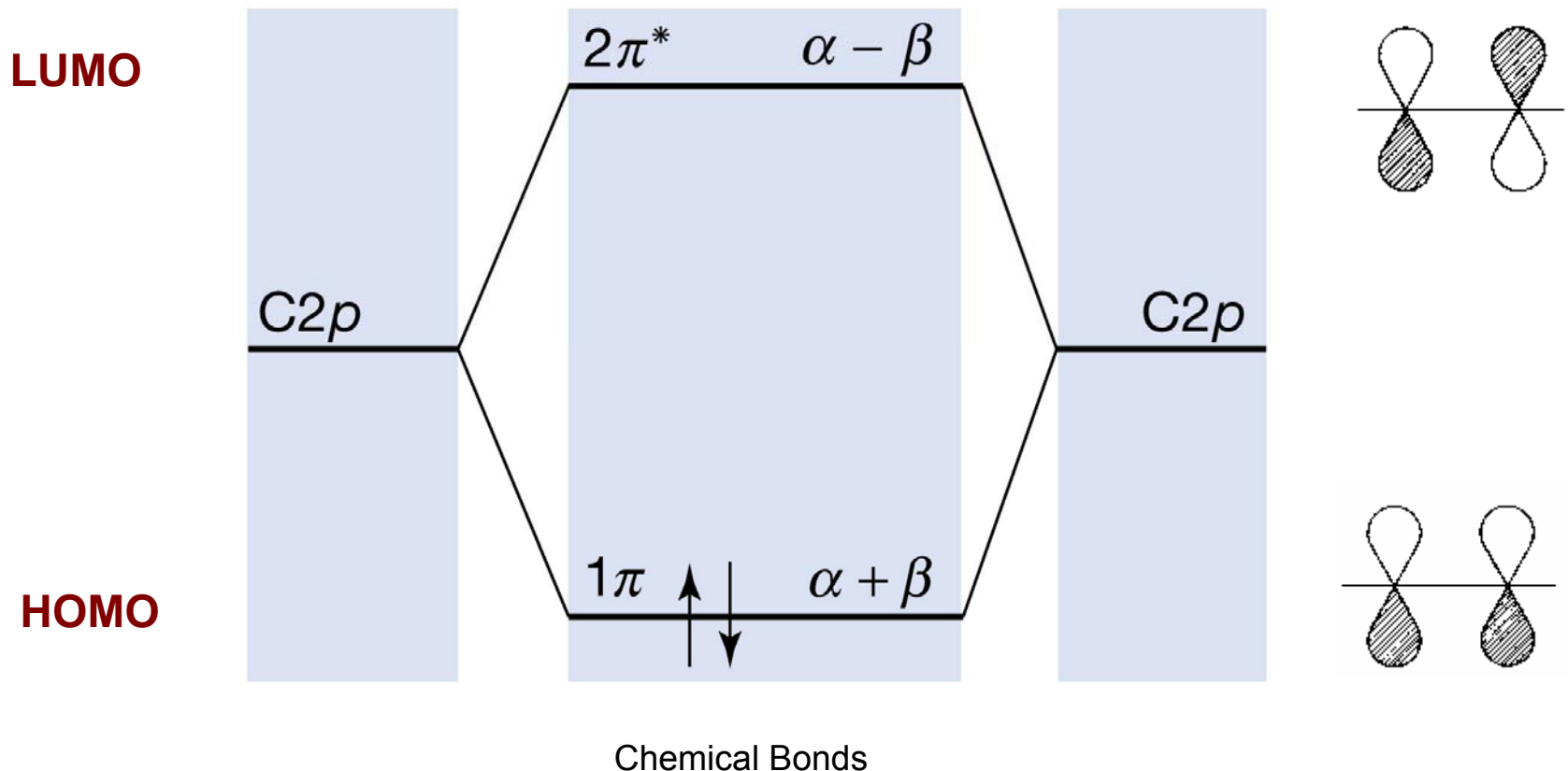
The solution are two energies: $E_{\pm} = \alpha \pm \beta$

where the energy E_+ corresponds to the bonding orbital and the energy E_- corresponds to the antibonding orbital. The Aufbau principle leads to the configuration $1\pi^2$ where each carbon atom supplies one electron to the π bond.

π -Orbitals in ethene (C_2H_4)

The molecule can be viewed as system where π electrons move relatively freely and are extending over the entire molecular skeleton which is formed by the σ electrons. The Frontier π orbitals are of particular importance:

The Frontier π Orbitals { **HOMO: The Highest Occupied Molecular Orbital**
{ **LUMO: The Lowest Unfilled Molecular Orbitals**



π -Orbitals in Butadiene (C_4H_6)

There are four $2p_z$ orbitals from each of the four C atom which form four π molecular orbitals contributing to the double bonds. The π orbitals in C_4H_6 can be expressed by as LCAO of four $C2p_z$ orbitals:

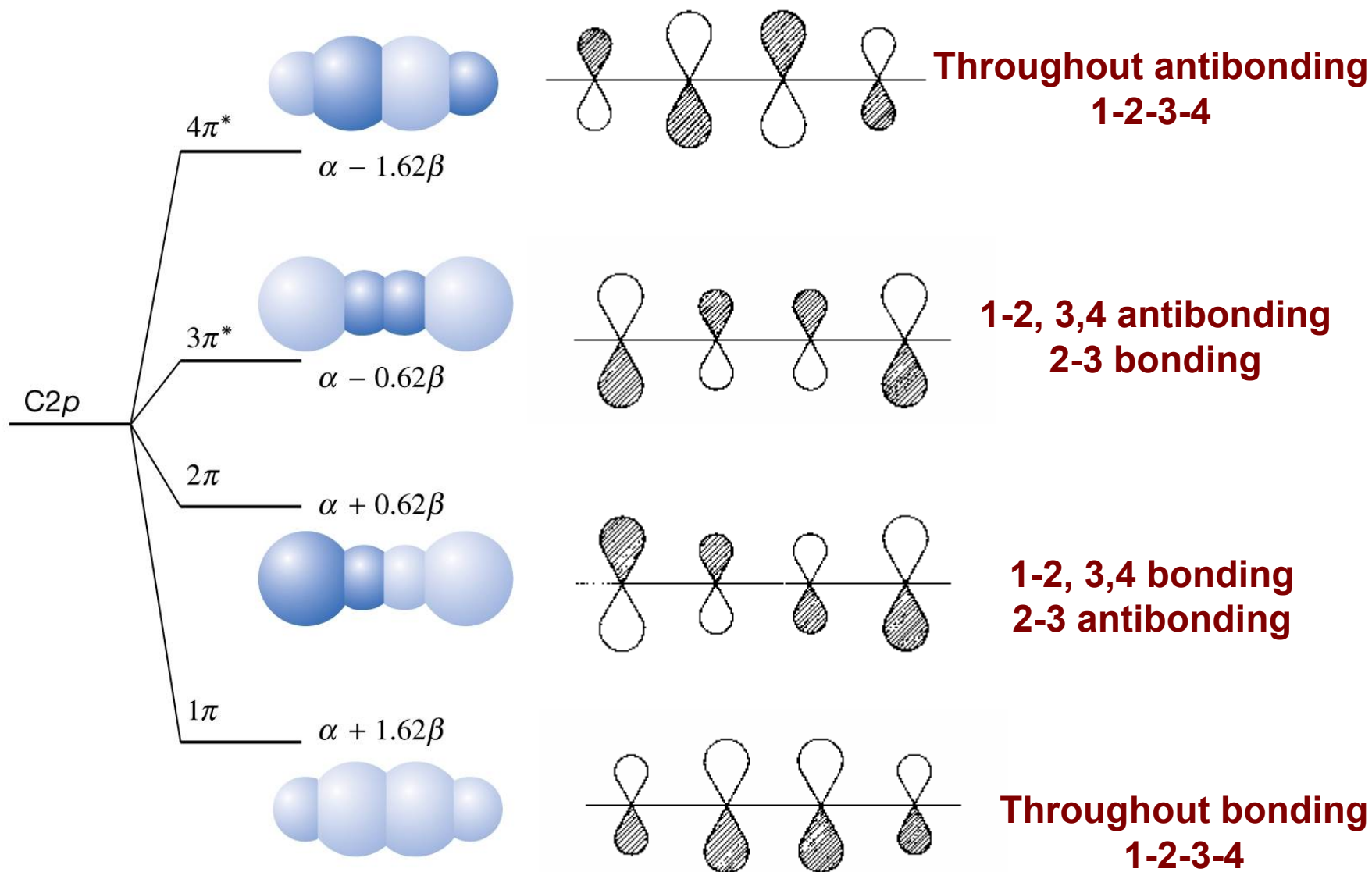
$$\Psi = c_1 \Phi_1 + c_2 \Phi_2 + c_3 \Phi_3 + c_4 \Phi_4$$

For obtaining the expansion coefficients $c_1 - c_4$ and the energies we have to solve the fourth-order secular determinant:

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{vmatrix} = 0$$

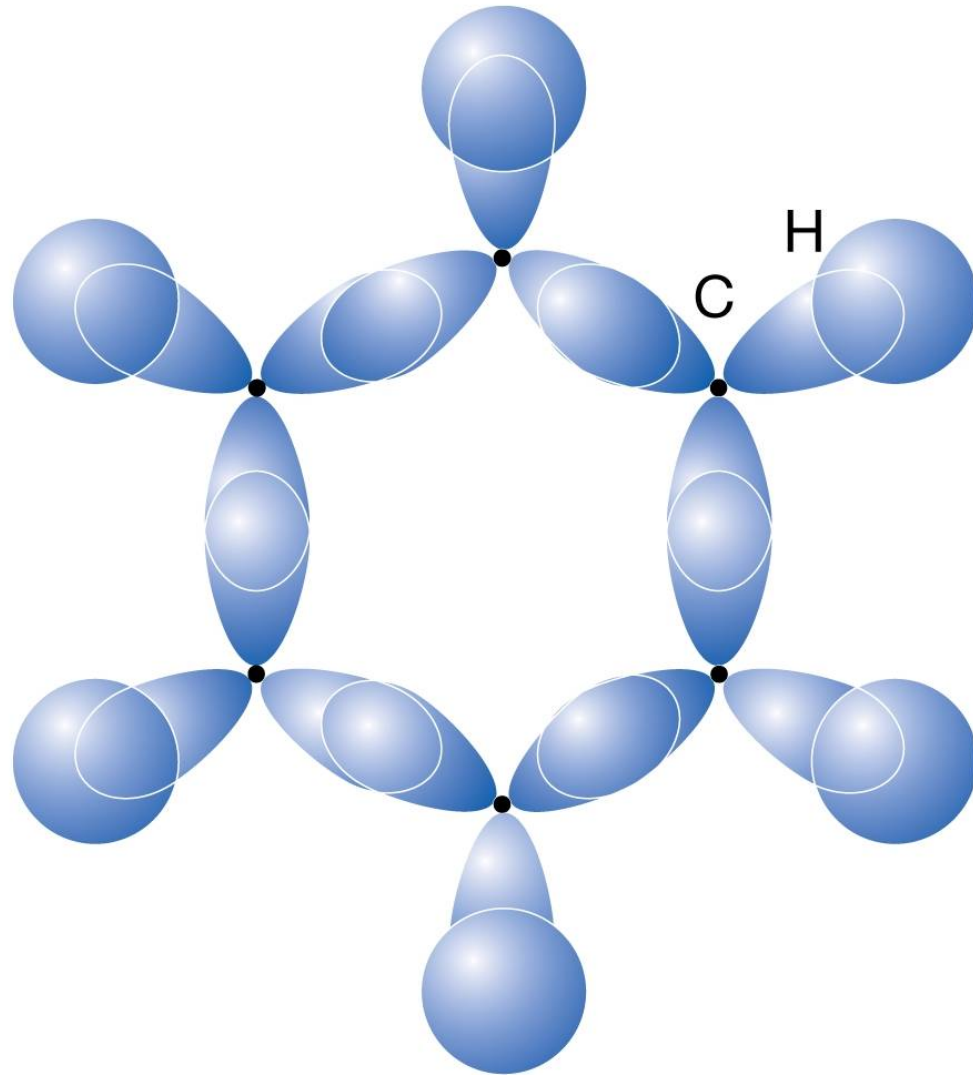
which is equivalent to the fourth-order algebraic equation. The solution are **four energies $E_1 - E_4$** and **four sets of the coefficients c_i** , where $i = 1,2,3,4$.

π -Orbitals in Butadiene (C_4H_6)



Chemical Bonds

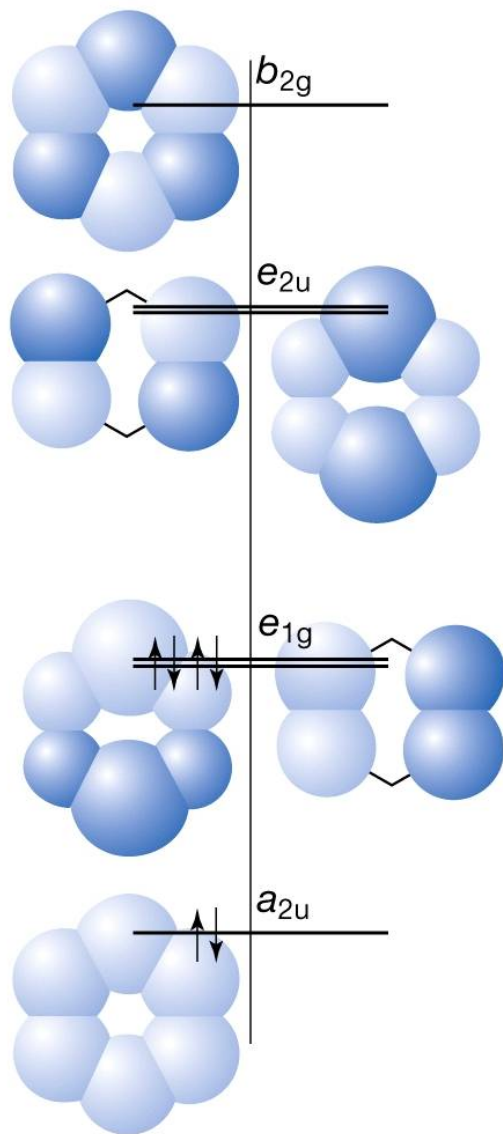
σ Framework in Benzene (C_6H_6):



sp^2 hybrid orbitals of C and s orbitals of H

Chemical Bonds

π -Orbitals in Benzene (C_6H_6)



**Throughout antibonding
1-2-3-4-5-6**

**Mixture of bonding, antibonding,
and nonbonding**

**Mixture of bonding, antibonding,
and nonbonding**

**Throughout bonding
1-2-3-4-5-6**