

Part 4. Many-Electron Molecules

In our analysis of H_2^+ and H_2 molecules, we used linear combinations of 1s orbitals to estimate the molecular structure. This is a major oversimplification, but the calculated bond energies, bond lengths, force constants, *etc.* are quite reasonable. For our purposes, the treatment provides insight regarding the consequences of the exclusion principle and the origins of chemical bonding and excited molecular states.

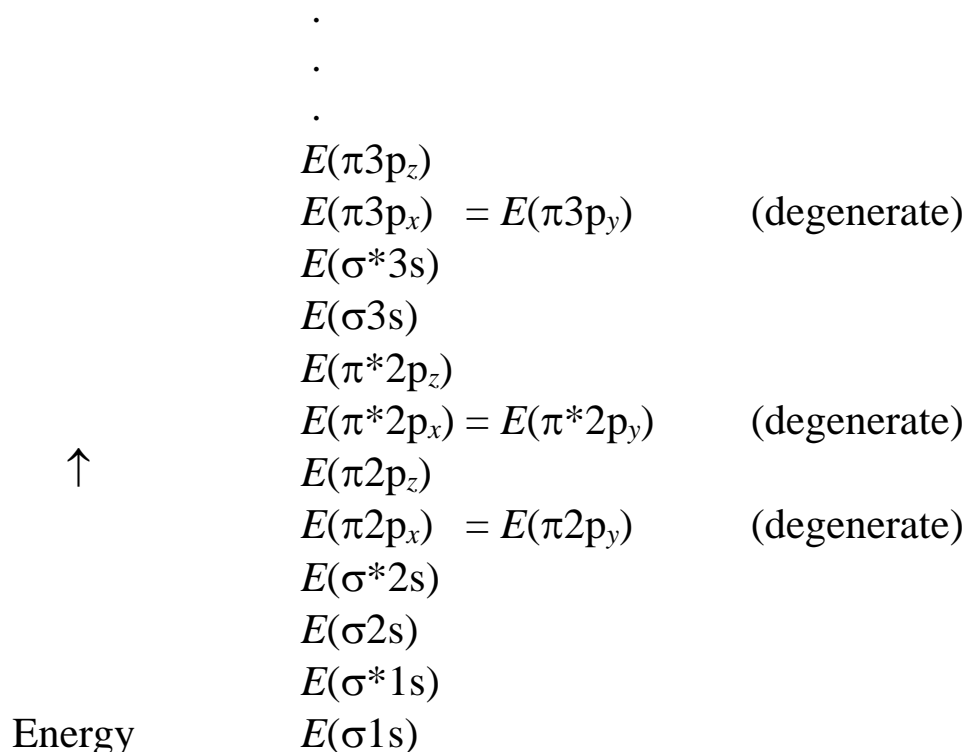
The linear combination of two 1s orbitals gave us:

a **bonding** σ_{1s} molecular orbital

a higher energy **antibonding** σ^*_{1s} molecular orbital

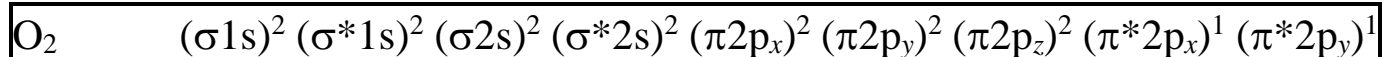
To carry out more accurate calculations on H_2^+ and H_2 , and to extend the treatment to more complicated diatomic molecules, all we have to do is repeat the calculations using additional orbitals: 2s, $2p_x$, $2p_y$, $2p_z$, 3s, ...

This approach leads to the molecular energy levels for diatomics (The bond is along the z axis. * denotes an antibonding molecular orbital.):



Molecular Orbital (MO) Theory Correctly Predicts that Oxygen Molecules are Paramagnetic

According to MO theory, the ground-state electron configuration of an oxygen molecule (16 electrons) is:



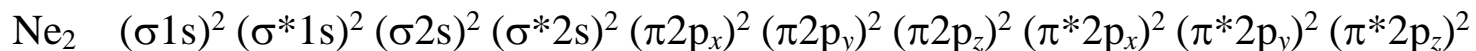
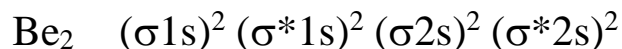
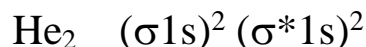
Hund's rule #1, which also applies to molecules, tells us that the $\pi^* 2p_x$ and $\pi^* 2p_y$ molecular orbitals are occupied by one unpaired electron each, with parallel spins, so an oxygen molecule has net electron spin and is paramagnetic.

Magnetic sensors are used to monitor oxygen levels.

Molecular Orbital (MO) Theory Correctly Predicts that He₂, Be₂, Ne₂, etc. Do Not Exist

Another test of MO theory:

The predicted ground-state electron configuration of molecules formed by filled-shell atoms are:



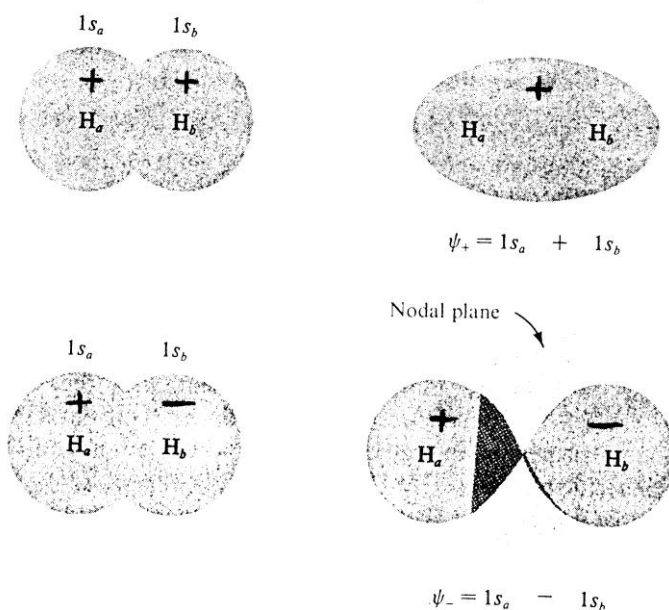
and so on. These molecules do not have a net excess of bonding electrons and are therefore predicted to be **unstable**. Consistent with this prediction, He₂, Be₂, Ne₂, etc. have never been detected by spectroscopists

What do molecular orbitals “look like”?

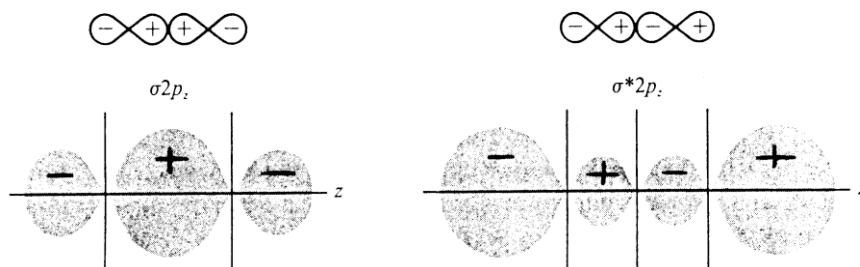
Linear combinations of two 1s atomic orbitals give:

the bonding σ_{1s} (or $\sigma_g 1s$) molecular orbital

the antibonding σ^*_{1s} (or $\sigma_u 1s$) molecular orbital



Linear combinations of two $2p_z$ atomic orbitals to give the bonding σ_{2p_z} (or $\sigma_g 2p_z$) molecular orbital and the antibonding $\sigma^*_{2p_z}$ (or $\sigma_u 2p_z$) molecular orbital:



Linear combinations of two $2p_x$ atomic orbitals to give the bonding $\pi 2p_x$ (or $\pi_u 2p_x$) molecular orbital and the antibonding $\pi^* 2p_x$ (or $\pi_g 2p_x$) molecular orbital

What do the σ and π symbols mean?

Historically, chemists have used the notation σ , π , δ , ... to denote **the number of nodes in the bonding orbital**.

Atomic Orbitals	m	nodal planes in bonding orbital	designation
s	0	0	σ
p_z	0	0	σ
p_x or p_y	± 1	1	π
d_{zx} or d_{zy}	± 1	1	π
$d_{x^2-y^2}$	± 2	2	δ
d_{xy}	± 2	2	δ

What do the Asterisks Mean?

As the internuclear distances decreases from infinity, the energy of **bonding orbitals** becomes negative and passes through a minimum (stable configuration).

Antibonding orbitals have positive energy (relative to the constituent atoms at infinite separation) and no stable minima. They are indicated by an asterisk *.

Nomenclature for Molecular Orbitals

Simple LCAO-MO		SCF-LCAO-MO
$\sigma 1s$	$\sigma_g 1s$	$1\sigma_g$
$\sigma^* 1s$	$\sigma_u 1s$	$1\sigma_u$
$\sigma 2s$	$\sigma_g 2s$	$2\sigma_g$
$\sigma^* 2s$	$\sigma_u 2s$	$2\sigma_u$
$\pi 2p_x$	$\pi_u 2p_x$	$1\pi_u$
$\pi 2p_y$	$\pi_u 2p_y$	$1\pi_u$
$\sigma 2p_z$	$\sigma_g 2p_z$	$3\sigma_g$
$\pi^* 2p_x$	$\pi_g 2p_x$	$1\pi_g$
$\pi^* 2p_y$	$\pi_g 2p_y$	$1\pi_g$
$\sigma^* 2p_z$	$\sigma_u 2p_z$	$3\sigma_u$

In the self-consistent field LCAO calculations, linear combinations of many atomic orbitals are used, and the electron density is “smeared out” to give a symmetrical charge density to estimate the screening of electrons from the nuclear charge. In this case, orbitals such as $\pi 2p_x$ and $\pi 2p_y$ lose their meaning and are lumped together as $1\pi_u$ orbitals in SCF-LCAO nomenclature.

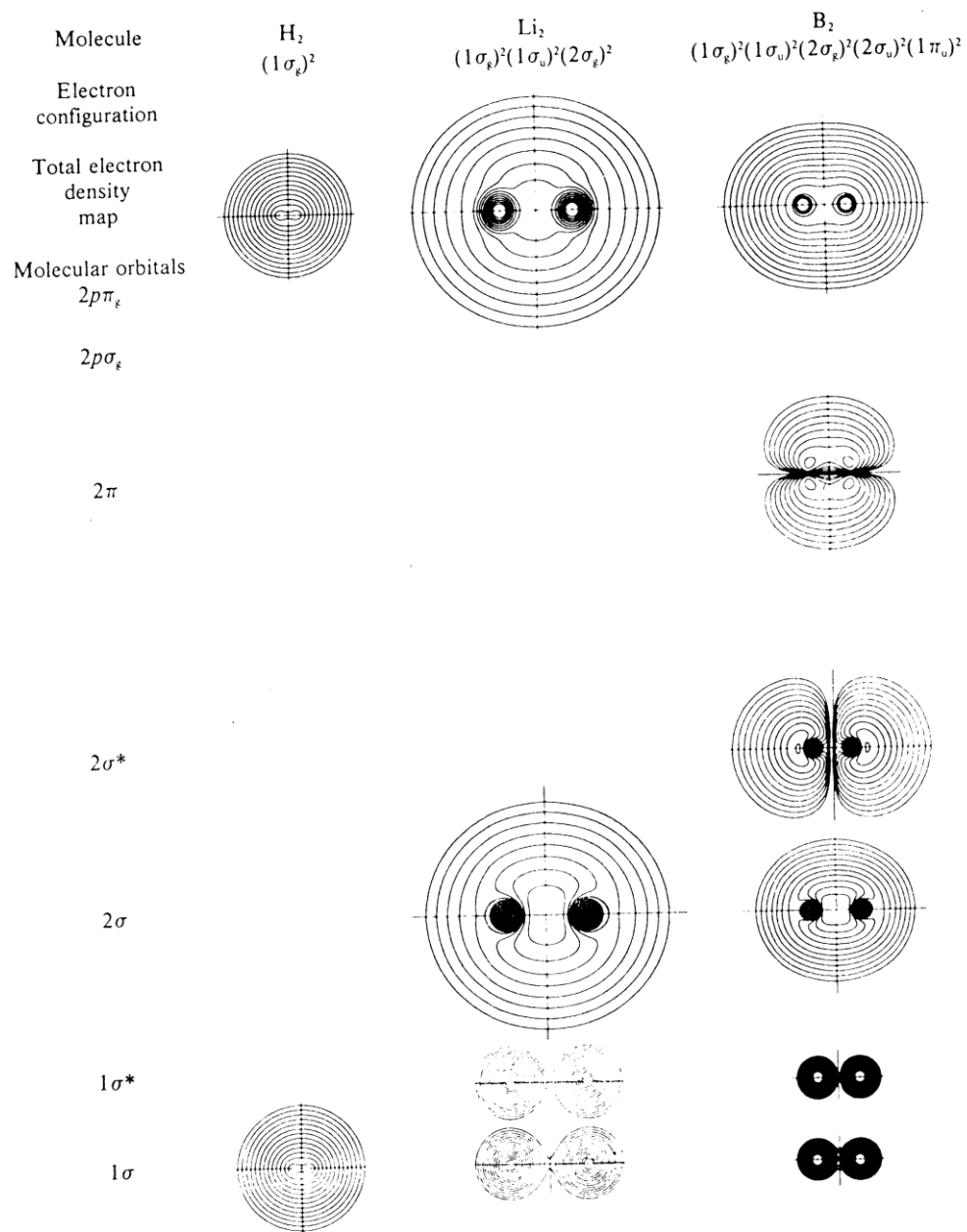
Homonuclear Diatomic Molecules, LCAO Configurations

molecule	no. of electrons	Ground-state electronic configuration LCAO	
H ₂ ⁺	1	(σ1s) ¹	
H ₂	2	(σ1s) ²	
He ₂ ⁺	3	(σ1s) ² (σ*1s) ¹	
He ₂	4	(σ1s) ² (σ*1s) ²	← (<i>not observed</i>)
Li ₂	6	(σ1s) ² (σ*1s) ² (σ2s) ²	
Be ₂	8	(σ1s) ² (σ*1s) ² (σ2s) ² (σ*2s) ²	← (<i>not observed</i>)
B ₂	10	(σ1s) ² (σ*1s) ² (σ2s) ² (σ*2s) ² (π2p) ²	
C ₂	12	(σ1s) ² (σ*1s) ² (σ2s) ² (σ*2s) ² (π2p) ⁴	
N ₂	14	(σ1s) ² (σ*1s) ² (σ2s) ² (σ*2s) ² (π2p) ⁴ (σ2p _z) ²	
O ₂	16	(σ1s) ² (σ*1s) ² (σ2s) ² (σ*2s) ² (π2p) ⁴ (σ2p _z) ² (π*2p) ²	
F ₂	18	(σ1s) ² (σ*1s) ² (σ2s) ² (σ*2s) ² (π2p) ⁴ (σ2p _z) ² (π*2p) ⁴	
Ne ₂	20	(σ1s) ² (σ*1s) ² (σ2s) ² (σ*2s) ² (π2p) ⁴ (σ2p _z) ² (π*2p) ⁴ (σ*2p _z) ²	← (")

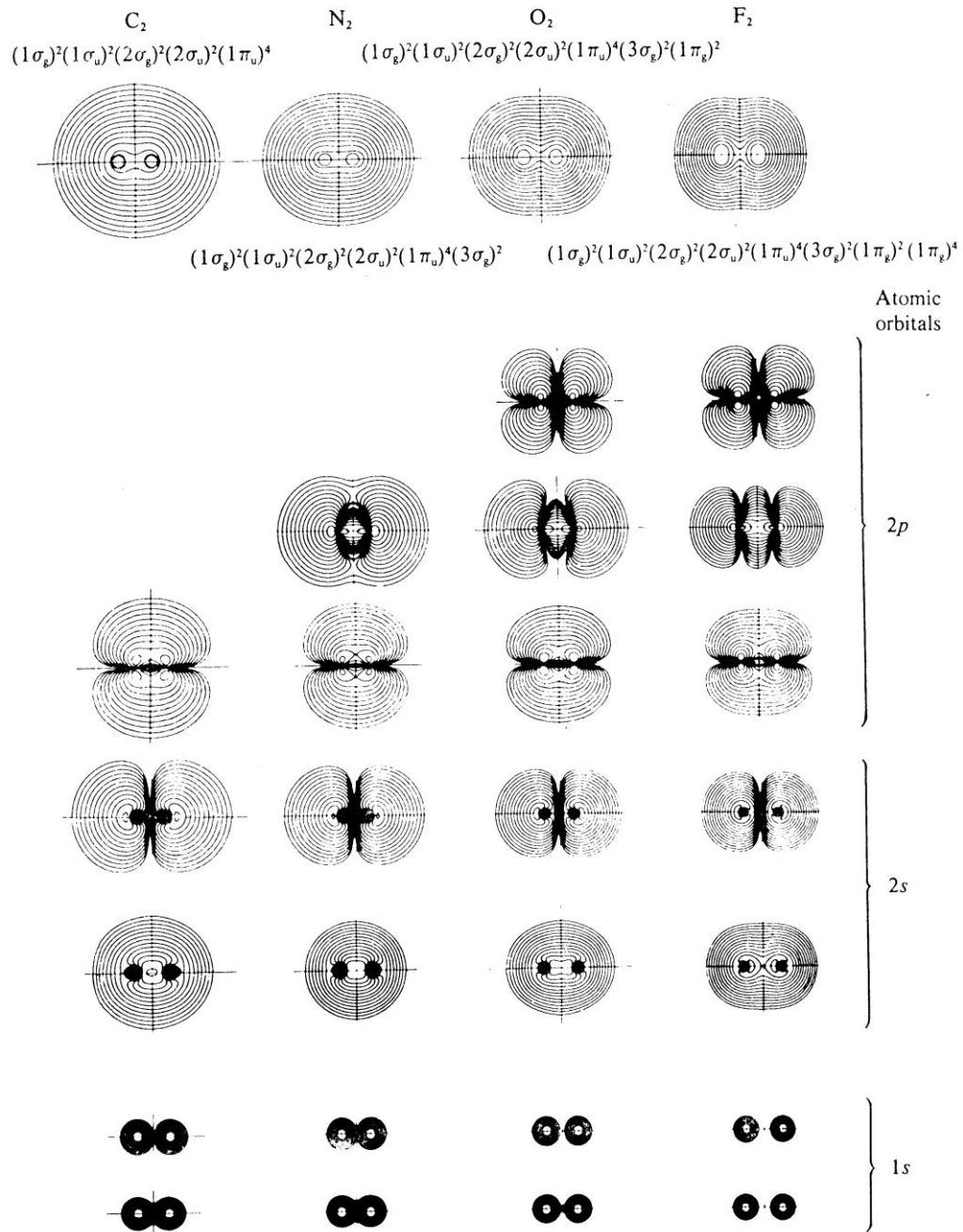
Homonuclear Diatomic Molecules, SCF-LCAO Configurations

molecule	no. of electrons	Ground-state electronic configuration SCF-LCAO	
H ₂ ⁺	1	(1σ _g) ¹	
H ₂	2	(1σ _g) ²	
He ₂ ⁺	3	(1σ _g) ² (1σ _u) ¹	
He ₂	4	(1σ _g) ² (1σ _u) ²	← (<i>not observed</i>)
Li ₂	6	(1σ _g) ² (1σ _u) ² (2σ _g) ²	
Be ₂	8	(1σ _g) ² (1σ _u) ² (2σ _g) ² (2σ _u) ²	← (<i>not observed</i>)
B ₂	10	(1σ _g) ² (1σ _u) ² (2σ _g) ² (2σ _u) ² (1π _u) ²	
C ₂	12	(1σ _g) ² (1σ _u) ² (2σ _g) ² (2σ _u) ² (1π _u) ⁴	
N ₂	14	(1σ _g) ² (1σ _u) ² (2σ _g) ² (2σ _u) ² (1π _u) ⁴ (3σ _g) ²	
O ₂	16	(1σ _g) ² (1σ _u) ² (2σ _g) ² (2σ _u) ² (1π _u) ⁴ (3σ _g) ² (1π _g) ²	
F ₂	18	(1σ _g) ² (1σ _u) ² (2σ _g) ² (2σ _u) ² (1π _u) ⁴ (3σ _g) ² (1π _g) ⁴	
Ne ₂	20	(1σ _g) ² (1σ _u) ² (2σ _g) ² (2σ _u) ² (1π _u) ⁴ (3σ _g) ² (1π _g) ⁴ (3σ _u) ²	← (")

Electron Density Contour Diagrams



Electron Density Contour Diagrams



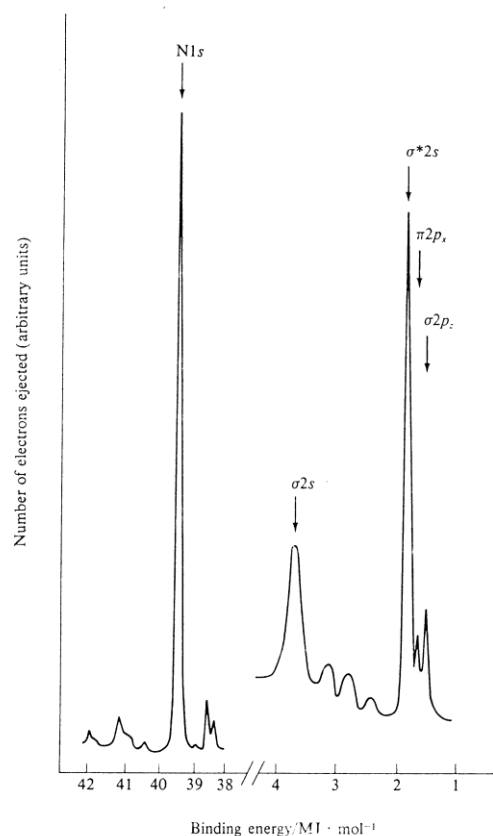
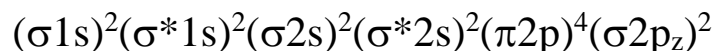
Orbital energies can be measured by photoelectron spectroscopy!

Atomic and molecular orbitals are abstract, nonclassical, and might appear to be far from reality.

But atomic and molecular orbital energies can be measured experimentally!

A beam of high energy electromagnetic radiation, usually X-rays, of variable wavelength is passed through a sample of gas-phase atoms or molecules. When the photon energy $h\nu$ matches the ionization energy of an electron in an orbital, some of those photons are absorbed and the appropriate electron is ejected, which produces a measurable electric current through a collection electrode.

Photoelectron Spectrum of N₂ Molecules



The Electronic States of Diatomic Molecules are Described by Molecular Term Symbols

The electronic states of atoms are designated by atomic term symbols.

To determine the analogous term symbols for diatomic molecules, the magnetic quantum numbers for the z -component of the orbital angular momentum of each electron are simply added:

$$M_L = m_{\ell 1} + m_{\ell 2} + m_{\ell 3} + \dots + m_{\ell N}$$

for the N electrons. m_{ℓ} is zero for a σ orbital, ± 1 for a π orbital, ± 2 for a δ orbital, ...

Then M_S is calculated by adding the quantum numbers for the electron spin along the z axis.

$$M_S = m_{s1} + m_{s2} + m_{s3} + \dots + m_{sN}$$

The possible values of M_L and M_S are arranged in a table to find the quantum number S for the total spin angular moment to arrive at the molecular term symbol

$$^{2S+1}|M_L|$$

with upper case Greek letters corresponding to S, P, D, F, ...

$ M_L $	Greek Letter
0	Σ
1	Π
2	Δ
3	Φ

Example 1. What is the molecular term symbol for the H_2 molecule?

The electronic configuration is $(1\sigma_g)^2$ and so $m_{\ell_1} = m_{\ell_2} = 0$ and $M_L = 0$. The electron spins must be in opposite direction according to the exclusion principle, and so $M_S = 0$. This is a singlet Sigma state:

$${}^1\Sigma$$

Example 2. What is the molecular term symbol for the He_2^+ molecular ion?

The electronic configuration is $(1\sigma_g)^2(1\sigma_u)^1$. In this case, $m_{\ell_1} = m_{\ell_2} = m_{\ell_3} = 0$ which gives $M_L = 0$ and another Sigma state. The first two electrons in the filled $1\sigma_g$ orbital must have opposite spins, which cancel each other. The third electron in the $1\sigma_u$ orbital can be spin up or spin down: $m_{s_3} = 1/2$ or $m_{s_3} = -1/2$. This gives $M_S = \pm 1/2$ corresponding to the projection of electron spin with quantum number $S = 1/2$ and spin multiplicity $2S + 1 = 2$ (a doublet).

$${}^2\Sigma$$

Example 3. What is the molecular term symbol for the C_2 molecule?

The electronic configuration is $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^4$. All of the electrons are paired, so $M_S = 0$. The 8 electrons in the σ orbitals have $m_{\ell_1} = m_{\ell_2} = \dots = m_{\ell_8} = 0$. The remaining 4 electrons in the π orbital have $m_{\ell} = 1, -1, 1, -1$ for a total $M_L = 0$. This is a singlet Sigma state.

$${}^1\Sigma$$

Example 4. What is the molecular term symbol for the B_2 molecule?

In this case, the electronic configuration is $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^2$.

All of the electrons are paired, except for the unpaired $(1\pi_u)^2$ electrons (corresponding to an electron in a $\pi 2p_x$ orbital and another electron in a $\pi 2p_y$ orbital). Each of these electrons can have m_ℓ values of ± 1 and m_s values of $\pm 1/2$. The following table can be constructed to summarize the number of different combinations of magnetic and spin quantum numbers for the z -component of the angular momentum.

	$m_{\ell 1}$	m_{s1}	$m_{\ell 2}$	m_{s2}	M_L	M_S
	1	+1/2	1	+1/2*		
1.	1	+1/2	1	-1/2	2	0
	1	-1/2	1	+1/2**		
2.	1	+1/2	-1	+1/2	0	1
3.	1	+1/2	-1	-1/2	0	0
4.	1	-1/2	-1	+1/2	0	0
5.	1	-1/2	-1	-1/2	0	-1
6.	-1	+1/2	-1	-1/2	-2	0

*not allowed, exclusion principle

**not allowed, electrons 1 and 2 are indistinguishable

An equivalent way of writing out the six possible arrangements is:

$m = 1$	$\uparrow\downarrow$	\uparrow	\uparrow	\downarrow	\downarrow	—
$m = -1$	—	\uparrow	\downarrow	\uparrow	\downarrow	$\uparrow\downarrow$

Entries number 1 and 6 in the table have $|M_L| = 2$ and $M_S = 0$. This is a singlet Delta state: ${}^1\Delta$.

Entries 2, 3, and 5 have $M_L = 0$ (Sigma state) and M_S values of $-1, 0, 1$. Recalling that

$$-S \leq M_S \leq S$$

these entries indicate a triplet ($S = 1$) Sigma state: ${}^3\Sigma$

The remaining entry (no. 4) has $M_L = 0$ and $M_S = 0$. This is a singlet Sigma state: ${}^1\Sigma$.

In summary, the **term symbols for the ground-state B₂ molecule are:** ${}^1\Delta, {}^3\Sigma, {}^1\Sigma$.

Hund's rules apply ($Z < 40$), so the triplet Sigma state (with the largest spin multiplicity) will have the lowest energy. For the two singlets, the Delta state (larger L) will have the lower energy. The energies of the states increase in the order

$${}^3\Sigma < {}^1\Delta < {}^1\Sigma$$

Molecular Structure Prediction

Hartree-Fock calculations have been carried out for a large number of molecules. Ground-state molecular geometries (bond lengths, bond angles) can be calculated to a high degree of accuracy for small molecules.

The bond lengths and bond angles are usually reliable to within a few picometers (10^{-12} m) and a degree or two. The results are impressive considering that *no empirical parameters are used*. These kinds of calculations are called ***ab initio* calculations**.

A wide range of Hartree-Fock calculations have been reported. Some studies employ small sets of basis functions to approximate the molecular orbitals and do not actually reach self consistency. More reliable calculations employ large basis sets of functions or solve the Schrödinger equations numerically.

Hartree-Fock calculations can be improved by using perturbation methods (and other techniques) to represent electron-electron interactions more accurately than using average electron distributions. The additional electron-electron interaction energy not described by using the SCF approximation is called **electron correlation**.

Current topics of interest:

- ◆ protein structures
- ◆ base pair interactions in DNA
- ◆ substrate-enzyme structures
- ◆ transition metal complexes and catalysts
- ◆ excited molecular states and free radicals
- ◆ molecular collisions and dynamics
- ◆ transition states and chemical reactions

Comparison of Measured and Predicted Molecular Structures

(bond lengths in pm, bond angles in degrees)

molecule	geometrical parameter	Hartree-Fock	Improved Hartree-Fock	Experiment
H-H	$r(\text{HH})$	73.0	73.8	74.1
Li-Li	$r(\text{LiLi})$	280.7	277.2	267
Li-H	$r(\text{LiH})$	163.6	164.0	159.5
Li-F	$r(\text{LiF})$	156.6	157.0	156.4
O=O	$r(\text{OO})$	116.8	124.5	120.7
HC≡CH	$r(\text{CC})$	118.5	121.7	120.3
	$r(\text{CH})$	105.7	106.3	106.1
H-C-H	$r(\text{CH})$	109.6	110.9	111.1
	$\angle(\text{HCH})$	103.0	102.1	102.4
CH ₄	$r(\text{CH})$	108.4	109.0	108.6
NH ₃	$r(\text{NH})$	100.2	101.7	101.2
	$\angle(\text{HNH})$	107.2	106.4	106.7
H-O-H	$r(\text{OH})$	94.7	96.9	95.9
	$\angle(\text{HOH})$	105.5	104.0	103.9
H-O-O-H	$r(\text{OO})$	139.3	146.7	147.5
	$r(\text{OH})$	94.9	97.6	95.0
	$\angle(\text{OOH})$	102.2	98.7	94.8
	$\angle(\text{HOOH})$	115.2	121.3	120.0

Valence Bond Methods

Almost all of the quantum mechanical calculations of the electronic structure of molecules use some form of molecular orbital theory.

When applied to large polyatomic molecules, the calculated electronic energy will depend on many different bond angles and bond lengths which must be adjusted to find the minimum energy. The minimization procedure becomes very-time consuming for complicated molecules with many electrons and nuclei.

Most chemists think about molecular structure in a different way in terms of **valence bond models** in which chemical bonds are viewed as pairing of electrons between atomic orbitals located on the bonded atoms = *ball and stick models!*

A valence bond can be formed by the pairing of unpaired electrons with opposite spin functions (**covalent bond**) or by the donation of an electron pair on one atom into an empty orbital on another atom (**coordinate covalent bond**). In both cases **the electrons are assumed to be localized between the bonded atoms**, rather than spread over the whole molecule in a molecular orbital.

Valence bond models are based on the idea that a chemical bond is formed when there is good overlap between the atomic orbitals of the participating atoms.

They provide convenient approximations to help understand bonding, but are not used in quantitative quantum chemistry calculations

Valence-bond models are based on the assumption of “perfect pairing”. There are four steps in the preparation of a wave function for a valence bond:

Step 1

Form a set of atomic orbitals on each atom into which the bonding pair of electrons will be placed. The set of atomic orbitals on each atom can be a single orbital (*e.g.*, 2s) or a linear combination of atomic orbitals (*e.g.*, $c_1 2s + c_2 2p_z$). In the Heitler-London treatment of the H₂ molecule, for example, 1s orbitals on each H atom were used.

Let φ_A and φ_B be the atomic orbitals chosen for atoms A and B.

Step 2

Spin atomic orbitals are formed so the electrons bonding the atoms have paired spins ($\uparrow\downarrow$).

There are two possible choices:

$$\varphi_A\alpha \text{ and } \varphi_B\beta \qquad \text{or} \qquad \varphi_A\beta \text{ and } \varphi_B\alpha$$

Step 3

Next, **Slater determinants of the atomic spin orbitals** are constructed for each of the two choices

$$D_1 = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_A(1)\alpha(1) & \varphi_A(2)\alpha(2) \\ \varphi_B(1)\beta(1) & \varphi_B(2)\beta(2) \end{vmatrix} \qquad D_2 = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_A\beta(1) & \varphi_A\beta(2) \\ \varphi_B\alpha(1) & \varphi_B\alpha(2) \end{vmatrix}$$

to form all possible combinations of the spin orbitals.

Step 4

The final step, the two determinant functions are combined to give the valence bond wave functions

$$\psi_1^{\text{VB}} = \frac{1}{\sqrt{2}}(D_1 - D_2)$$

$$\psi_2^{\text{VB}} = \frac{1}{\sqrt{2}}(D_1 + D_2)$$

Multiplying out the determinants gives the following expressions for the valence bond wave functions

$$\psi_1^{\text{VB}} = \frac{1}{\sqrt{2}}[\varphi_A(1)\varphi_B(2) + \varphi_B(1)\varphi_A(2)][\alpha(1)\beta(2) - \beta(1)\alpha(2)] \quad \text{bonding}$$

$$\psi_2^{\text{VB}} = \frac{1}{\sqrt{2}}[\varphi_A(1)\varphi_B(2) - \varphi_B(1)\varphi_A(2)][\alpha(1)\beta(2) + \beta(1)\alpha(2)] \quad \text{no bond (node)}$$

A few points to notice:

- a) ψ_1^{VB} and ψ_2^{VB} are both antisymmetric with respect to the interchange of electrons 1 and 2, as required by the exclusion principle. ψ_1^{VB} is the product of a symmetric spatial function and an antisymmetric spin function, and *vice versa* for ψ_2^{VB} .
- b) As a consequence of the minus sign in the spatial function ψ_2^{VB} has a node (zero electron density) along the z -axis between atoms A and B. ψ_2^{VB} is therefore a “no bond” wave function representing an excited state.
- c) ψ_1^{VB} is the bonding wave function (no node along the bonding z -axis).

What's the Difference Between Molecular Orbital and Valence Bond Models?

Valence Bond Model of the H₂ Molecule

To apply the valence bond model to the ground-state hydrogen molecule, we used 1s orbitals on each H atom

$$\varphi_A = 1s_A \quad \varphi_B = 1s_B$$

and the wave function for the H-H bond is

$$\psi_1^{\text{VB}} = \frac{1}{\sqrt{2}} [1s_A(1)1s_B(2) + 1s_B(1)1s_A(2)] [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

LCAO Molecular Orbital Model of the H₂ Molecule

To apply the molecular orbital model to the ground-state hydrogen molecule, we also use 1s orbitals on each H atom, but now we use **Slater functions of linear combinations of the atomic orbitals**. The electrons are assumed to be “free” to roam the entire molecule.

For the bonding MO (spatially symmetric wave function), we obtain:

$$\begin{aligned} \psi_1^{\text{MO}} &= \frac{1}{\sqrt{2}} \begin{vmatrix} [1s_A(1) + 1s_B(1)]\alpha(1) & [1s_A(2) + 1s_B(2)]\alpha(2) \\ [1s_A(1) + 1s_B(1)]\beta(1) & [1s_A(2) + 1s_B(2)]\beta(2) \end{vmatrix} \\ &= \frac{1}{\sqrt{2}} [1s_A(1) + 1s_B(1)] [1s_A(2) + 1s_B(2)] [\alpha(1)\beta(2) - \beta(1)\alpha(2)] \end{aligned}$$

$$= \frac{1}{\sqrt{2}} [1s_A(1)1s_B(2) + 1s_B(1)1s_A(2)] [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

$$+ \frac{1}{\sqrt{2}} [1s_A(1)1s_A(2) + 1s_B(1)1s_B(2)] [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

Comparing the valence bond and LCAO-MO wave functions

$$\psi_1^{\text{MO}} = \psi_1^{\text{VB}} + \frac{1}{\sqrt{2}} [1s_A(1)1s_A(2) + 1s_B(1)1s_B(2)] [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

shows the LCAO-MO contains extra terms representing ionic states where both electrons are on atom A or on atom B. Ionic states are important for molecules such as LiF which are formed from atoms with widely different electronegativities.

[The Linear BeH₂ Molecule and Valence Bond sp Hybrid Orbitals](#)

Adding the concept of hybrid orbitals (linear combinations of atomic orbitals on the *same* atom) to valence bond theory vastly increases the number of molecular structures that can be rationalized.

For example, experiments show that beryllium and hydrogen form the stable compound BeH₂. Spectroscopic measurements indicate a linear molecule with the structure H–Be–H (*i.e.*, the HBeH bond angle is 180°).

Question. How can Be atoms with the filled-shell electronic configuration (1s)²(2s)² form bonds with two hydrogen atoms with electronic configuration (1s)¹?

Answer. A 2s electron in the Be atom is promoted to a 2p orbital. The remaining 2s electron and the promoted 2p electron to form two hybrid (*i.e.*, mixed) sp orbitals for bonding with two H atoms.

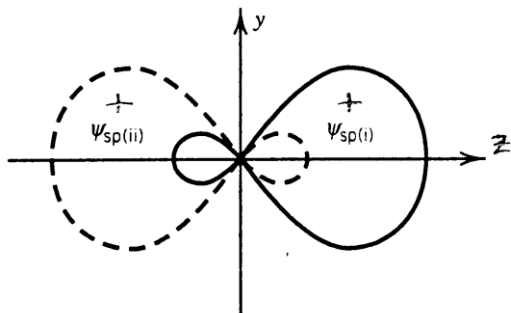
Energy is of course required to excite a 2s electron into a 2p orbital, but this energy is more than recovered by the formation of two Be–H bonds.

The two sp orbitals are formed by taking linear combinations of the atomic 2s and 2p orbitals on beryllium. For bonding along the z-axis, we use the 2p_z orbital.

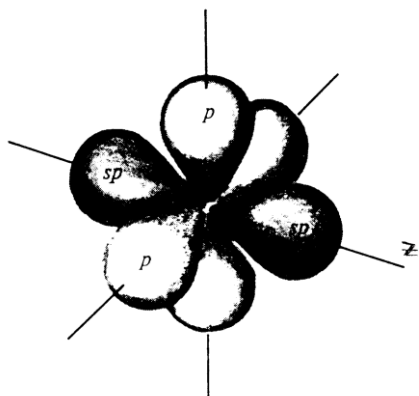
$$\varphi_{A(i)} = \frac{1}{\sqrt{2}}(2s + 2p_z)$$

$$\varphi_{A(ii)} = \frac{1}{\sqrt{2}}(2s - 2p_z)$$

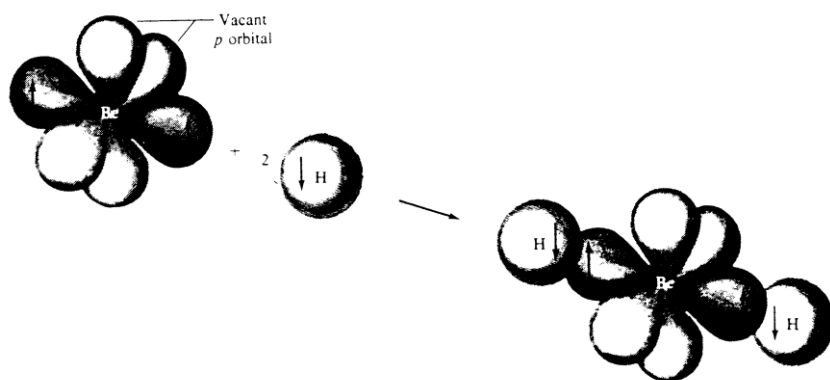
The 2p_z orbital is positive for $z > 0$ and negative for $z < 0$, whereas the 2s orbital is spherically symmetric. This means that the $\varphi_{A(i)}$ hybrid orbital will be positive for $z > 0$ to overlap favorably with the 1s orbital of a hydrogen atom, and the $\varphi_{A(ii)}$ hybrid orbital will be positive for $z < 0$ to overlap with the other hydrogen atom to form a stable BeH₂ molecule, and give the correct 180° HBeH bond angle!



Electron Density for sp Hybrid Orbitals



Formation of BeH_2 (the p_x and p_y orbitals are vacant)



The Planar BH₃ Molecule and Bond sp² Hybrid Orbitals

Boron, with the electronic configuration (1s)²(2s)²(2p)¹ and a single unpaired electron, might be expected to form the stable molecule BH. And it does!

More interestingly, boron and hydrogen also form the stable compound BH₃. Spectroscopic measurements indicate a planar molecule with HBH bond angles of 120°. How can this be rationalized?

B atoms with the electronic configuration (1s)²(2s)²(2p)¹ can form bonds with three hydrogen atoms by promoting a 2s electron to a 2p orbital to form three sp² hybrid orbitals for bonding with two H atoms.

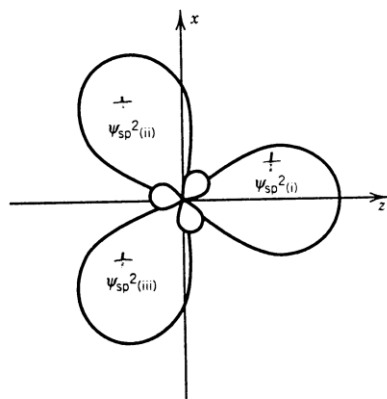
The three sp² orbitals are formed by taking linear combinations of the atomic 2s and the two 2p orbitals on boron.

$$\varphi_{A(i)} = \frac{1}{\sqrt{3}} \left(2s + \sqrt{2} 2p_z \right)$$

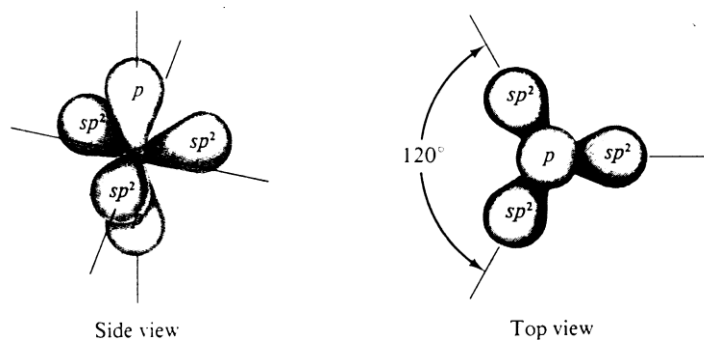
$$\varphi_{A(ii)} = \frac{1}{\sqrt{3}} \left(2s - \frac{1}{\sqrt{2}} 2p_z + \frac{\sqrt{3}}{\sqrt{2}} 2p_x \right)$$

$$\varphi_{A(iii)} = \frac{1}{\sqrt{3}} \left(2s - \frac{1}{\sqrt{2}} 2p_z - \frac{\sqrt{3}}{\sqrt{2}} 2p_x \right)$$

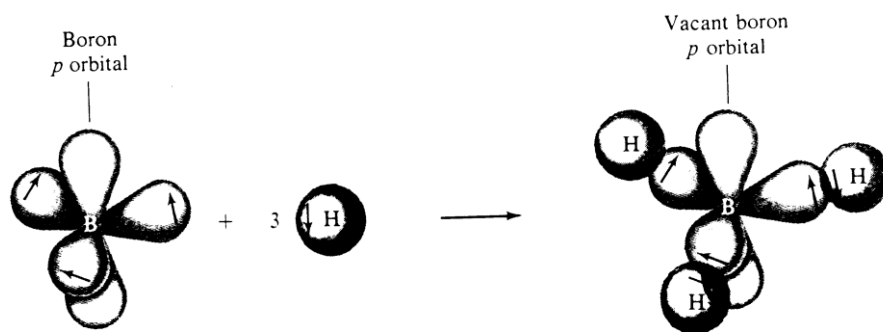
The three hybrid orbitals constructed in this manner lie in the *x-z* plane with lobes pointing in directions separated by 120°.



Electron Density of sp^2 Hybrid Orbitals



Formation of BH_3



Extending these ideas, sp^3 can be used to rationalize the tetrahedral structure of CH_4 and the approximately tetrahedral structure of ammonia (three N–H bonds plus a nonbonding “lone pair” of electrons) and water (two O–H bonds and two lone pairs), and many other bonding geometries.

Hückel Molecular Orbital Theory

Molecular orbital theory is a triumph of modern science, providing accurate properties of molecules calculated *ab initio* (from *first principles*, without empirical parameters). As computers continue to become faster and more powerful, MO calculations are becoming routine, but are still time consuming, especially for large molecules with many bond angles and bond lengths to be optimized.

Valence bond theory provides a much simpler description of chemical bonding. Though only qualitative, VB models are very useful in practice because they do not require long, complicated computer calculations.

Molecules with extensive π -bonding systems, such as benzene and many other important molecules, are not described very well by valence bond methods.

Why?

Hückel developed a variation of MO theory for π -bonded molecules. Though approximate, Hückel methods are very useful in practice, mostly in organic chemistry, because the calculations are relatively simple. As a bonus, valuable information about excited states is provided.

In addition, Hückel theory is a good example of **semi-empirical quantum mechanical methods**. Instead of trying to calculate everything from first principles (can be very time consuming), spectroscopy and other experimental methods are used to evaluate some of the energy terms and other molecular properties that are difficult to calculate.

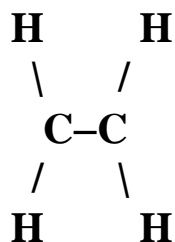
In Hückel MO theory, the key assumptions are:

1. sp^2 hybridization on carbon and the resulting C–C and C–H σ bonding (no nodes on the bond axis) provides the molecular framework.
2. The remaining p_z orbitals provide the π bonding (one node on the bond axis), superimposed on the sigma C–C bonds to form double C=C bonds.

Hückel Theory for Ethylene ($\text{H}_2\text{C}=\text{CH}_2$)

Ethylene illustrates the simplest application of Hückel theory. Both carbon atoms are assumed to be sp^2 hybridized, resembling the planar BH_3 molecule discussed previously.

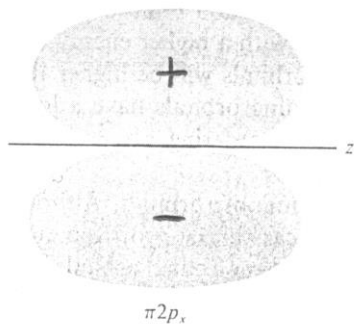
sp^2 hybridization in ethylene provides the sigma C–H bonds and the sigma C–C bond between the carbon atoms:



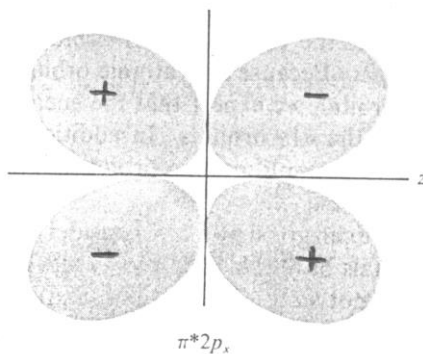
sigma bonds in ethylene

The double C=C bond is produced by the additional overlap of the third remaining 2p orbital on each carbon atom, perpendicular to the plane of the molecule:

π bond



nonbonding π orbital (more nodes)



The key feature of the Hückel model is the assumption that the π electrons, which are responsible for the special properties of conjugated and aromatic systems, do not interact with each other or with other electrons in the molecule.

For ethylene, the wave function for the π electrons is assumed to be a linear combination of the p_z orbitals on the two carbon atoms.

$$\psi = c_1 p_{z1} + c_2 p_{z2}$$

π Electron Energies Applying the variational principle, the calculated energy of the π electrons

$$E' = \frac{\int \psi^* \hat{H} \psi \, d\tau}{\int \psi^* \psi \, d\tau}$$

is minimized by setting $\partial E'/c_1$ and $\partial E'/c_2$ equal to zero. As we have seen before, the energy minimization leads to the secular equation

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = 0$$

With

$$H_{ik} = \int p_{zi}^* \hat{H} p_{zk} \, d\tau \qquad S_{ik} = \int p_{zi}^* p_{zk} \, d\tau$$

The following reasonable (*why?*) assumptions are made:

1. The overlap integrals S_{ik} are zero, unless $i = k$ and $S_{ii} = 1$ (complete overlap).
2. The **coulomb integrals** H_{ii} are assumed to be identical and are set equal to α .
3. The **exchange integrals** H_{ik} ($i \neq k$) are zero, except for those on neighboring atoms which are set equal to β .

In this context, notice that α and β are not spin states!

With these approximations, the secular equation simplifies considerably

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

which is equivalent to

$$E^2 - 2\alpha E + \alpha^2 - \beta^2 = 0$$

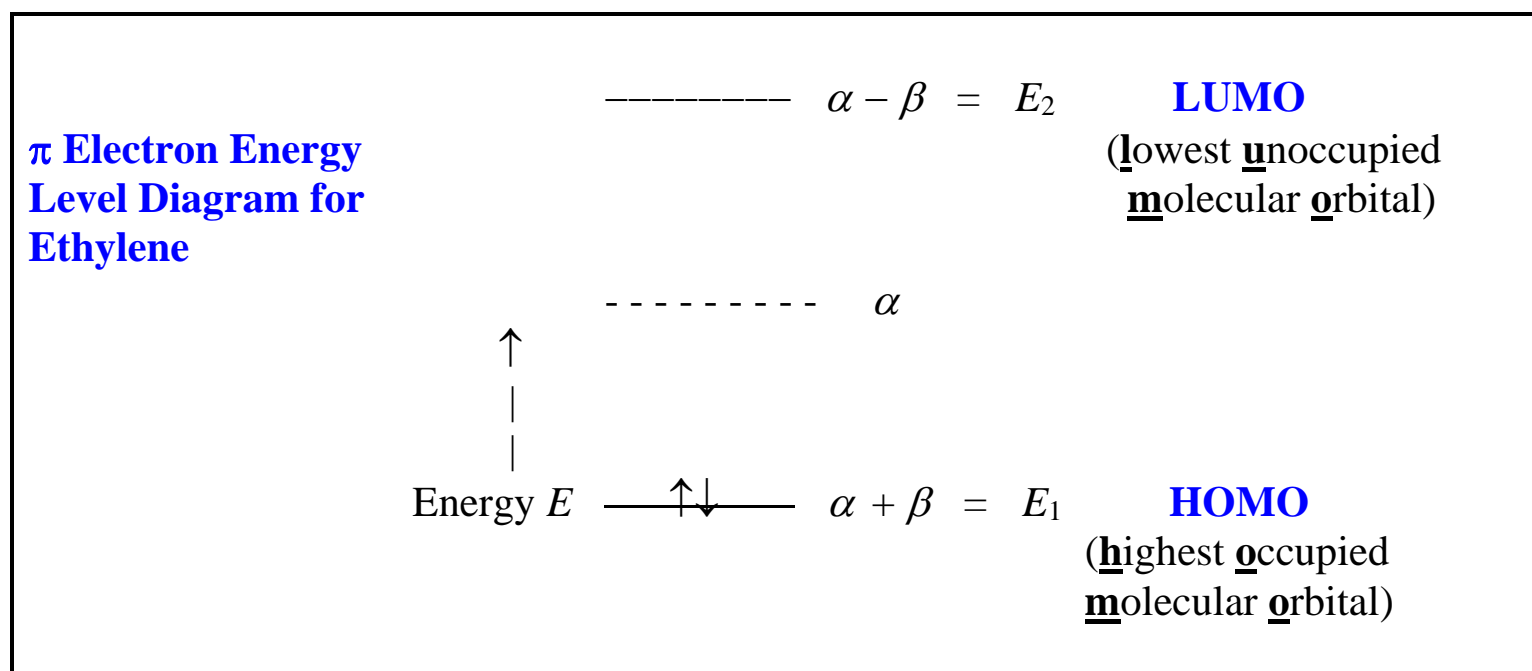
Solving the quadratic equation for the energy (*try it!*) gives

$$E = \alpha \pm \beta$$

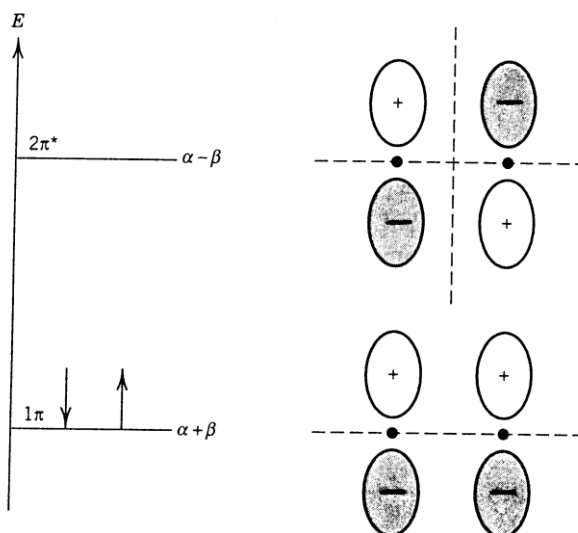
The usual practice is to evaluate α (the **coulomb integral**) and β (the **exchange integral**, $\approx -75 \text{ kJ mol}^{-1}$) empirically, from spectroscopic or calorimetric measurements. The exchange integral is negative (“stabilizing”), so the energy of the ground state is $\alpha + \beta$. The energy of the excited state is $\alpha - \beta$.

$$E_2 = E(\text{excited } \pi \text{ state}) = \alpha - \beta = \int p_{z1}^* \hat{H} p_{z1} d\tau - \int p_{z1}^* \hat{H} p_{z2} d\tau$$

$$E_1 = E(\text{ground } \pi \text{ state}) = \alpha + \beta = \int p_{z1}^* \hat{H} p_{z1} d\tau + \int p_{z1}^* \hat{H} p_{z2} d\tau$$



**Energy Levels for
the π Electrons
in Ethylene**



In the ground state ethylene molecule, the π electrons are in the lower energy and the total π electron energy is $2E_1 = 2(\alpha + \beta)$.

The energy difference between the ground level and the excited level is

$$E(\text{excited } \pi \text{ state}) - E(\text{ground } \pi \text{ state}) = E_2 - E_1 = -2\beta$$

-2β is about 150 kJ mol^{-1} , so ultraviolet photons are required to promote a π electron from the ground state to the excited state.

Bonding and Nonbonding Wave Functions The wave functions for the two energy levels can now be evaluated by solving the secular equation for c_1 and c_2 .

$$(\alpha - E)c_1 + \beta c_2 = 0$$

$$\beta c_1 + (\alpha - E)c_2 = 0$$

Substituting the lower energy $E = \alpha + \beta$ into either of these equations (*try it!*) gives $c_1 = c_2$ and the symmetric (gerade) wave function.

$$\psi_{1g} = \frac{1}{\sqrt{2}}(p_{z1} + p_{z2})$$

for the **bonding orbital**.

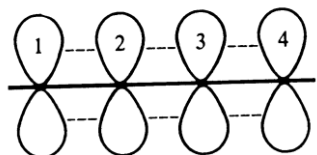
For the higher energy level, $E = \alpha - \beta$, we obtain $c_1 = -c_2$ and the asymmetric (ungerade) wave function

$$\psi_{1u} = \frac{1}{\sqrt{2}}(p_{z1} - p_{z2})$$

for the **nonbonding orbital**. Notice that these results are analogous to the LCAO energies obtained for the H_2^+ molecule ion. This is not accidental!

Hückel Theory for π electrons in Butadiene ($H_2C=CH-CH=CH_2$)

The application of Hückel to butadiene is more interesting. Although butadiene molecules have *cis* and *trans* configurations, we will treat the molecule as simply a linear sequence of four carbon atoms.



Each of the four carbon atoms contributes a π electron orbital. Proceeding as before, we write

$$\psi = c_1 p_{z1} + c_2 p_{z2} + c_3 p_{z3} + c_4 p_{z4}$$

for the wave equation for the π electrons. The secular equation is

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & H_{13} - ES_{13} & H_{14} - ES_{14} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & H_{23} - ES_{23} & H_{24} - ES_{24} \\ H_{31} - ES_{31} & H_{32} - ES_{32} & H_{33} - ES_{33} & H_{34} - ES_{34} \\ H_{41} - ES_{41} & H_{42} - ES_{42} & H_{43} - ES_{43} & H_{44} - ES_{44} \end{vmatrix} = 0$$

With the help of the Hückel approximations, the secular equation simplifies to

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

Dividing each row by β and defining $x = (\alpha - E)/\beta$ gives

$$\begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} = 0$$

which is equivalent to

$$x^4 - 3x^2 + 1 = 0$$

This equation is easily solved for x^2

$$x^2 = \frac{3 \pm \sqrt{5}}{2}$$

to obtain the four roots

$$x = \pm 0.61804, \pm 1.61804$$

Recalling that $x = (\alpha - E)/\beta$ and also that β is negative, we find

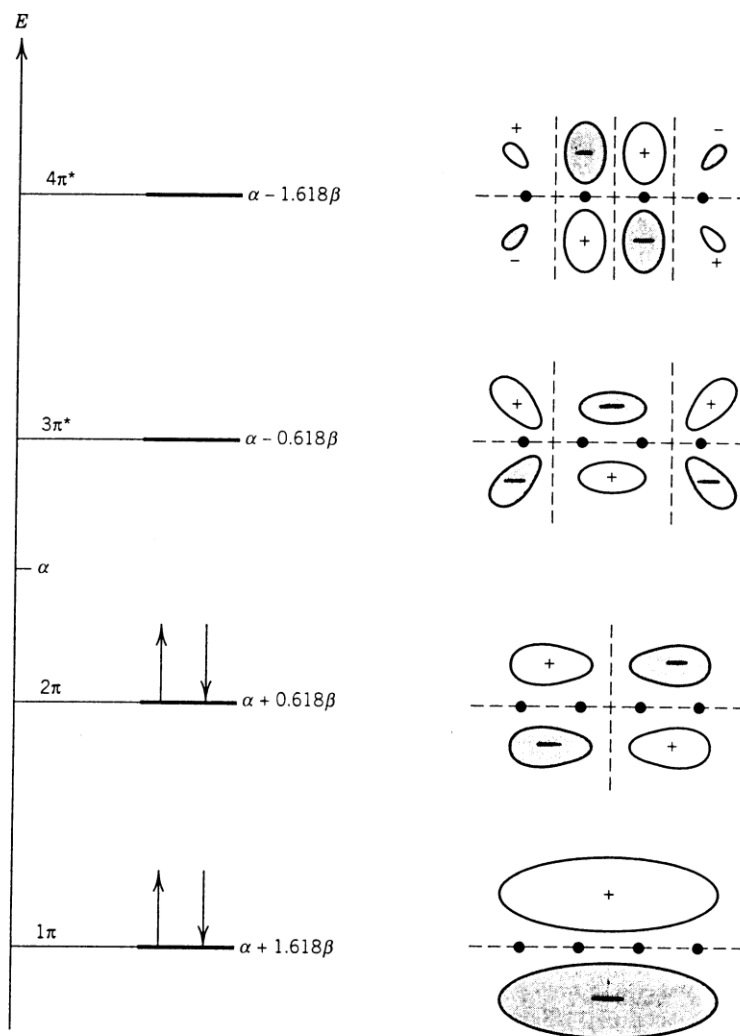
butadiene π electron energy levels

$$E_4 = \alpha - 1.618\beta \quad \text{highest energy}$$

$$E_3 = \alpha - 0.618\beta \quad \text{LUMO}$$

$$E_2 = \alpha + 0.618\beta \quad \text{HOMO}$$

$$E_1 = \alpha + 1.618\beta \quad \text{lowest energy}$$



In the ground-state butadiene molecule, the four π electrons fill the lowest two energy levels. The total π electron energy is $2E_1 + 2E_2 = 4\alpha + 4.472\beta$.

Notice that the energy difference between the ground level and the first excited level for butadiene is $E_3 - E_2 = -1.236\beta$ compared to -2β for ethylene, illustrating that the energy levels become closer together as the length of the molecule increases.

The particle in a box strikes again!

Delocalization Energy It is interesting to compare the energy of the butadiene π electrons to the energy of the localized structure in which the two double bonds are localized between carbon atoms 1 and 2 and between carbon atoms 3 and 4.

For the localized π bond in ethylene, the calculated energy for a single π electron is $\alpha + \beta$. Subtracting $4(\alpha + \beta)$ from the energy for butadiene energy gives

butadiene π delocalization energy

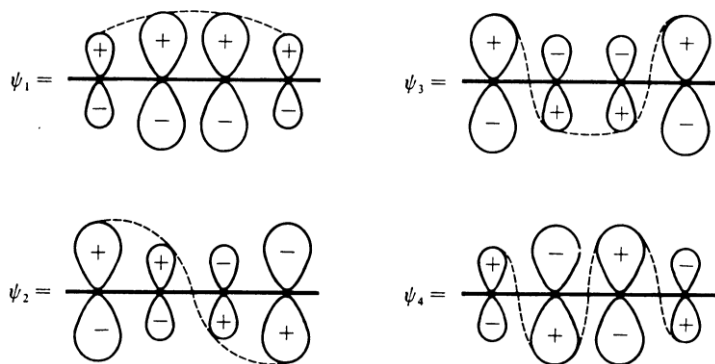
$$\begin{aligned} E_{\pi}(\text{butadiene}) - 2E_{\pi}(\text{ethylene}) &= 4\alpha + 4.472\beta - 4(\alpha + \beta) \\ &= 0.472\beta \\ &\approx -35 \text{ kJ mol}^{-1} \end{aligned}$$

Wave Functions The wave functions for the four energy levels can be evaluated by solving the secular equation for c_1 through c_4 and taking linear combinations of the p_z orbitals on carbon atoms $n = 1$ to $n = 4$.

$$\psi_i = \sum_{n=1}^4 c_{in} p_{zn}$$

	$\psi_4 = 0.3717 p_{z1} - 0.6015 p_{z2} + 0.6015 p_{z3} - 0.3717 p_{z4}$
LUMO	$\psi_3 = 0.6015 p_{z1} - 0.3717 p_{z2} - 0.3717 p_{z3} + 0.6015 p_{z4}$
HOMO	$\psi_2 = 0.6015 p_{z1} + 0.3717 p_{z2} - 0.3713 p_{z3} - 0.6015 p_{z4}$
ground state	$\psi_1 = 0.3717 p_{z1} + 0.6015 p_{z2} + 0.6015 p_{z3} + 0.3717 p_{z4}$

Notice that the number of nodes increases with the energy:



π Electron Density We have assumed no overlap of neighboring orbitals ($S_{ik} = 0$ for $i \neq k$), so the p_{zn} functions are orthonormal

$$\sum_{n=1}^4 c_{in}^2 = 1$$

The total π electron density on the n th carbon atom is therefore

$$q_n = \sum_{i=1}^4 n_i c_{in}^2$$

where n_i is the number of electrons in the i th orbital. The π electron density on the first carbon atom in butadiene is

$$\begin{aligned} q_1 &= 2c_{11}^2 + 2c_{21}^2 + (0)c_{31}^2 + (0)c_{41}^2 \\ &= 2(0.3717)^2 + 2(0.6015)^2 \\ &= 1.0000 \end{aligned}$$

The other q_n 's are also 1.0000, indicating that the π electrons are uniformly distributed over the butadiene molecule.

π Bond Order Another interesting quantity we can calculate is the π electron density between adjacent carbon atoms r and s .

$$P_{rs} = \sum_{i=1}^4 n_i c_{ir} c_{is}$$

Between carbon atoms 1 and 2, the π electron density is

$$\begin{aligned} P_{12} &= 2c_{11}c_{12} + 2c_{21}c_{22} + (0)c_{31}c_{32} + (0)c_{41}c_{42} \\ &= 2(0.3717)(0.6015) + 2(0.6015)(0.3717) \\ &= 0.8942 \end{aligned}$$

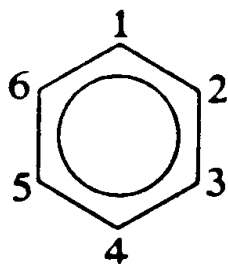
For comparison, the π electron density between carbon atoms 2 and 3 is

$$\begin{aligned}
 P_{23} &= 2c_{12}c_{13} + 2c_{22}c_{23} + (0)c_{32}c_{33} + (0)c_{42}c_{43} \quad \text{the We have} \\
 &= 2(0.6015)(0.6015) + 2(0.3717)(-0.3717) \\
 &= 0.4473
 \end{aligned}$$

This result shows that the π electrons in butadiene are not uniformly distributed and are more likely to be found between the outer two carbon atoms than the middle two carbon atoms.

Hückel Theory for Benzene

The benzene molecule has six carbon atoms in a ring.



The Hückel secular determinant for the π electrons in benzene is

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

Because benzene is cyclic, carbon atoms 1 and 6 are adjacent, so the 1,6 and 6,1 elements of the determinant are nonzero.

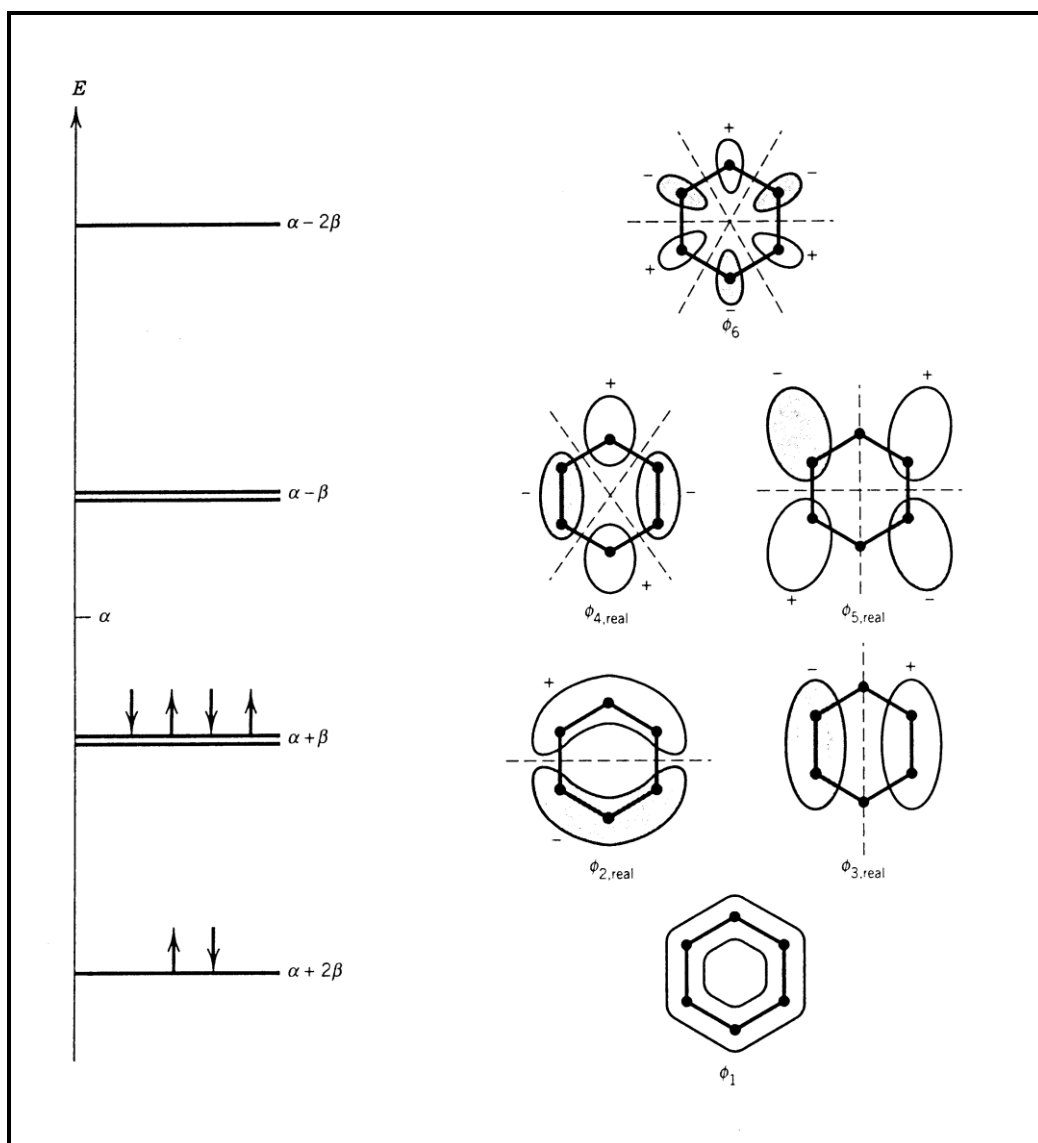
Solving the 6th degree polynomial for the energies gives four different energy levels, two of which are doubly degenerate:

$$E_6 = \alpha - 2\beta$$

$$E_4, E_5 = \alpha - \beta \quad (\text{LUMO, doubly degenerate})$$

$$E_2, E_3 = \alpha + \beta \quad (\text{HOMO, doubly degenerate})$$

$$E_1 = \alpha + 2\beta$$



Benzene Delocalization Energy The total π electronic energy in ground-state benzene is

$$\begin{aligned} 2E_1 + 2E_2 + 2E_3 &= 2(\alpha + 2\beta) + 2(\alpha + \beta) + 2(\alpha + \beta) \\ &= 6\alpha + 8\beta \end{aligned}$$

If the six π electrons were in three localized double bonds, then the π electronic energy would be equivalent to the energy of three ethylene π bonds $= 3(2\alpha + 2\beta) = 6\alpha + 6\beta$, so the delocalization (or resonance) energy of benzene is therefore

Benzene Delocalization Energy

$$\begin{aligned} E_{\pi}(\text{benzene}) - 3E_{\pi}(\text{ethylene}) &= 6\alpha + 8\beta - 6\alpha - 6\beta \\ &= 2\beta \\ &\approx -150 \text{ kJ mol}^{-1} \end{aligned}$$

Wave Functions The wave functions for the energy levels are linear combinations of the p_z orbitals on carbon atoms $n = 1$ to $n = 6$.

$$\psi_i = \sum_{n=1}^6 c_{in} p_{zn}$$

The constants c_{1n} through c_{6n} are evaluated by substituting the energies into the secular equation to and solving to obtain the π electron wave functions:

Benzene π Electron Wave Functions

$$\psi_6 = \frac{1}{\sqrt{6}} (p_{z1} - p_{z2} + p_{z3} - p_{z4} + p_{z5} - p_{z6})$$

$$\psi_5 = \frac{1}{\sqrt{3}} (p_{z1} - \frac{1}{2}p_{z2} - \frac{1}{2}p_{z3} + p_{z4} - \frac{1}{2}p_{z5} - \frac{1}{2}p_{z6})$$

LUMO $\psi_4 = \frac{1}{\sqrt{4}} (p_{z2} - p_{z3} + p_{z5} - p_{z6})$

HOMO $\psi_3 = \frac{1}{\sqrt{3}} (p_{z1} + \frac{1}{2}p_{z2} - \frac{1}{2}p_{z3} - p_{z4} - \frac{1}{2}p_{z5} + \frac{1}{2}p_{z6})$

HOMO $\psi_2 = \frac{1}{\sqrt{4}} (p_{z2} + p_{z3} - p_{z5} - p_{z6})$

$$\psi_1 = \frac{1}{\sqrt{6}} (p_{z1} + p_{z2} + p_{z3} + p_{z4} + p_{z5} + p_{z6})$$

π Electron Density The π electron density on the first carbon atom in benzene is

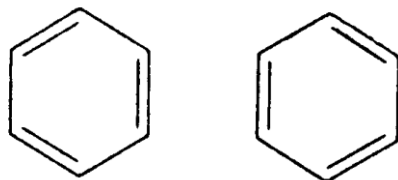
$$q_1 = 2c_{11}^2 + 2c_{21}^2 + 2c_{31}^2 + (0)c_{41}^2 + (0)c_{51}^2 + (0)c_{61}^2$$

$$= 2\left(\frac{1}{\sqrt{6}}\right)^2 + 2(0) + 2\left(\frac{1}{\sqrt{3}}\right)^2 = \frac{1}{3} + 0 + \frac{2}{3}$$

$$= 1$$

The other q_n 's are also 1 (*try it!*), indicating that the π electrons are uniformly distributed over the benzene molecule.

π Bond Order and Resonance It is customary to write the structure of the benzene molecule as the Kekule structures



implying alternating single and double bonds in the ring. Double C=C bonds, which are shorter and stronger than the corresponding single C–C, can be detected by experimental techniques such as x-ray crystallography. Measurements indicate, however, that all of the carbon-carbon bonds in benzene are equivalent.

This result can be understood by assuming that the two structures for benzene written above are in resonance, producing a uniform distribution of π electrons around the ring.

Hückel theory can be used to illustrate the quantum mechanics of resonance structures. by calculating the π electron density between adjacent carbon atoms in the benzene ring.

$$P_{rs} = \sum_{n=1}^4 n_i c_{ir} c_{is}$$

Between carbon atoms 1 and 2, the π electron density is

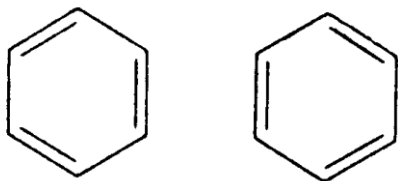
$$\begin{aligned} P_{12} &= 2c_{11}c_{12} + 2c_{21}c_{22} + (2)c_{31}c_{32} + (0)c_{41}c_{42} + (0)c_{51}c_{52} + (0)c_{61}c_{62} \\ &= 2 \frac{1}{\sqrt{6}} \frac{1}{\sqrt{6}} + 2(0) \frac{1}{\sqrt{4}} + 2 \frac{1}{\sqrt{3}} \frac{1}{2\sqrt{3}} = \frac{1}{3} + 0 + \frac{1}{3} \\ &= 2/3 \end{aligned}$$

For comparison, the π electron density between carbon atoms 2 and 3 is

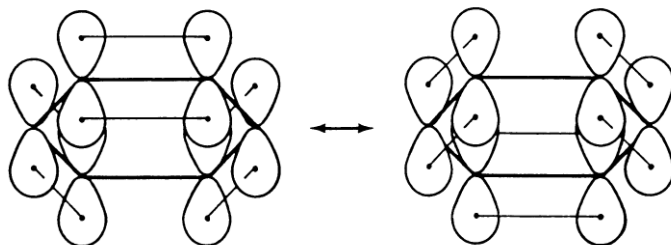
$$\begin{aligned} P_{23} &= 2c_{12}c_{13} + 2c_{22}c_{23} + (2)c_{32}c_{33} + (0)c_{42}c_{43} + (0)c_{52}c_{53} + (0)c_{62}c_{63} \\ &= 2 \frac{1}{\sqrt{6}} \frac{1}{\sqrt{6}} + 2 \frac{1}{\sqrt{4}} \frac{1}{\sqrt{4}} + 2 \frac{1}{2\sqrt{3}} \frac{-1}{2\sqrt{3}} = \frac{1}{3} + \frac{1}{2} - \frac{1}{6} \\ &= 2/3 \end{aligned}$$

P_{34} , P_{45} , P_{56} , and P_{61} are also $2/3$, illustrating the important result, verified by experiment, that all of the bonds in benzene are equivalent.

The uniform distribution of π electrons in benzene can be visualized by assuming that the two equivalent Kekule structures



are in rapid “resonance”:



Spin-Orbit Coupling

For “light” atoms (Z less than about 40), the interactions between the orbital angular momentum and spin angular momentum is sufficiently weak to be ignored in calculating the total angular momentum. This is the key assumption in the Russell-Saunders scheme for determining atomic term symbols.

The interaction between orbital and spin angular momentum, though very small, is not zero. When an electron has orbital angular momentum, a small magnetic dipole and a correspondingly weak magnetic field are generated. This magnetic field interacts with the electron spin magnetic moment and produces a very small change in the energy.

The magnitude of spin-orbit interaction energy is proportional to the dot product of the orbital and spin angular momentum vectors

$$\Delta E_{\text{spin-orbit}} = c \vec{L} \cdot \vec{S}$$

c is a proportionality constant.

The expression

$$\vec{J} \cdot \vec{J} = [\vec{L} + \vec{S}] \cdot [\vec{L} + \vec{S}] = \vec{L}^2 + \vec{S}^2 + 2\vec{L} \cdot \vec{S}$$

for the square of the total angular momentum and

$$\vec{J} \cdot \vec{J} = J(J + 1)\hbar^2$$

$$\vec{L} \cdot \vec{L} = \ell(\ell + 1)\hbar^2$$

$$\vec{S} \cdot \vec{S} = S(S + 1)\hbar^2$$

to derive

$$\Delta E_{\text{spin-orbit}} = c[J(J + 1) - \ell(\ell + 1) - S(S + 1)]$$

for the energy change caused by spin orbit coupling. (In the notation used here, note that J , ℓ and S are quantum numbers, not the magnitudes of the angular momentum vectors.)

Experiments give $c \approx 0.000023 Z^4$ eV.