

CHAPTER 10

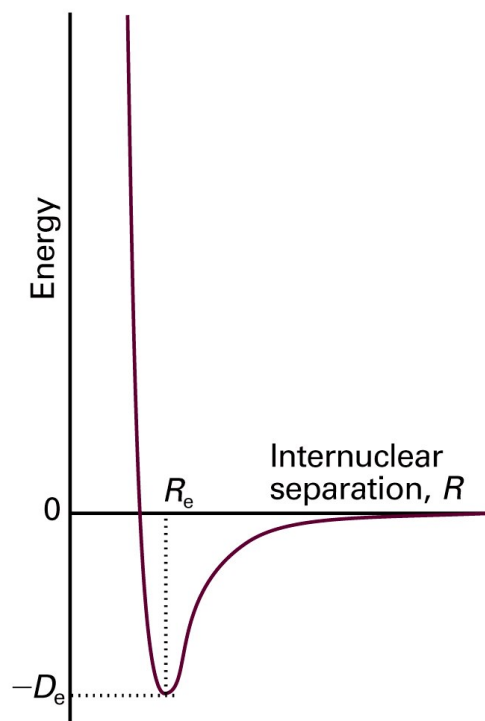
Molecular Structure

I. Basic Concepts

A. Born-Oppenheimer Approximation.

1. All theories of molecular bonding make the same simplification to start - the B.O. approximation
2. Nuclei are sluggish relative to e^- motion due to their masses. (Time scale separation)
3. e^- cloud responds instantaneously to slowly changing nuclear positions.
4. Separate problem into a) nuclear vibrations and b) electron wave function around fixed nuclear separation R .
5. For H_2^+ , 3 body problem \rightarrow 1 body (1 e^- moving around fixed nuclei)
6. Potential energy curve for nuclear motion:
7. Nuclei vibrate around R_e , the equilibrium bond Length
8. D_o = bond dissociation energy

$$D_e = \text{well depth} \\ = D_o + \frac{1}{2} h\nu$$



II. Valence Bond (VB) Theory

A. Introduction.

1. First theory of the chemical bond, developed by Linus Pauling.
2. VB theory still largely affects the thinking of organic chemists.
3. Concepts such as spin pairing, orbital overlap, sigma and pi bonding, and hybridization carry over to all bonding theories, including Molecular Orbital Theory.
4. Bond forms when an electron in an atomic orbital on one atom pairs its spin with another electron in an atomic orbital on another atom.
5. 2 electrons = one bond

B. Homonuclear Diatomics.

1. Consider formation of the bond in H_2 diatomic. Label the atoms A and B, each with one electron.

2. At large distance $\psi_{\text{molecule}} = A(1)B(2)$

where $A()$ and $B()$ are atomic orbitals, i.e. $1s$.

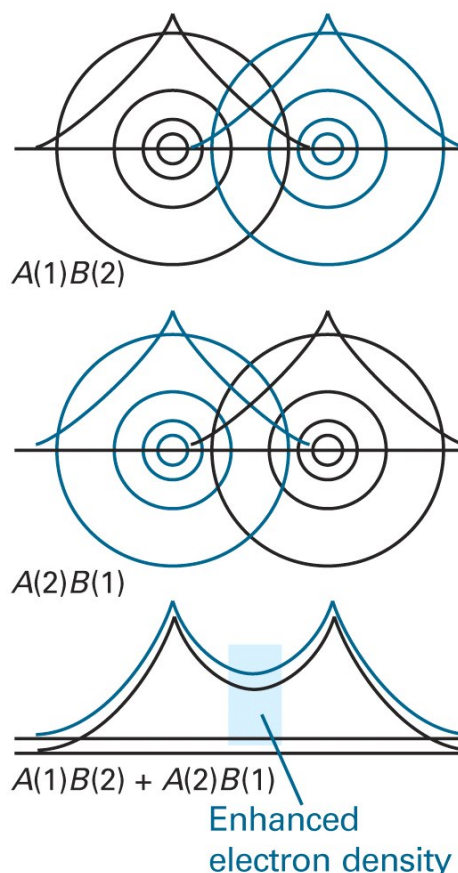
3. As atoms begin to interact at short distance, it is impossible to distinguish whether electron 1 is on A, or electron 2. An equally valid description would be:

$$\psi_{\text{molecule}} = A(2)B(1)$$

4. The true wavefunction is a superposition of these two possibilities, so in QM we construct two linear combinations:

$$\psi_{\pm} = A(1)B(2) \pm A(2)B(1)$$

5. The combination with the + sign is the lower energy one, so that becomes the VB wavefunction for H_2 .



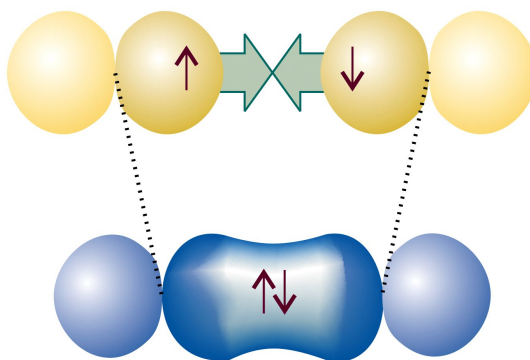
6. The electron distribution is called a sigma (σ) **bond**, meaning it has cylindrical symmetry around the bond axis.
7. The VB wavefunction $\psi_{\sigma} = A(1)B(2) + A(2)B(1)$ is only the *spatial* part of the wavefunction, and is *symmetric* with respect to interchange of electron labels 1 and 2. Pauli Principle requires a total wavefunction which is *antisymmetric*, so the spin part of the wavefunction must be antisymmetric.

Therefore the spin wavefunction we saw before must be used, and that means **spins paired**. (one up, one down)

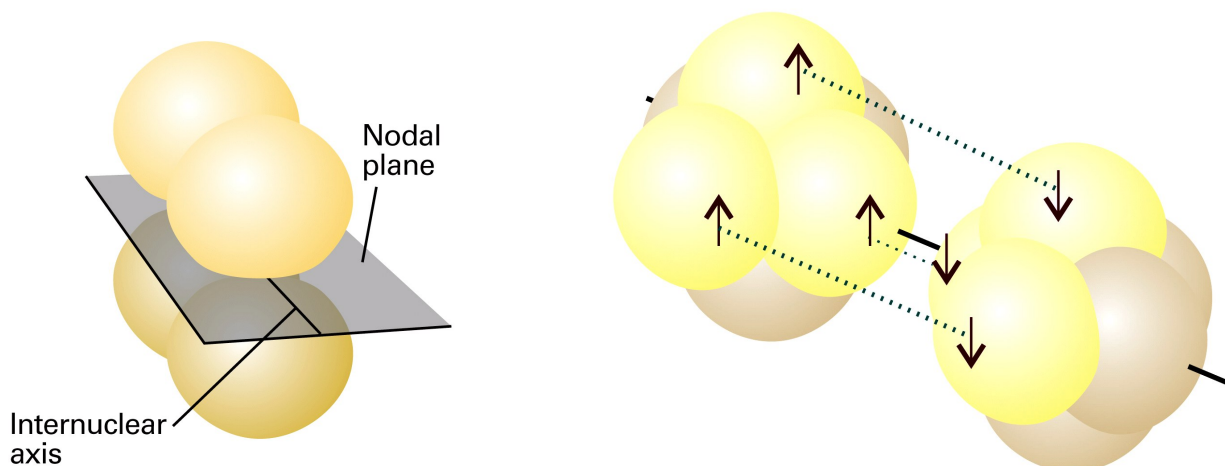
8. VB can easily treat other homonuclear diatomics, like N_2 .

Each N atom has $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$

Take z-direction to be the internuclear axis. The two $2p_z^1$ orbitals from separate atoms overlap to produce a σ bond.



The two neighboring $2p_x^1$ orbitals overlap to give a π **bond**, and the two neighboring $2p_y^1$ orbitals overlap to give another π **bond**.

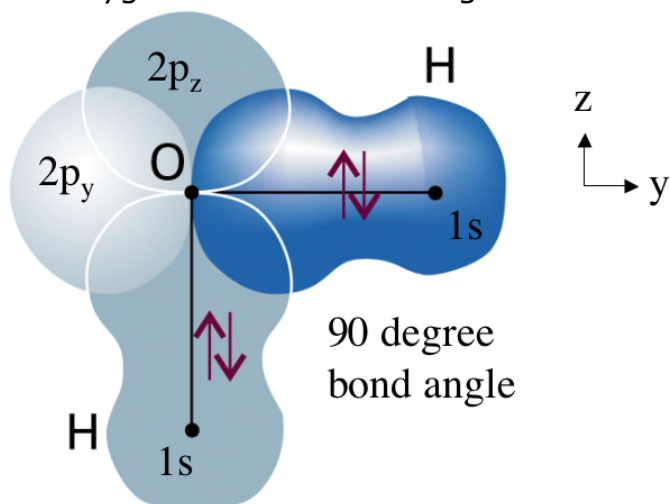


C. VB treatment of polyatomic molecules.

1. Now let's try to use this idea to predict the bonding in water.

Each H atom brings one electron to the molecule as $1s^1$

The central oxygen atom has a configuration $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$



Uh, oh! This is not a good prediction. It predicts two single bonds form, but the molecular geometry is not quite correct. Angle should be 104° , not 90° .

2. Let's try a different molecule, methane, CH₄.

central atom Carbon = $[\text{He}]2s^2 2p_x^1 2p_y^1 2p_z^0$

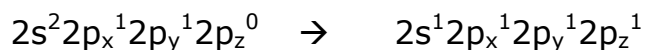
Only possibility of pairing up with a $\text{H}=1s^1$ in two orbitals - prediction CH₂.

Carbon's known valency is 4, not 2.

3. VB Theory must introduce another two new ideas ("fixes") here:

promotion and **hybridization**

1st, promote an electron out of $2s$ into the empty $2p$



Now there are four locations for pairing up an electron from incoming atoms.

Problem: It would still not produce the known tetrahedral geometry of CH₄.

2nd, form hybrid atomic orbitals by taking **linear combinations** of the 2s and the three 2p atomic orbitals to form four equivalent and **orthogonal** hybrid atomic orbitals. These hybrid orbitals are called **sp³ hybrid atomic orbitals**.

$$(\text{sp}^3)_1 = 2s + 2p_x + 2p_y + 2p_z$$

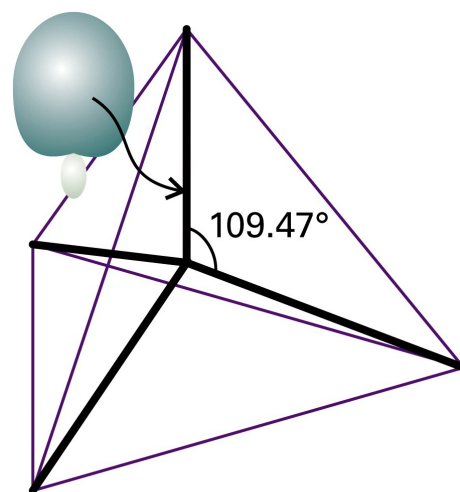
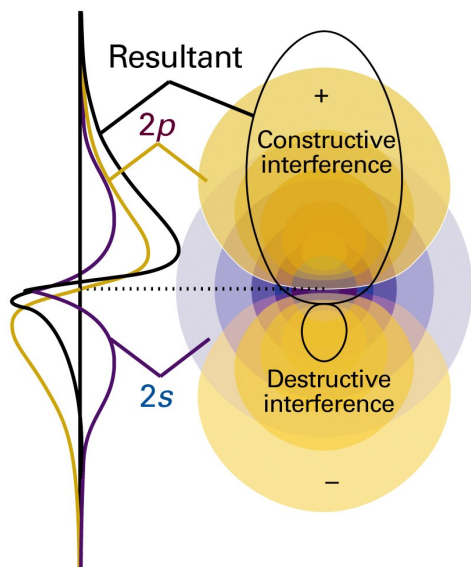
$$(\text{sp}^3)_2 = 2s - 2p_x - 2p_y + 2p_z$$

$$(\text{sp}^3)_3 = 2s - 2p_x + 2p_y - 2p_z$$

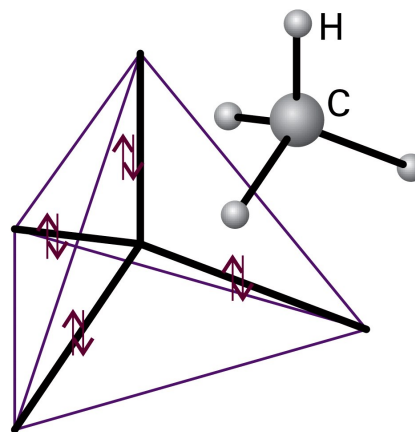
$$(\text{sp}^3)_4 = 2s + 2p_x - 2p_y - 2p_z$$

These have a tetrahedral geometry around carbon.

The shape of the hybrids result from constructive and destructive interference that results from adding 2s to a 2p.



Resulting molec. geometry of methane



4. Other hybridizations explain geometries of other molecular systems.

What about Carbon in Ethene? Makes use of **sp² hybridization**.

$$(\text{sp}^2)_1 = 2s + 2^{1/2} 2p_y$$

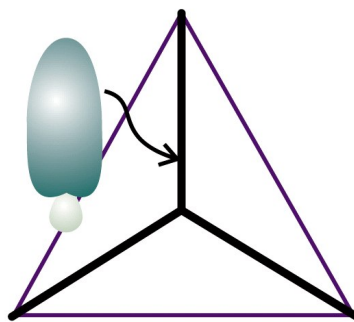
$$(\text{sp}^2)_2 = 2s + (3/2)^{1/2} 2p_x - (1/2)^{1/2} 2p_y$$

$$(\text{sp}^2)_3 = 2s - (3/2)^{1/2} 2p_x - (1/2)^{1/2} 2p_y$$

These need to be normalized.

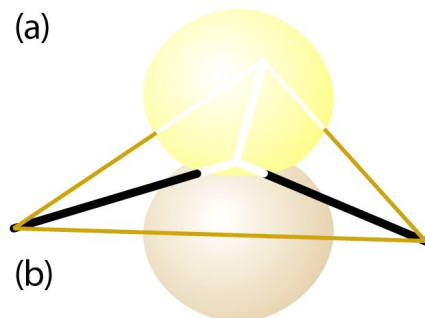
Note that the $2p_z$ orbital did not enter into the hybridization mix.

Trigonal planar geom.
Of sp^2 hybrids



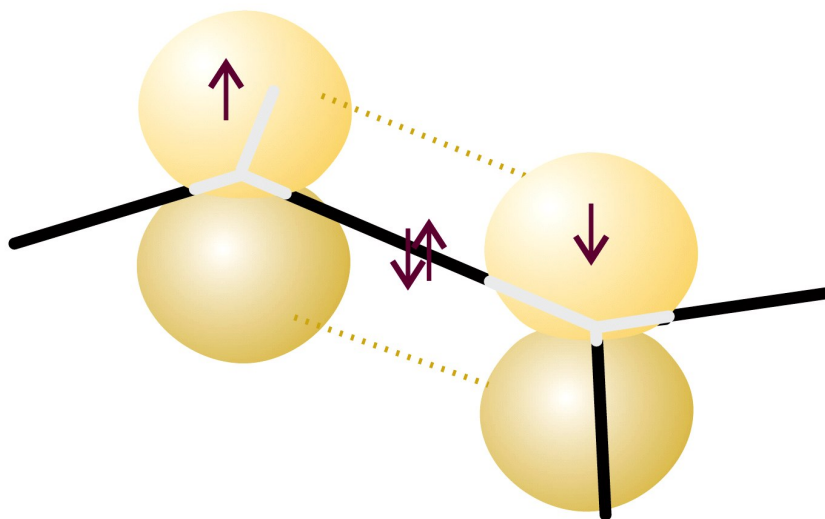
(a)

Perpendicular
Orientation of
Un-utilized $2p_z$



(b)

The un-utilized perpendicular $2p_z$ on each carbon in ethene may overlap to create a π **bond**, non-cylindrically symmetric around the bond axis.



5. Hybrid atomic orbitals do not always form bonds. They may also contain a non-bonding pair of electrons, as in water or ammonia.

6. Other hybridization schemes:

Table 10.1 Some hybridization schemes

Coordination number	Arrangement	Composition
2	Linear	sp, pd, sd
	Angular	sd
3	Trigonal planar	sp^2, p^2d
	Unsymmetrical planar	spd
	Trigonal pyramidal	pd^2
	Tetrahedral	sp^3, sd^3
4	Irregular tetrahedral	spd^2, p^3d, dp^3
	Square planar	p^2d^2, sp^2d
	Trigonal bipyramidal	sp^3d, spd^2
5	Tetragonal pyramidal	$sp^2d^2, sd^4, pd^4, p^3d^2$
	Pentagonal planar	p^2d^3
	Octahedral	sp^3d^2
6	Trigonal prismatic	spd^4, pd^5
	Trigonal antiprismatic	p^3d^2

* Source: H. Eyring, J. Walter, and G.E. Kimball, *Quantum chemistry*, Wiley (1944).

7. Can you show that a set of hybrid AO's are mutually orthogonal?

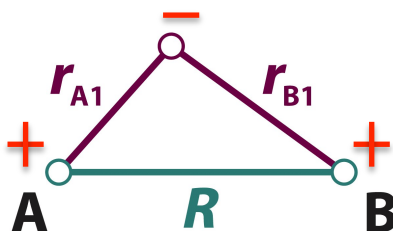
III. Molecular Orbital Theory

A. Basic Concepts.

1. Electrons are no longer regarded as belonging to particular bonds but are spread throughout the molecule to varying degrees.
2. Like VB Theory, the hydrogenic atomic orbitals are still the building blocks for the molecular orbitals.
3. MO Theory is less physically appealing to working chemists than VB in describing organic molecules, but it achieves much greater accuracy in predicting properties.

B. The Hydrogen molecule-ion H_2^+ .

2 protons, 1 e^-



Simplest molecular species known. H_2^+ problem may be solved in terms of known functions, but they are too complicated to extend to polyatomics, so we adopt the LCAO-MO approximation.

C. The LCAO - MO Approximation.

Is an orbital approximation= Electrons in a *molecule* reside in one-electron orbitals, just like we saw for many-electron atoms. Thus the whole wavefunction is the product of one-electron wavefunctions.

Wave function ψ for one e^- in a molecule = "molecular orbital" = "M.O."

ψ^2 = distribution of e^- in the molecule.

"LCAO-MO approximation." (linear combination of atomic orbitals [to give] molecular orbitals)

For H_2 , take overlaps of 1s orbital from atom A and atom B

$$\psi_{1s\sigma} = N \{ \psi_{1s}(A) + \psi_{1s}(B) \}$$

e^- occupies this orbital

norm. cons.
has cylindrical sym around internucl axis
= σ molecular orbital, specific $1s\sigma$

The probability density for locating the e^- occupying $1s\sigma$ orbital is:

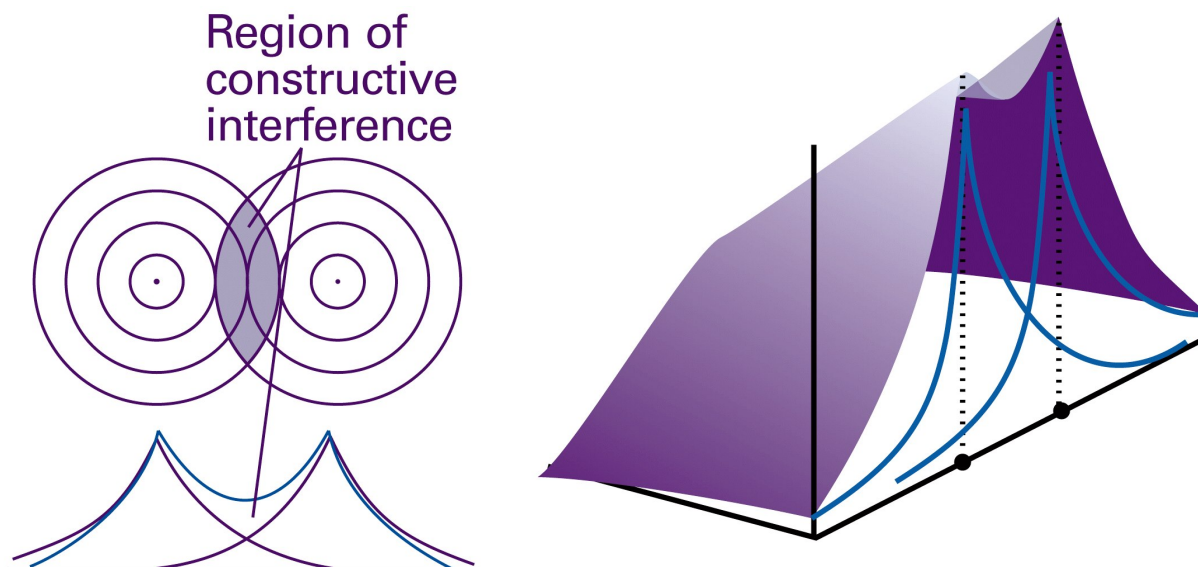
$$\psi_{1s\sigma}^2 = N^2 \{ \psi_{1s}(A) + \psi_{1s}(B) \}^2$$

$$= N^2 \{ \psi_{1s}^2(A) + \underbrace{2\psi_{1s}(A)\psi_{1s}(B)}_{\text{cross term}} + \psi_{1s}^2(B) \}$$

prob dens
if e^- were
confined to
 $1s$ orbital on
atom A

extra contrib
called
"overlap density"
(Constructive interference)

same for B

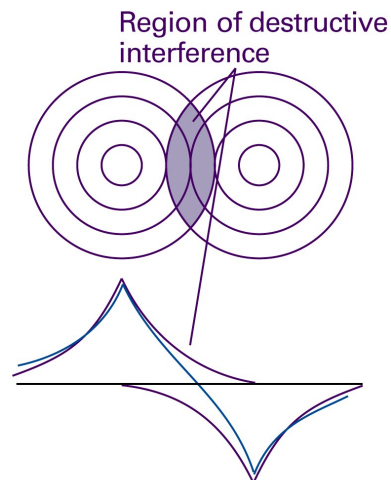


$1s\sigma$ is a bonding orbital, since there is enhanced amplitude in ψ^2 between the nuclei that hold molec together.

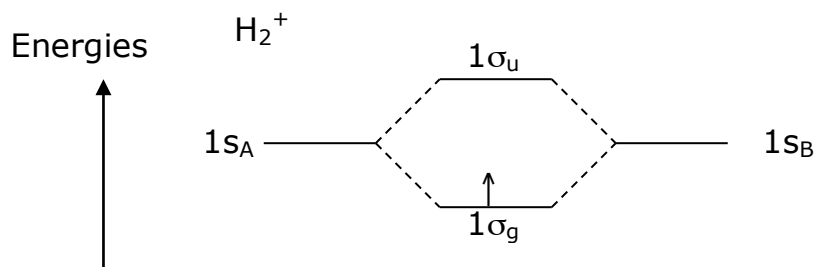
Can also construct antibonding orbital $1s\sigma^*$.

$$\psi_{1s\sigma^*} = N \{ \psi_{1s}(A) - \psi_{1s}(B) \}$$

Note: little electron probability in the internuclear region, so does not give rise to stability.

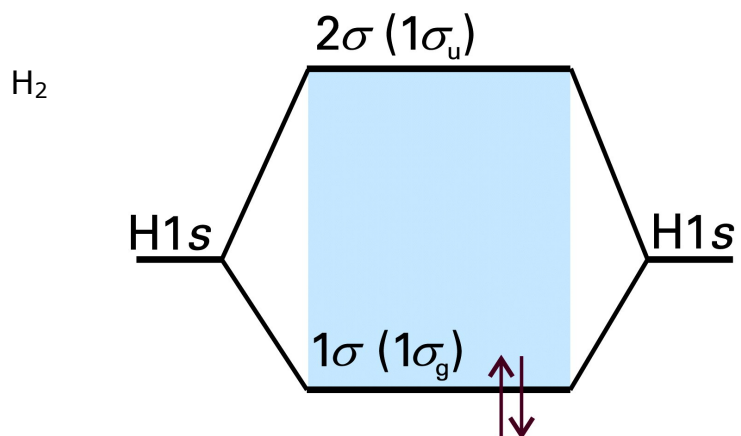
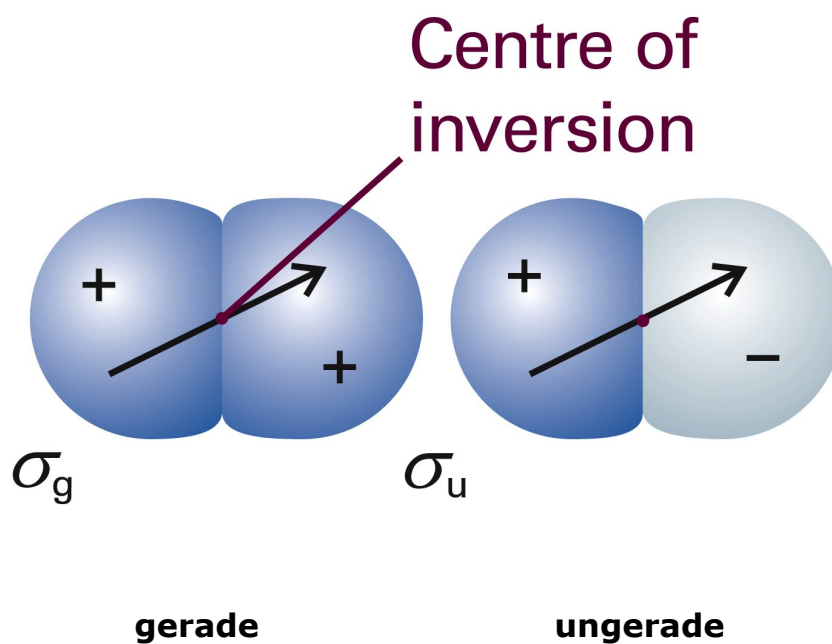


Conventional MO energy diagram



Modern notation focuses on the symmetry of the MO's. For homonuclear diatomics we classify MO's by looking at their **inversion symmetry**.

= the symmetry of MO through its center (a point midway between atoms A and B).

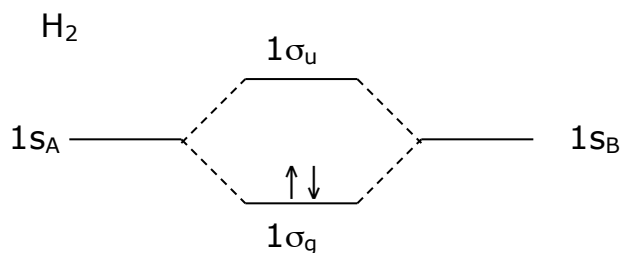


IV. Homonuclear Diatomic Molecules

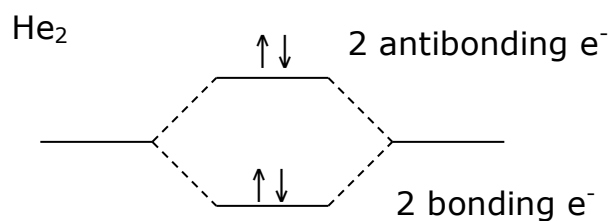
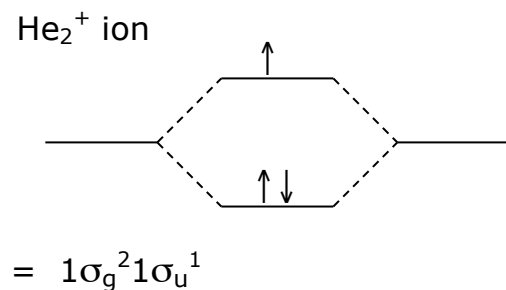
Form M.O.'s by LCAO, overlapping AO's.

Then fill MO's with electrons just like Aufbau filling of AO's.

A. Hydrogen and Helium.



H₂ = 1σ_g² (electron configuration)



He₂ = 1σ_g²1σ_u² not stable

Bond order of diatomics $b = 1/2(n - n^*)$

n = # of e⁻ in bonding orbitals

n^* = # of e⁻ in antibonding orbitals

He₂⁺ $b = 1/2(2 - 1) = 1/2$ 1/2 a bond

H₂ $b = 1/2(2 - 0) = 1$ "single bond"

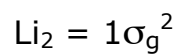
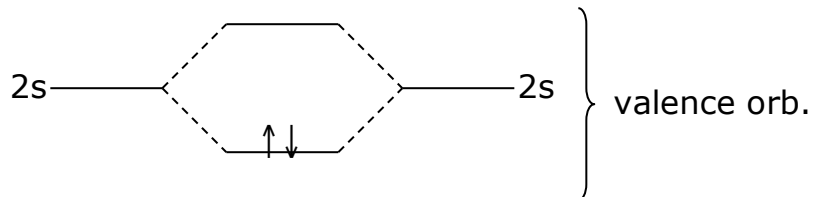
He₂ $b = 1/2(2 - 2) = 0$ no bond

B. Period-2 homonuclear diatomics.

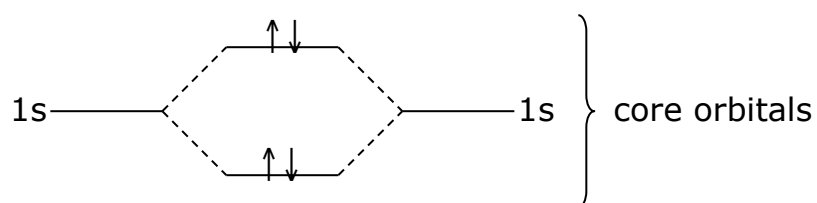
Homonuclear diatomics
Hetero diatomics

N_2 , etc.
 LiH , NO , etc.

Li_2

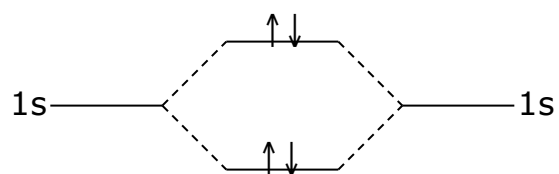
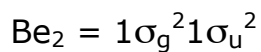
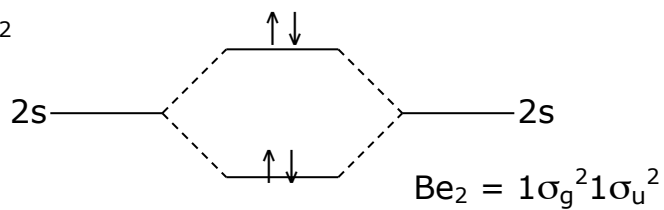


(written config focuses on valence electrons only)



$$b = 1/2(4-2) = 1$$

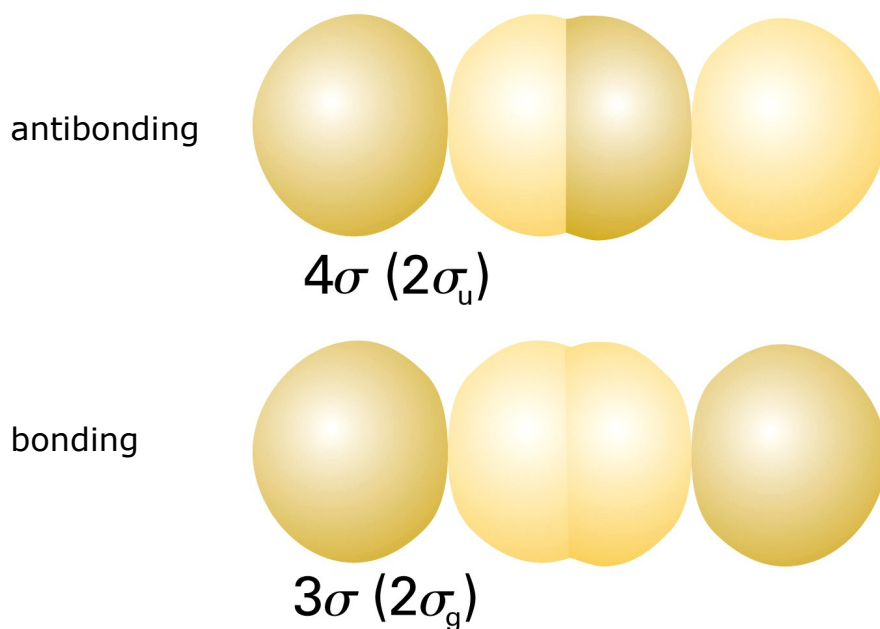
Be_2



$b = 0$ unstable

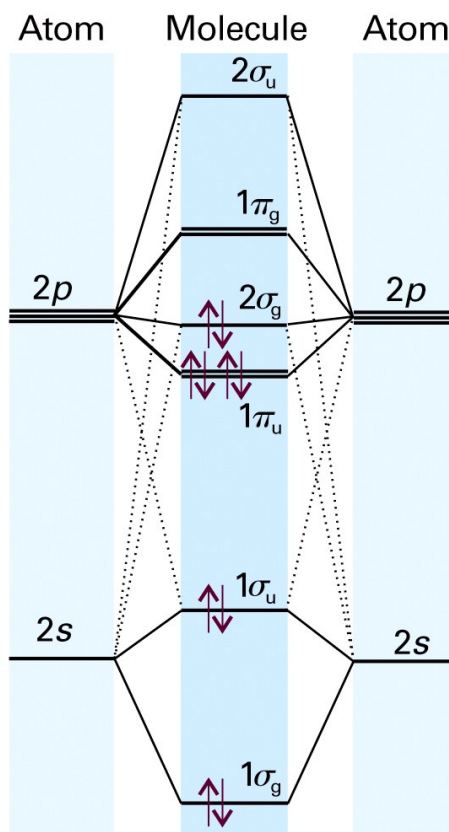
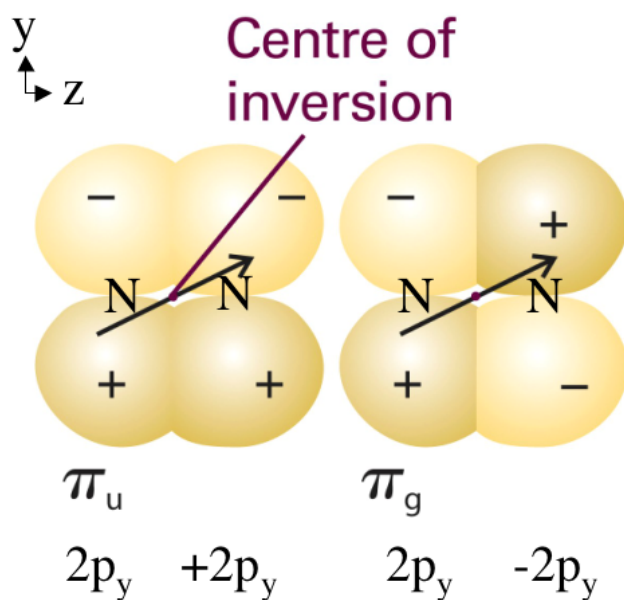
Beyond Be_2 , the 2p orbitals begin to get involved.

Here are the two linear combinations of the $2p_z$, which are oriented along the bond axis.



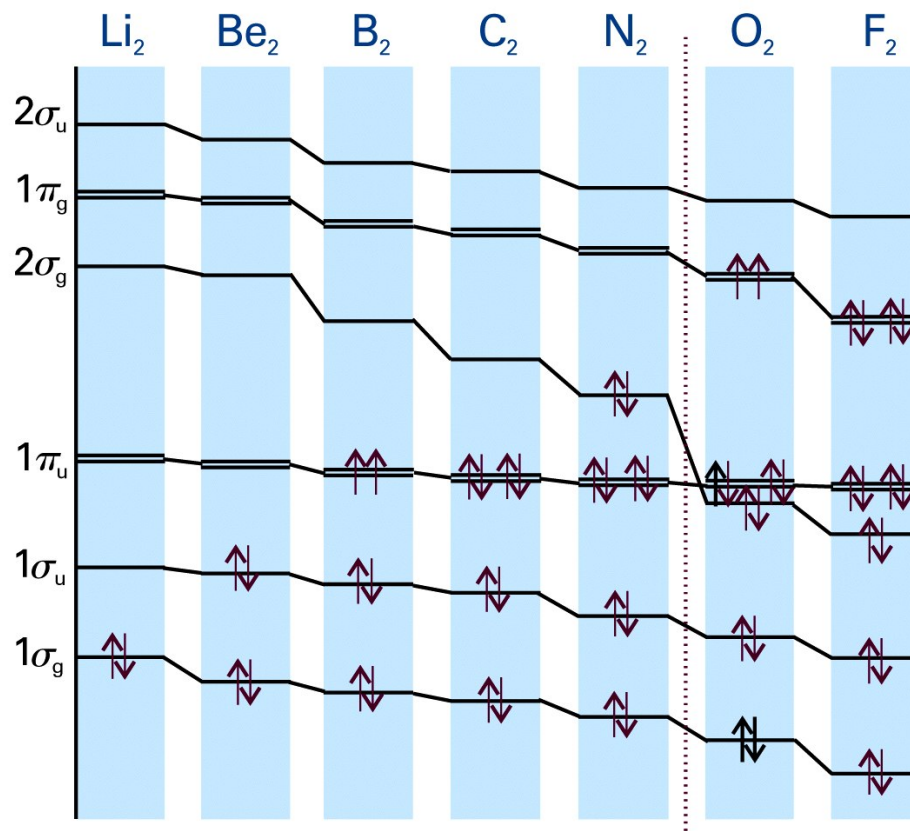
N_2

bond order = 3



$2p_x$'s overlap the same way to give another π M.O. with same energy.

Relative energies of the 2σ and 1π M.O.'s vary across Row 2 diatomics



Why does 2σ take dip down underneath 1π ?

So far have constructed M.O.'s by adding together $(1s + 1s)$, $(2s + 2s)$, $(2p_z + 2p_z)$, $(2p_{x,y} + 2p_{x,y})$

In general however:

$$\psi_{MO} = \sum_{i=\text{orbitals}}^{\text{on A}} c_i \psi_i + \sum_{j=\text{orbitals}}^{\text{on B}} c_j \psi_j$$

in principle, all AO's contribute to all MO's

It just turns out that especially for diatomics, "like" orbitals seems to have the largest overlap with each other.

e.g.

$$\psi_{2\sigma g} \approx \underbrace{2p_z(A) + 2p_z(B)}_{\text{dominant terms}} + \text{minor contribution from } 2s(A) + 2s(B)$$

Minor contributions do affect relative energies however.

O₂

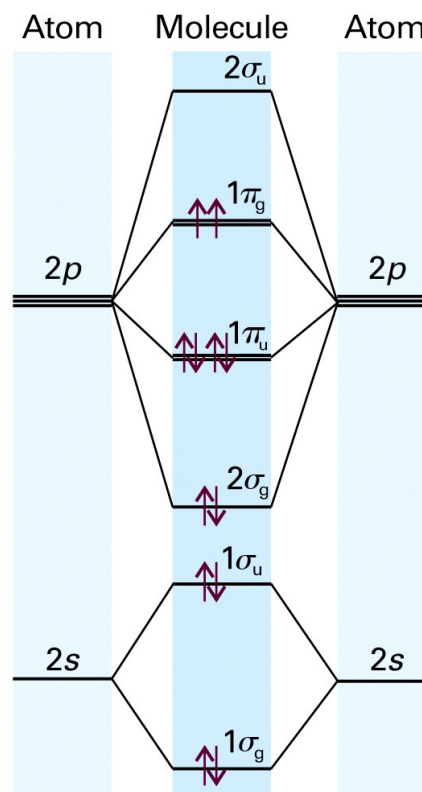
Bond order = 2

By Hund's Rule, the two electrons in the 1 π_g antibonding level go into separate MO's, giving rise to two unpaired electrons.

Molecular oxygen is paramagnetic.

F₂ has two more electrons into 1 π_g antibonding level and so has bond order = 1 and no unpaired electrons.

Ne₂ has two more electrons going into antibonding MO, and has bond order = 0. Unstable.

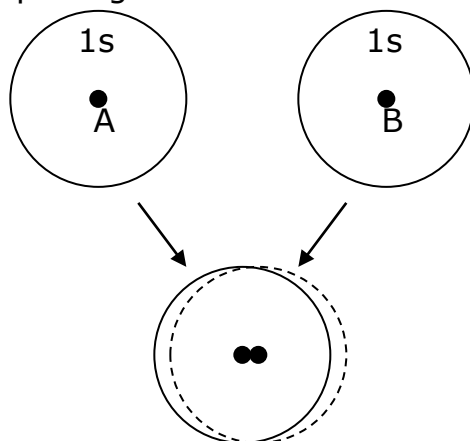


Effectiveness of overlap:

The overlap integral S , determines the extent of overlap of two atomic orbitals, which determines whether they will form good M.O.

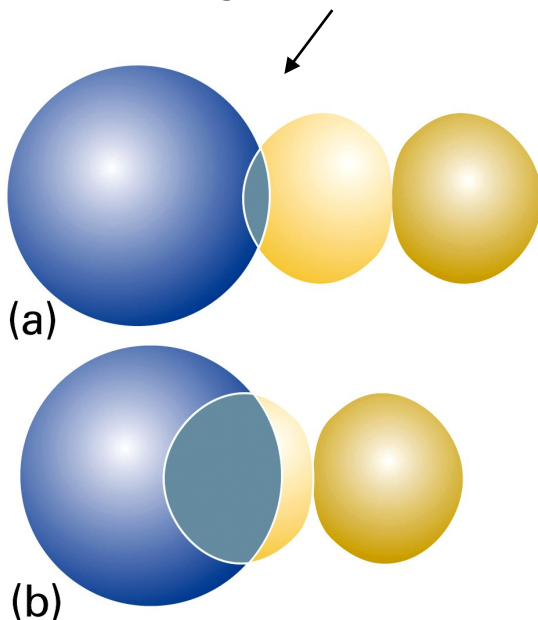
$$S = \int \psi(A)\psi(B)d\tau$$

E.g. If two 1s orbitals approach one another, one on A and one on B, their overlap integral increases to 1.

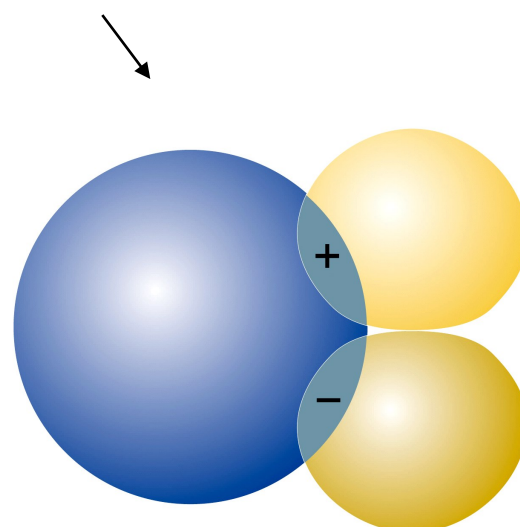


$$S = \int \psi_{1s}(A)\psi_{1s}(A) = 1$$

Overlap of s and p increases up to a point, then begins to decrease.



This s and p gives ZERO net overlap.



Bond strength:

The greater the bond order, the greater the bond strength.

The greater the bond order, the shorter the bond.

Table 10.2 Bond lengths

Bond	Order	R_e/pm
HH	1	74.14
NN	3	109.76
HCl	1	127.45
CH	1	114
CC	1	154
CC	2	134
CC	3	120

* More values will be found in the *Data section*.
Numbers in italics are mean values for polyatomic molecules.

Table 10.3 Bond dissociation energies

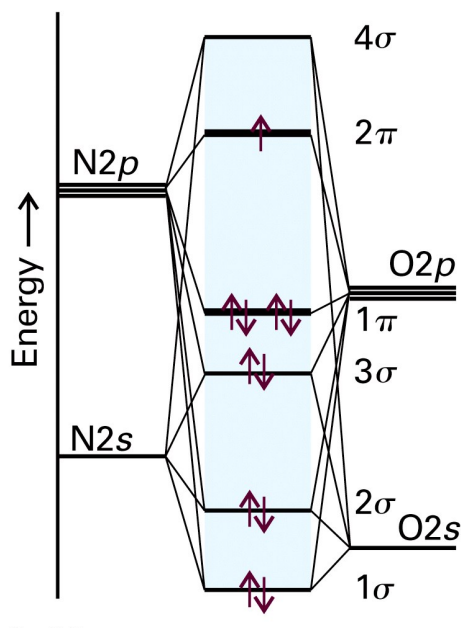
Bond	Order	$D_0/(\text{kJ mol}^{-1})$
HH	1	432.1
NN	3	941.7
HCl	1	427.7
CH	1	435
CC	1	368
CC	2	720
CC	3	962

* More values will be found in the *Data section*.
Numbers in italics are mean values for polyatomic molecules.

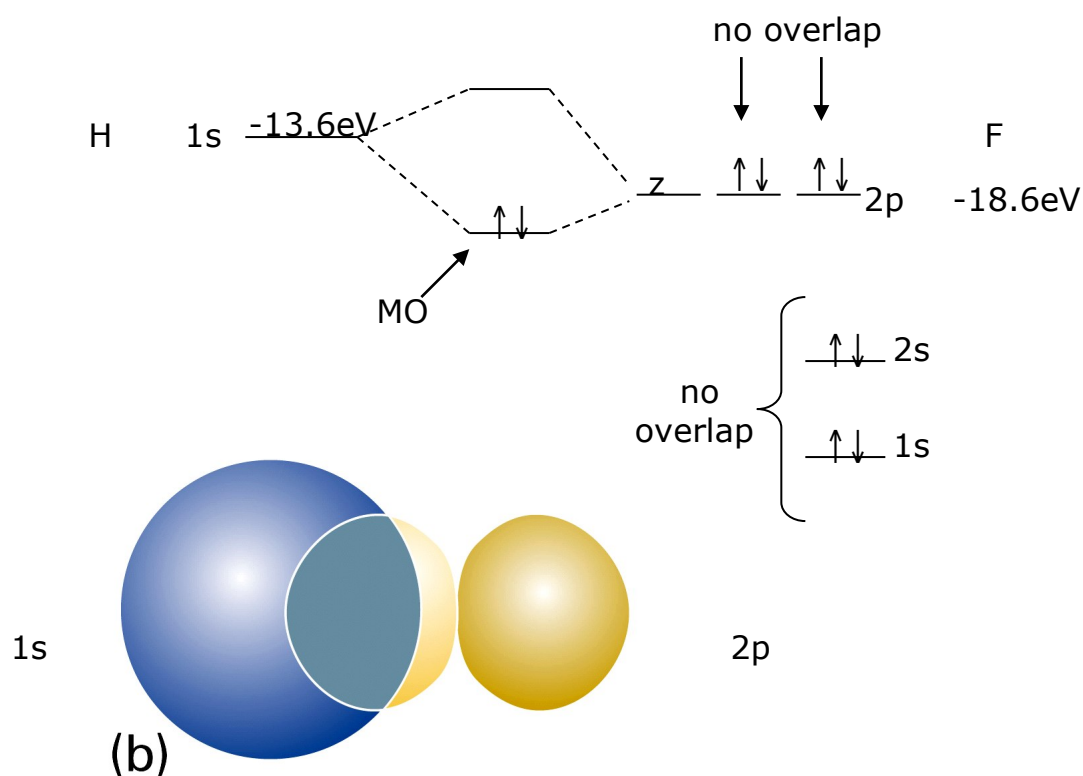
C. Heteronuclear Diatomics.

M.O.'s are somewhat like homonuclear diatomics, but less so as EN difference between atoms increase.


e.g. NO



Now what about HF $EN_F \gg EN_H$

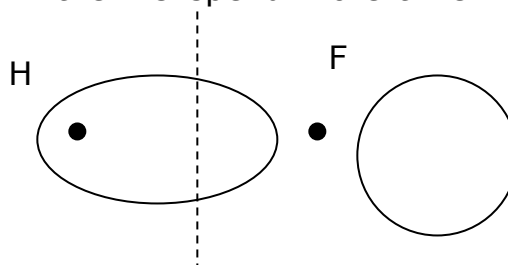


$$\psi_{\text{MO}} = 0.19\psi_{1s}(\text{H}) + 0.98\psi_{2p_z}(\text{F})$$


 different weighting
contribution

M.O. produced has much greater contrib. from $2p_z$ on F (high E_a) than from $1s$ of H.

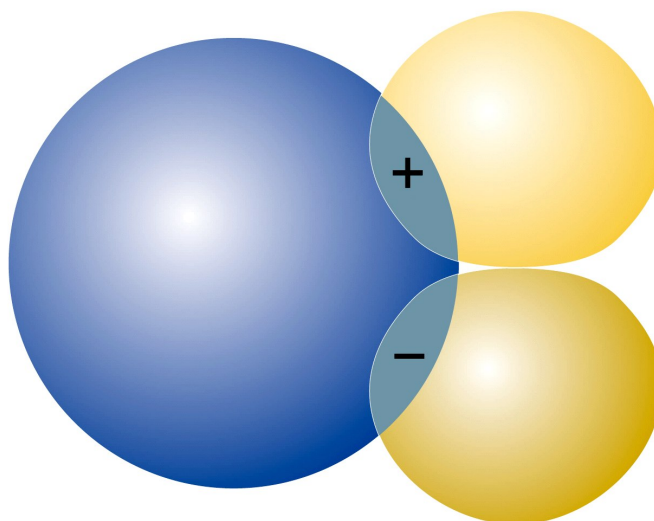
→ a **polar covalent bond**. $2e^-$ in the MO spend more time near F than near H. Shared unequally.



General Rule: atomic orbitals most effectively combine (overlap) to form M.O.'s when:

- 1) their energies are similar in the separated atoms.
- 2) their shapes are conducive to good overlap.

E.g. these give no overlap due to their shape and sign of wave function.



The construction of energy level diagrams for arbitrary heteronuclear diatomics is not straightforward, and requires calculation.

- D. The Variation Principle – a systematic way of taking linear combinations of atomic orbitals in correct proportions to produce the most optimum approximation to the M.O.'s.

V.P. is based on the fact that approximate M.O.'s will always have a higher energy than the true exact M.O.'s energy.

E.g. in HF, if I had constructed the M.O. as:

$$\psi_{MO} = 1.0\psi_{1s}(H) + 1.0\psi_{2p_z}(F) \quad \text{with equal coefficients}$$

the energy of this $\psi_{mo} > E_{true}$

Consequence of V.P. → vary the weighting coefficients until you get the lowest energy you can find. This will be the best approx you can make to the true wave function.

$$\psi_{trial} = C_A\psi(A) + C_B\psi(B) \quad \text{unknown coeff which are to be varied}$$

$$E_{trial} = \frac{\int \psi_{trial}^* \hat{H} \psi_{trial}}{\int \psi_{trial}^* \psi_{trial}}$$

Vary C_A and C_B until E_{trial} attains its lowest value.

Suppose ψ_{trial} is real:

$$\begin{aligned} \text{Denom} &= \int \psi_{trial}^2 d\tau = \int (C_A\psi(A) + C_B\psi(B))^2 d\tau \\ &= C_A^2 \underbrace{\int \psi(A)^2 d\tau}_{=1} + C_B^2 \underbrace{\int \psi(B)^2 d\tau}_{=1} + 2C_A C_B \int \psi_A \psi_B d\tau \end{aligned}$$

using normalized wave functions from the separated atoms A + B

← overlap integral S

$$\text{Denominator} = C_A^2 + C_B^2 + 2C_A C_B S$$

$$\begin{aligned}
 \text{Numerator} &= \int \psi_{\text{trial}} \hat{H} \psi_{\text{trial}} \\
 &= C_A^2 \underbrace{\int \psi(A) \hat{H} \psi(A) d\tau}_{\alpha_A} + C_B^2 \underbrace{\int \psi(B) \hat{H} \psi(B) d\tau}_{\alpha_B} + 2C_A C_B \underbrace{\int \psi(A) \hat{H} \psi(B) d\tau}_{\beta}
 \end{aligned}$$

α_A, α_B = "Coulomb integrals"

β = "Resonance integral"

$$\text{Numerator} = C_A^2 \alpha_A + C_B^2 \alpha_B + 2C_A C_B \beta$$

$$E_{\text{trial}} = \frac{C_A^2 \alpha_A + C_B^2 \alpha_B + 2C_A C_B \beta}{C_A^2 + C_B^2 + 2C_A C_B S}$$

Must evaluate integrals $\alpha_A, \alpha_B, \beta$ and S to obtain #'s. Then vary C_A, C_B until E_{trial} achieves a minimum.

i.e. set $\frac{\partial E_{\text{trial}}}{\partial C_A} = 0$ this gives equation:

$$(\alpha_A - E_{\text{trial}})C_A + (\beta - E_{\text{trial}} S)C_B = 0$$

Then set $\frac{\partial E_{\text{trial}}}{\partial C_B} = 0$ this gives equation:

$$(\beta - E_{\text{trial}} S)C_A + (\alpha_B - E_{\text{trial}})C_B = 0$$

Two equations, two unknowns C_A and C_B .

This set of eqns has a solution when the determinant is zero:

$$\begin{vmatrix}
 \alpha_A - E_{\text{trial}} & \beta - E_{\text{trial}} S \\
 \beta - E_{\text{trial}} S & \alpha_B - E_{\text{trial}}
 \end{vmatrix} = 0$$

↑
this is called the "secular determinant"

Definition of “determinant”

$$\begin{vmatrix} A & B \\ C & D \end{vmatrix} = AD - BC$$

$$(\alpha_A - E)(\alpha_B - E) - (\beta - ES)^2 = 0$$

Solve for E (a quadratic equation)

Has 2 roots (corresponding to bonding and antibonding orbital energies)

Simple case: $A = B$ (homonuclear diatomic)

$$\alpha_A = \alpha_B = \alpha$$

Two solutions: (1) bonding $E_+ = \frac{\alpha + \beta}{1 + S}$ $C_A = \left(\frac{1}{2(1 + S)} \right)^{1/2} = C_B$

(2) anti $E_- = \frac{\alpha - \beta}{1 - S}$ $C_A = \left(\frac{1}{2(1 - S)} \right)^{1/2} = -C_B$

$$\psi_{\pm} = \left(\frac{1}{2(1 \pm S)} \right)^{1/2} (\psi(A) \pm \psi(B))$$

Even better approximate wave functions and energies for the molecule can be constructed by taking linear combinations of **lots** of atomic orbitals, not just two.

This is called expanding your basis set.

In principle, by using a “complete” basis set, you should obtain an exact solution upon using the variation principle.

In practice, a complete set would need to have all atomic orbitals (full and empty) on all the atoms in your molecule, and that is an infinite set.

HF - MNDO CALCULATION RESULTS MOPAC: VERSION 6.00 CALC'D. 21-Oct-94
 XYZ GEO-OK LARGE VECTORS FOCK MULLIK BONDS DENOUT 1ELECTRON

INPUT CARTESIAN COORDINATES

NO.	ATOM	X	Y	Z
1	H	0.0000	0.0000	0.0000
2	F	0.9200	0.0000	0.0000

FINAL HEAT OF FORMATION = -59.73416 KCAL
 TOTAL ENERGY = -494.25877 EV
 ELECTRONIC ENERGY = -576.87098 EV
 CORE-CORE REPULSION = 82.61221 EV
 IONIZATION POTENTIAL = 14.89120
 NO. OF FILLED LEVELS = 4
 MOLECULAR WEIGHT = 20.006
 SCF CALCULATIONS = 7
 COMPUTATION TIME = 0.180 SECONDS

ATOM NUMBER	CHEMICAL SYMBOL	BOND LENGTH (ANGSTROMS)
1	H	
2	F	0.95633 *

EIGENVECTORS

ROOT NO.		1	2	3	4	5
		-43.77134	-17.93881	-14.89120	-14.89120	5.80377
1S	H	-0.37307	0.46609	0.00000	0.00000	0.80223
2S	F	-0.91567	-0.32434	0.00000	0.00000	-0.23738
2Px	F	0.14956	-0.82314	0.00000	0.00000	0.54779
2Py	F	0.00000	0.00000	0.92376	-0.38298	0.00000
2Pz	F	0.00000	0.00000	0.38298	0.92376	0.00000

NET ATOMIC CHARGES AND DIPOLE CONTRIBUTIONS

	ATOM NO.	TYPE	CHARGE	ATOM ELECTRON DENSITY
	1	H	0.2872	0.7128
	2	F	-0.2872	7.2872

	X	Y	Z	TOTAL
DIPOLE				
POINT-CHG.	-1.319	0.000	0.000	1.319
HYBRID	-0.670	0.000	0.000	0.670
SUM	-1.989	0.000	0.000	1.989

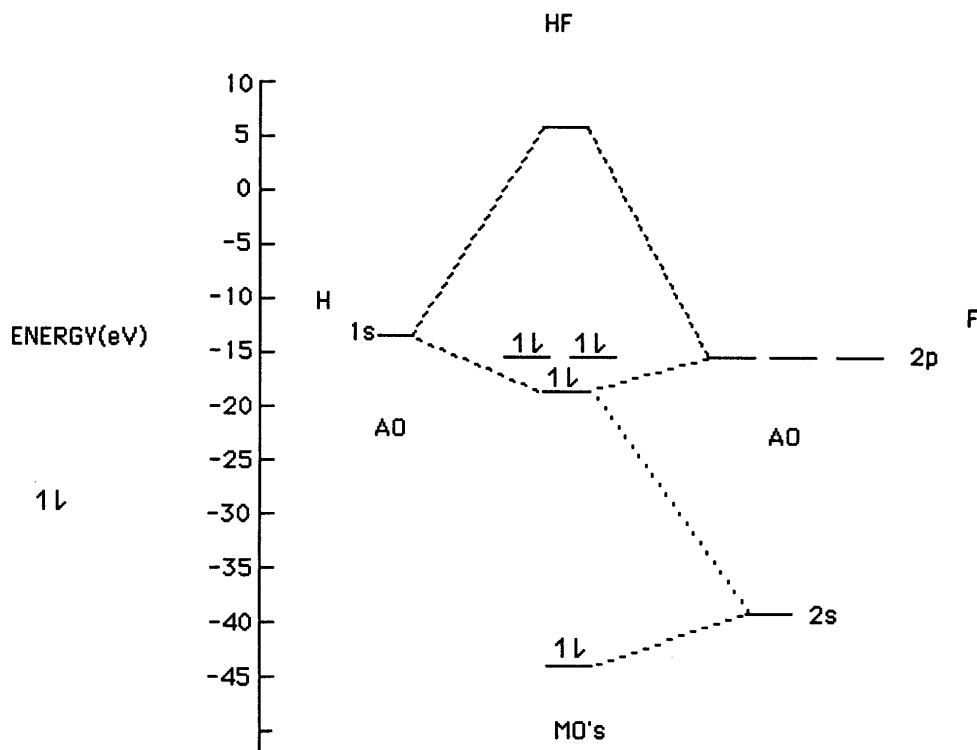
FOCK MATRIX IS

		1S	H	1	2S	F	2	2Px	F	2	2Py	F	2	2Pz	F	2
1S	H	1	-6.329743													
2S	F	2	-12.932297	-38.008471												
2Px	F	2	11.390509	0.183063	-11.327472											
2Py	F	2	0.000000	0.000000	0.000000	-14.824289										
2Pz	F	2	0.000000	0.000000	0.000000	0.000000	-14.824289									

BONDING CONTRIBUTION OF EACH M.O.

0.7166 1.1185 0.0000 0.0000 -1.8351
 TOTAL CPU TIME: 0.23 SECONDS

MNDO QUANTUM MECHANICAL CALCULATION



E.g. The $2p\sigma$ M.O. of homonuclear diatomics can be improved by adding in 2s AO's.

$$\psi_{\text{trial}} = \underbrace{C_A \psi_{2p_z}(A) + C_B \psi_{p_z}(B)}_{\text{usual combination}} + \underbrace{C'_A \psi_{2s}(A) + C'_B \psi_{2s}(B)}_{\text{extra}}$$

The Variation procedure will generate 4 eqns and 4 unknowns C_A , C_B , C'_A , C'_B .

Secular detm will be 4×4 .

It will turn out that $C_A, C_B \gg C'_A, C'_B$

Therefore minor contrib. from 2s A.O.'s.

Using computers, basis sets can include dozens of A.O.'s to produce and solve huge matrices of numbers and extremely accurate solutions.

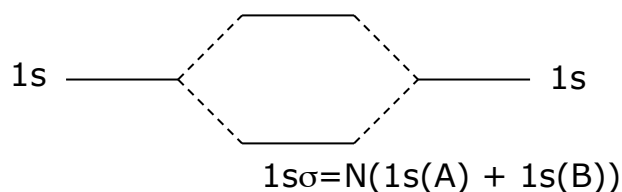
Still must evaluate α , β and S integrals These are done two ways:

- 1) semi empirical – estimate them from spectroscopic data.
- 2) ab initio – evaluate them numerically on the computer (Simpson's rule)

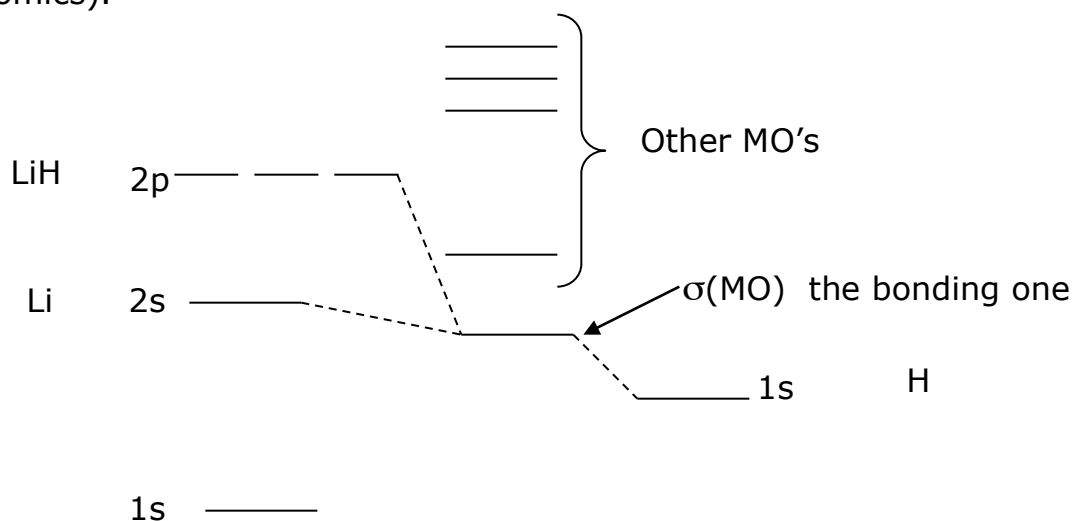
E. Hybridization can be used in MO theory also.

Introduced to try to preserve the idea that every MO is constructed by linear combination of only 2 AO's.

E.g.



In reality, in advanced MO calcs, every MO is produced by a LC of all the atomic orbitals in the basis set. Turns out that usually only a single AO from each atom contributes significantly to a given MO (esp in homonuclear diatomics).



$$\psi_{\sigma} = 0.414\psi_{2s}(\text{Li}) + 0.331\psi_{2p_x}(\text{Li}) + 0.848\psi_{1s}(\text{H})$$

From Variation treatment, 3 AO's end up contributing to σ bond in Li-H.

To preserve concept of overlap of 2 AO's to get MO hybridization idea is introduced.

1s H is seen as overlapping with a hybrid orbital (call it $\phi(\text{Li})$),

$\phi(\text{Li})$ = mixture of Li atomic orbitals prior to interaction with H.

$$\phi_L(\text{Li}) = \phi(\text{Li}) + 0.715 \psi_{2p}(\text{Li})$$

$$\text{Now } \psi_{\sigma} = 0.323 \phi(\text{Li}) + 0.685 \psi_{1s}(\text{H})$$

See that hybrid concept is cumbersome here.

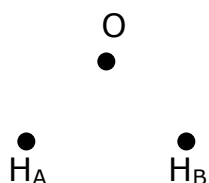
III. Polyatomic Molecules.

MO's are still constructed by LCAO, but using more atomic orbitals.

Ordinary procedure is to use all the AO's from the valence shell of every atom as our basis set.

A. Treat H₂O by LCAO-MO theory.

1. Position nuclei at a trial starting position.



2. Choose appropriate basis set =
(6 AO's in basis set)
- | | |
|-----------------|----------------|
| 1s | H _A |
| 1s | H _B |
| 2s | O |
| 2p _x | O |
| 2p _y | O |
| 2p _z | O |

3. Use Variation Principle. Will solve 6 x 6 secular determinant.

Will find 6 roots which are the 6 energies of 6 MO's produced.

6 MO's produced
6 energies

4. Walsh diagram – plot of energies of the different MO's as we bend the molecule.

Procedure: vary angles until lowest energy is obtained, always putting the valence e⁻ in the lowest energy orbitals possible.

* MOPAC: VERSION 6.00
Water, linear 180 degrees

CALC'D. 26-Oct-94

			FINAL HEAT OF FORMATION =		-16.01362 KCAL			
			EIGENVECTORS					
ROOT NO.			1	2	3	4	5	6
			-38.36620	-20.43460	-11.11085	-11.11085	3.66569	9.72546
S	H	1	-0.29829	0.47730	0.00000	0.00000	-0.64111	0.52171
S	O	2	-0.90667	0.00000	0.00000	0.00000	0.42185	0.00000
PX	O	2	0.00000	-0.73782	0.00000	0.00000	0.00000	0.67500
PY	O	2	0.00000	0.00000	-0.99961	-0.02782	0.00000	0.00000
PZ	O	2	0.00000	0.00000	-0.02782	0.99961	0.00000	0.00000
S	H	3	-0.29829	-0.47730	0.00000	0.00000	-0.64111	-0.52171

NET ATOMIC CHARGES AND DIPOLE CONTRIBUTIONS				
ATOM NO.	TYPE	CHARGE	ATOM ELECTRON DENSITY	
1	H	0.3664	0.6336	
2	O	-0.7328	6.7328	
3	H	0.3664	0.6336	
DIPOLE POINT-CHG.	X	Y	Z	TOTAL
HYBRID	0.000	0.000	0.000	0.000
SUM	0.000	0.000	0.000	0.000

Water, optimum

			FINAL HEAT OF FORMATION =		-60.92461 KCAL			
ATOM		CHEMICAL	BOND LENGTH	BOND ANGLE	TWIST ANGLE			
NUMBER	SYMBOL	(ANGSTROMS)	(DEGREES)	(DEGREES)				
(I)		NA:I	NB:NA:I	NC:NB:NA:I	NA	NB	NC	
1	H							
2	O	0.94000			1			
3	H	0.94000	106.92268	*	2	1		
EIGENVECTORS								
ROOT NO.		1	2	3	4	5	6	
		-40.47670	-18.16014	-15.45354	-12.31455	5.85841	5.97957	
S	H	1	-0.33152	0.43899	-0.34044	0.00000	-0.49342	0.58139
S	O	2	-0.87433	0.01750	0.37543	0.00000	-0.01728	-0.30659
PX	O	2	0.10787	-0.54937	0.54118	0.00000	-0.51874	0.35296
PY	O	2	-0.12305	-0.50143	-0.61997	0.00000	-0.42241	-0.41308
PZ	O	2	0.00000	0.00000	0.00000	1.00000	0.00000	0.00000
S	H	3	-0.31444	-0.50373	-0.25673	0.00000	0.55562	0.52228

NET ATOMIC CHARGES AND DIPOLE CONTRIBUTIONS			
ATOM NO.	TYPE	CHARGE	ATOM ELECTRON DENSITY
1	H	0.1630	0.8370
2	O	-0.3259	6.3259
3	H	0.1630	0.8370

DIPOLE	X	Y	Z	TOTAL
POINT-CHG.	-0.522	0.704	0.000	0.876
HYBRID	-0.539	0.728	0.000	0.906
SUM	-1.061	1.432	0.000	1.782

Water, 90 degree

FINAL HEAT OF FORMATION = -54.37055 KCAL
EIGENVECTORS

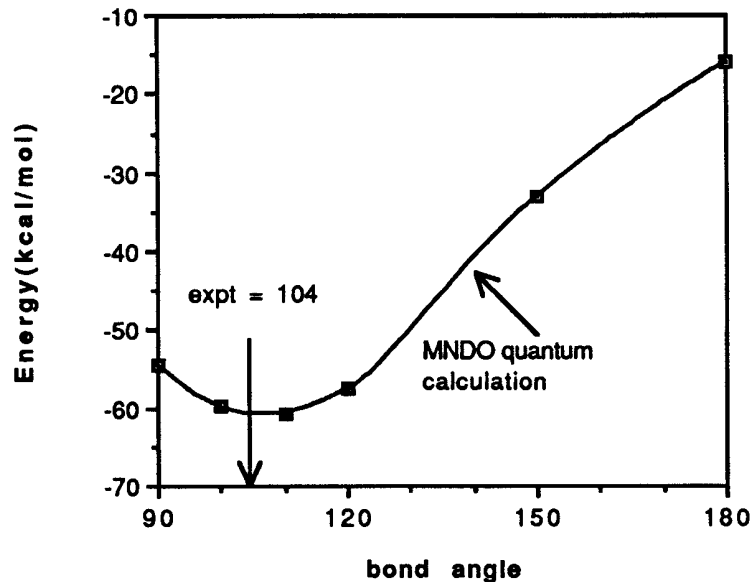
ROOT NO.	1	2	3	4	5	6
	-40.47670	-18.16014	-15.45354	-12.31455	5.85841	5.97957
S H 1	-0.32425	0.46451	-0.32988	0.00000	-0.53313	0.53483
S O 2	-0.87368	0.00000	0.39231	0.00000	0.00000	-0.28771
PX O 2	0.11491	-0.53313	0.56056	0.00000	-0.46451	0.41541
PY O 2	-0.11491	-0.53313	-0.56056	0.00000	-0.46451	-0.41541
PZ O 2	0.00000	0.00000	0.00000	1.00000	0.00000	0.00000
S H 3	-0.32425	-0.46451	-0.32988	0.00000	0.53313	0.53483

NET ATOMIC CHARGES AND DIPOLE CONTRIBUTIONS

ATOM NO.	TYPE	CHARGE	ATOM ELECTRON DENSITY
1	H	0.1405	0.8595
2	O	-0.2811	6.2811
3	H	0.1405	0.8595

DIPOLE	X	Y	Z	TOTAL
POINT-CHG.	-0.635	0.635	0.000	0.897
HYBRID	-0.650	0.650	0.000	0.919
SUM	-1.284	1.284	0.000	1.816

Walsh Diagram Bending of Water



B. Huckel Molecular Orbital theory (HMO theory).

An approximate theory that gives us a very quick picture of the MO energy diagram and MO's of molecules without doing a lot of work.

Structure and bonding of the π electrons in highly conjugated systems nicely treated by HMO. Look at examples:

1. Ethene – look at the π bond in this simple molecule first.

Each carbon has a $2p_z$ orbital perpendicular to plane of molecule. Use LCAO-MO to get two MO's, which gives rise to 2×2 secular determinant:

$$\begin{vmatrix} \alpha_A - E_{\text{trial}} & \beta - E_{\text{trial}} S \\ \beta - E_{\text{trial}} S & \alpha_B - E_{\text{trial}} \end{vmatrix} = 0$$

HMO approx:

Set all overlap integrals $S = 0$

Recognize the α integrals are equal

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

This gives quadratic $(\alpha - E)^2 - \beta^2 = 0$
 Roots $E = \alpha + \beta, \alpha - \beta$

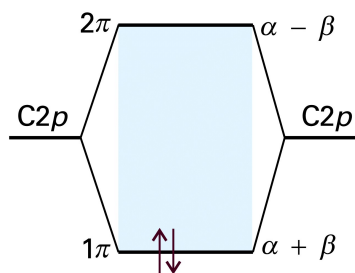


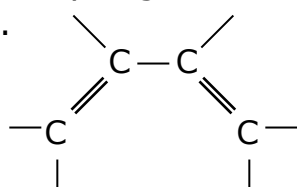
Figure 11-18
 Atkins Physical Chemistry, Eighth Edition
 © 2006 Pearson Education, Inc. and W. H. Freeman

$$\text{Total } \pi \text{ bond energy} = 2 (\alpha + \beta)$$

$$\text{Stabilization due to bond formation} = 2\beta$$

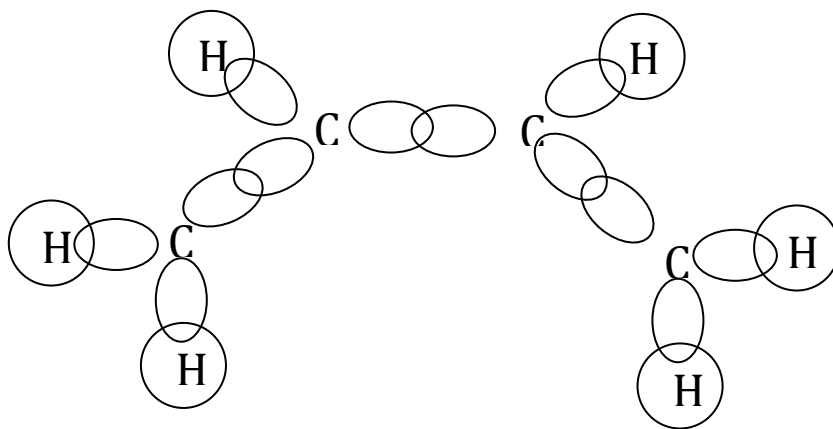
β is intrinsically negative and ~ -2.4 eV for C-C bond (~ -230 kJ/mol)

2. Butadiene.



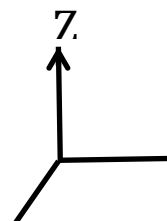
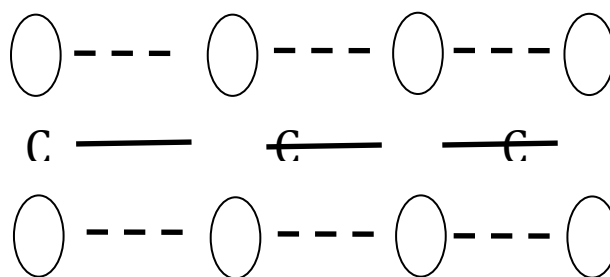
Treat sigma bonding framework using VB theory as follows:

sp^2 around each C forms σ -bonding framework



Still have an unused p orbital available on each C, perpendicular to plane of molecule.

Edge on view:



These extensively overlap to form a delocalized π system.

Treat π system by HMO as follow:

- basis set is composed of four $2p_z$ orbitals (perpendicular to plane).

Therefore will get 4×4 matrix or secular determinant

b. HMO approx:

- 1) Set all overlap integrals $S = 0$
- 2) Set all resonance integrals between non-neighbors = 0
 $\beta_{13}, \beta_{14}, \beta_{24}$ etc. = 0
- 3) Set all other resonance integrals (β) equal to one another.

Resulting Sec detm

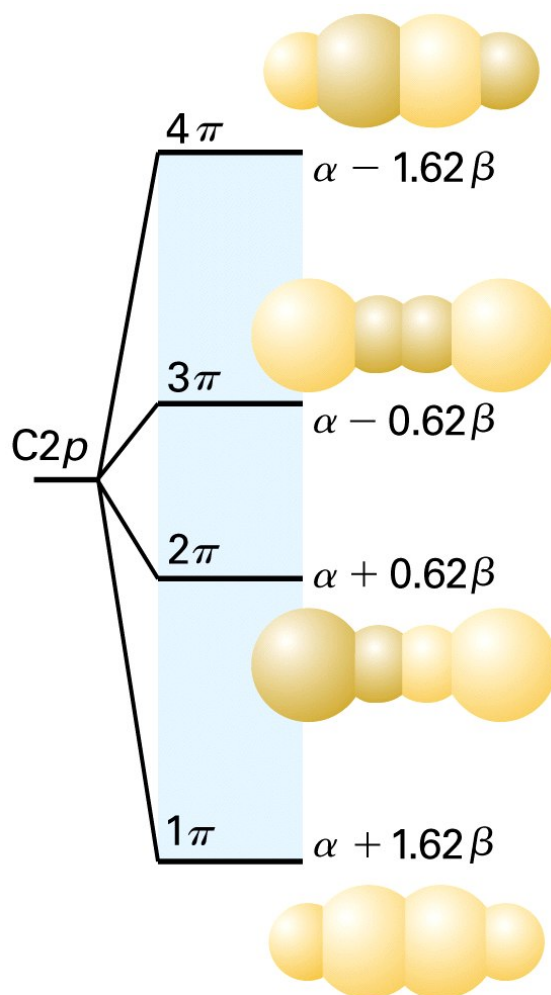
$$\begin{vmatrix} \alpha-E & \beta & 0 & 0 \\ \beta & \alpha-E & \beta & 0 \\ 0 & \beta & \alpha-E & \beta \\ 0 & 0 & \beta & \alpha-E \end{vmatrix} = 0$$

Generates a quartic polynomial in E which has four roots.

Therefore 4 π -orbital MO
 4 energies (roots of secular determinant)

They are: $E = \alpha \pm 1.62 \beta, \alpha \pm 0.62 \beta$

Energy diagram:



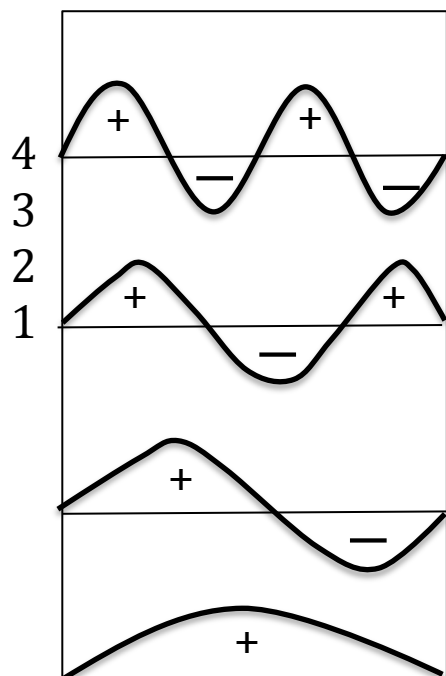
Spectroscopic transition HOMO \rightarrow LUMO (called frontier orbitals)

HOMO= highest occupied molecular orbital (here MO 2π)

LUMO = lowest unoccupied molecular orbital (here MO 3π)

$$\Delta E_{\text{trans}} = \text{LUMO} - \text{HOMO} = (\alpha - 0.62 \beta) - (\alpha + 0.62 \beta) = -1.24\beta$$

Compare wave functions with particle in box:



Delocalized system have extra stability (=deloc energy ΔE_{deloc})

Calculate it:

$$\Delta E_{\text{deloc}} = \text{Energy of c-c-c-c} - \text{Energy of c=c-c=c}$$

\uparrow Allow electrons To delocalize \uparrow 2 separate π bonds like in ethene

$$= [2(\alpha + 1.62 \beta) + 2(\alpha + 0.62 \beta)] - 2(2\alpha + 2\beta)$$

$$= 4\alpha + 4.48\beta - (4\alpha + 4\beta)$$

$$= 0.48\beta \sim -110 \text{ kJ/mol of stabilization}$$

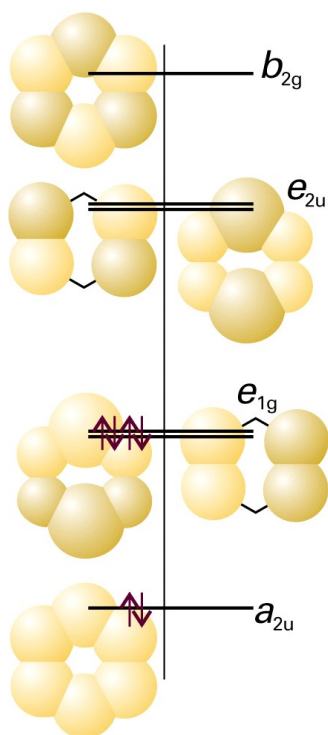
3. Benzene – cyclic delocalized system.

6x6 secular determinant =

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

due to cyclic connection

=Energy eigenvalues are $E = \alpha \pm 2\beta, \alpha \pm \beta, \alpha \pm \beta$



Calculate delocalization energy DE:

$$\text{Total pi electron energy} = 2(\alpha + 2\beta) + 4(\alpha + \beta) = 6\alpha + 8\beta$$

$$\text{Energy of C=C in ethene} = 3(2\alpha + 2\beta) = 6\alpha + 6\beta$$

$$\text{DE} = \text{difference} = 2\beta = -460 \text{ kJ/mol}$$

4. Solids are extreme case of delocalization.

Graphite is like benzene stretching to infinity.

C. Computational Chemistry: Solving the Schrodinger Equation for Molecules.

1. The molecular orbitals ϕ_i are produced by a linear combination of atomic orbitals ψ_k that are the basis set. N atomic orbitals produce N molecular orbitals.

$$\phi_i = \sum_{k=1}^N C_{ik} \psi_k$$

Finding the weighting coefficients C_{ik} is the essence of the problem to be solved.

C_{ik} = contribution AO k makes to MO i .

2. The *variation principle* forms the basis for making sure we have the "best", most accurate wave function for our molecule.

$$\text{Approximate MO energy} = \frac{\int \phi_i^* H \phi_i d\vec{r}}{\int \phi_i^* \phi_i d\vec{r}} \text{ is always } > E_i \text{ (true)}$$

So, by varying the coefficients C_{ik} which make up the MO function ϕ_i until we find the *minimum* energy possible, we are ensured of having the best ϕ_i and energy E_i afforded by the *basis set* we have chosen. The more robust the basis set, the more accurate the ϕ_i and E_i for the molecule.

3. The actual procedure for the above involves lots of matrix algebra with matrix elements derived from the following integral expressions:

$$\begin{aligned} S_{ik} &= \int \psi_i \psi_k d\vec{r} && \text{overlap integrals} \\ H_{ik} &= \int \psi_i H \psi_k d\vec{r} && \text{Coulomb integrals} \end{aligned}$$

4. The S_{ik} are a snap to solve. The harder problem is the H_{ik} . Different MO methods vary according to the way they handle this problem.
5. In the Coulomb integrals, H is an effective one-electron Hamiltonian which is complicated by the fact that it accounts for interactions with all the other electrons. H then has within it terms which require the electron density of *all the other electrons*.

Therefore one must "know" the solution ϕ_i before one starts, just to have the effective one-electron Hamiltonians H .

6. This implies an iterative solution called the Hartree-Fock self-consistent field (SCF) iteration. The Hartree-Fock one-electron

$$H^{\text{SCF}} = H^{\text{N}} + \sum_j J + \sum_j' K$$

Hamiltonian is often written as, where sum j is over all the other e-.

$$J_j = \int \phi_j^2(2) \frac{1}{r_{12}} d\vec{r}_2 \quad \text{Coulomb electronic interactions}$$

$$K_j = \int \phi_j(1)\phi_i(2) \frac{1}{r_{12}} d\vec{r}_2 \quad \text{exchange terms (due to Pauli)}$$

H^N = attraction of electrons to fixed nuclei and simple kinetic energy terms.

D. *Ab Initio* Hartree-Fock (HF) Methods:

1. All integrals are actually directly solved for the basis set employed, then the matrix diagonalization is performed.

The number of integrals needing to be solved increases as N^4 , where N = atoms.

2. ab initio HF methods then differ by the *basis set* employed.
3. Most intuitively obvious choice for basis set would be Slater-type atomic orbitals (STO). (Hydrogen-like with good $\zeta = Z_{\text{eff}}/n$ values):

$$\psi_k = C e^{-\zeta r} Y_{lm}(\theta, \phi)$$

Then, e.g. for each Carbon atom we use a 1s, a 2s, and three 2p atomic orbitals.

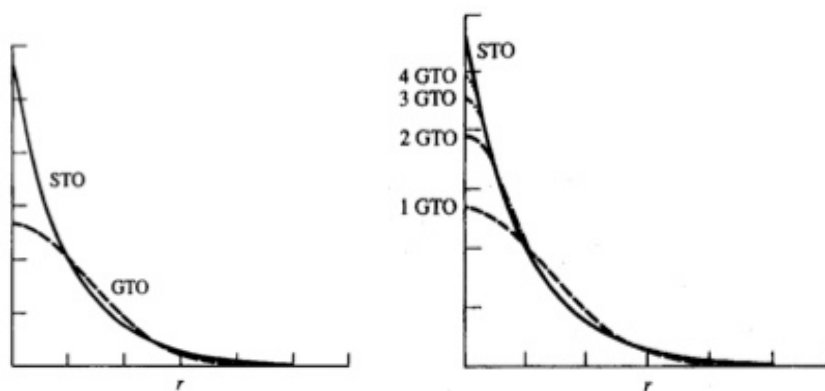
4. Easier to do integrals if ψ_k are of a Gaussian form instead of a Slater exponential:

$$e^{-ar^2} \text{ instead of } e^{-\zeta r}$$

But the true wave function is more nearly like $e^{-\zeta r}$ around nuclei, so we might use 3 Gaussian functions combined to approximate the Slater exponential. This is called:

STO - 3G

meaning "Slater-type orbitals built up using 3 Gaussians" or STO - 4G is more accurate. (3 seems to be the absolute minimum number of Gaussians to treat each AO.



5. Gaussian basis sets:

- Each Gaussian shape is determined by an exponential parameter and an expansion coefficient.
- Most flexible basis allow these to be varied independently. (Uncontracted or *primitive* Gaussians)
- More commonly use *contracted* Gaussians = exponents are pre-set and remain constant during calculation.
- Further, it is common for efficiency's sake to use the same Gaussian exponents for the s and p orbitals in a given shell on a given atom. (Restricts flexibility but reduces number of integrals).

6. Minimal basis set = contains AO up through the valence shell on each atom.

e.g. all the atomic orbitals in the shell

H and He, use 1s

Li to Ne, use 1s, 2s, three 2p

Third row, start adding 3d.

STO-nG are all minimal basis sets, using n Gaussians for each AO

Deficiencies in STO-nG:

- atoms at the end of a period are described using same number of basis functions as atoms at the beginning. Oxygen and Fluorine versus Lithium. (Contracted Gaussian radial exponents are not allowed to vary – expand or contract according to molecular environment.)
- Can't treat non-spherical anisotropies in wave function because $2p_x$, $2p_y$ and $2p_z$ are all the same size.

7. Short-hand notation schemes for the basis set used.

Double-zeta basis set uses a linear combination of two radial

exponents, one contracted and one diffuse, whose weightings are varied during the calc.

Split-valence double-zeta 3-21G basis set:

3 Gaussians to describe each core orbital.

3 Gaussians to describe each valence shell orbital,
with 2 being contracted and one being diffuse.

6-31G is also common and works the same way.

8. Strong anisotropic charge distributions: all basis sets above use functions centered on atomic nuclei.

Treating non-isotropic charge distribution around an atom done by introducing *polarization* functions into the basis set.

e.g., electron cloud around a H atom bonded to another atom is distorted in direction of the other atom. Can mimic this by mixing with the 1s a p-type orbital to give a form of sp hybrid.

Similarly, p orbitals can be enhanced by adding in d type orbitals to give pd hybrids which are more flexible in treating the distortion.

Use of polarization basis functions is denoted with asterisk:

3-21G* or 6-31G*

A single asterisk means polarization functions are used on only non-H atoms.

** is used when polarization is also applied to H atoms (good for treating H-bonding better).

See reference books for other commonly used abbreviations.

9. Another challenge is atoms with lone pairs, significant density away from nuclei. Highly diffuse functions are added to the basis set, denoted by using a "+" or "++"

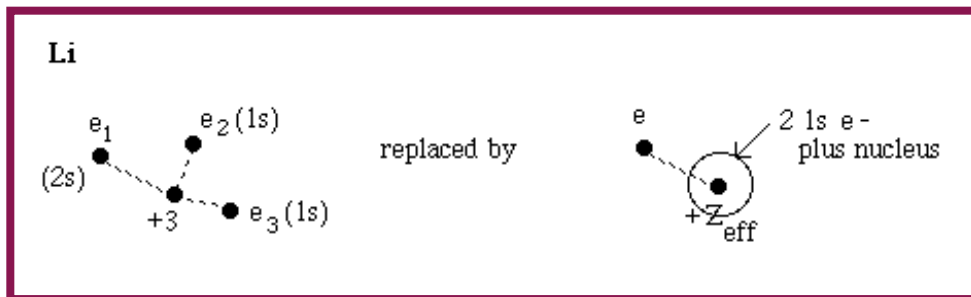
6-311++G(3df,3pd)

E. Semi-Empirical Methods:

1. Less computationally intensive than ab initio.
2. Many of the integrals are not actually directly solved, but are substituted for by parameters determined empirically, i.e., so as to

give good fit to specific experimental properties for a given class of molecules.

- Particularly the H^N integrals, which treat electron interaction with nuclei, are replaced by H^{core} , which involves attractions to the inner core rather than a bare nucleus. Then only valence shell electrons are treated explicitly.



- Some common semi-empirical quantum mechanics methods include:

CNDO - complete neglect of differential overlap
 INDO - intermediate neglect of differential overlap
 MNDO
 AM1 - Austin Model 1
 PM3 - Parameterized Model revision 3

Reference books abound which describe these various formulations.

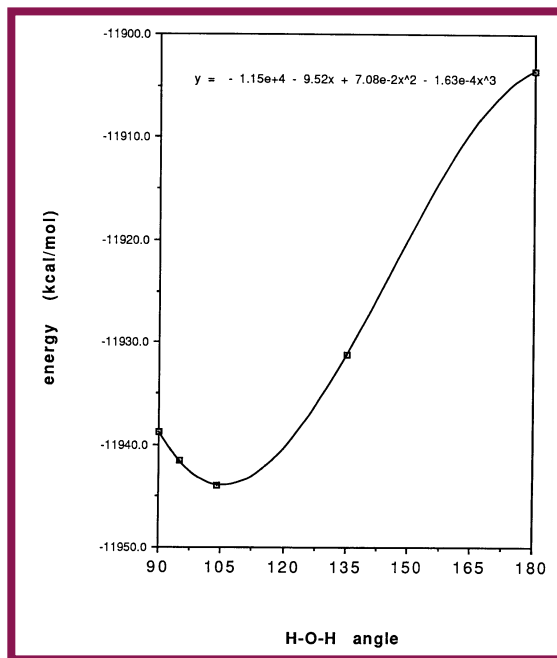
F. Molecular Geometry Optimization:

- All QM methods can solve the Schrodinger equation for MO's and energies (and everything else) for a **fixed** set of nuclear coordinates input by the user. This is called a *single point energy calculation*.
- They are also capable of computing forces on the atoms and moving them in a direction of decreasing total energy until an optimum geometry is reached. This is called *geometry optimization*, and is done iteratively through many steps.
- In the HF example, the user inputs starting positions of H and F such that the bond distance was 1.07Å. After 7 cycles of iteration, the energy decreased almost 30 kcal/mol and a final bond distance of 0.827Å was achieved. This is thus the predicted equilibrium bond length of H-F according to the AM1 Hamiltonian.
- In a **manual** geometry optimization of H₂O using the CNDO method, I performed a single-point energy calculation for a series of H-O-H bond angles starting from bent configuration (90°) and going to

linear configuration (180°). The following potential energy curve was derived.

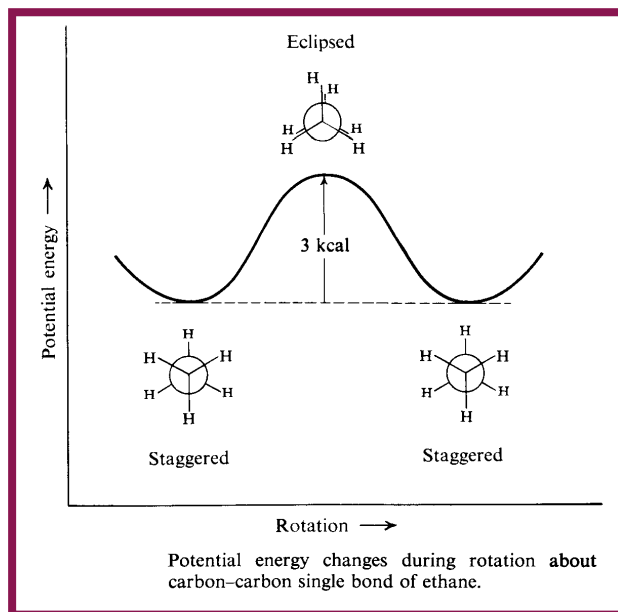
e.g. CNDO Calculation Energy of Bending Water

Note that CNDO predicts an equilibrium bond angle of 105°, compared with the experimental value of 104°. Further, we see that it costs 40 kcal/mol energy to "straighten out" water to 180°.



G. Molecular Conformation:

1. Most organic and biological molecules have freedom to rotate about bonds (A torsion angle rotation) and can exist in several conformational states. An example is butane, which rotates around the center C-C bond to produce g₊, trans, and g₋ conformations.
2. Conformational analysis is the process of systematically exploring the conformational states of a molecule, at each point doing single-point calculation to generate potential energy surface.

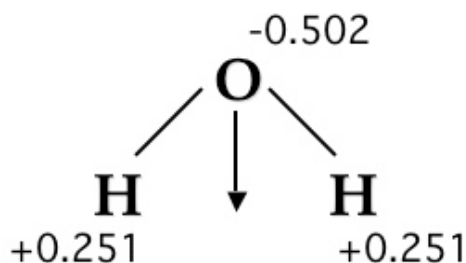


H. Other Quantities Accessible to QM Calculations:

1. Vibrational spectra can be calculated by normal mode analysis. (useful for vibrational spectroscopy)
2. Ionization potentials and electron affinities.
3. Charge distribution and dipole moment.

Mulliken population analysis: Partitions the electron density between the nuclei so that each nucleus has a non-integer number of electrons associated with it.

e.g. H₂O calculation with AM1 (Dipole moment = 1.66 D)



Then these point charges can be used to estimate the electrostatic potential around a molecule in molecular mechanics methods.

4. Electrostatic potential maps.
5. Frontier orbitals electron density:

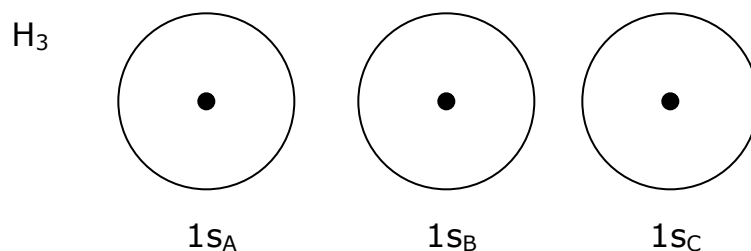
LUMO = lowest unoccupied molecular orbital

HOMO = highest occupied molecular orbital

Used to predict site of reactivity of molecules. Most highly reactive site on a molecule in an electrophilic reaction is the HOMO (the molecule is the e⁻ donor). For a nucleophilic attack it is the LUMO (the molecule is the e⁻ acceptor).

6. QSAR properties - (Quantitative Structure-Activity Relationships) can be calculated:
 - a. hydrophobicity = log P , where P=partition coefficient between octanol and water.
 - b. molecular volume
 - c. molecular surface area.

I. Problem in Homework: Use HMO to treat a hypothetical molecule H_3 .



The secular determinant would be:

$$\begin{vmatrix} \alpha-E & \beta_{AB}-E S_{AB} & \beta_{AC}-E S_{AC} \\ \beta_{BA}-E S_{BA} & \alpha-E & \beta_{BC}-E S_{BC} \\ \beta_{CA}-E S_{CA} & \beta_{CB}-E S_{CB} & \alpha-E \end{vmatrix} = 0$$

Now, the HMO approximations are:

non-neighbor resonance integrals β 's = 0
 all overlap integrals $S=0$
 all resonance integrals between neighbors = β

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

Cyclic add β

Cyclic add β

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

$$(\alpha-E) \{ (\alpha-E)^2 - \beta^2 \} - \beta \{ \beta(\alpha-E) - 0 \} = 0$$

$$(\alpha-E)^3 - (\alpha-E)\beta^2 - \beta^2(\alpha-E) = 0$$

Cubic equation but one root is $E = \alpha$, so factor out $(\alpha - E)$.

$$(\alpha - E)^2 - \beta^2 - \beta^2 = 0$$

$$(\alpha - E)^2 - 2\beta^2 = 0$$

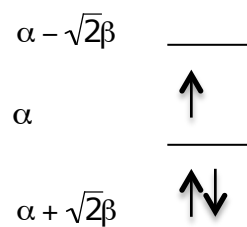
$$\alpha^2 - 2\alpha E + E^2 - 2\beta^2 = 0$$

This is a quadratic equation that can be solved for E .

$$E = \alpha \pm \sqrt{2}\beta$$

$E = \alpha$ is also a root

Energy diagram for linear H_3 :



NOTES: