PART FIVE: The Covalent Bond

- We can model bonding in molecules in essentially two ways.

- Localized Bounds (retains electron pair concept of Lewis Structures).

- Delocalized Molecular Orbitals.

![Diagram of Covalent Bond]

- COVALENT BOND
- Localized
- Valence Bond Theory (Heitler & London 1927)
- Hybridization (Pauling)
- Delocalized
- Molecular Orbitals
Valence Bond Theory For $H_2$

- $H + H \rightarrow H_2$ (Ch. 3 deK & G.)

- Combine wavefunctions $\psi_{1a}$ and $\psi_{1b}$.

- Multiply the functions.

\[
\psi_1 = 1sa(1) \ 1sb(2) \\
\begin{array}{c}
\uparrow \\
\text{Atom a} \\
\text{Electron 1}
\end{array}
\]

- This is a lousy guess
- Also it doesn’t take into account that we will not be able to distinguish electrons 1 and 2 at short internuclear distances.

Better is: $\psi_{II}^{(+)} = 1sa(1) \ 1sb(2) + 1sa(2) \ 1sb(1)$

$\psi_{II}^{(-)} = 1sa(1) \ 1sb(2) - 1sa(2) \ 1sb(1)$
- Further improvements can be made.

- Vary $z$ in atomic hydrogen wavefunction

$$\psi(1s) = \frac{1}{\sqrt{\pi}} \left( \frac{z}{a_0} \right)^{\frac{3}{2}} e^{-\frac{zr}{a_0}}$$

(Electron now attracted to 2 nuclei)

Effective $z \rightarrow \sim 1.7$ (NOT 2)
**Better Still: Hybridize !?!!**

- Remember hybridization?

- Mixing together orbitals to get hybrids that point at atoms.

This is quite reasonable—after all the orbitals are only functions.
• Why invoke hybridization for H₂?

Because it gives a lower energy. We know the real measured energy so this is clearly nearer the “truth”.

AND

• Represents Bond Better.

• Each H atom distorts the electron cloud on the other.

• Since 1s is spherically symmetric this does not represent the bond very well.

• 2pz orbital is not spherically symmetric, so we can add in a bit of this to make the bond look better.
Wavefunctions now are.

\[ \phi_a = N(1sa + \gamma za) \]

\[ \phi_b = N(1sb + \gamma zb) \quad (N = \text{Normalization constant to make sure } \int \phi^2 = 1) \]
• Best fit with experiment when $\gamma = 0.1$

• 99% of bonding is via 1s.

• But 1% p. character improves stability by 5%

- Polarized orbitals enhance electron density in bonding region of molecule.

  (d is the Heitler-London wavefunction)

Mixing is called HYBRIDIZATION

- creates more overlap.

- more bonding.
• wavefunction is still not that good-curve (d) is not that close to the experimental value.

• Further improvements can be obtained by adding terms to wavefunction where both electrons are on one atom.

Contribution of these is weighted (Factor $\lambda$)

i.e. $\psi = \phi_a(1) \phi_b(2) + \phi_a(2) \phi_b(1)$

$$+ \lambda \phi_a(1) \phi_a(2) + \lambda \phi_b(1) \phi_b(2)$$

($\lambda = 0.25; \lambda^2 \sim 0.06$, contribution is about 6%)

• These terms are related to the Resonance forms of the Lewis dot forms.
• So in QM we have to use a trial wavefunction and improve it to fit experiment.

• For H\textsubscript{2} a 50 term wavefunction reproduces the experiment bond energy to within 0.0001 ex.

WOW!

Today this is done with computers
Valence bond picture for HF: A nice example

\[ \text{H : F :} \]

Lewis Structure \[
\begin{align*}
\text{H} & : 1s^2 \\
\text{F} & : 1s^2 2s^2 2p_x^1 2p_y^2 2p_z^2 \\
\downarrow \\
\text{Simplest VB wavefunction for HF is} \\
\psi & = 1s_F^2 2s_F^2 2p_{xF}^2 2p_{yF}^2 [1s_H(1)2p_{2F}(2) + 1s_H(2)2p_F] \\
\end{align*}
\]

• This doesn’t work very well.

• Improvements made by using 2s on Fluorine.

• Done by hybridizing F 2s and F 2p_z

i.e. \( 2p_{ZF} \) is replaced by

\[ \phi_F = N(2p_{ZF} + \gamma 2s_F) \]
• Ionic terms can be introduced into the wavefunction.

• Good Idea! Based upon electronegativity considerations.

\[ H^+ F^- \text{ will contribute more than } H^- F^+ \]

Now

\[ \psi = 1S_H(1) \phi_F(2) + 1s_H(2) \phi_F(1) + \lambda(\phi_F(1) \phi_F(2)) \]

\[ \left\uparrow \right\uparrow \]

Both e\(^{-}\)s on F

“Ionic Term”

• Ionic term Contributes \(~50\%\) (compare only 6\% in H\(_2\)).
Advantages in Hybridization

Electron Density concentrated between nuclei

Decrease in e-e repulsion

Since part of 2s was mixed with the 2p the LONE PAIR is not simply $2s^2$.

$\phi_{ep} = N(2s - \gamma 2p)$

See Over ⇒
See deKock & Gray, p. 232.

Hybrids for HF
(a) Formation of bonding hybrid $\phi_F$
(b) Overlap with H 1s
(c) Formation of lone pair hybrid
(d) Electron density in of lone pair- note it points away from bond

Note Normalization:

\[ \phi_F = N(2p_{zF} + \gamma 2s_F) \]

\[ \int \phi_F^2 = N^2 \int (2p_{zF})^2 + N^2 \gamma^2 \int (2s_F)^2 \]

\[ 1 = N^2 + N^2 \gamma^2 \Rightarrow N = \frac{1}{\sqrt{1 + \gamma^2}} \]

Normalization is a funny word but basically means that when an orbital is "scanned" over all space you must find 1 electron.
Water: Hybrid Model

• Form bonding & lone pair hybrids.
• Like the Lewis Structure H₂O (2 lone pairs).
• If we only use 2pₓ 2pᵧ orbitals we end up with 2 bonds but H-Ô-H bond angle of 90° (0: 1s² 2s² 2pₓ² 2pᵧ² 2pₓ¹ 2pᵧ¹).
• One way out is to mix in 2s orbital.

See deKock & Gray pages 146-147.

• Hybrids of 2s, 2pᵧ 2pₓ.
See deKock & Gray, Fig 3.9

Bonding hybrids

Lone pair hybrids
• Like \( \text{sp}^3 \) but “fiddled” with to get bond angles right. In other words the 4 lobes are not quite a perfect tetrahedron. We can rationalize this by thinking about the \( s \) and \( p \) characters of the hybrids.

First we will write down the wavefunction and see what this means and then we will rationalize it.

In this course I will write \( \text{sp} \) hybrids in the general form:

\[
\phi = N (p + \gamma s)
\]

\( N \) is the normalization coefficient (see next page)
\( \gamma \) tells us how much \( s \) is added to the \( p \). It must be related to the \( s \) character of the hybrid. In order to get at this we need to normalize the wavefunction

All this means is that the new orbital contains 1 electron. So the integral of the function squared over all space = 1

So: \( \int \phi^2 \cdot dv = 1 \)

\[ \int N^2 (p + \gamma s)^2 = 1 \]

\[ = N^2 \int p^2 + N^2 \gamma^2 \int s^2 + 2 \gamma \int sp \]

\[ = N^2 + N^2 \gamma^2 + 0 \]
Note \[ \int \text{sp} = 0 \]

As much as ++ constructively interfere – balances this.

So:

\[ N^2 + N^2 \gamma^2 = 1 : N = 1 / \sqrt{1 + \gamma^2} \]

sp hybrid wavefunction is then:

\[ \phi = 1 / \sqrt{1 + \gamma^2} \cdot (p + \gamma s) \]
The s and p characters are now easy to get: It is the square of that part of the wavefunction:

\[
\text{s character} = \frac{\gamma^2}{1 + \gamma^2}
\]

\[
\text{p character} = \frac{1}{1 + \gamma^2}
\]

Finally:

\[\gamma\] the mixing coefficient is clearly related to the bond angle.
For example a 50:50 mix (sp hybrid)

\[\phi = N(s + p)\]

and \[N = 1/\sqrt{2}\] : i.e., \[N^2 \int s^2 + N^2 \int p^2 = 1\]
We will not prove it here but it transpires that:

\[ \cos \theta = -\gamma^2 \]

So for a sp hybrid the bond angle is 180°
Cos 180 = -1 so \( \gamma = 1 \)

\[ \phi_{sp} = 1/\sqrt{2} (s + p) \]

As we go through the sp hybrids you will see how this works. Lets go back to water for a moment and finish that molecule.

**********************************************************************************
Water: The bond angle is 104.5° (see CHEM 2070)

\[ \text{p character in O-H bonds} \]

\[
\begin{align*}
s \text{ character} &= \frac{\gamma^2}{1 + \gamma^2} \\
p \text{ character} &= \frac{1}{1 + \gamma^2}
\end{align*}
\]

\[
p \text{ character} = \frac{1}{1 + 0.25} = 0.8
\]

(cos 104.5° = - 0.25)

so the OH bonds are 80% p. (and 20% s)
p character of lone pairs:
Without the angle we cannot get $\gamma$- but we do know there are 3 p orbitals. So the TOTAL p character count must be 3. Let $x$ be the p character in the lone pairs.

$$0.8 + 0.8 + x + x = 3$$

There are 3p orbitals $\therefore x = 0.7$ (70% p) and 20%s

Angle between lone pairs

$p$ character $= 1/(1 + \gamma^2) = 0.7$

so: $-\gamma^2 = 1/0.7 - 1 = -0.42$

$\theta = 115^\circ$

Lone pairs are more separated than bonding pairs (More s character – “fatter”)

Q: Can you now write down the full wavefunctions for the water hybrids?
Ammonia, \( \text{NH}_3 \),

Lewis Structure: One lone pair

\[
\text{N: } 1s^2 \ 2s^2 \ 2p_x^1 \ 2p_y^1 \ 2p_z^1
\]

\[
\text{H} \cdot \circ \text{N} \cdot \circ \text{H} \\
\cdot \circ \text{H}
\]

Observed Bond Angle is 107.3°
* Hybrid involves N 2s

Hybrids have general form

\[ \phi = \frac{1}{\sqrt{1+\gamma^2}} \ (2p + \gamma 2s) \]

\[ (\cos \theta = -\gamma^2) \]

\[ p_{ch} = \frac{1}{1+\gamma^2}, \quad s_{ch} = \frac{\gamma^2}{1+\gamma^2} \]

\[ \cos \theta = \gamma^2 \]

• \[ \cos 107.3 = -\gamma^2; \quad \text{so } \gamma^2 = 0.29 \]

⇒ Each bonding hybrid has 77% p
Each bonding hybrid has 23% s
lone pair

Once again we have 3 p orbitals. 0.7 of each has been used up: Let $x$ be the p character of the lone pair:

So $x = 3 - 3(0.77) = 0.69$

2s character is then 31%

inserting values for $\gamma$ leads to

$$\phi = 0.88(2p) + 0.48 (2s)$$

$$\phi^2 = (0.88)^2 + (0.48)^2$$

77% 23%

Each hybrid has the form

$$\phi = 0.882p + 0.48 2s$$
Bonding molecule orbital picture for ammonia, NH₃

Lewis structure

Orbital picture

ACID

BASE

ammonia accepts a hydrogen ion

lone pair: two non-binding electrons in sp³ hybrid

net charge repels other bonds: bond angle < tetrahedron

hydrogen ion can "accept" electron pair

empty 1s orbital
**s and p Characters** (A final review)

For a 50/50 sp hybrid we can write

\[ \phi = (s + p) \]

but \( \int \phi^2 = 1 \)

\[ (s + p)^2 = 2 \quad \text{so we need to "normalize"} \]

\[ \phi = N(s + p); \quad \text{then } \int \phi^2 = 2N^2 = 1 \]

\[ \therefore \quad N = \frac{1}{\sqrt{2}} \]

\[ \phi = \frac{1}{\sqrt{2}} (s+p) \]

s character = \( \left( \frac{1}{\sqrt{2}} \right)^2 = 50\% \)

p character = \( \left( \frac{1}{\sqrt{2}} \right)^2 = 50\% \)
sp$^3$

Methane: c. 1s$^2$ 2s$^2$ 2p$^1$ 2p$^1$ 2p$^0$

- Hybridize 2s & 3 2p orbitals

\[ \phi = \frac{1}{\sqrt{1+\gamma^2}} (\gamma 2s + 2p) \]

Bond Angle = 109.5

\[ \cos \theta = -\gamma^2 = -0.33 \]

2s character = \[ \frac{\gamma^2}{(1+\gamma^2)} = 0.25(25\%) \]

2p character 75%
sp hybrid orbitals (for linear geometry, example BeF₂)

sp² hybrid orbitals (for trigonal planar geometry, example BF₃)

sp³ hybrid orbitals (for tetrahedral geometry, example CH₄)
**Orbital Electronegativity**

- s orbitals “pull” electrons more than p.
- s orbitals are none electronegative.
- \( \therefore \) electronegative substituents will have less s character to hybrid.

e.g.

\[
\begin{align*}
\text{Cl} & \quad \text{C} & \quad \text{H} \\
\text{Cl} & \quad \text{C} & \quad \text{H}
\end{align*}
\]

\[\text{Cl} \quad \text{C} \quad \text{Cl} < \quad \text{H} \quad \text{C} \quad \text{H}\]

\[\text{more s character.}\]

\[\text{bond s}\]

\[\therefore \text{is less s character}\]

\[(\text{pulls more p electrons } \Rightarrow \text{“skinnier bond”})\]
Molecular Orbitals

- VB Theory emphasizes electron pair bond (actually overemphasis).

- Very good for ground state properties (Geometries, Bond Dissociation Energies)

- Difficult to apply VB to excited states.

- MO theory better for spectroscopy (Also see 19-207).

Exited State Properties; Ionization,

VB – Products of atomic orbitals.

MO – Adds atomic orbitals.
• Molecular orbitals are formed by using a Linear Combination of atomic orbitals.

\[ \psi = \sum C_v \phi_v \]

• MO’s are **Delocalized**: Does not emphasize electron pairs in bonds.

First Example \( \text{H}_2^+ \) (deK & G. p. 184)
$H^+_2$; one electron held in MO

Ground State: $\psi = C_1 \phi_1 + C_2 \phi_2$

For $H_2$ there are 2 possibilities (add or subtract)

$\psi = 1sa + 1sb$ Bonding

$\psi^* = 1sa - 1sb$ Antibonding

\( \psi \) and \( \psi^* \)

\( \psi^2 \)

\( (\psi^*)^2 \)
• $1s_a + 1s_b \Rightarrow$ concentrates electron density between nuclei (reduces nuclear-nuclear repulsion).

• $1s_a - 1s_b \Rightarrow$ concentrated outside internuclear region. Has a NODE.
deKock & Gray, p. 246.

- Can think of concentration of electrons as an **Overlap** of the 1s atomic orbitals.
• MO’s can be classified according to *symmetry*.

\[ \sigma \sim \text{Rotational Symmetry} \]

\[ \sigma_\text{g} \sim \text{inversion centre} \]

\[ \sigma_\text{u} \sim \text{inversion centre} \]

\[ (\text{gerade} = \text{even}) \]

\[ (\text{ungerade} = \text{odd}) \]

\[ \sigma_\text{u}^* \equiv \text{Antibonding} \]

Wavefunction changes sign.

(N.B. *Not all* antibonding MO’s are u).
Normalized Wavefunctions

Bonding

\[ \psi = C_1 \ 1s_1 + C_2 \ 1s_2 \]

\[ \int \psi^2 = 1 \]

\[ \therefore \int (C_1 \ 1s_1 + C_2 \ 1s_2)^2 = 1 \text{ "overlap integral"} \]

\[ \int 1s^2 = 1 \]

so:

\[ C_1^2 + C_2^2 + 2C_1 C_2 \int 1s_1 \ 1s_2 \bigg|_{S=0} = 1 \]

* The approximation that \( \int 1s_1 \ 1s_2 = 0 \) involves a fairly substantial error in the case of \( H_2^+ \). The overlap in \( H_2^+ \) is actually 0.585. In most cases however \( s = 0 \) is an O.K. approximation.
So, $C_1^2 + C_2^2 = 1$, $C_1 = C_2$ by symmetry

$$\therefore \psi = \frac{1}{\sqrt{2}} (1s_1 + 1s_2) \quad \text{Bonding}$$

and

$$\psi^* = \frac{1}{\sqrt{2}} (1s_1 - 1s_2) \quad \text{Antibonding}$$

**SUMMARY:**

- Constructive overlap
- Destructive overlap
Overall, the energy of the \( \sigma_g \) is lower than the original 1s, and the \( \sigma_u^* \) is higher.

We will meet \( \alpha \) and \( \beta \) later.

**Bond Order** (see dek. & G., p. 198)

- Electrons in bonding orbitals give stability – cancelled by electrons in antibonding orbitals.

<table>
<thead>
<tr>
<th></th>
<th>Bonding Electrons</th>
<th>Anti-bonding Electrons</th>
<th>Net Bonding Electrons</th>
<th>Bond Length (Å)</th>
<th>Experimental Bond Energy kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>He(_2)</td>
<td>2</td>
<td>2</td>
<td>0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>H(_2^+)</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>1.06</td>
<td>256</td>
</tr>
<tr>
<td>He(_2^+)</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>1.08</td>
<td>231</td>
</tr>
<tr>
<td>H(_2)</td>
<td>2</td>
<td>0</td>
<td>2</td>
<td>0.74</td>
<td>432</td>
</tr>
</tbody>
</table>
Molecular Orbitals for Homonuclear Diatomics

- Molecular orbitals can be formed pictorially by looking at the way in which atomic orbitals overlap.

- For the 1st row we can simplify matters by using s and p orbitals.
p\pi - \pi orbitals change sign when rotated 180° about internuclear axis.

Here are the ways in which p – orbitals can overlap
Rules for filling molecular orbitals:
1. Electrons first occupy the MO’s of lowest energy: they enter higher-energy MO’s only when the lower energy orbitals are filled.
2. Each MO can accommodate a maximum of two electrons (Pauli exclusion principle).
3. MO’s of equal energy are occupied single electrons before electron pairing begins (Hund Principle).
• The MO’s are switched over at O and F.
• We will see why later.

\[ \text{Li}_2 \rightarrow \text{N}_2 \quad \text{O}_2, \text{F}_2 \]

\[ \text{B}_2 \text{ is paramagnetic- only works in this scheme (10 electrons)}. \]
Paramagnetism can be experimentally verified. Note that both MO schemes give an unpaired electron. This makes liquid oxygen sense a magnetic field which causes the unpaired electrons to line up in the field.
The orbitals are three dimensional of course. Make sure you can draw them in 2D.
Liquid oxygen is blue and is attracted to the poles of a magnet. Oxygen is said to have a triplet ground state (2 unpaired electrons). If the MO’s were otherwise oxygen would occur in the atmosphere with a singlet ground state. Singlet oxygen can be created for example photochemically. Such a small energy difference (about 1 ev) has massive ramifications for life on earth.

Singlet oxygen attacks cellular structures by oxidation. Such oxidative damage might be oxidation of cell membranes or proteins. When the accumulation of oxidative damage exceeds a threshold level, the cell begins to die.
Why are N$_2$, O$_2$ Different?

- Evidence is spectroscopic – See 19-207 photoelectron spectroscopy.
- If you are interested now, see dek. & G. ,p 212-217.

MO scheme depends on how close s and p orbitals are in energy.

Pictorially (hybrids)

Note: orbitals are also of correct symmetry to interact.
The key here is that the 2s – 2p energy gap dictates how strongly the orbitals interact. Orbitals interact only when (a) they are of the same symmetry and (b) are close in energy. As we go across the periodic table from left to right the 2s orbitals feel the pull of the additional nuclear charge to a greater extent than the 2p (why? they are on average closed to the nucleus and screen the 2p’s – see the radial wavefunctions). It is a matter of degree really- there IS sp mixing for all cases – it’s just so small for oxygen and fluorine that the σ orbital remains lower than the π-orbitals.
Note effect of increased $z^*$ on 2s vs. 2p.

- This modifies our ideas about bonding and antibonding orbitals.

<table>
<thead>
<tr>
<th>Orbital Character</th>
<th>Orbital Notation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma^*(z)$</td>
<td>$\sigma^<em>(s) - \sigma^</em>(z)$</td>
</tr>
<tr>
<td>$\pi^<em>(x) = \pi^</em>(y)$</td>
<td>$\pi_v^<em>(x) = \pi_v^</em>(y)$</td>
</tr>
<tr>
<td>$\sigma^*(z)$</td>
<td>$\sigma^<em>_v(z) - \sigma^</em>_v(z)$</td>
</tr>
<tr>
<td>$\sigma^*(z)$</td>
<td>$\sigma^<em>_v(z) + \sigma^</em>_v(z)$</td>
</tr>
<tr>
<td>$\sigma^*(z)$</td>
<td>$\sigma^<em>_v(z) + \sigma^</em>_v(z)$</td>
</tr>
<tr>
<td>$\sigma^*(z)$</td>
<td>$\sigma^<em>_v(z) + \sigma^</em>_v(z)$</td>
</tr>
</tbody>
</table>

**Orbital (no s-p mixing) | Bonding Character**

- Antibonding
- Bonding

**Orbital (with s-p mixing) | Bonding Character**

- Antibonding
- Bonding
- Slightly bonding
- Slightly antibonding

**Note**

- $\sigma^*(z)$
- $\pi^*(x) = \pi^*(y)$
- $\sigma^*(z)$
- $\sigma^*(z)$
- $\sigma^*(z)$
- $\sigma^*(z)$
- $\sigma^*(z)$
- $\sigma^*(z)$

**Diagram**

- Visualization of molecular orbitals with and without s-p mixing.
MO's for Diatomics
Summary: MO's explain well the following trends: see Fig 4.30 deK and G.
Heteronuclear Diatomics

- MO’s can only be classified by rotational symmetry (Inversion Symmetry is lost).

Now we look at HF and CO (See Problem set #8, Q8.)

Which orbitals do we use?

<table>
<thead>
<tr>
<th></th>
<th>VALENCE</th>
<th>ORBITAL</th>
<th>IP's</th>
</tr>
</thead>
<tbody>
<tr>
<td>IE's H</td>
<td>1s 13.6 eV</td>
<td>2s 40.2 eV</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>2p 18 eV</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Leave out the F2s atomic orbital (for now). We will see that there is some 2s mixing a bit later.

- Only use 2p_z (p_x & p_y have zero overlap).
Overlap of valence orbitals for HF molecule

So, \( \sigma_b = C_1[1s(H)] + C_2[2p_z(F)] \)

\( C_2 > C_1 : X_F > X_H \)

\( \sigma^* \) - composed mostly of H 1s.

\( \sigma_b \) composed mostly of F 2p\(_Z\).

Three "Lone Pairs" – corresponds to \( H—\overset{\cdot}{F} \):
• Note u and g labels do not apply.

• \( \psi = C_1 \phi_{1s} (H) + C_2 \phi_{2s} (F) + C_3 \phi_{2p_z} (F) \)

• 1\( \sigma \) is really very bonding
  2\( \sigma \) almost non-bonding

\[ \begin{align*}
\text{Single Bond} \\
\text{Sharing MOs}
\end{align*} \]

Hydrogen: 1s, \(-13.6\) eV
Fluorine: 2s, \(-40.2\) eV; 2p. \(-18.6\) eV

Actually the 2s orbital does contribute.
Hydrogen: 1s, -13.6 eV
Fluorine: 2s, -40.2 eV; 2p, -18.6 eV

Figure 4.9 Approximate MO energy-level diagrams for LiH and HF.

Bigger and Better

• We saw earlier that one of the more important distinctions between atomic orbitals of different energy is the number of nodes.

• This is also true for molecular orbitals.

• All Molecular Orbital Nodes must be symmetrically disposed.

“Linear” Molecules

→ Provides some “Intuition” of orbital shapes.

See pictures on next pages.

1. Successively higher energy orbitals have mo nodes symmetrically placed and increasing in number by one, in order from most stable to least stable.
2. An mo node through a nucleus means that the mo from that atom does not contribute.
3. The mo energy increases with increasing numbers of node because the net number of bonding interactions (between neighboring atoms) decreases by two as the number of mo nodes increases by one.
First let us start with a row of 1s orbitals. Once we have done this you will see how easy it is to write down both mo’s from s and p purely using symmetry. (No math involved).

<table>
<thead>
<tr>
<th>( n = 2 )</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( n = 3 )</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( n = 4 )</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( n = 5 )</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( n = 6 )</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>number of nodes</th>
<th>number of net bonding interactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>-2</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>-3</td>
</tr>
<tr>
<td>2</td>
<td>-1</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>-4</td>
</tr>
<tr>
<td>3</td>
<td>-2</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>0</td>
<td>4</td>
</tr>
<tr>
<td>5</td>
<td>-5</td>
</tr>
<tr>
<td>4</td>
<td>-3</td>
</tr>
<tr>
<td>3</td>
<td>-1</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>0</td>
<td>5</td>
</tr>
</tbody>
</table>
So:

Rules for constructing the linear MO pattern:
1. Left most atomic orbital is +
2. Right most atomic orbital is + in lowest energy MO the alternates sign.
3. The lowest mo has no nodes between neighbours
4. Nodes increase by 1 and are symmetrically placed, in successively higher mo’s.

**Words of encouragement**

By way of an example we can see how this works for the MO’s of a triatomic inorganic molecule. Now don’t freak out here – it is more important to be able to look at the MO scheme and understand it than be able to set it up from scratch. There are shortcuts to doing the latter and some you will learn a bit later – mostly we will be looking at organic molecules and see how the mo’s actually dictate reactivity. Believe it or not we will be able to make predictions about reactivity from the MO’s we will generate. Soon you will be able to write down the MO’s for benzene – literally on the back of an envelope
**p and s σ orbitals for triatomics**

Here are the overlaps. You can see how the p atomic orbitals overlap with each other now as well (5 above). See how they were drawn – first draw them as single (like 1s) and then add a "tail" of the appropriate sign.

BeH₂ looks like this: you can trace which are the major overlaps.
In deK and G they are drawn like this. Note the appearance and number of nodes:
We can extend these ideas to cyclic molecules.

Cyclic (Two-Dimensional) Molecules

A second important structural class of molecules is those with cyclic structures; you are aware of many from organic chemistry, and there are many inorganic types as well. The results given in Figure 4-1 for “linear” molecules provide a nice basis for introducing the forms of molecular orbitals of cyclic compounds. A convenient mnemonic device to use for the cyclic structures is to start with the orbital sketches of the linear molecule with the same number of atoms, and to “wrap” the linear arrangement into the cyclic arrangement:

When there are nodes present it can be a little tricky
Key is to make lines pass through centers of polygons.
This may seem a little esoteric (putting 3, 4 and 5 H atoms in a circle).

However it is actually incredibly useful. As before the circles can be turned into p orbitals very easily.

As we will see these form the $\pi$- molecular orbitals of organic molecules and control reactivity (we will do this very soon now).
So something you are familiar with:

\[ n = 6 \]

\[
\begin{array}{c}
\text{Original Structure} \\
1 \quad 2 \quad 3 \quad 4 \quad 5 \quad 6
\end{array}
\]

\[
\begin{array}{c}
\text{Transformed Structure} \\
1 \quad 2 \quad 3 \quad 4 \quad 5 \quad 6
\end{array}
\]

Leading to benzene: (see Fig 5-36 deK and G)

Each carbon 1 p electron to \( \pi \) system.
Summary:

So we can get the mo’s of some largish organics.

That’s not all – you will see how we can order them in the correct energy sequence by using “magic circles” soon.

These circles will let us identify the “Frontier Orbitals” of the molecules – those that collide when molecules react.

But first a side-step. We are going to determine the relative energies of the orbitals. This first will require some math – but then I will show you how to do it with the “magic circles”
ENERGIES

Lets go back to good old molecular hydrogen. **First recall this:**

\[
\begin{align*}
\text{Bonding} \\
\psi &= C_1 \ 1s_1 + C_2 \ 1s_2 \\
\int \psi^2 &= 1 \\
\therefore \int (C_1 \ 1s_1 + C_2 \ 1s_2)^2 &= 1 \text{ “overlap integral”} \\
\int 1s^2 &= 1
\end{align*}
\]
so: \[ C_1^2 + C_2^2 + 2C_1 C_2 \int \psi_1 \psi_2 = 1 \]

So, \( C_1^2 + C_2^2 = 1 \), \( C_1 = C_2 \) by symmetry

\[ \therefore \quad \psi = \frac{1}{\sqrt{2}} (1s_1 + 1s_2) \quad \text{Bonding} \]

and

\[ \psi^* = \frac{1}{\sqrt{2}} (1s_1 - 1s_2) \quad \text{Antibonding} \]

* The approximation that \( \int \psi_1 \psi_2 = 0 \) involves a fairly substantial error in the case of \( H_2^+ \). The overlap in \( H_2^+ \) is actually 0.585. In most cases however \( s = 0 \) is an O.K. approximation.
So bonding and antibonding orbitals are formed by addition and subtraction of ao’s.

- Formed by adding/subtracting $\phi_a$, $\phi_b$
Let us imagine 2 orbitals and form an MO.

$$\psi = C_A \phi_A + C_B \phi_B$$

Assuming $C_A = C_B$, then $(C_A = C_B = C)$: reasonable: each orbital contributes equally – no dipole moment
\int \psi^2 = 1 = 2C^2 + (2c\phi_a\phi_b) \quad \text{set to zero}

see p. 247, xxx of lecture notes.

\[ \psi = \frac{1}{\sqrt{2}}(\phi_A + \phi_B) \]

we have; \[ \psi = \frac{1}{\sqrt{2}}(\phi_a + \phi_b) \] Bonding

\[ \psi^* = \frac{1}{\sqrt{2}}(\phi_a - \phi_b) \] Antibonding

The energies of these are given by

\[ \psi(E = \alpha + \beta); \quad \psi^*(E = \alpha - \beta) \]

• What are \( \alpha \) and \( \beta \)?

• Can we work out their values – Yes very easy.
Schrodinger Equation: Recall \( \hat{H} \) is the Hamiltonian Operator and \( E \) is the energy.

\[
\frac{-\hbar^2}{8\pi^2m} \nabla^2 \psi = (E - V)\psi
\]
OR: \( \hat{H}_\psi = E\psi \)

So: \( \hat{H} \frac{1}{\sqrt{2}}(\phi_A + \phi_B) = E \frac{1}{\sqrt{2}} (\phi_A + \phi_B) \)

Left multiply by \( \psi \)

\[
\frac{1}{\sqrt{2}} (\phi_A + \phi_B) \hat{H} \frac{1}{\sqrt{2}} (\phi_A + \phi_B) = \frac{1}{\sqrt{2}} (\phi_A + \phi_B) E \frac{1}{\sqrt{2}} (\phi_A + \phi_B)
\]

Remembering that \( E \) is a number and that \( \phi_A \) is normalized. Integrate both sides over all space-gives (left-hand side)

\[
\frac{1}{2} \int \phi_A \hat{H} \phi_A + \frac{1}{2} \int \phi_B \hat{H} \phi_B + \frac{1}{2} \int \phi_B \hat{H} \phi_B + \frac{1}{2} \int \phi_B \hat{H} \phi_A + \frac{1}{2} \int \phi_B \hat{H} \phi_A = \alpha + \beta
\]
Right Hand side (EΦ)

\[ E \frac{1}{\sqrt{2}} (\phi_A + \phi_B) \]

Left multiply by Φ

\[ = \frac{1}{\sqrt{2}} (\phi_A + \phi_B) E \frac{1}{\sqrt{2}} (\phi_A + \phi_B) \]

\[ E + E \int \phi_A \phi_B \, dv \]

\[ = E + ES \]

\[ E = \frac{\alpha + \beta}{1 + S}, \quad E^* = \frac{\alpha - \beta}{1 - S} \]

(To a 1\(^{st}\) approx. \( S = 0 \))

so \( E = \alpha + \beta \)
\[ \alpha = \int \phi_A H \phi_A : \text{Coulomb Integral} \]

\[ \beta = \int \phi_A \hat{H} \phi_B : \text{Resonance Integral}. \]

- We have assumed \( C_A = C_B \) (Homonuclear Diatomic)

\[
E = \frac{\alpha + \beta}{1 \pm S} \quad \psi = \frac{\phi_A \pm \phi_B}{\sqrt{2(1 \pm S)}}
\]

- Bigger interaction the bigger \( \beta \).

- Bigger \( \beta \), bigger overlap

More bonding. Small \( \Delta \alpha \) and large \( \beta \)
\[ \alpha_A = \int \phi_A \hat{H} \phi_A \cdot dv \]
\[ \hat{H} \phi_A = E \phi_A \]
\[ \phi_A \hat{H} \phi_A = E \phi_A \phi_A \Rightarrow \int \phi_A \hat{H} \phi_A = E = \alpha_A \]

Roughly the energy of an electron in \( \phi_A \) (But A does have attraction. of nucleus 2 also).

\[ \alpha_A = \int \phi_A \hat{H} \phi_B \quad \alpha_B = \int \phi_B \hat{H} \phi_B \]

\[ \beta_A = \int \phi_A \hat{H} \phi_B \quad S = \int \phi_A \hat{H} \phi_B \]

- The bonds get stronger with more overlap.

s orbitals

No overlap \quad Small \quad S_{12} \to 1

- Principle of maximum overlap.
- Can be governed by symmetry.
e.g. $\text{sp}_x$

- zero overlap
- no bonding
Energies: Pictorial Route:
That wasn’t too bad was it? But you can imagine with more than two orbitals it can get a bit hairy. There are many approximate methods for getting MO energies. Here we look at some pictorial methods.

We will focus on the π- molecular orbitals of cyclic and linear polyenes (alternating single and double bonds.

The reactivity of organic molecules is governed largely by their FRONTIER ORBITALS

These are the Highest (Energy) occupied molecular Orbital: HOMO

And

Lowest (energy) unoccupied molecular Orbital
(More on this later)
The π-mo’s for linear and cyclic polyenes always contain the HOMO and LUMO: more examples soon.

ENERGIES
Frost Circles: Cyclic Systems. Place the molecule in a circle (point down). Where the corners touch marks a mo. So we see below FOUR π-mo’s, two of which are degenerate.

Example: cyclobutadiene

radius of Frost Circle = 2β; Centre = α
Not only that you can immediately write down the symmetries of the orbitals:

Remember:
You can add tails to get:

Each carbon atom contributes one p electron to the $\pi$- system (the other goes to the $\sigma$ bonds – "head to head p overlap).

So: the HOMO and LUMO here are

HOMO $\pi_2 \pi_3$

LUMO $\pi_4$
Another example: Benzene:

Frost Circle:

![Frost Circle Diagram]

Orbitals:

![Orbitals Diagram]
six \( \pi \)- electrons

what are the HOMO and LUMO??

And now linear dienes:

Soon we will be looking at reactions of linear polyynes (really) – first we need the HOMO and LUMO and the symmetries.
**Linear polyenes: Baker circles: 1984**

his brother

our Mark Baker

---

**A Geometric Method for Determining the Hückel Molecular Orbital Energy Levels of Open-Chain, Fully Conjugated Molecules**

A. D. Baker  
The City University of New York, Queens College, Flushing, NY 11367

M. D. Baker  
University of Toronto, Toronto, Ontario, Canada M5S 1A1

Texts dealing with the application of elementary quantum mechanics to organic systems generally include a description of the Frost circle mnemonic for calculating the Hückel molecular orbital energy levels of cyclic conjugated polyenes.1-3 The use of this mnemonic simplifies the time-consum ing task of creating and solving the appropriate secular equations.

Curiously, there is lacking in these texts any description of mnemonic devices for similar calculations on open-chain systems.4 We describe here such a device which is straightforward and which uses a line drawing of the molecule in setting up the geometric mnemonic.

The procedure is to draw a circle of diameter 4R and center A, exactly as would be done when using the Frost circle. Inside the circle, a line drawing of the open-chain molecule is constructed following the rules:

1. The line drawing should reflect the number of C=C bonds in the open-chain molecule, e.g., for ethylene for the allyl system, and for butadiene. (See figure and steps below.)

2. The line drawing should be symmetric with respect to the horizontal axis of the circle.

3. The termini of the line drawing should be equidistant from the top and bottom of the circle.

4. Each side of the line drawing should be of equal length, and this length should also be the same as the distance from either the top or bottom of the circle to the terminus of the line drawing (i.e., the dashed line and the heavy lines in the figure are of the same length).

The energy levels of the system are now given by the points at which the line drawing touches the circle.

The success of the method is readily established by simple trigonometry. The orbital energy levels are given by

\[ E = \alpha + n\beta \]

where \( m_j = (2\cos j\pi/(n + 1)) \) for \( j = 1, 2, \ldots, n \) and \( \alpha \) and \( \beta \) have their usual designations as the Coulomb and resonance integrals, in agreement with values found by solution of the appropriate secular equations.

**Acknowledgement**

We are grateful to W. F. Beerkowitz of Queens College for helpful discussion and suggestions.

---


6. Nevertheless, Frost and Musilis (J. Chem. Phys., 21, 572, 1953) have pointed out that the Hückel molecular orbital energy levels for an open-chain, open-chain-conjugated system are identical to some of the levels of an \((n + 4)\) atom, cyclic-conjugated molecule. On this basis a modification of the Frost circle approach to open-chain systems is possible. For teaching purposes, however, this is not particularly useful since it requires a knowledge of the Hückel results for cyclic systems to solve problems involving open-chain systems, while it is natural and the usual practice to consider the latter type of system first. The mnemonic described in the present paper avoids this difficulty, requiring prior knowledge of results for cyclic molecules.
The circle has a radius of $2\beta$ and the centre is $\alpha$. In order to get the energies right, “dummy” atoms are entered so that the molecule lies symmetrically within the circle.

For example: ethylene
Orbitals:

LUMO $\pi_g$

HOMO $\pi_u$

Make sure you can do $n=2$ to $n=6$ with Frost and Baker circles and write down the HOMO and LUMO and their symmetries.

See problem sets and tutorials.
A final word on the MO’s of ethylene.

We have written down the Mo’s of ethylene, their symmetries and their energies. These were only the $\pi$-orbitals. The others are:
(see deK and G Fig 5.32 and 5.33)

$\psi_6$ and $\psi_7$ are the orbitals we just wrote down.

(do not try to remember this figure – it is for understanding purposes only)
We can see the electrons come out of these orbitals with photoelectron spectroscopy.

And they all look like:
Frontier Orbitals

(see DeKock & Gray, p. 316)

Proton Affinity: (Like electron affinity)

\[ B(g) + H^+(g) \rightarrow BH^+ \quad PA(B) = -\Delta H \]

We can arbitrarily divide this into two steps:

\[ B + H^+ \rightarrow B^+ + H \]

\[ (\Delta H_1 = IE(B) - IE(H)) \]

AND

\[ B^+ + H \rightarrow BH^+ \]

\[ \Delta H_2 = -DE(BH) \]
• First Step \((B + H^+ \rightarrow B^+ + H)\)

  - Proton attacks \(B\) and one electron is transferred from \(B\) to \(H^+\).

  - Point of proton attack is HOMO

• Second Step \((B^+ + H \rightarrow BH)\)

  - Proton attaches at point of attack.

\[
\text{BASE} \quad \text{HOMO} \quad \begin{array}{c}
\uparrow \\
\downarrow \\
\end{array} \\
\begin{array}{c}
\uparrow \\
\downarrow \\
\end{array} \quad H^+
\]

• So we need to know what the HOMO looks like.
So \( PA(B) = IE(H) - IE(B) + DE(BH) \)

\[ IE(H) = 13.598 \text{ eV} \]

So: The smaller IP of molecule B, the \textit{larger} is its proton affinity.

\( H^+ \) is an \textit{Electrophile}:

- can remove electron density from B is IP is low)

- Using Frontier Orbitals (i.e. HOMO) we can predict shape of protonated form.
For molecules isoelectronic with Ne, we can use the Lewis electron-dot structures to depict their reaction with the proton:


$$\text{Ne}^2 + \text{H}^+ \rightarrow [\text{NeH}]^+$$

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Structure</th>
<th>$P_A$ (kcal mole$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{F}_2^+ + \text{H}^+$</td>
<td>$[\text{FH}]^+$</td>
<td>112</td>
</tr>
<tr>
<td>$\text{O}_2^+ + \text{H}^+$</td>
<td>$[\text{OH}]^+$</td>
<td>164</td>
</tr>
<tr>
<td>$\text{NH}_3 + \text{H}^+$</td>
<td>$[\text{NH}_2]^+$</td>
<td>201</td>
</tr>
<tr>
<td>$\text{CH}_4 + \text{H}^+$</td>
<td>$\text{CH}_5^+$</td>
<td>126</td>
</tr>
</tbody>
</table>

- Trends: $P_A$ increases from Ne $\rightarrow$ NH$_3$.
  - Each has lone pair that H can attack
  - and IP decreases NE$>$HF$>$H$_2$O$>$NH$_3$.
- But $P_A$ CH$_4$ $>$ $P_A$ HF – WHY?
  - (0 lone pairs) (3 lone pairs)
First We Look at Point of Attack

Homo in HF is $1\pi$ MO localized on F
H orbital HF orbitals F orbitals

Increasing energy
• Crucial Factor is Ionization Energy of HOMO (Doesn’t have to be a lone pair)

\[ \text{IP}\sigma \ CH_4 \ 12.05 \text{ eV} < \text{IP}(1\pi) \ HF \ 16.05 \text{ eV} \]

(Bonding)  (Lone Pair)

\[ \therefore \text{ PA CH}_4 > \text{ PA HF} \]
Organic Reactions: Diels-Alder Reactions

First recall:

- HOMO’s, LUMO’s etc. for $\pi$ MO’s.
- Method as before.

e.g. butadiene.

\[\text{Diagram of molecular orbitals and \pi orbitals for butadiene}\]
Add symmetry labels.

e.g. LUMO

\[ \pi_u \]

**Energies**

\[ \alpha - 1.62 \beta \]
\[ \alpha - 0.62 \beta \]
\[ \alpha + 0.62 \beta \]
\[ \alpha + 1.62 \beta \]
See also Frost Circle for Cyclics
Diels Alder Cycloaddition Reactions

\[ \text{heat} \]

\[ \text{no reaction} \]

\[ \text{light} \]
WHY?

HOMO of diene  LUMO of diene

LUMO of alkene  HOMO of alkene

Photochemical Stimulation

\[
2 
\xrightarrow{hv} 
\text{75% yield}
\]

In these reactions it is very easy to see if there is a reaction or not:

\[ \pi_u \pi_u \quad \text{+ve overlap} \]

\[ \pi_g \pi_g \quad \text{+ve overlap} \]

\[ \pi_g \pi_u \quad \text{-ve overlap} \]

LIGHT (reacts)

HEAT (no reaction)
We made it. That’s all folks.

Good Luck with the final. Come and see me with any problems. Come as groups or by yourselves.

Last Revision – October 2008