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PERIODIC PROPERTIES

**TYPE-I:**

* Noble Gases-Inert Gases (zero group) -He, Ne, Ar, Kr, Xe, Rn.
* Stable configuration (ns²np⁶) this implies 8e⁻.

**TYPE-II:**

Elements with all (or) almost outermost shell in complete.

\[ 1s^15^2s^3s^- \text{block (or) P-block 2s}^22p^1 \]

**S-block metals:**

1. All are metals.
2. CS, Rb-Highly reactive.
3. Melting and boiling point is lower compared to transition metals (Loosely bounded e.s).
4. Lower density:
5. Ionisation energy is very low this implies energy required to removed the e.s readily form positive ions.
6. Good electrical conductors.
7. High lattice energy due to greater ionic character and greater inner ionic forces of attraction.
Licl > Nacl > Kcl > Rbcl > Cscl
7. Oxidation state this implies +1 only.
8. Alkaline earth metals this implies +2.
9. Except Li, Be all are ionic compounds.

**Buli-co-valent Bond:**
2. Diamagnetic.

**B-block elements:**
1. Non Metals, Metalloids and metals. {B, Si, Ge, As, Sb, Te, Bi, etc}.

   Left → Right (ionization potential and electro-negativity increases).

2. High electron affinity.
   Smaller size compared to S-block elements.
   Left → Right (Atomic size decreases).

3. Oxidizing power:
   Left → Right (increases)

4. Halogens are strong oxidizing.
   Al-Reducing.
5. It forms hydrides:
   NH₃, PH₃, ASH₃, SbH₃, BiH₃

   Basic Character
   NH₃ > PH₃ > ASH₃ > SbH₃ > BiH₃ ← stability order

6. P₄g₈ Elemental Sulphur.
**d-Block elements:**
1. Incomplete outermost shells.
2. Generally contains two electrons in ns orbital.

**Properties:**
Transition metals (elements) between S and P.
1. All are metals.
2. High melting and boiling point.
3. W - High melting point.
5. Many are paramagnetic (variable oxidation states).

**Molecular orbital theory:**

*Valence bond theory* gave us a qualitative picture of chemical bonding. Useful for predicting shapes of molecules, bond strengths, etc. It fails to describe some bonding situations accurately because it ignores the wave nature of the electrons.

*Molecular orbital (MO) theory* has the potential to be more quantitative. Usually we settle for simplified models here too. These simple models do not give very accurate orbital and bond energies, but they do explain concepts such as resonance (e.g., in the ferrocene molecule) that are hard to represent otherwise.

We can get accurate energies from MO theory by computational "number crunching". While MO theory is more "correct" than VB theory and can be very accurate in predicting the properties of molecules, it is also rather complicated even for fairly simple molecules.

For example, you should have no trouble drawing the VB pictures for CO, NH₃, and benzene, but we will find that these are increasingly challenging with MO theory.

*Constructing the molecular orbitals for a molecule:*
We use atomic orbitals (AO) as a basis for constructing MO's.
Molecular orbital theory

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Constructing the molecular orbitals for a molecule:

We use atomic orbitals (AO) as a basis for constructing MO's.

LCAO-MO = linear combination of atomic orbitals
Physicists call this the "tight binding approximation."

The molecular orbitals, also called wavefunctions (ψ), are obtained by adding and subtracting atomic orbitals (φ). The φ's are multiplied by scalar coefficients (c) to give normalized linear combinations.

For example, to make MO's from two AO's φ₁ and φ₂, we write:

ψ₁ = c₁φ₁ ± c₂φ₂; or
ψ₁ = c₁φ₁ + c₂φ₂ and ψ₂ = c₁φ₁ - c₂φ₂

e.g.,

atomic orbital 1
 e.g., H 1s
φ₁(x,y,z)

atomic orbital 2
 e.g., Cl 3pₓ
φ₂(x,y,z)
Nodes. The wavefunctions $\phi$ and $\psi$ are probability amplitudes. They have lobes with (+) or (-) signs, which we indicate by shading or color. Wherever the wavefunction changes sign we have a node. As you can see in the picture above, nodes in MOs result from destructive interference of (+) and (-) wavefunctions. Generally, the more nodes, the higher the energy of the orbital.

In this example we have drawn a simplified picture of the Cl 3p$_z$ orbital and the resulting MOs, leaving out the radial node. Recall that 2p orbitals have no radial nodes, 3p orbitals have one, 4p have two, etc. The MOs we make by combining the AOs have these nodes too.

Normalization. We square the wave functions to get probabilities, which are always positive or zero. So if an electron is in orbital $\phi_1$, the probability of finding it at point xyz is the square of $\phi_1(x,y,z)$. The total probability does not change when we combine AOs to make MOs, so for the simple case of combining $\phi_1$ and $\phi_2$ to make $\psi_1$ and $\psi_2$,

$$\psi_1^2 + \psi_2^2 = \phi_1^2 + \phi_2^2$$

Overlap integral and $c$ values. The spatial overlap between two atomic orbitals $\phi_1$ and $\phi_2$ is described by the overlap integral $S$,

$$S = \int \phi_1 \phi_2 d\tau$$

where the integration is over all space ($d\tau = dx dy dz$).

From the normalization criterion we get:

$$\psi_1 = \frac{1}{\sqrt{2}} \left( \frac{1}{1 + S} \right) (\phi_1 + \phi_2) \quad \text{(bonding orbital)}$$

and

$$\psi_2 = \frac{1}{\sqrt{2}} \left( \frac{1}{1 - S} \right) (\phi_1 - \phi_2) \quad \text{(antibonding orbital)}$$

In the case where $S=0$, this simplifies to $c_1 = c_2 = \frac{1}{\sqrt{2}}$.

Energies of bonding and antibonding MOs:

The energies of the bonding and antibonding molecular orbitals ($\psi_1, \psi_2$) are lower and higher, respectively, than the energies of the atomic basis orbitals $\phi_1$ and $\phi_2$. 

For the simple case where $\phi_1$ and $\phi_2$ have the same energy (e.g., the two H 1s orbitals that combine to make the MO's of the H$_2$ molecule) we have the following picture:

The energy of an electron in one of the atomic orbitals is $\alpha$, the Coulomb integral.

$$\alpha = \int \phi \, H \, \phi \, d\tau = \int \phi_2 \, H \, \phi_2 \, d\tau,$$

where $H$ is the Hamiltonian operator. Essentially, $\alpha$ represents the ionization energy of an electron in atomic orbital $\phi_1$ or $\phi_2$.

The energy difference between an electron in the AO's and the MO's is determined by the exchange integral $\beta$,

$$\beta = \int \phi \, H \, \phi \, d\tau$$

Note that the bonding orbital is stabilized by an energy $\frac{\beta}{1 + S}$ and the antibonding orbital is destabilized by $\frac{\beta}{1 - S}$. That is, the antibonding orbital goes up in energy more than the bonding orbital goes down. This means that H$_2$ ($\psi_1^2 \psi_2^0$) is energetically more stable than two H atoms, but He$_2$ with four electrons ($\psi_1^2 \psi_2^2$) is unstable relative to two He atoms.

**Heteronuclear case** (e.g., HCl):
The bigger the electronegativity difference between atomic orbitals (the larger $\Delta \alpha$ is) the more “$\phi_2$ character” the bonding orbital has, i.e., the more it looks like the Cl $3p_z$ orbital in this case. This is consistent with the idea that H-Cl has a polar single bond.

The antibonding orbital (empty) has more H-character.

*Extreme case - ionic bonding (NaF):* very large $\Delta \alpha$

\[
\begin{align*}
\phi_1 & \quad \text{(Na 3s)} \\
\psi_2 & \\
\psi_1 & \quad \phi_2 \quad \text{(F 2p_z)}
\end{align*}
\]

In this case, there is not much mixing between the AO’s because their energies are far apart. The two bonding electrons are localized on the F atom, so we can write the molecule as Na$^+$F$^-$. Note that if we were to excite an electron from $\psi_1$ to $\psi_2$ using light, the resulting electronic configuration would be ($\psi_1^+, \psi_2^-$) and we would have Na$^{0+}$F$^0$. This is called a *charge transfer* transition.

**Summary of MOs so far:**

- Add and subtract AO wavefunctions to make MOs. Two AOs $\rightarrow$ two MOs. More generally, the total number of MOs equals the number of AO basis orbitals.

- We showed the simplest case (only two basis orbitals). More accurate calculations use a much larger basis set (more AOs) and solve for the matrix of $c$’s that gives the lowest total energy, using mathematically friendly models of the potential energy function that is part of the Hamiltonian operator $H$.

- More nodes $\rightarrow$ higher energy MO

- Bond order $= \frac{1}{2} (\# \text{ of bonding electrons} - \# \text{ of antibonding electrons})$

- Bond polarity emerges in the MO picture as orbital “character.”
MO theory

AOs that are far apart in energy do not interact much when they combine to make MOs.

**Orbital symmetry**

The MO picture gets complicated when many AOs are involved. We can simplify the problem enormously by noting (without proof here) that orbitals of different symmetry with respect to the molecule do not interact.

AO’s must have the same nodal symmetry (as defined by the molecular symmetry operations), or their overlap is zero.

For example, in the HCl molecule, the molecular symmetry axis is $z$.

![HCl molecule diagram]

Because these two orbitals have different symmetries, the Cl 3$p_y$ orbital is nonbonding and doesn’t interact with the H 1$s$. The same is true of the Cl 3$p_x$ orbital. The $p_x$ and $p_y$ orbitals have π symmetry (nodal plane containing the bonding axis) and are labeled $\pi_{nb}$ in the MO picture.

The H 1$s$ and Cl 3$p_z$ orbitals both have σ symmetry and make the bonding and antibonding combinations shown on p.1.

Inorganic compounds use s, p, and d orbitals (and more rarely f orbitals) to make bonding and antibonding combinations. These combinations result in σ, π, and δ bonds (and antibonds).

In organic compounds, σ and π bonding is found naturally. In inorganic chemistry, π bonds can be made from p- and/or d-orbitals. δ bonds are more rare and occur by face-to-face overlap of d-orbitals, as in the ion $Re_2Cl_8^{2-}$. The fact that the Cl atoms are eclipsed in this anion is evidence of δ bonding.

Because π-π bonding involves sideways overlap of π-orbitals, it is most commonly observed with second-row elements (C, N, O). π-bonded compounds of heavier elements are rare because the larger cores of the atoms prevent good π-overlap. For this reason, compounds containing C=C double bonds are very common, but those with Si=Si bonds are rare. δ bonds are generally quite weak compared to σ and π bonds. Compounds with metal-metal δ bonds occur in the middle of the transition series.
The $\sigma$, $\pi$, and $\delta$ bonding geometries are sketched below:

- $\sigma$ MO: no nodes passing through nuclei
  - $\sigma (s,s)$
  - $\sigma (p,p)$
  - $\sigma (s,p)$

- $\pi$ MO: one node passing through nuclei
  - $\pi (p,p)$

- $\delta$ MO: two nodes passing through nuclei
  - $\delta (d,d)$
  - $\delta (p,d)$

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**Diatom molecules**

Valence bond theory fails for a number of the second row diatomics, most famously for O$_2$, where it predicts a diamagnetic, doubly bonded molecule with four lone pairs. O$_2$ does have a double bond, but it has two unpaired electrons in the ground state, a property that can be explained by the MO picture. We can construct the MO energy level diagrams for these molecules as follows:

![Diagram of MO energy level diagrams for Diatomic molecules](Diagram)

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We get the simpler picture on the right when the 2s and 2p AOs are well separated in energy, as they are for O, F, and Ne. The picture on the left results from mixing of the $\sigma_{2p^*}$ and $\sigma_{2p}$ MO's, which are close in energy for Li$_2$, Be$_2$, B$_2$, C$_2$, and N$_2$. The effect of this mixing is to push the $\sigma_{2p^*}$ down in energy and the $\sigma_{2p}$ up, to the point where the $\pi$ orbitals are below the $\sigma_{2p}$.

**Orbital filling**

MO’s are filled from the bottom according to the Aufbau principle and Hund’s rule, as we learned for atomic orbitals.

**Question:** what is the quantum mechanical basis of Hund’s rule?

(hint: it has something to do with the Pauli exclusion principle)

For O$_2$ (12 valence electrons), we get this MO energy diagram:
This energy ordering of MOs correctly predicts two unpaired electrons in the $\pi^*$ orbital and a net bond order of two (8 bonding electrons and 4 antibonding electrons).

Other interesting predictions of the MO theory for second-row diatomics are that the C$_2$ molecule has a bond order of 2 and that the B$_2$ molecule has two unpaired electrons (both verified experimentally).

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We can also predict (using the O$_2$, F$_2$, Ne$_2$ diagram above) that NO has a bond order of 2.5, and CO has a bond order of 3.

The symbols "g" and "u" in the orbital labels, which we only include in the case of centrosymmetric molecules, refer to their symmetry with respect to inversion. Gerade (g) orbitals are symmetric, meaning that inversion through the center leaves the orbital unchanged. Ungereade (u) means that the sign of the orbital is reversed by the inversion operation. Because g and u orbitals have different symmetries, they have zero overlap with each other. As we will see below, factoring orbitals according to g and u symmetry simplifies the task of constructing molecular orbitals in more complicated molecules.

The orbital shapes shown above were computed using a one-electron model of the molecule, as we did for hydrogen-like AOs to get the shapes of s, p, and d-orbitals. To get accurate MO energies and diagrams for multi-electron molecules, we must include the fact that electrons are “correlated,” i.e. that they avoid each other in molecules because of their negative charge. This problem cannot be solved analytically, and is solved approximately in numerical calculations by using density functional theory (DFT).
π-bonding must involve a second-row element!

We encounter π-bonding from the sideways overlap of p-orbitals in the MO diagrams of second-row diatomics (B₂...O₂). It is important to remember that π-bonds are weaker than σ bonds made from the same AOs, and are especially weak if they involve elements beyond the second row.

Example:

Ethylene: stable molecule
Doesn’t polymerize without a catalyst

Silylene: never isolated, spontaneously polymerizes
Calculations indicate 117 kJ/mol stability in gas phase relative to singly-bonded (triplet) H₂Si-SiH₂

Large Ne core of Si atoms inhibits sideways overlap of 3p orbitals → weak π-bond

Other examples: P₄ vs. N₂

P cannot make π-bonds with itself, so it forms a tetrahedral molecule with substantial ring strain. This allotrope of P undergoes spontaneous combustion in air.

N can make π-bonds, so N₂ has a very strong triple bond and is a relatively inert diatomic gas

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(CH₃)₂SiO vs. (CH₃)₂CO

<table>
<thead>
<tr>
<th>-Si-O-</th>
<th>H₃C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C=O</td>
</tr>
</tbody>
</table>

“RTV” silicone polymer (4 single bonds to Si) vs. acetone (C=O double bond)

Also compare: SiO₂ (mp ~1600 °C) vs. CO₂ (sublimes at -78 °C)

S₈ (solid, ring structure) vs. O₂ (gas, double bond)

2nd row elements can form reasonably strong π-bonds with 3rd row elements, e.g., in sulfur-nitrogen compounds such as S₂N₂, S₃N₃⁻, etc.
Three-center bonding

Many (but not all) of the problems we will solve with MO theory derive from the MO diagram of the \( \text{H}_2 \) molecule, which is a case of two-center bonding. The rest we will solve by analogy to the \( \text{H}_3^+ \) ion, which introduces the concept of three-center bonding.

We can draw the \( \text{H}_3^+ \) ion (and also \( \text{H}_3 \) and \( \text{H}_3^- \)) in either a linear or triangular geometry.

Walsh correlation diagram for \( \text{H}_3^+ \):

A few important points about this diagram:

- For the linear form of the ion, the highest and lowest MO’s are symmetric with respect to the inversion center in the molecule. The term symbol “\( g \)” (from German gerade) means that an orbital has this kind of symmetry, whereas “\( u \)” means antisymmetric with respect to inversion. Note that the central 1s orbital has \( g \) symmetry, so by symmetry it has zero overlap with the \( u \) combination of the two 1s orbitals on the ends. This makes the \( \sigma_u \) orbital a nonbonding orbital.

- In the triangular form of the molecule, the orbitals that derive from \( \sigma_u \) and \( \sigma^*_g \) become degenerate (i.e., they have identically the same energy by symmetry). The term symbol “\( e \)” means doubly degenerate. We will see later that “\( t \)” means triply degenerate. Note that we drop the “\( g \)” and “\( u \)” for the triangular orbitals because a triangle does not have an inversion center.
The triangular form is most stable because the two electrons in H$_3^+$ have lower energy in the lowest orbital. Bending the molecule creates a third bonding interaction between the 1s orbitals on the ends.

MO diagram for XH$_2$ ($X = \text{Be, B, C...}$):

This is more complicated than H$_3$ because the X atom has both s and p orbitals. However, we can symmetry factor the orbitals and solve the problem by analogy to the H$_2$ molecule:

Some key points about this MO diagram:

In the linear form of the molecule, which has inversion symmetry, the 2s and 2p orbitals of the X atom factor into three symmetry classes:

- $2s = \sigma_g$
- $2p_x = \sigma_u$
- $2p_y = \pi_u$

Similarly, we can see that the two H 1s orbitals make two linear combinations, one with $\sigma_g$ symmetry and one with $\pi_u$ symmetry. They look like the bonding and antibonding MO’s of the H$_2$ molecule (which is why we say we use that problem to solve this one).
The $\pi_u$ orbitals must be non-bonding because there is no combination of the H 1s orbitals that has $\pi_u$ symmetry.

In the MO diagram, we make bonding and antibonding combinations of the $\sigma_g$'s and the $\sigma_u$'s. For BeH$_2$, we then populate the lowest two orbitals with the four valence electrons and discover (not surprisingly) that the molecule has two bonds and can be written H-Be-H. The correlation diagram shows that a bent form of the molecule should be less stable.

An interesting story about this MO diagram is that it is difficult to predict a priori whether CH$_2$ should be linear or bent. In 1970, Charles Bender and Henry Schaefer, using quantum chemical calculations, predicted that the ground state should be a bent triplet with an H-C-H angle of 135°. The best experiments at the time suggested that methylene was a linear singlet, and the theorists argued that the experimental result was wrong. Later experiments proved them right!

“A theory is something nobody believes, except the person who made it. An experiment is something everybody believes, except the person who made it.” – Einstein

**MO diagram for NH$_3$**

We can now attempt the MO diagram for NH$_3$, building on the result we obtained with triangular H$_3^+$. 

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Notes on the MO diagram for ammonia:

Viewed end-on, a p-orbital or an sp³ hybrid orbital looks just like an s-orbital. Hence we can use the solutions we developed with s-orbitals (for H⁺) to set up the σ bonding and antibonding combinations of nitrogen sp³ orbitals with the H 1s orbitals.

We now construct the sp³ hybrid orbitals of the nitrogen atom and orient them so that one is “up” and the other three form the triangular base of the tetrahedron. The latter three, by analogy to the H⁺ ion, transform as one totally symmetric orbital (“a₁”) and an e-symmetry pair. The hybrid orbital at the top of the tetrahedron also has a₁ symmetry.

The three hydrogen 1s orbitals also make one a₁ and one e combination. We make bonding and antibonding combinations with the nitrogen orbitals of the same symmetry. The remaining a₁ orbital on N is pushed up in energy above the level of the AO because it interacts with the lower energy a₁ bonding orbital. In the molecule this orbital is approximately non-bonding.

The result in the 8-electron NH₃ molecule is three N-H bonds and one lone pair localized on N, the same as the valence bond picture.

**P₄ molecule and P₄²⁺ ion:**

By analogy to NH₃ we can construct the MO picture for one vertex of the P₄ tetrahedron, and then multiply the result by 4 to get the bonding picture for the molecule. An important difference is that there is relatively little s-p hybridization in P₄, so the lone pair orbitals have more s-character and are lower in energy than the bonding orbitals, which are primarily pσ.

P₄: 20 valence electrons

3pₓ, pᵧ, pzano 6 σ* orbitals (empty)

Large energy gap
Not much s-p mixing

6 σ orbitals (12 e = 6 bonds)

3s x 4 = 4 nonbonding orbitals (8 e = 4 lone pairs)

Square form relieves ring strain

(60° → 90°)

Highest occupied MO is a bonding orbital → break one bond, 5 bonds left

2 π electrons aromatic
(4n + 2 rule)
Homology of $\sigma$ and $\pi$ orbitals in MO diagrams

The ozone molecule (and related 18e molecules that contain three non-H atoms, such as allene) is an example of 3-center 4-electron $\pi$-bonding. Our MO treatment of ozone is entirely analogous to the 4-electron $H_3^+$ ion. We map that solution onto this one as follows:

Ozone: 18 e

\[ \begin{array}{c}
\sigma \text{ framework:} \\
3 \text{ H1s} \\
\pi \text{ framework:} \\
\text{orthogonal to } \sigma, 4e
\end{array} \]

\[ \begin{array}{c}
\sigma \text{ framework:} \\
2 \text{ bonds + 5 lp = 14e} \\
\pi \text{ framework:} \\
\text{orthogonal to } \sigma, 4e
\end{array} \]

Map $H_3$ solution onto $\pi$-orbitals:

The nonbonding $\pi$-orbital has a node at the central O atom. This means that the non-bonding electron pair in the $\pi$-system is shared by the two terminal O atoms, i.e., that the formal charge is shared by those atoms. This is consistent with the octet resonance structure of ozone.

An analogous (and seemingly more complicated) case of 3-center 4-electron bonding is $I_3^-$. Each I atom has 4 valence orbitals ($5s$, $5p_x$, $5p_y$, $5p_z$), making a total of 12 frontier orbitals, and the $I_3^-$ has 22 electrons.

We can simplify the problem by recalling two periodic trends:

- The s-p orbital splitting is large, relative to the bond energy, after the second row of the periodic table. Thus, the 5s orbital is low in energy and too contracted to make bonds with its neighbors.
- $\pi$-overlap of 5p orbitals is very weak, so the 5p_x and 5p_y orbitals will also be non-bonding.
This leaves only the three 5p\(_z\) orbitals to make bonding/nonbonding/antibonding combinations. Again, the problem is entirely analogous to ozone or \(\text{H}_3^+\).

![MO theory](image)

Counting orbitals we obtain 9 lone pairs from the nonbonding 5s, 5p\(_x\), and 5p\(_y\) orbitals, as well as one bond and one lone pair from the 5p\(_z\) orbital combinations above. The total of 10 nonbonding pairs and one bond accounts for the 22 electrons in the ion. The non-bonding 5p\(_z\) pair is localized on the terminal I atoms, giving each a -1/2 formal charge. This MO description is entirely consistent with the octet no-bond resonance picture of \(\text{I}_3^-\) that we developed before.

\[
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\]

\[
\begin{align*}
\text{I} & \quad \text{I} & \quad \text{I} \\
\text{I} & \quad \text{I} & \quad \text{I}
\end{align*}
\]

Bond order = 1/2

*Chains and rings of \(\pi\)-conjugated systems*

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Ethylene: The \(\pi\) system is analogous to \(\sigma\)-bonding in \(\text{H}_2\)

![Ethylene](image)

Viewed from the top or bottom, the ethylene \(\pi\)-orbitals look like the \(\text{H}_2\) \(\sigma\) orbitals. Thus we can map solutions from chains and rings of H atoms onto chains and rings of \(\pi\)-orbitals (as we did for the three-orbital case of \(\text{O}_3\)).
Chains and rings of four H atoms or $\pi$-orbitals ($H_4$ or butadiene):

Center H atoms

$\sigma_g$

$\sigma_u$

$\sigma^*$

$\sigma_g$

End H atoms

In the linear form of the molecule, the combination of AOs makes a ladder of evenly spaced energy levels that alternate $g-u-g-u$ .... Each successive orbital has one more node. This is a general rule for linear chains of $\sigma$ or $\pi$ orbitals with even numbers of atoms.

In the cyclic form of the molecule, there is one non-degenerate orbital at the bottom, one at the top, and a ladder of doubly degenerate orbitals in between. This is also a general rule for cyclic molecules with even numbers of atoms. This is the origin of the $4n+2$ rule for aromatics.

$H_4$ has four valence electrons, and by analogy butadiene has four $\pi$-electrons. These electrons fill the lowest two MOs in the linear form of the molecule, corresponding to two conjugated $\pi$-bonds in butadiene ($H_2C=CH-CH=CH_2$).
In the cyclic form of the butadiene molecule, the degenerate orbitals are singly occupied. The molecule can break the degeneracy (and lower its energy) by distorting to a puckered rectangle. This is a general rule for anti-aromatic cyclic molecules (4n rule). Thus cyclobutadiene should be anti-aromatic and have two single and two double bonds that are not delocalized by resonance.

Cyclobutadiene is actually a very unstable molecule because it polymerizes to relieve ring strain. Sterically hindered derivatives of the molecule do have the puckered rectangular structure predicted by MO theory.
Benzene π-orbitals:
How do we get from a 4-atom to 6-atom chain?

It should now be evident that we can keep adding atomic orbitals to make chains and rings of 8, 10, 12... atoms. In each case, the g and u orbitals form a ladder of MOs. At the bottom rung of the ladder of an N-atom chain, there are no nodes in the MO, and we add one node for every rung until we get to the top, where there are N-1 nodes. Another way of saying this is that the wavelength of an electron in orbital x, counting from the bottom (1,2,3...x,...N), is 2Na/x, where a is the distance between atoms. We will find later in the course that we can learn a great deal about the electronic properties of metals and semiconductors from this model, using the infinite chain of atoms as a model for the crystal.
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