Chemical Bonding

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Intermolecular Forces

All forces in chemistry ultimately arise from Coulomb's law, the attraction between opposite charges. But sometimes that fundamental fact is not so obvious, due to the large number of charged particles (electrons and nuclei) in the system.

Coulomb's Law for the force between two charges Q_1 and Q_2, when separated by distance r :

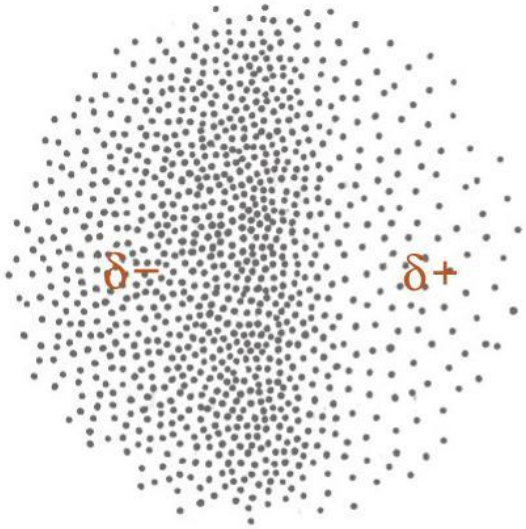
$$F = \frac{Q_1 Q_2}{4\pi\varepsilon_0 r^2}$$

Specific Variations on this Theme (weakest to strongest):

1. Van der Waals or Dispersion Forces
2. Dipole-dipole attraction
3. Hydrogen bonding
4. Coulomb attraction between ions

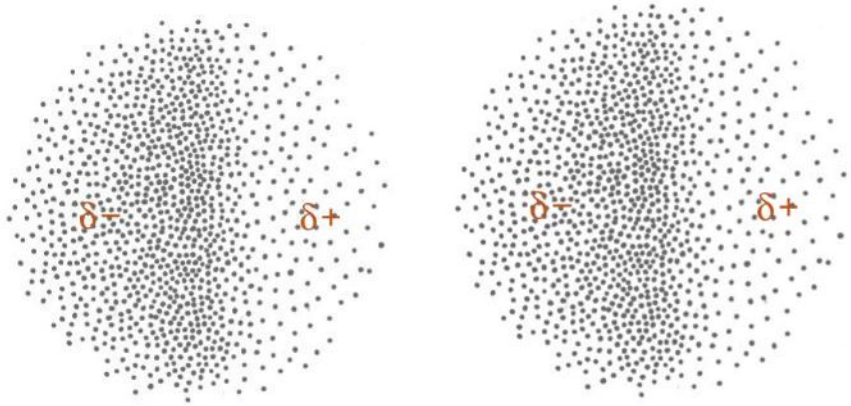
Dispersion Forces

Even in highly symmetric molecules (CH_4, for example) or atoms (He, Ne, Ar,…), the charge distribution is not always symmetric. There is always a probability that the electrons at any instant will be asymmetric, as illustrated here:



This leads to a momentary dipole moment (asymmetric charge distribution) that is always possible. On average, however the dipole moment vanishes.

Dispersion Forces (continued)



When two atoms or molecules are close to each other, these random fluctuations in dipole moment become correlated, so the random dipoles tend to align to give a weak attraction – the dispersion force. It is roughly proportional to the number of electrons, so it becomes more important for larger molecules. It is always present, even when other forces are more important.

Dispersion Forces (continued)

This is why melting or boiling points tend to go up as the size of the molecule increases, even if there are no dipole moments, hydrogen bonds, or ion-ion interactions present.

Boiling Points:

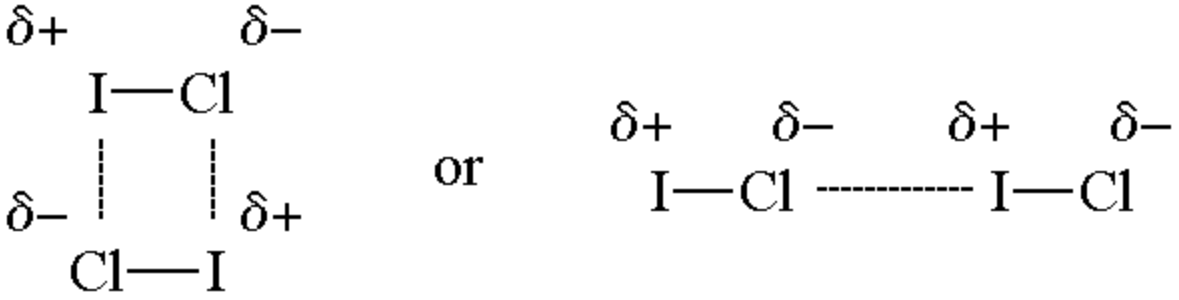
He	4.6 K
Ne	25 K
Ar	87 K
Kr	116 K
Xe	161 K
Rn	211 K

Boiling Points:

CH_4	methane	109 K
C_2H_6	ethane	184 K
C_3H_8	propane	231 K
C_4H_{10}	butane	273 K
C_5H_{12}	pentane	309 K
C_6H_{14}	hexane	342 K

Dipole-Dipole Forces

Stronger, longer-range forces, because the molecules can orient to align dipoles favorably. However, in larger molecules, dispersion forces (which grow in magnitude with molecular size) become equally or even more important.



Dipole-dipole forces can lead to cyclic structures or linear chain-like structures.

Dipole-Dipole Forces (continued)

Dipole-dipole forces grow as the dipole moment grows:

Molecule	Dipole Moment	Boiling Point
CH_4	0 Debye	109 K
CH_3F	1.81 Debye	195 K
CH_2F_2	1.98 Debye	221 K
CHF_3	1.649 Debye	157 K
CF_4	0 Debye	145 K

The difference between the nonpolar CH_4 and CF_4 molecules is greater dispersion forces in CF_4.

Hydrogen Bonding

When H is bonded to an electronegative atom (F, O, or N), the single electron of the hydrogen atom is strongly pulled toward the electronegative atom, leaving the positive charge of the proton exposed. Naturally, atoms with negative partial charges are attracted, leading to a hydrogen bond.

Like a dipole-dipole interaction, but stronger because the proton has almost no electron density to hide behind.

Hydrogen Bonding (continued)

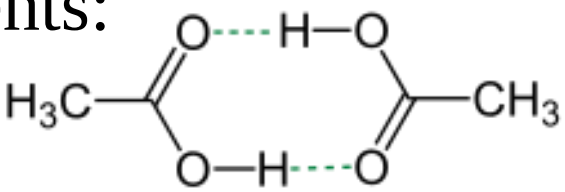
Strengths of hydrogen bonds

System	Typical Bond Energy
$F\text{-}H\text{-}F^-$	161 kJ/mol (the bifluoride ion)
$HOH\bullet\bullet\bullet NH_3$	29 kJ/mol
$HOH\bullet\bullet\bullet OH_2$	21 kJ/mol
$H_2NH\bullet\bullet\bullet NH_3$	13 kJ/mol
$N\text{-}H\bullet\bullet\bullet O$	8 kJ/mol

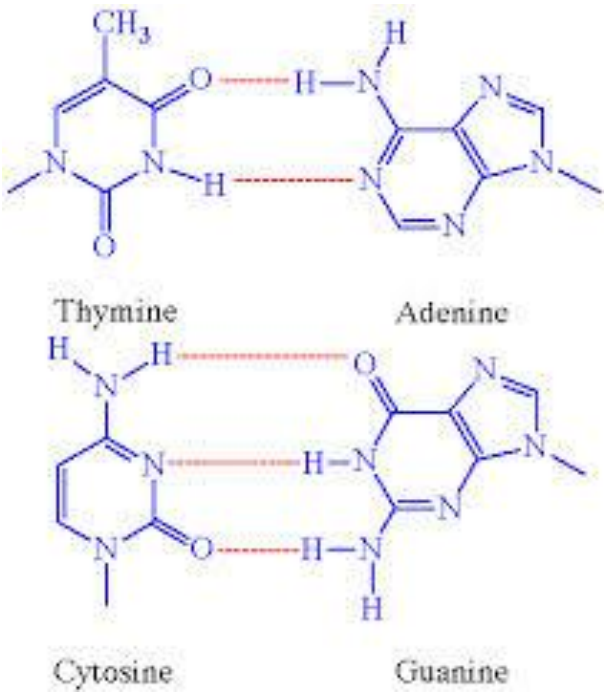
Hydrogen Bonding (continued)

Interesting hydrogen bonded facts and structures:

- In the vapor phase over liquid HF, $(HF)_2$ and $(HF)_3$ are abundant.
- In the vapor phase over liquid carboxylic acids, double hydrogen bonded structures, are stable – also in nonpolar solvents:

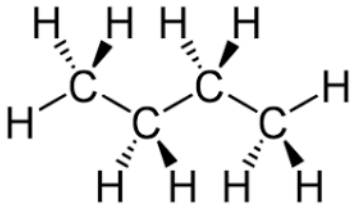


- Finally, the most important hydrogen bonded structure:
  DNA – held together by hydrogen bonds.

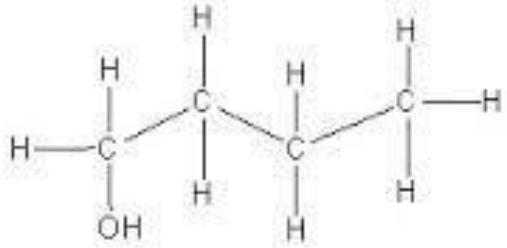


Which will have the strongest intermolecular attraction?

1. C_4H_{10}, butane, 0.00 Debye

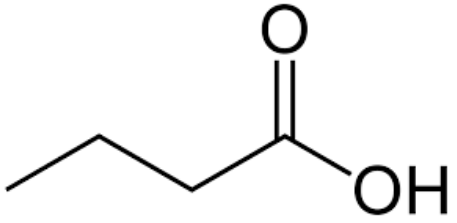


2. C_4H_9OH, butanol, 1.66 Debye



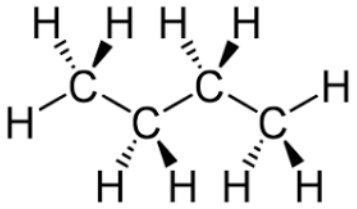
3. C_4H_9Cl, butyl chloride, 2.05 Debye

4. $C_4H_7O_2H$, butanoic acid, 1.65 Debye

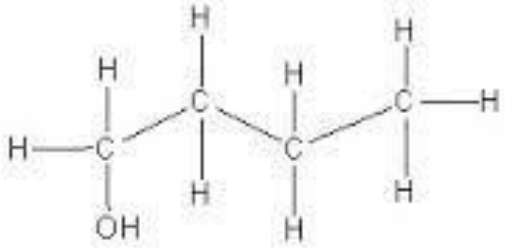


Which will have the strongest intermolecular attraction?

1. C_4H_{10}, butane, 0.00 Debye
   B.P. 272 K (-1 °C)

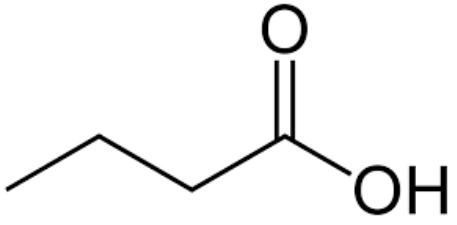


1. C_4H_9OH, butanol, 1.66 Debye
   B.P. 391 K (117 °C)



3. C_4H_9Cl, butyl chloride, 2.05 Debye
   B.P. 352 K (78 °C)

4. $C_4H_7O_2H$, butanoic acid, 1.65 Debye
   B.P. 437 K (164 °C)



Now, for “real” chemical bonds

Actually, even the best chemical researchers still debate what is, and what isn’t a chemical bond. But we can still think of two limiting types of bonds:

Ionic Bonds – These are easily understood as arising from the Coulomb attraction between ions with opposite charges

Covalent Bonds – These are more difficult to understand, and really require quantum mechanics

Ionic Bonds

Bonding force given by Coulomb's Law directly:

$$F = \frac{Q_1 Q_2}{4\pi\varepsilon_0 r^2}$$

Binding energy is greatest for large charges, small separations.

Crystal	Melting Point	Crystal	Melting Point
LiF	1118 K	NaF	1266 K
NaCl	1074 K	Na_2O	1405 K
KBr	1007 K	MgF_2	1536 K
CsI	894 K	MgO	3125 K

Ionic Bonds

Which crystal will have the highest melting point?
Which will have the lowest melting point?

Crystal
BaS
CsCl
BaO
SrS
SrO

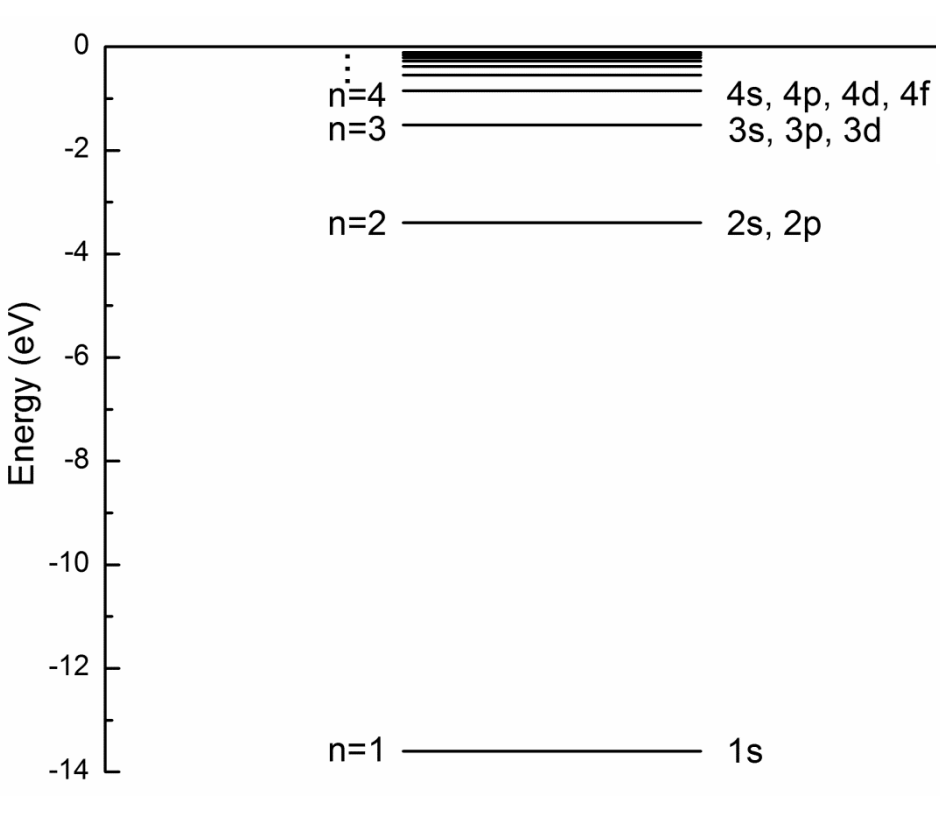
Ionic Bonds

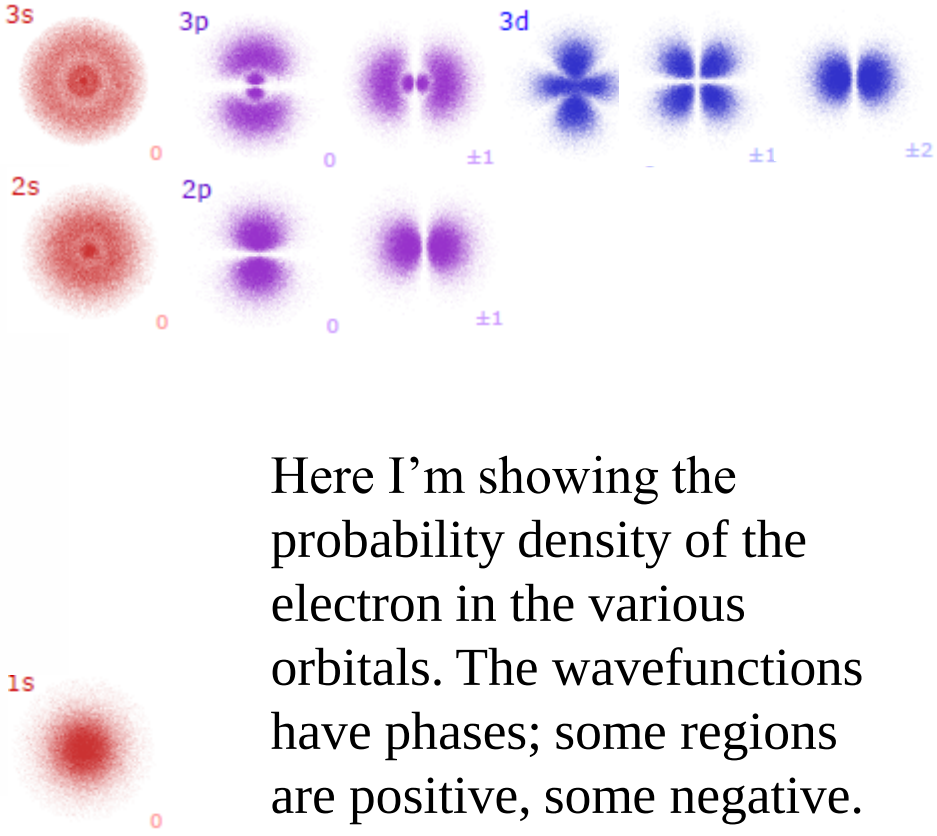
Which crystal will have the highest melting point?
Which will have the lowest melting point?

Crystal	Melting Point
BaS	1200 ºC
CsCl	645 ºC
BaO	1973 ºC
SrS	2002 ºC
SrO	2531 ºC

Covalent Bonds start with atomic orbitals

In atomic H, one electron moving in the field of one proton, gives us wavefunctions that are the atomic orbitals:





Here I'm showing the probability density of the electron in the various orbitals. The wavefunctions have phases; some regions are positive, some negative.

Covalent Bonds (continued)

Now move to the simplest molecule, H_2^+. Again, the single electron moves in the field of the nuclei, but now there are two of them. If we imagine fixing the two nuclei at a certain separation (R), we can solve for the orbitals of this molecule (molecular orbitals). As for atoms, there are many different solutions, with different energies.

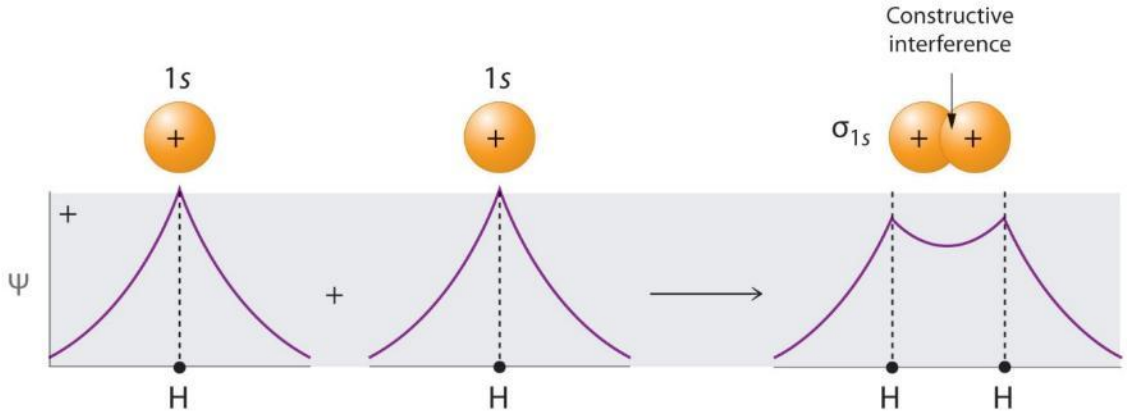
Usually, it is convenient to approximate the molecular orbitals as sums of atomic orbitals (the linear combination of atomic orbitals, or LCAO method).

Molecular Orbitals of H_2^+

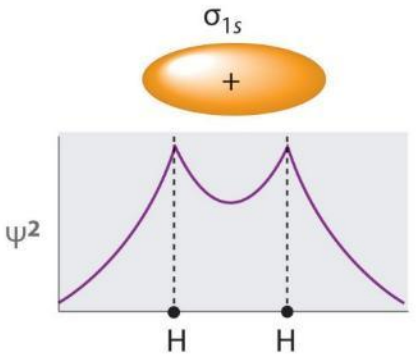
In the LCAO method, atomic orbitals of similar energies and of the same symmetry on the two atoms combine to give the molecular orbitals. For H_2^+, this means that the 1s orbitals combine.

A key point: You get as many molecular orbitals as you have atomic orbitals in the system. Since you have 2 hydrogen atoms, you get 2 molecular orbitals formed from the 1s orbitals on the two centers. For symmetric molecules like H_2^+, these are just the sum and difference of the atomic orbitals.

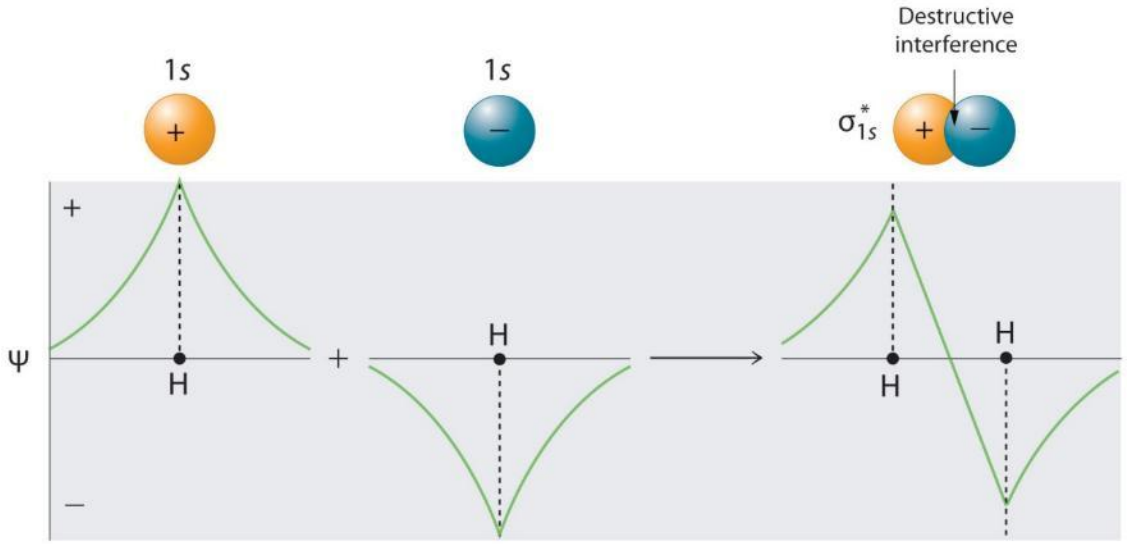
Molecular Orbitals of H_2^+



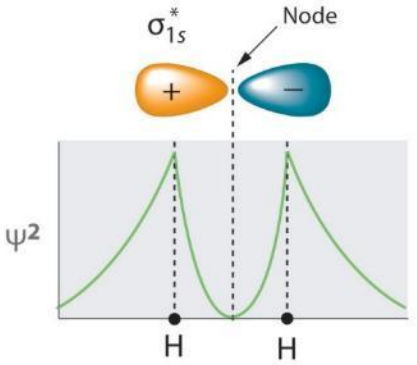
(a) Wave functions combined for σ_{1s}



(b) Bonding probability density

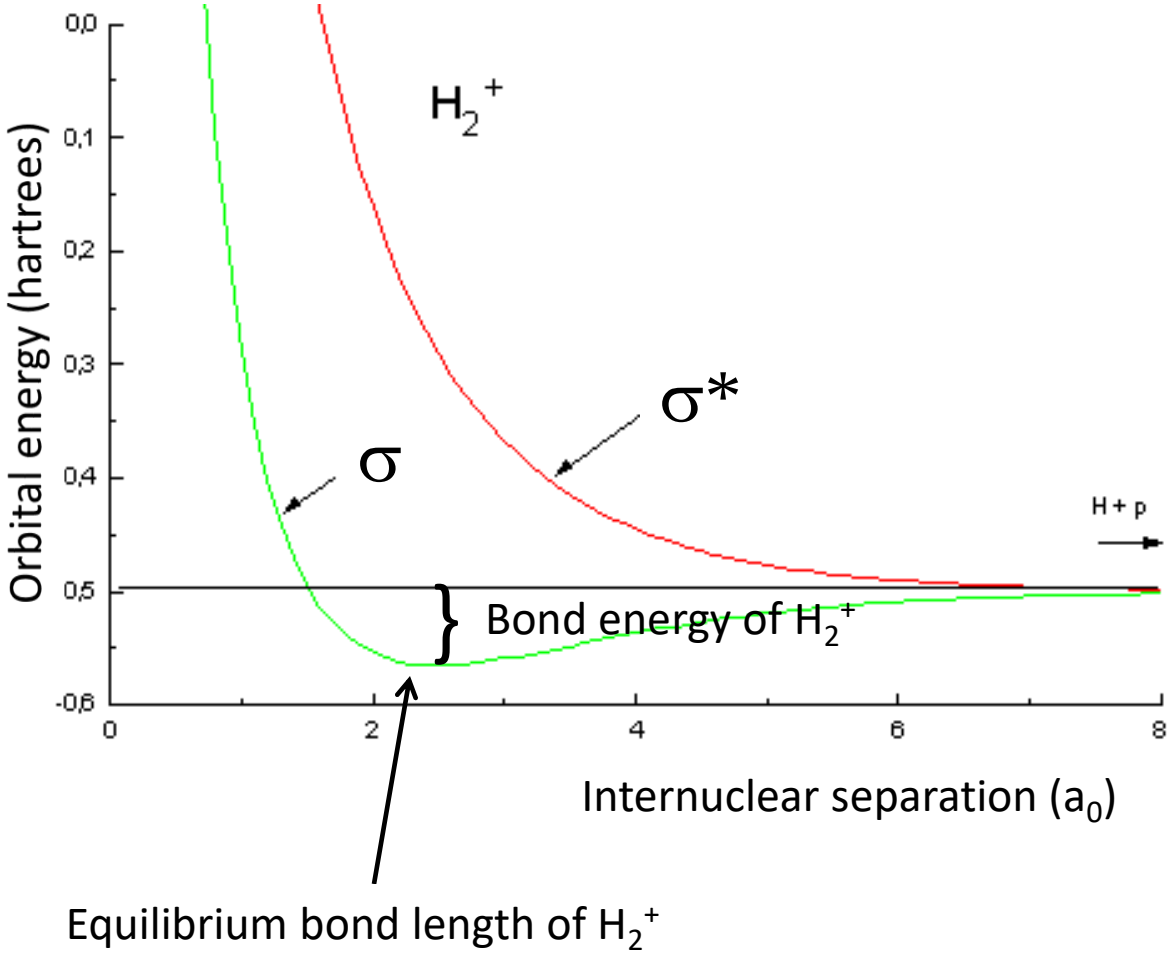


(c) Wave functions combined for σ^*_{1s}



(d) Antibonding probability density

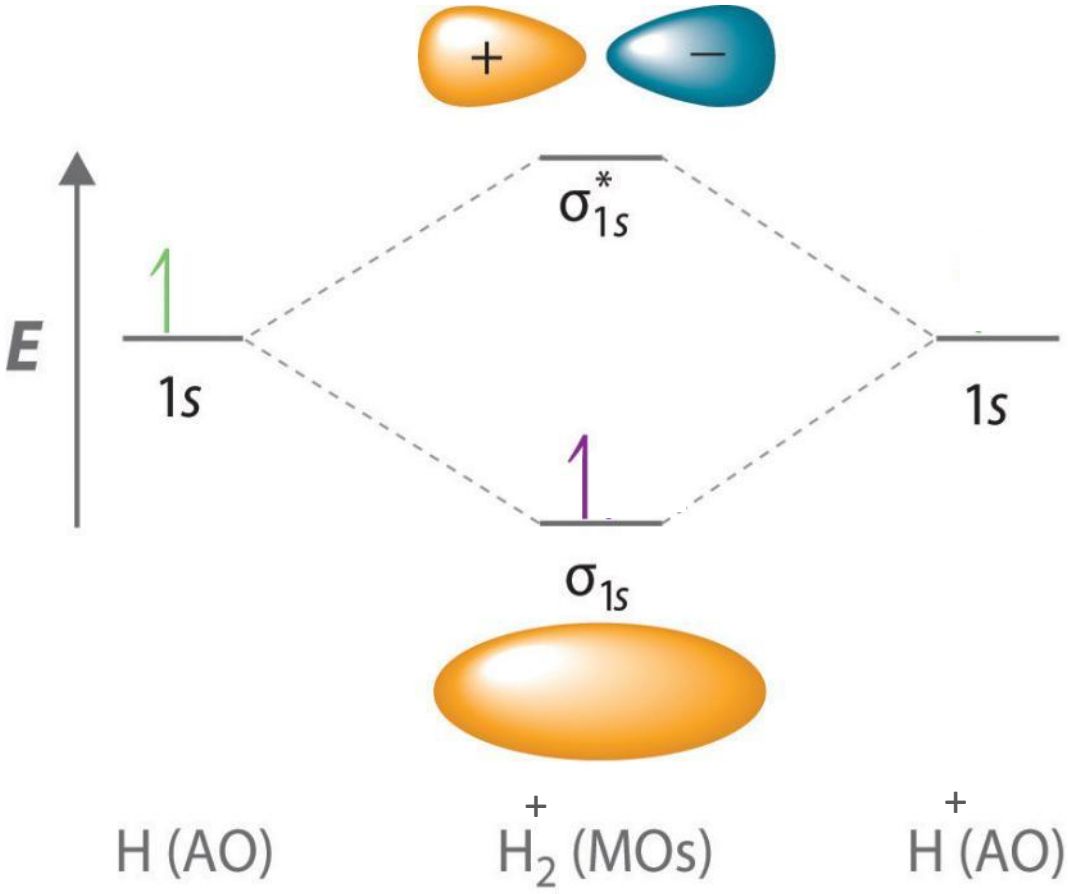
Molecular Orbitals of H_2^+



Higher energy orbitals also exist, but they are MUCH higher in energy, deriving from the 2s, 2p, etc. orbitals.

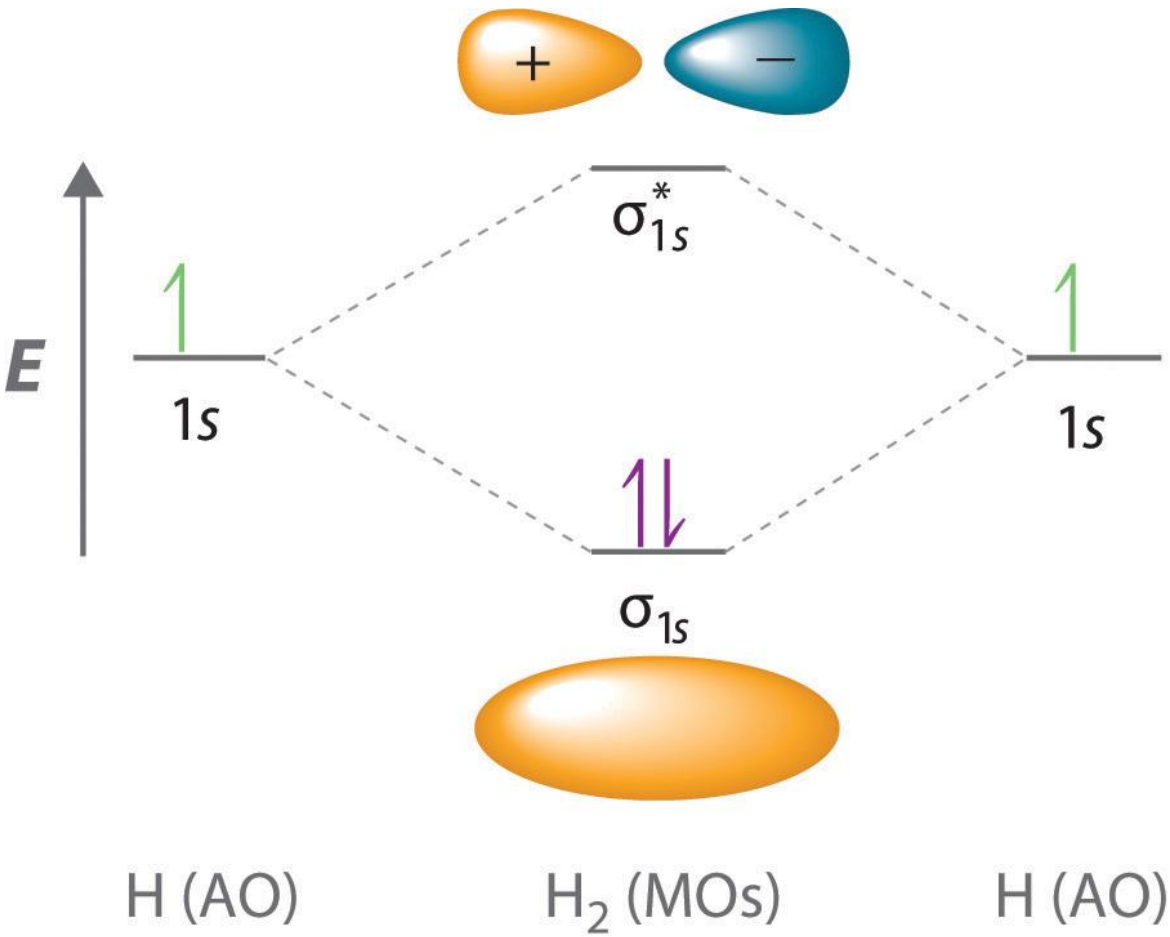
Molecular Orbitals of H_2^+

To simplify, we often only consider the molecule at its equilibrium geometry and don't consider how the energy changes as the molecule is formed. This lets us construct MO diagrams like this:



Molecular Orbitals of H_2

For H_2, there's not much difference, just add one more electron.

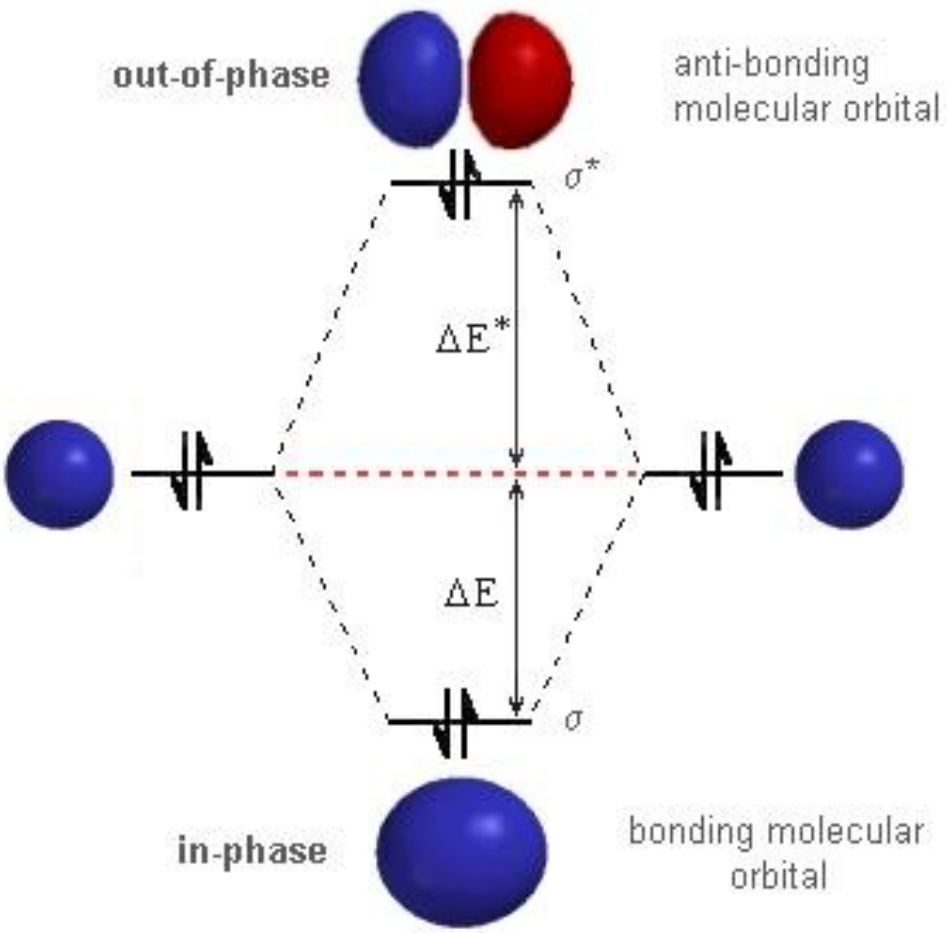


Both electrons drop in energy when H_2 is formed, so the bond energy is greater than in H_2^+:

$D(H_2^+) = 2.69$ eV
$D(H_2) = 4.48$ eV

Molecular Orbitals of He_2

For He_2 there are 4 electrons altogether, so the next two go into the antibonding orbital.



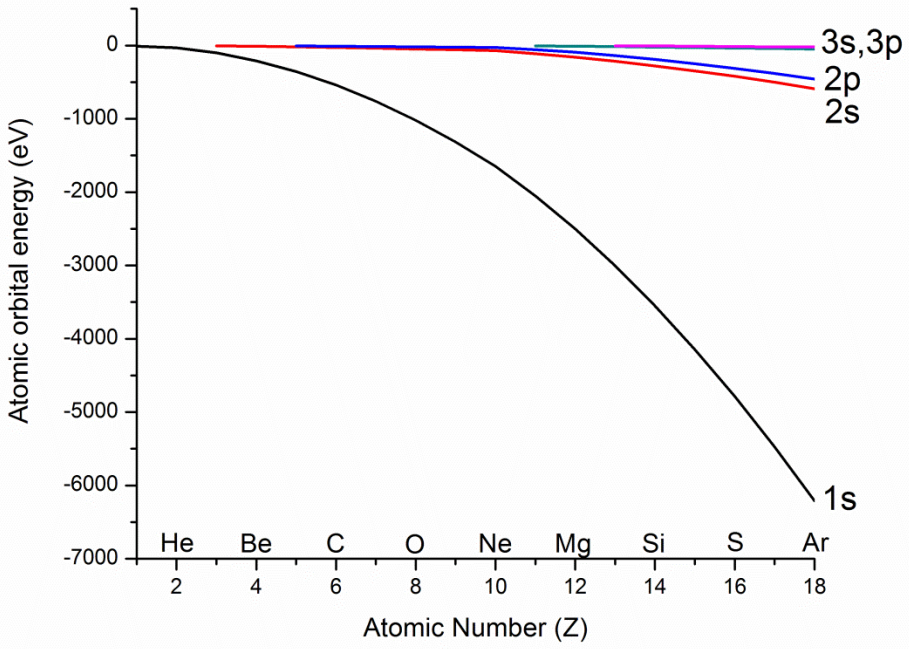
It turns out that the antibonding orbital is raised up in energy somewhat higher above the atomic orbital than the bonding orbital is lowered. The net affect is that the two atoms repel one another.

<u>However, dispersion forces still lead to a very slight attraction.</u>

He_2 does exist, but the "bond" energy is only 0.000000095 eV and its "bond" length is 52 Å (compared to 0.74 Å for H_2). This is the weakest and longest "bond" known.

Valence vs. Core Atomic Orbitals

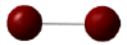
If we look at the atomic orbital energies as a function of atomic number, the energies drop very rapidly:



As they drop, they get much smaller too:

H_2 σ_{1s}

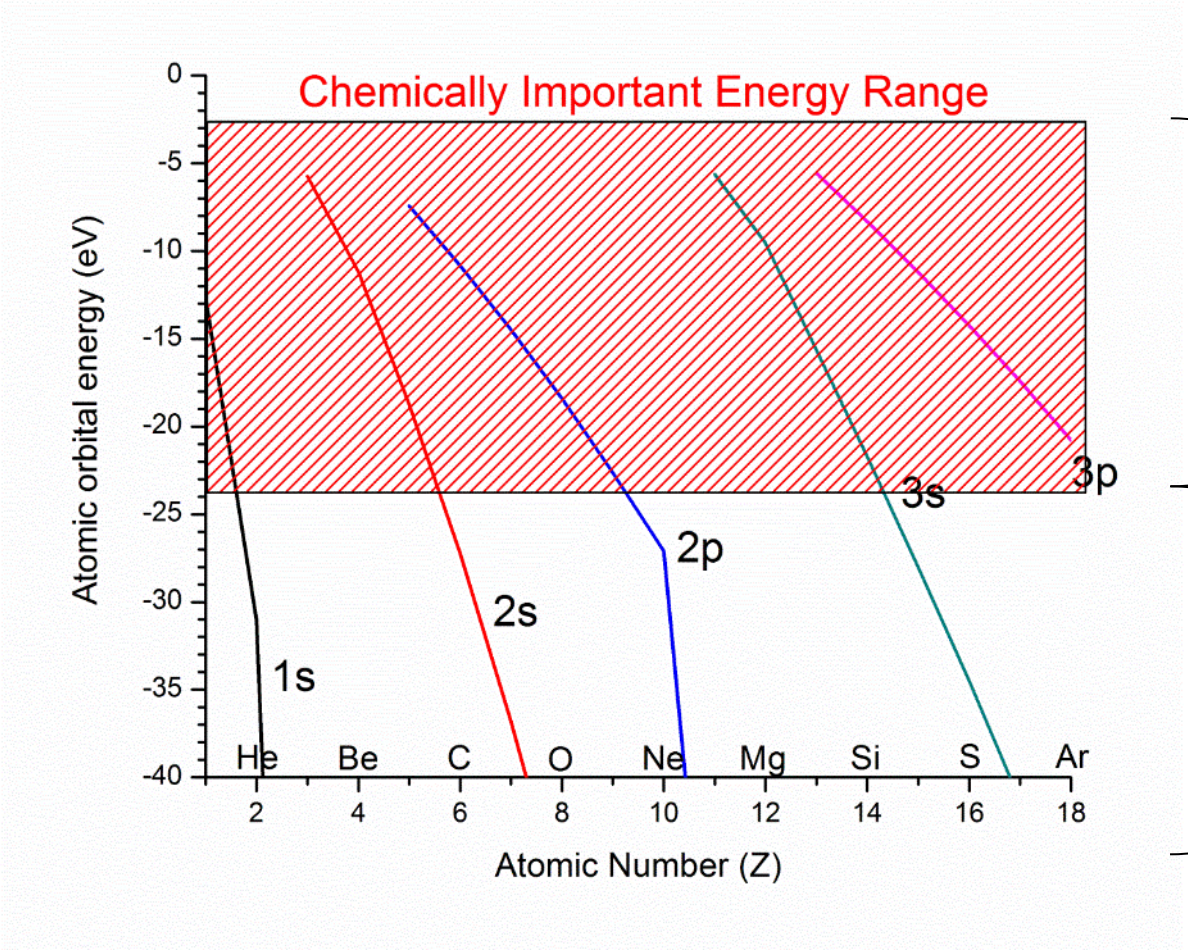
Li_2 σ_{1s}



No orbital overlap implies a core orbital, not a valence orbital.

Valence vs. Core Atomic Orbitals

Zooming in:



Valence Orbitals

Core Orbitals

Homonuclear Diatomic Molecules

Molecule	Electronic configuration	Bond Length	Bond Strength	B.O.
H_2	$\sigma_{1s}^{\ 2}$	0.74144 Å	4.478 eV	1
He_2	$\sigma_{1s}^{\ 2}\ \sigma_{1s}^{\ *2}$	52 Å	0.000000095 eV	0
Li_2	$[\sigma_{1s}^{\ 2}\ \sigma_{1s}^{\ *2}]\ \sigma_{2s}^{\ 2}$	2.673 Å	1.05 eV	1
Be_2	$[\sigma_{1s}^{\ 2}\ \sigma_{1s}^{\ *2}]\ \sigma_{2s}^{\ 2}\ \sigma_{2s}^{\ *2}$	2.445 Å	0.116 eV	0

Two electrons in a bonding orbital denote a bond, and antibonding electrons cancel out the effects of the bond. Therefore, we can define the bond order as

$$\text{B.O.} = \frac{1}{2}\ (number\ of\ bonding\ electrons\ -number\ of\ antibonding\ electrons)$$

There's no need to consider the core electrons (in square brackets []), because they don't overlap sufficiently to be considered either bonding or antibonding.

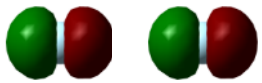
Note: All bonds are not of equal strength! The single bond in Li_2 is much weaker than that of H_2. That's because the 2s orbital of Li is much larger and more diffuse than the 1s orbital of H.

p-orbital bonding

When the p orbitals are involved, you can get two different types of bonds:
σ bonds and π bonds.

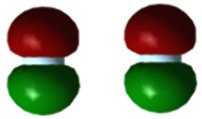
σ orbitals have cylindrical symmetry about the molecular axis,
no nodal planes containing the axis
π orbitals have one nodal plane containing the axis

σ interaction of 2p orbitals:



Atom A Atom B

π interaction of 2p orbitals:



Atom A Atom B

In each orientation, the orbitals can approach so they overlap constructively to form bonding orbitals, or destructively to form antibonding orbitals.

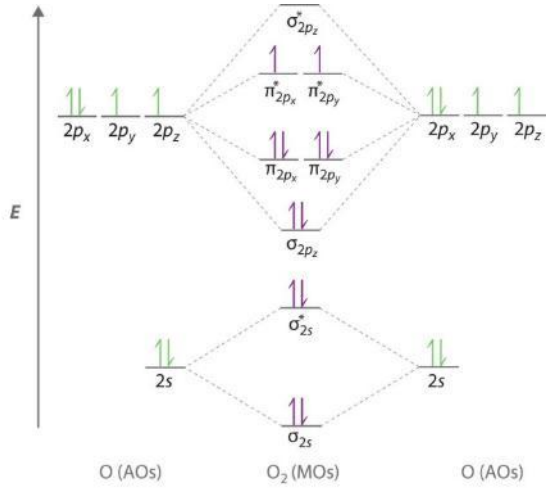
σ_{2p} σ_{2p}^*

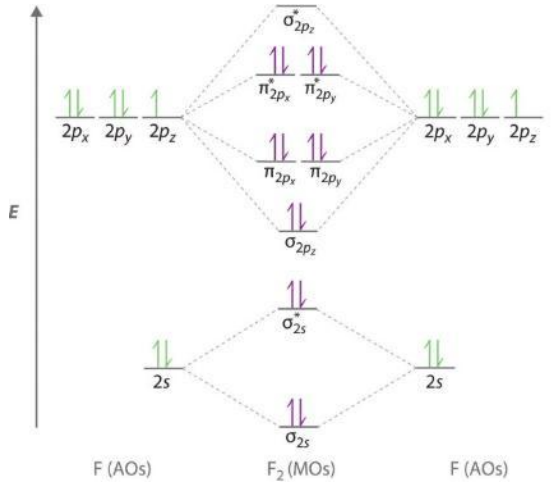
π_{2p} π_{2p}^*

Energy ordering of p-based MOs

Looking at the p-based molecular orbitals, it seems obvious that the greatest build-up of electron density between the nuclei will be in the σ_{2p} orbital, so it should be the strongest bond. Next would be the π_{2p}, which is also a good bonding orbital, then π_{2p}* should be less antibonding than σ_{2p}*. This is correct <u>unless</u> there is an outside influence.

This leads to the correct orbital diagrams for O_2, F_2, and Ne_2:



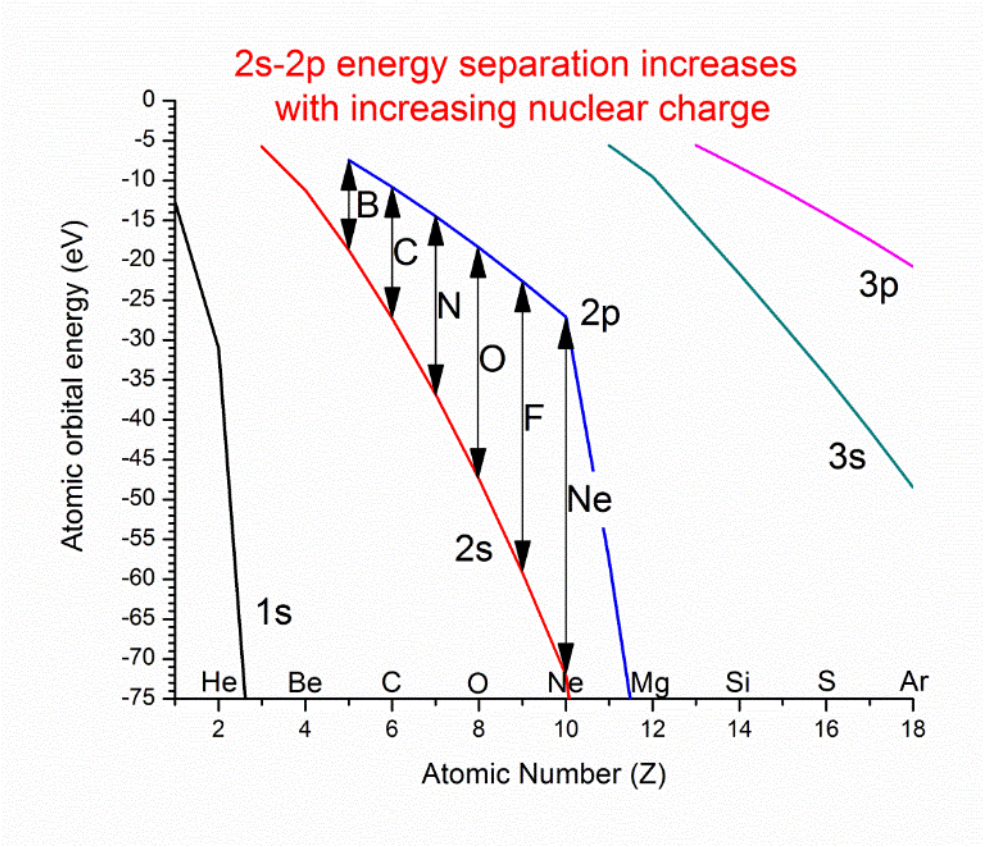


$$\text{B.O.}(O_2) = \frac{1}{2}(8-4) = 2 \qquad \text{B.O.}(F_2) = \frac{1}{2}(8-6) = 1$$

Energy ordering of p-based MOs

In B_2, C_2, and N_2, however, the ordering is different, with the π_{2p} orbitals lying below the σ_{2p} orbital. Why?

This comes back to the way the orbitals drop in energy as nuclear charge increases.

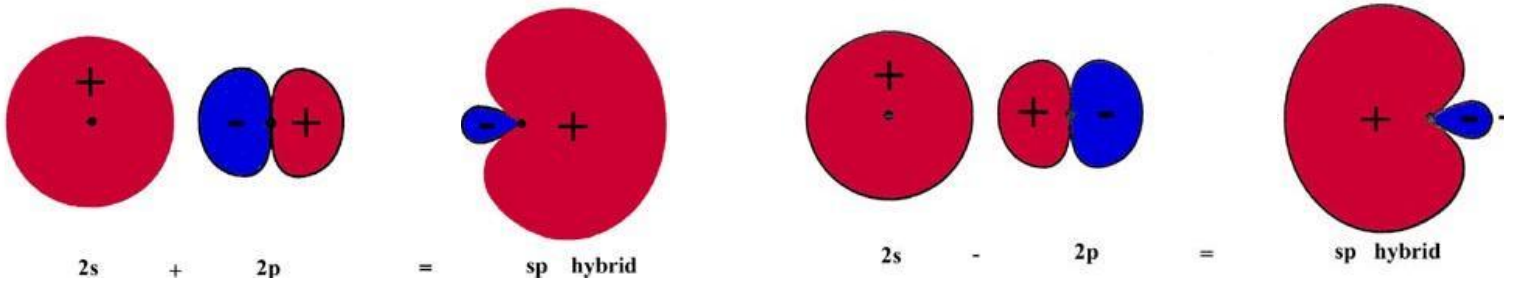


In B_2, C_2, and N_2, the 2s and 2p orbitals are close enough in energy that they can mix to form what are essentially 2s-2p hybrids. In the process the σ_{2s} (which is no longer purely 2s) becomes a better bonding orbital and the σ_{2p} (which is also no longer purely 2p) becomes a worse bonding orbital.

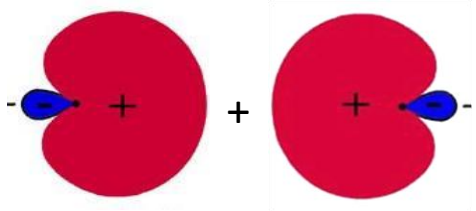
This interaction is strong enough to reverse the order of the σ_{2p} and π_{2p} orbitals in B, C, and N, where the 2s and 2p are close in energy, but not in O, F, and Ne.

sp-hybrid MOs

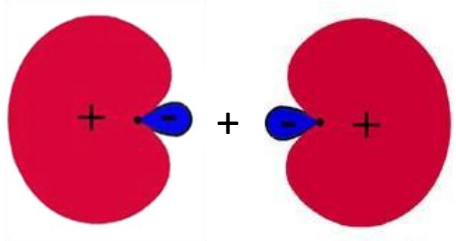
sp-hybrids are formed by first adding (or subtracting) the 2p orbital to the 2s orbital. Since two atomic orbitals are combined in this way, two hybrid orbitals are obtained.



Then the four sp-hybrids (2 on each atom) are combined to form a really good bonding orbital and a really bad bonding orbital, along with two antibonding orbitals:



= great overlap, good bonding orbital
hybridization lowers the energy of σ_{2s}

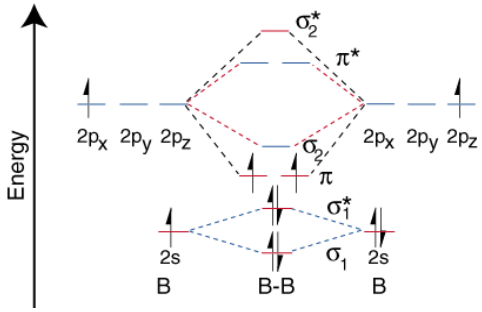


= poor overlap, poor bonding orbital
hybridization increases the energy of σ_{2p}, so it lies above the π_{2p} orbital in B_2, C_2, and N_2

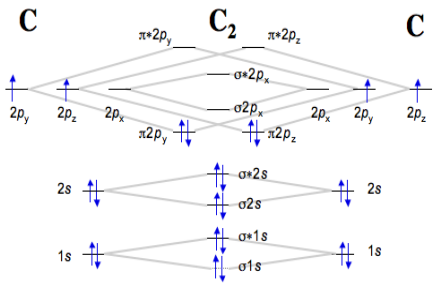
Energy ordering of p-based MOs

In B_2, C_2, N_2 the revised energy ordering is found:

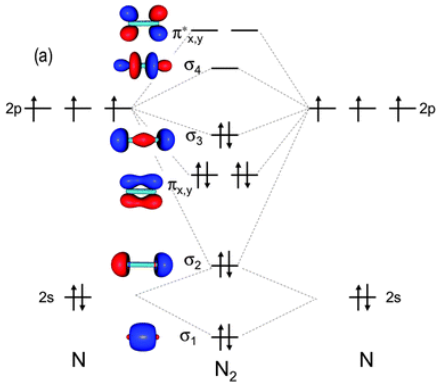
B_2



C_2



N_2



Electronic configuration (valence electrons only):

$\sigma_{2s}^2\ \sigma_{2s}^{*2}\pi_{2p}^2$ $\sigma_{2s}^2\ \sigma_{2s}^{*2}\pi_{2p}^4$ $\sigma_{2s}^2\ \sigma_{2s}^{*2}\pi_{2p}^4\ \sigma_{2p}^2$

Bond Order:

1	2	3
no σ bonds	no σ bonds	one σ bond
one π bond	two π bonds	two π bonds
Bond Length:		
1.590 Å	1.243 Å	1.098 Å
Bond Energy:		
3.02 eV	6.21 eV	9.76 eV

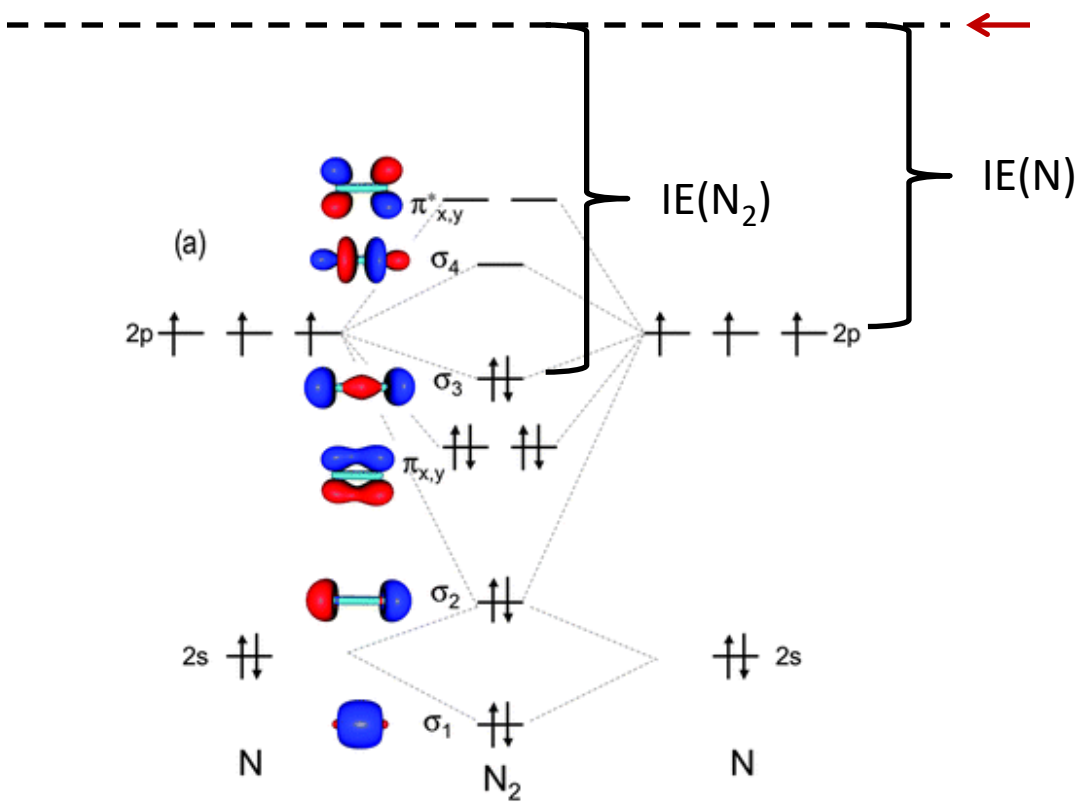
Homonuclear Diatomic Molecules

Molecule	Electronic configuration	Bond Length	Bond Strength	B.O.
H_2	σ_{1s}^{2}	0.74144 Å	4.48 eV	1
He_2	$\sigma_{1s}^{2}\,\sigma_{1s}^{*2}$	52 Å	0.000000095 eV	0
Li_2	σ_{2s}^{2}	2.673 Å	1.05 eV	1
Be_2	$\sigma_{2s}^{2}\,\sigma_{2s}^{*2}$	2.445 Å	0.12 eV	0
B_2	$\sigma_{2s}^{2}\,\sigma_{2s}^{*2}\,\pi_{2p}^{2}$	1.590 Å	3.02 eV	1
C_2	$\sigma_{2s}^{2}\,\sigma_{2s}^{*2}\,\pi_{2p}^{4}$	1.243 Å	6.21 eV	2
N_2	$\sigma_{2s}^{2}\,\sigma_{2s}^{*2}\,\pi_{2p}^{4}\,\sigma_{2p}^{2}$	1.098 Å	9.76 eV	3
O_2	$\sigma_{2s}^{2}\,\sigma_{2s}^{*2}\,\sigma_{2p}^{2}\,\pi_{2p}^{4}\,\pi_{2p}^{*2}$	1.208 Å	5.12 eV	2
F_2	$\sigma_{2s}^{2}\,\sigma_{2s}^{*2}\,\sigma_{2p}^{2}\,\pi_{2p}^{4}\,\pi_{2p}^{*4}$	1.412 Å	1.60 eV	1
Ne_2	$\sigma_{2s}^{2}\,\sigma_{2s}^{*2}\,\sigma_{2p}^{2}\,\pi_{2p}^{4}\,\pi_{2p}^{*4}\sigma_{2p}^{*2}$	unknown	tiny	0

Homonuclear Diatomic Molecules

GREAT QUESTIONS FOR AP STUDENTS:

1. Is the ionization energy of X_2 greater than that of the atom, or less than that of the atom? Let's compare N_2 and O_2.



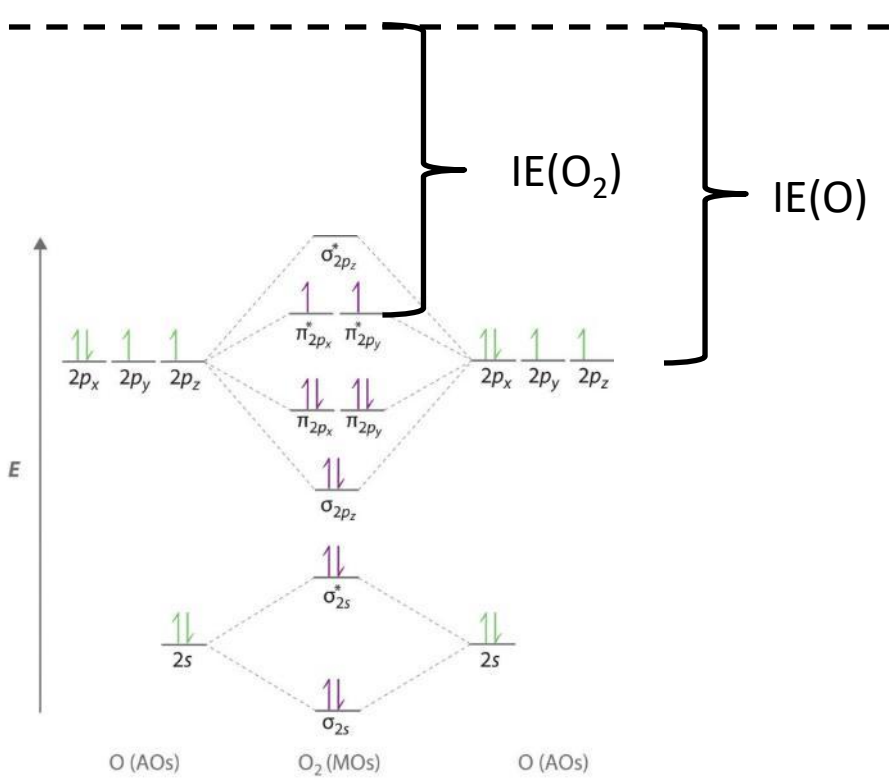
Because the HOMO of the N_2 molecule is a bonding orbital, that electron is held more tightly than it is in the atom. Thus, we expect $IE(N_2) > IE(N)$.

Experimentally:
$IE(N_2) = 15.581$ eV
$IE(N) = 14.534$ eV
YES! Just as we predicted.

Homonuclear Diatomic Molecules

GREAT QUESTIONS FOR AP STUDENTS:

1. Is the ionization energy of X_2 greater than that of the atom, or less than that of the atom? Let's compare N_2 and O_2.



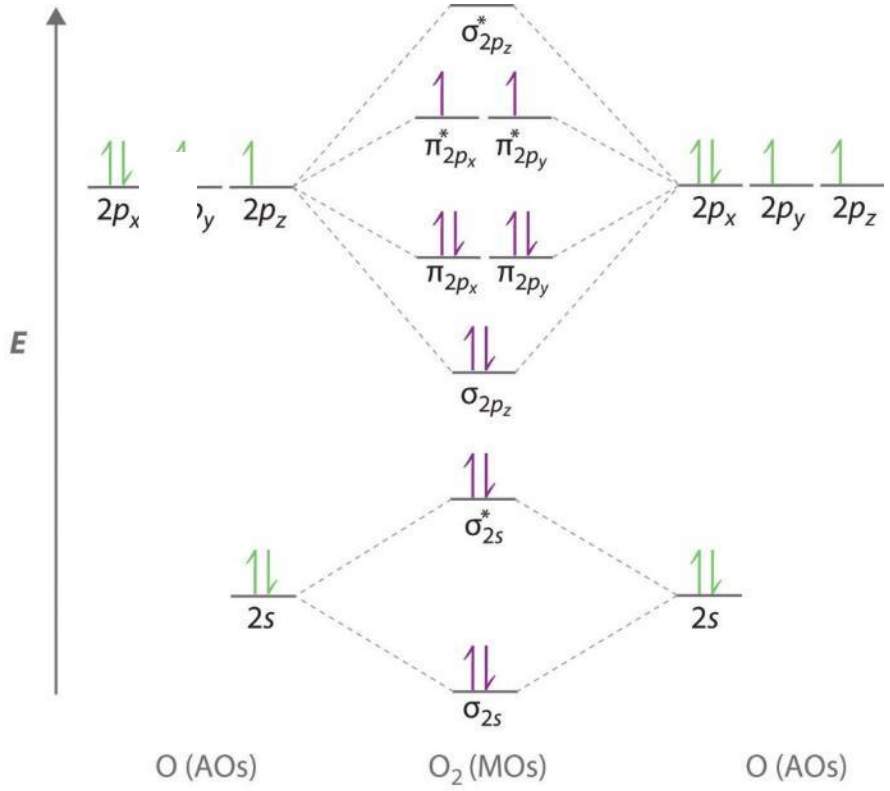
Because the HOMO of the O_2 molecule is an antibonding orbital, that electron is held less tightly than it is in the atom. Thus, we expect $IE(O_2) < IE(O)$.

Experimentally:
$IE(O_2) = 12.071$ eV
$IE(O) = 13.618$ eV
YES! Just as we predicted.

Homonuclear Diatomic Molecules

GREAT QUESTIONS FOR AP STUDENTS:

2. Is the bond energy of X_2 greater than that of X_2^+, or less? Let's compare O_2 and O_2^+.



For O_2, the bond order is 2, because there are 8 bonding electrons and 4 antibonding electrons. When it is ionized, we remove an antibonding electron, so the bond order of O_2^+ is 2.5.

The bond dissociation energy of O_2^+ should be greater than that of O_2.

Experimentally, the bond energies are:

O_2	5.116 eV
O_2^+	6.663 eV

Homonuclear Diatomic Molecules

GREAT QUESTIONS FOR AP STUDENTS:

3. Is X_2 diamagnetic (weakly repelled by a magnetic field) or paramagnetic (attracted into a magnetic field).

   This is just a hidden way of asking if the molecule has unpaired electrons. If it has unpaired electrons, the unpaired spin causes it to be paramagnetic.

   Examples of paramagnetic molecules that are stable:

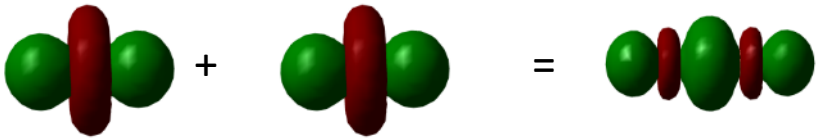
   O_2 $\sigma_{2s}^2 \sigma_{2s}^{*2} \sigma_{2p}^2 \pi_{2p}^4 \pi_{2p}^{*2}$ (Here the last two π_{2p}^* electrons go into the π_{2p}^* orbitals with parallel spins, causing O2 to be a high spin molecule that is attracted into a magnetic field.)

   NO $\sigma_{2s}^2 \sigma_{2s}^{*2} \sigma_{2p}^2 \pi_{2p}^4 \pi_{2p}^{*1}$ (Here there is only one unpaired electron, but that is enough! NO is a paramagnetic molecule.)

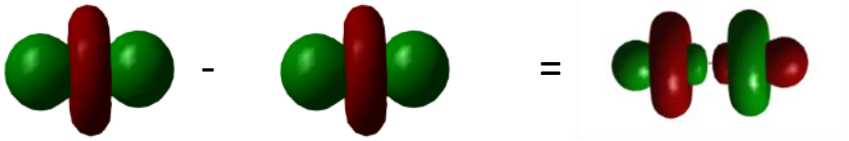
   All radicals (molecules with unpaired spins) are paramagnetic.

d-orbital bonding

If the bonding is between transition metals, you can get d-orbital bonding.
For the internuclear axis defined as the z-axis, you can combine the d_{z^2} orbtals to get bonding and antibonding dσ orbitals:



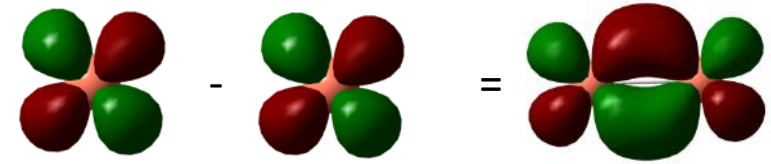
dσ bonding orbital



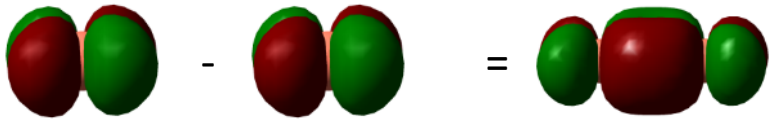
dσ* antibonding orbital

d-orbital bonding

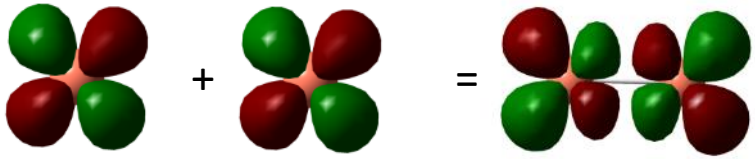
If you combine the d_{xz} orbitals (or the d_{yz} orbitals), you can get dπ bonding and antibonding orbitals.



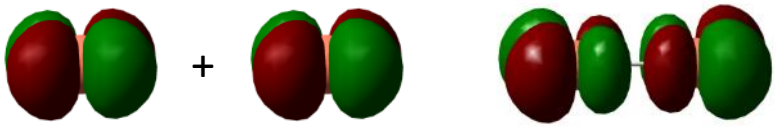
dπ bonding orbital



dπ bonding orbital



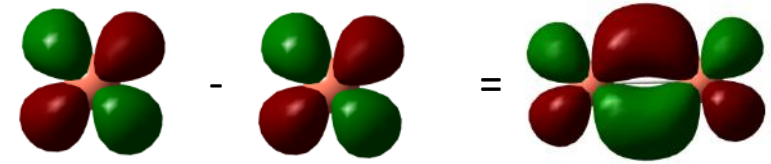
dπ antibonding orbital



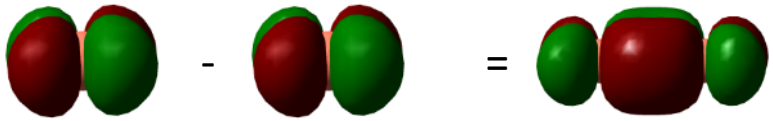
dπ antibonding orbital

d-orbital bonding

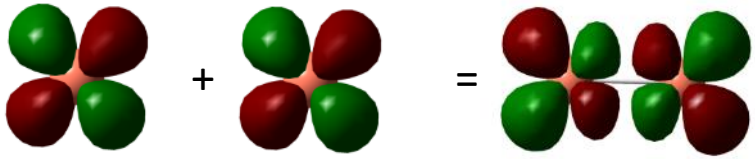
If you combine the d_{xz} orbitals (or the d_{yz} orbitals), you can get dπ bonding and antibonding orbitals.



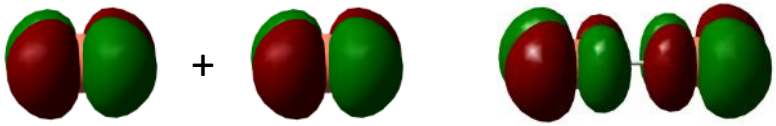
dπ bonding orbital



dπ bonding orbital



dπ* antibonding orbital



dπ* antibonding orbital

d-orbital bonding

If you combine the d_{xy} orbitals (or the d_{x2-y2} orbitals), you can get dδ bonding and antibonding orbitals.

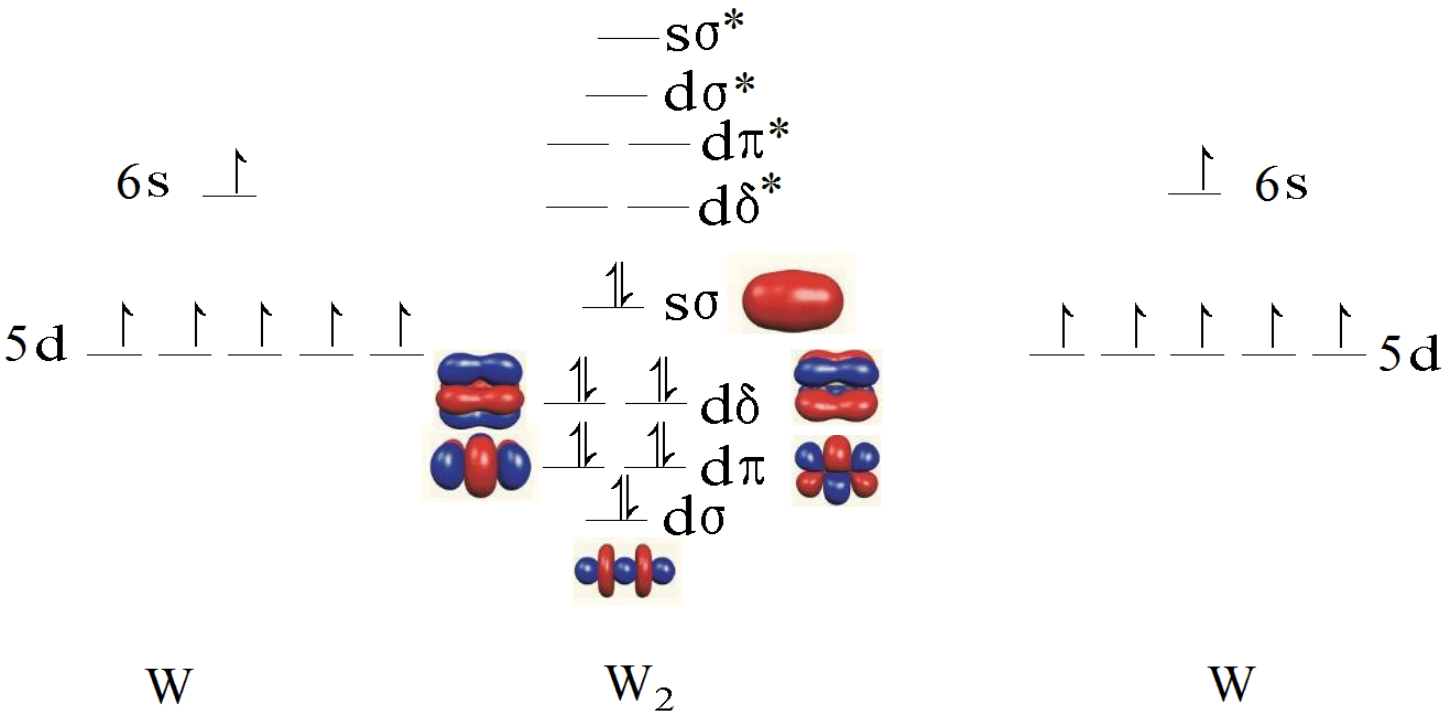
dδ bonding orbital

dδ bonding orbital

dδ* antibonding orbital

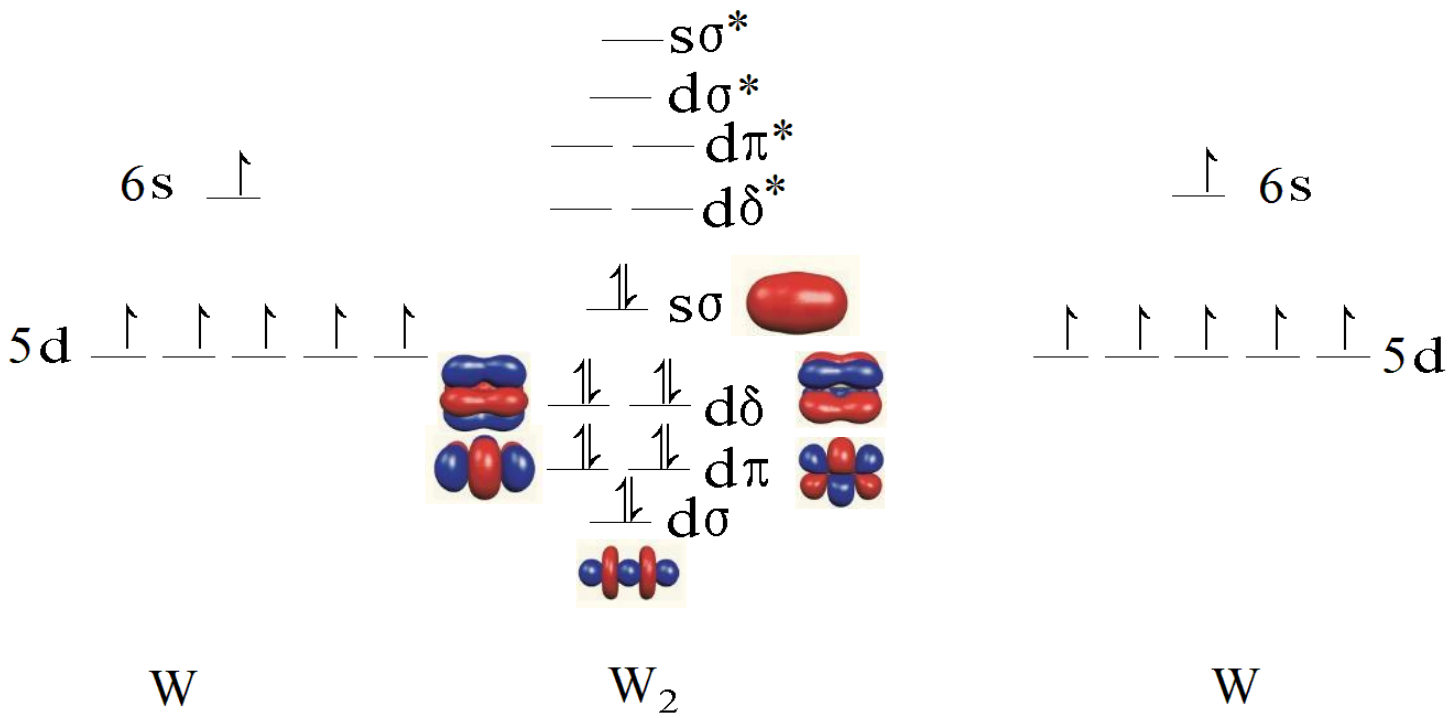
dδ* antibonding orbital

d-orbital bonding in W_2



Tungsten dimer has a sextuple bond!

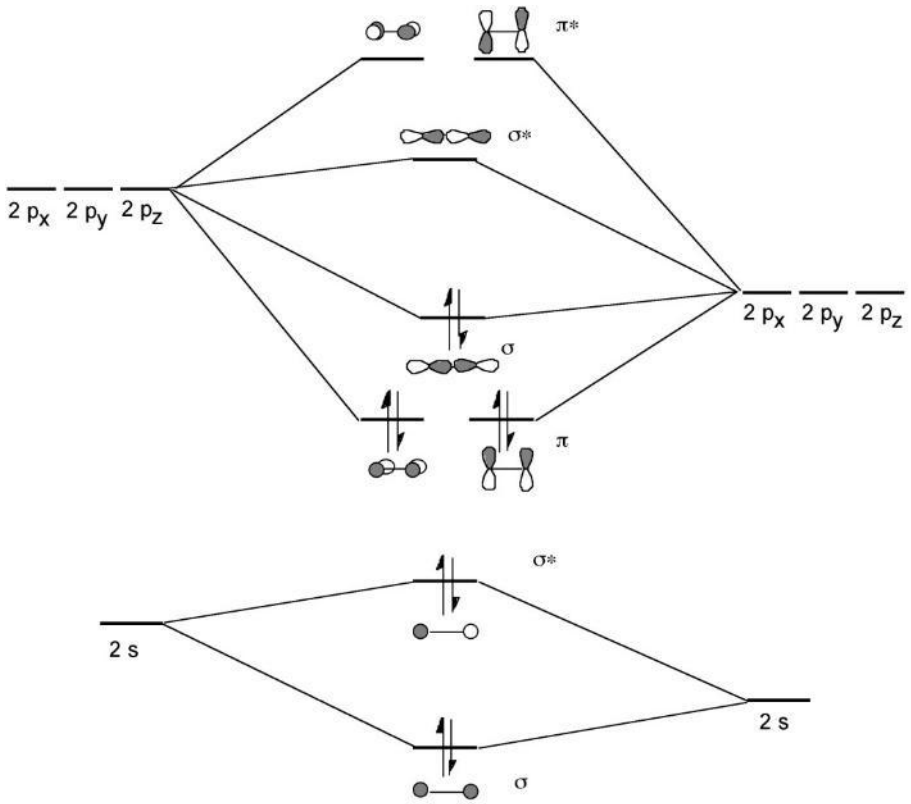
d-orbital bonding in W_2



$W \equiv W$

Heteronuclear Diatomic Molecules

If the nuclei are different, the more electronegative atom holds onto its electrons more tightly, so its atomic orbitals are pushed to lower energies. Molecular orbitals are formed by combining atomic orbitals that lie at similar energies, that have the same symmetry (σ or π), and that overlap well.

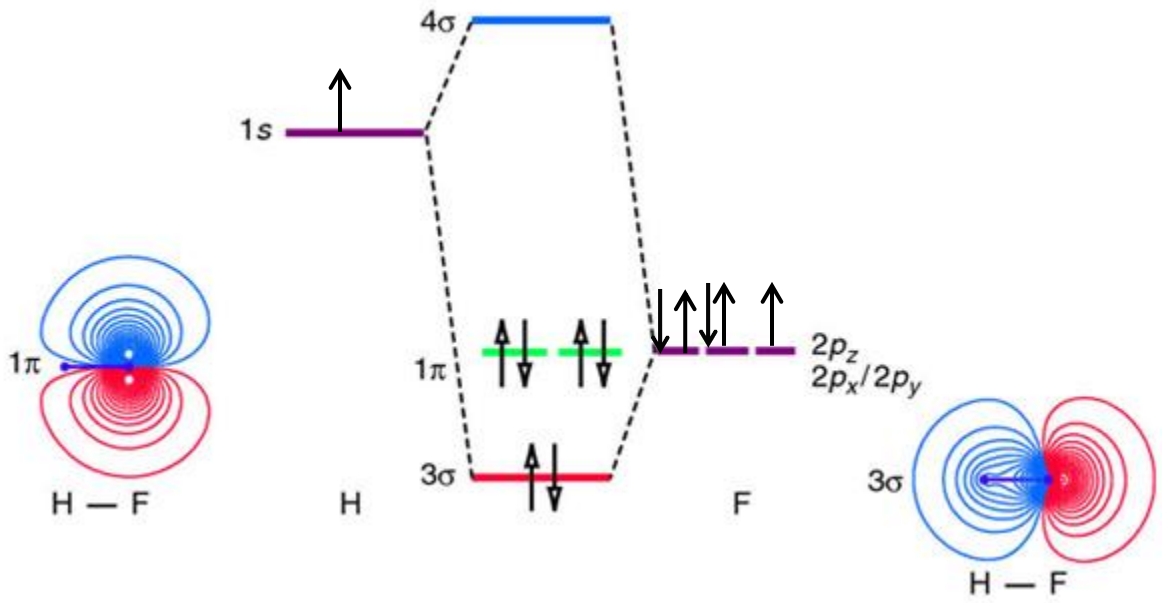


In CO, the two atoms aren't very different, so the molecular orbital diagram is just a slight change from N_2.

Heteronuclear Diatomic Molecules

If the nuclei are very different, the same rules apply.

For example, in HF, the F atom has a higher ionization energy, so its 2p orbitals lie below the 1s of hydrogen. However, the 1s of hydrogen has cylindrical symmetry about the H-F axis, so it is of σ-type and can only combine with the $2p_z$ orbital, which is also of σ-type. The $2p_x$ and $2p_y$ orbitals of F are of π-type, and have nothing to interact with on the hydrogen. They don't shift in energy.



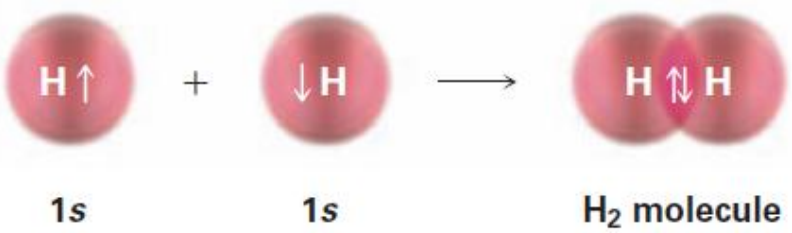
Valence Bond Theory

Molecular orbital theory – useful, explains small molecules well, good for understanding excited electronic states (and spectroscopy).

Valence bond theory – more obvious for extensions to polyatomics.

Basic Idea: Electrons stay in atomic orbitals but are spin-paired to form a bond when the atoms approach and the atomic orbitals overlap.

Valence Bond Theory of H_2



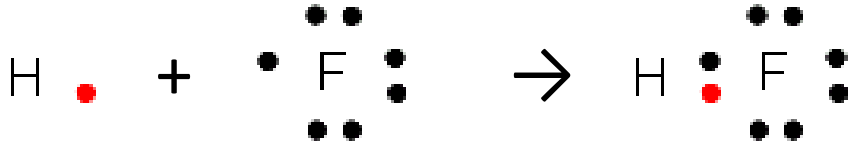
The VB and MO approaches represent different approximations in the solution of $\hat{H}\psi = E\psi$.

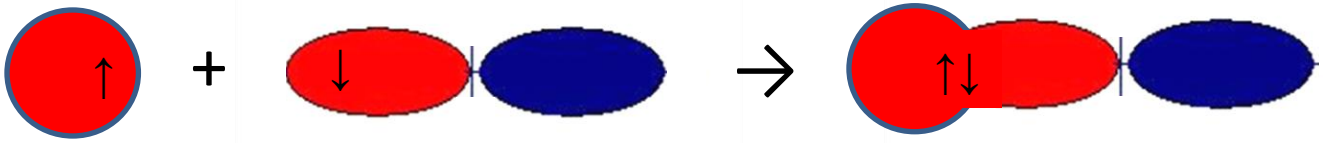
In the MO approach, both electrons are in the same molecular orbital, which extends over the entire molecule. There is therefore a certain probability that they'll be found on the same atom. Thus, you get equal contributions from structures like H^+H^- and H^-H^+ (ionic structures) and an equal contribution from covalent structures (where each atom has one electron on it). The MO method gives 50% covalent, 50% ionic character in the wavefunction.

In the VB approach, the ionic structures are completely eliminated and only covalent structures are included. The VB method gives a wavefunction that is 100% covalent.

A better method optimizes the amount of covalent vs. ionic character, and gets 93.7% covalent and 6.3% ionic character. So VB is closer to the truth for H_2.

Valence Bond Theory of HF





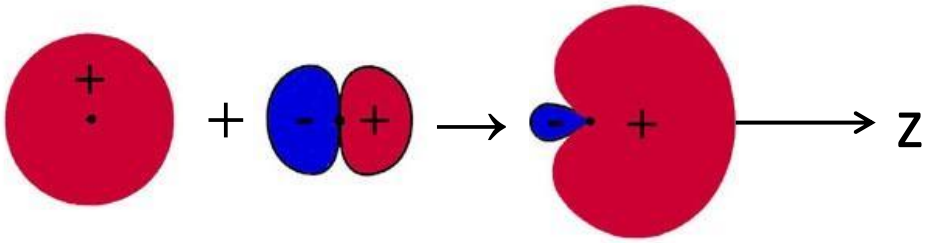
As you can see, VB theory has its origin in Lewis dot structures.

Unfortunately, actual calculations using VB theory are more difficult than MO theory, so it isn't used that much in actual computational chemistry.

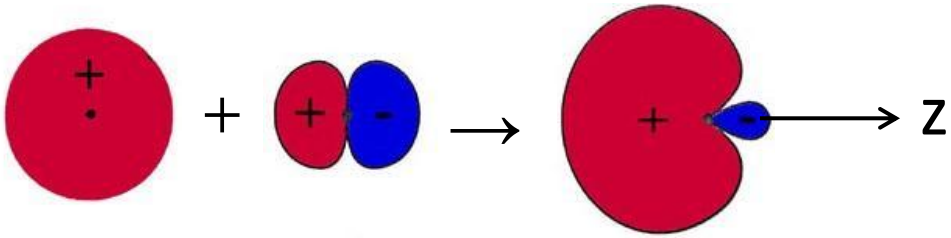
Bonds to multiple atoms: hybridization

To form equivalent bonds to multiple atoms, hybrid orbitals are formed by forming linear combinations of atomic orbitals on the central atom.

Example: sp hybrid orbitals:



2s + 2p → sp hybrid 1



2s - 2p → sp hybrid 2

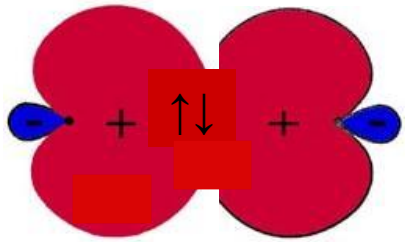
The other two 2p orbitals are then unused in forming the hybrids, and are oriented perpendicular to the z-axis.

sp hybrid orbitals (continued)

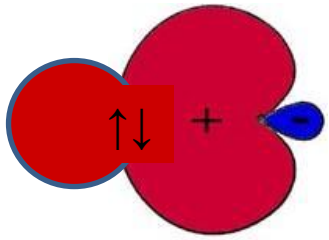
These sp hybrid orbitals are perfect for forming bonds to two different atoms to form a linear three-atom structure, like HCN.

Lewis dot structure: H:C:::N:
Each electron pair is represented by a different diagram here.

The nitrogen atom is also sp-hybridized, with the other hybrid projecting out the back as a lone pair.

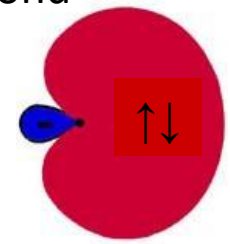


C N sigma bond



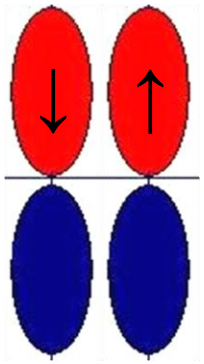
H C sigma bond

N lone pair



sp hybrid orbitals (continued)

Finally, the two p orbitals that weren't used on C combine with the two 2p orbitals that weren't used on N to form two sets of π bonds.



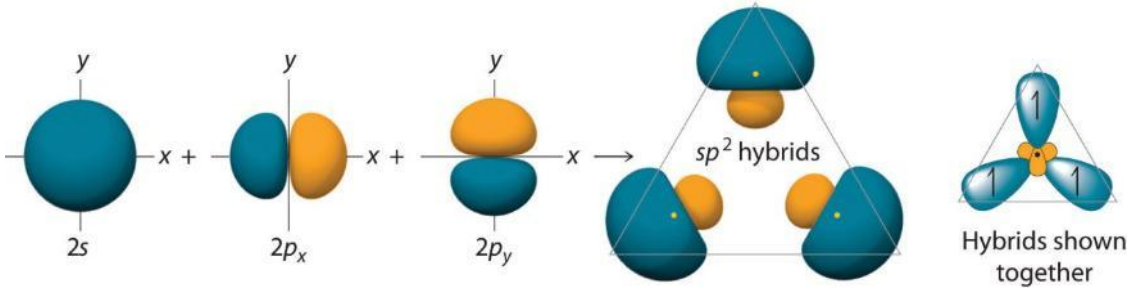
H C N

The other π bond is oriented 90 degrees to this one.

Other hybridizations: sp^2

For a central atom that has 3 sigma bonds to other atoms (or lone pairs), the hybridization is sp^2. This means that two p orbitals and one s orbital combine to make three equivalent hybrid atomic orbitals.

If the three equivalent orbitals are in the x-y plane, they are formed from s, p_x, and p_y, leaving the p_z orbital free to form a π bond. The three hybrid orbitals are then all in the same plane.

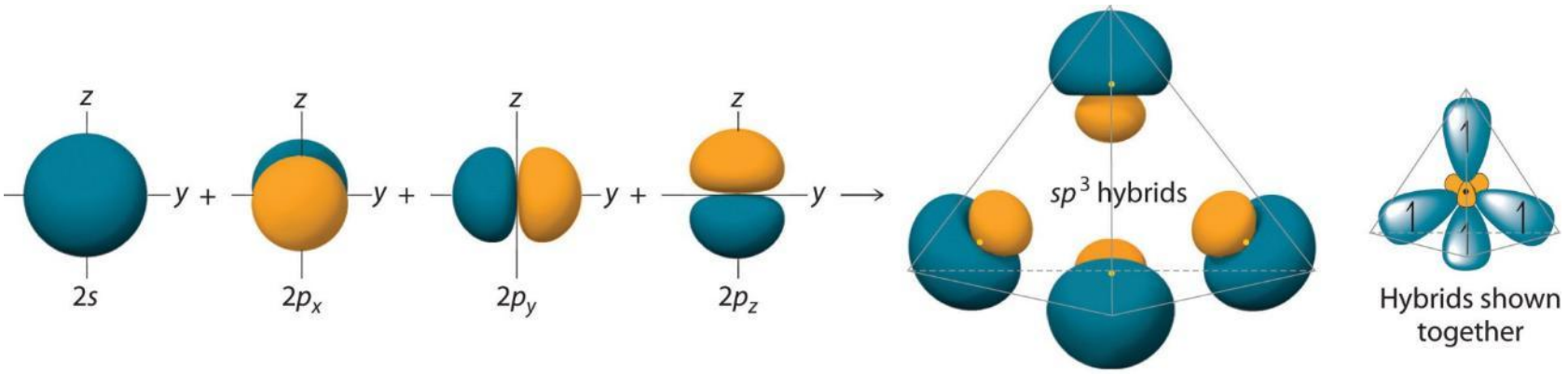


Examples: BF_3

CH_2O

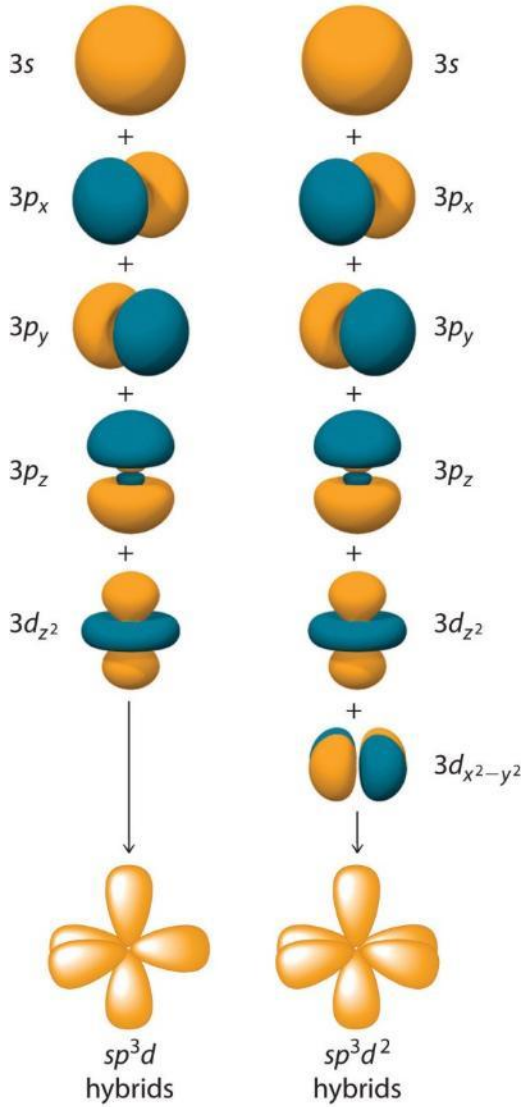
Other hybridizations: sp^3

For a central atom that has 4 sigma bonds to other atoms (or lone pairs), the hybridization is sp^3. This means that three p orbitals and one s orbital combine to make four equivalent hybrid atomic orbitals. These are formed from the s, p_x, p_y, and p_z orbitals.



Examples: CH_4, NH_3, H_2O

Other hybridizations: sp^3d and sp^3d^2



For 5 or 6 sigma bonds (or lone pairs) on a central atom, the atom must be hybridized sp^3d or sp^3d^2 , respectively.

For sp^3d, this is easily understood as forming sp^2 hybrids in one plane, leading to a trigonal planar portion of the molecule, then combining the remaining p_z orbital with the d_{z^2} to generate hybrids pointing along the +z and –z axis.