Localized Electron Model

Models for Chemical Bonding

Localized electron model

(Valence bond model)

Molecular orbital model

Localized Electron Model

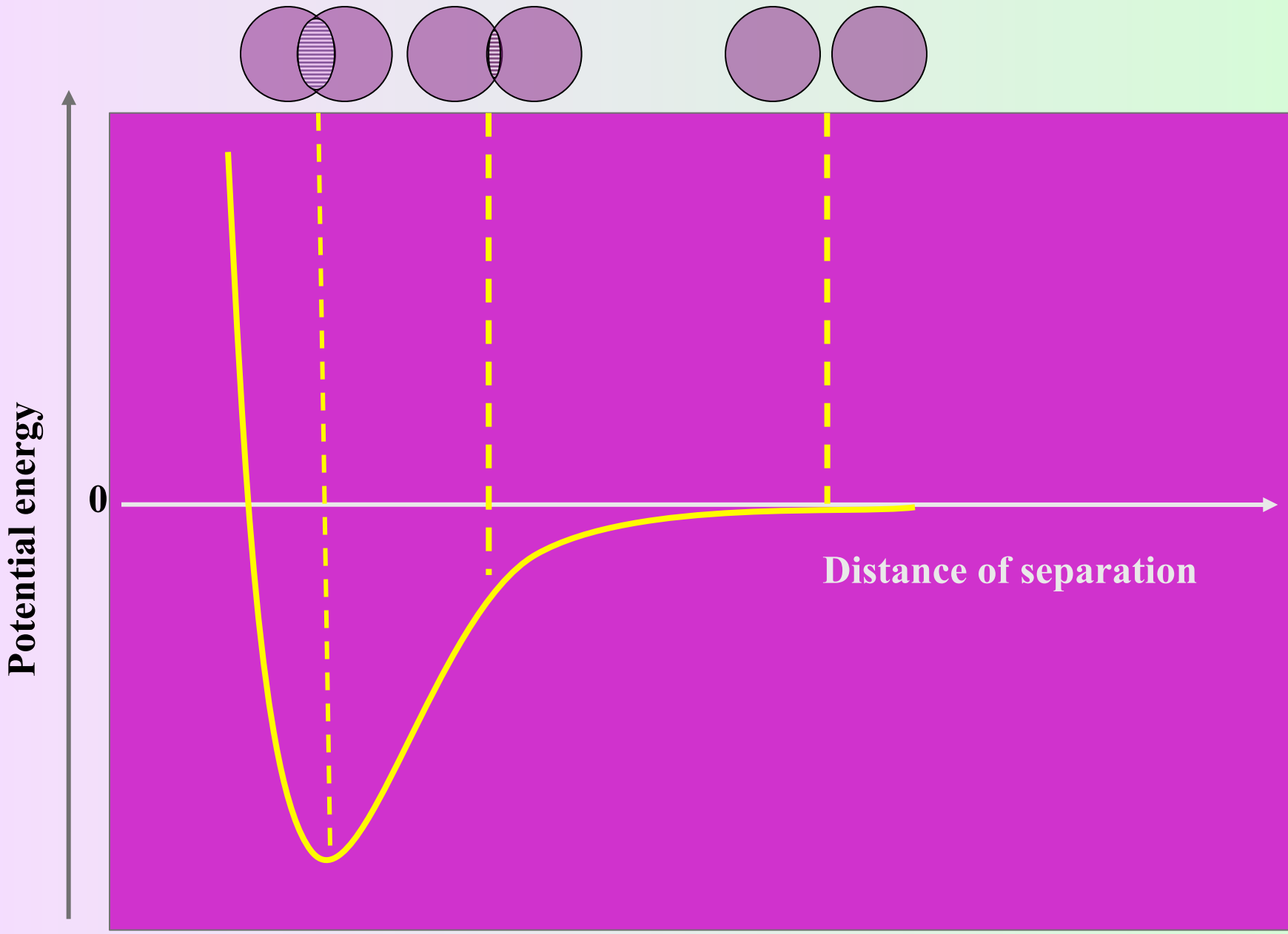
Useful for explaining the structure of molecules especially nonmetals bonded to nonmetals

Localized electron model

Electron pair can be shared when half-filled orbital of one atom overlaps with half-filled orbital of another.

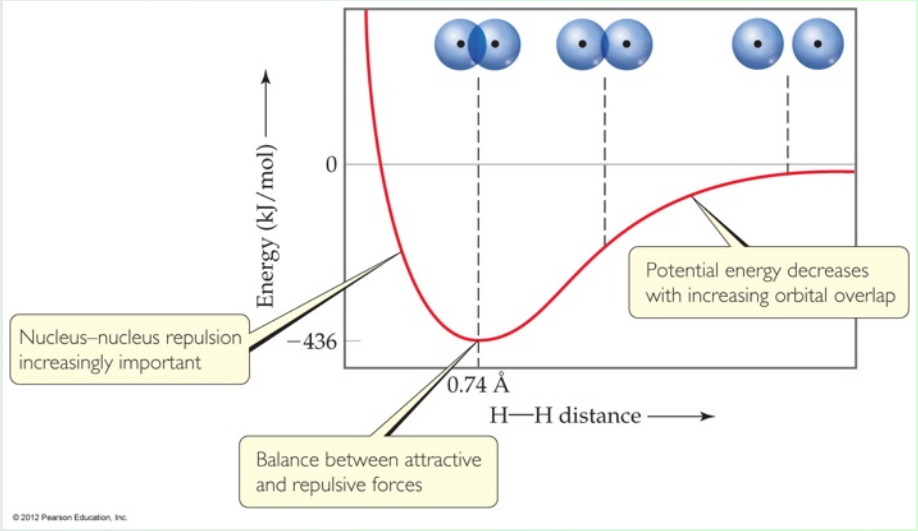
δ Bond: orbitals overlap along the internuclear axis

π Bond: side by side overlap of orbitals parallel to the internuclear axis


Potential energy
0
Distance of separation

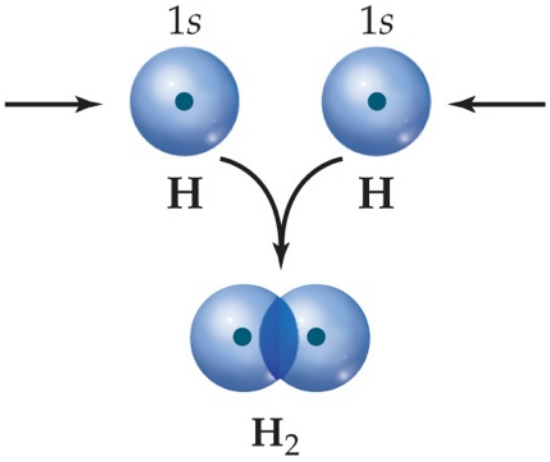
Overlap and Bonding

- Increased overlap brings the electrons and nuclei closer together while simultaneously decreasing electron–electron repulsion.

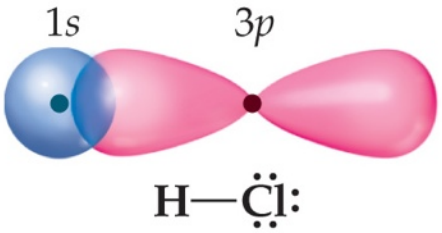


- However, if atoms get too close, the internuclear repulsion greatly raises the energy.

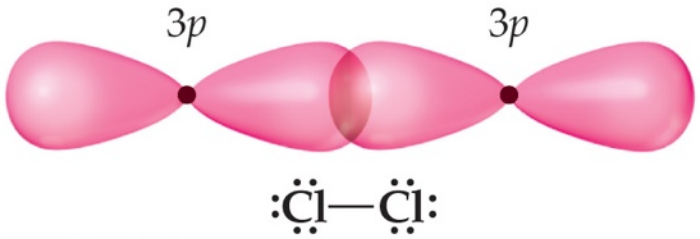
Overlap and Bonding



s,s δ bond



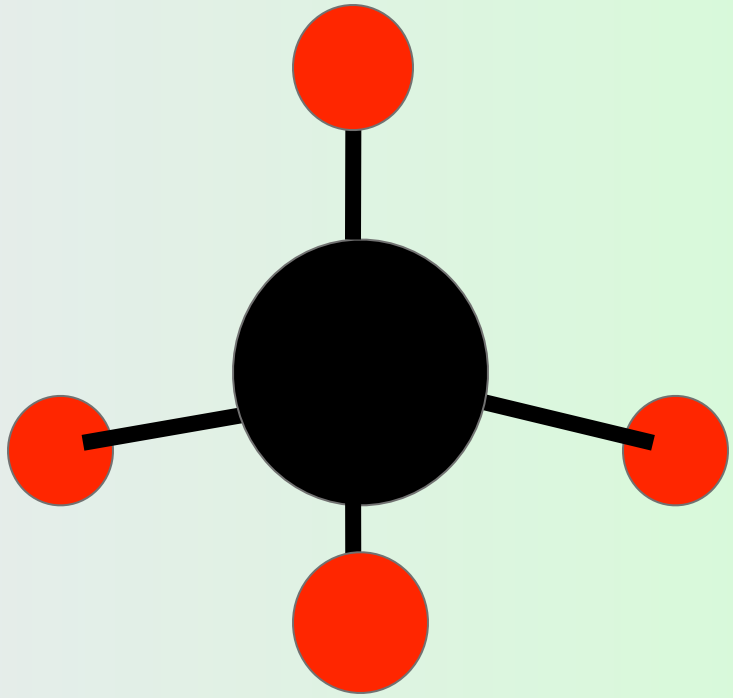
s,p δ bond



p,p δ bond

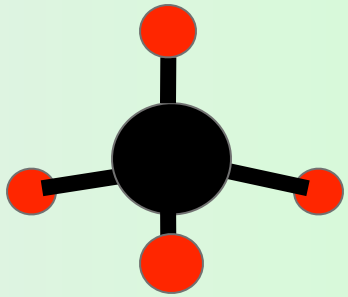
Structure of Methane (CH_4)

structure of methane seems inconsistent with electron configuration of carbon

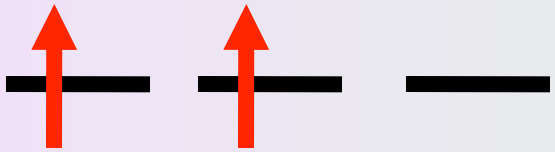


carbon

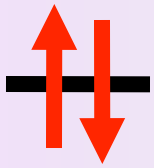
only two unpaired electrons



2p



2s



Carbon Should form δ –bonds with only two Hydrogen atoms ?

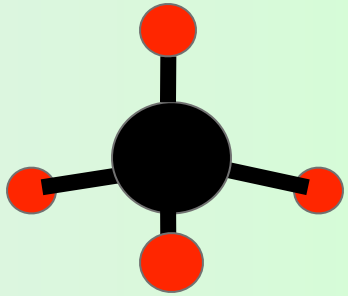
Hybridization of Atomic Orbitals

Hybrid orbitals

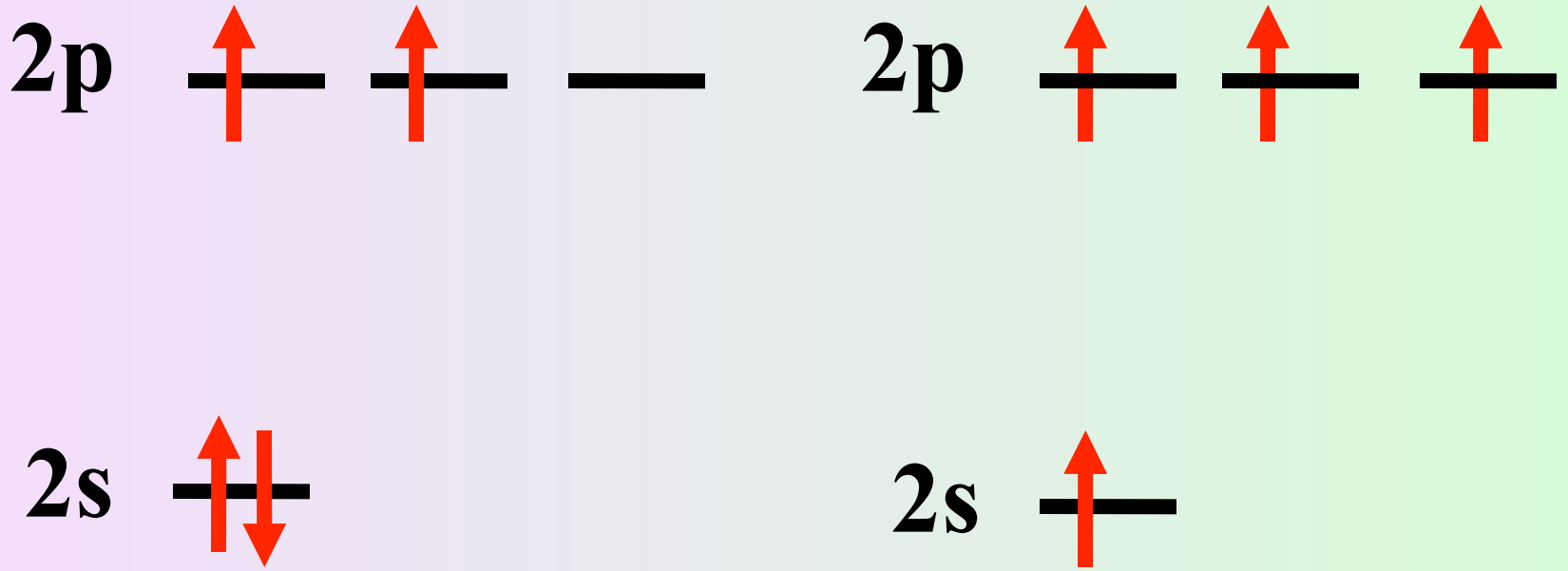
atomic orbitals obtained when two or nonequivalent orbitals of the same atom combine in preparation for covalent bond formation

sp^3 Hybridization

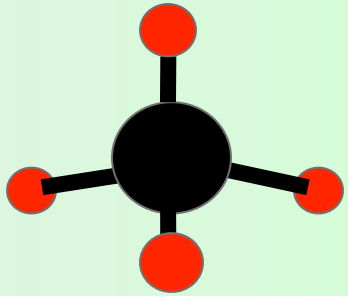
sp^3 Hybridization



Promote an electron from the 2s to the 2p orbital

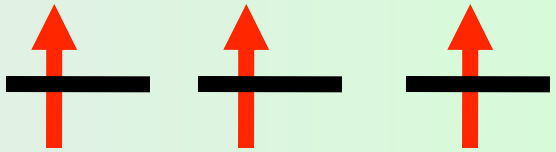


sp^3 Hybridization

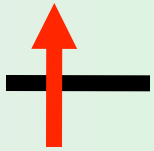


Mix together (hybridize) the 2s orbital and the three 2p orbitals

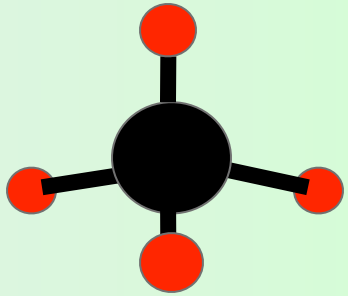
2p



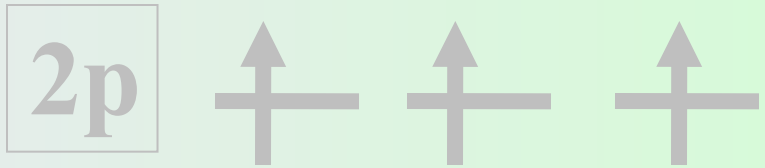
2s

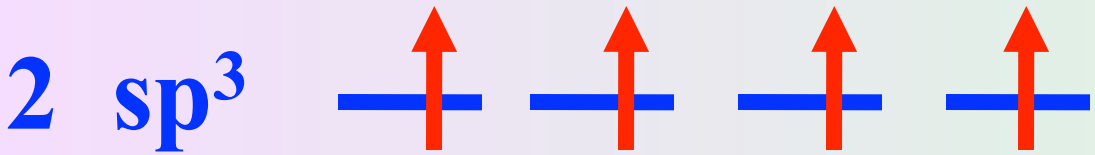


sp^3 Hybridization

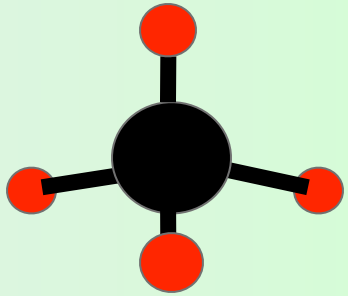


Mix together (hybridize) the 2s orbital and the three 2p orbitals



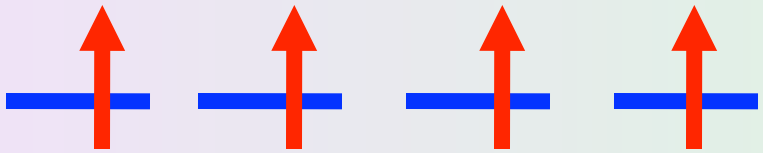


sp^3 Hybridization



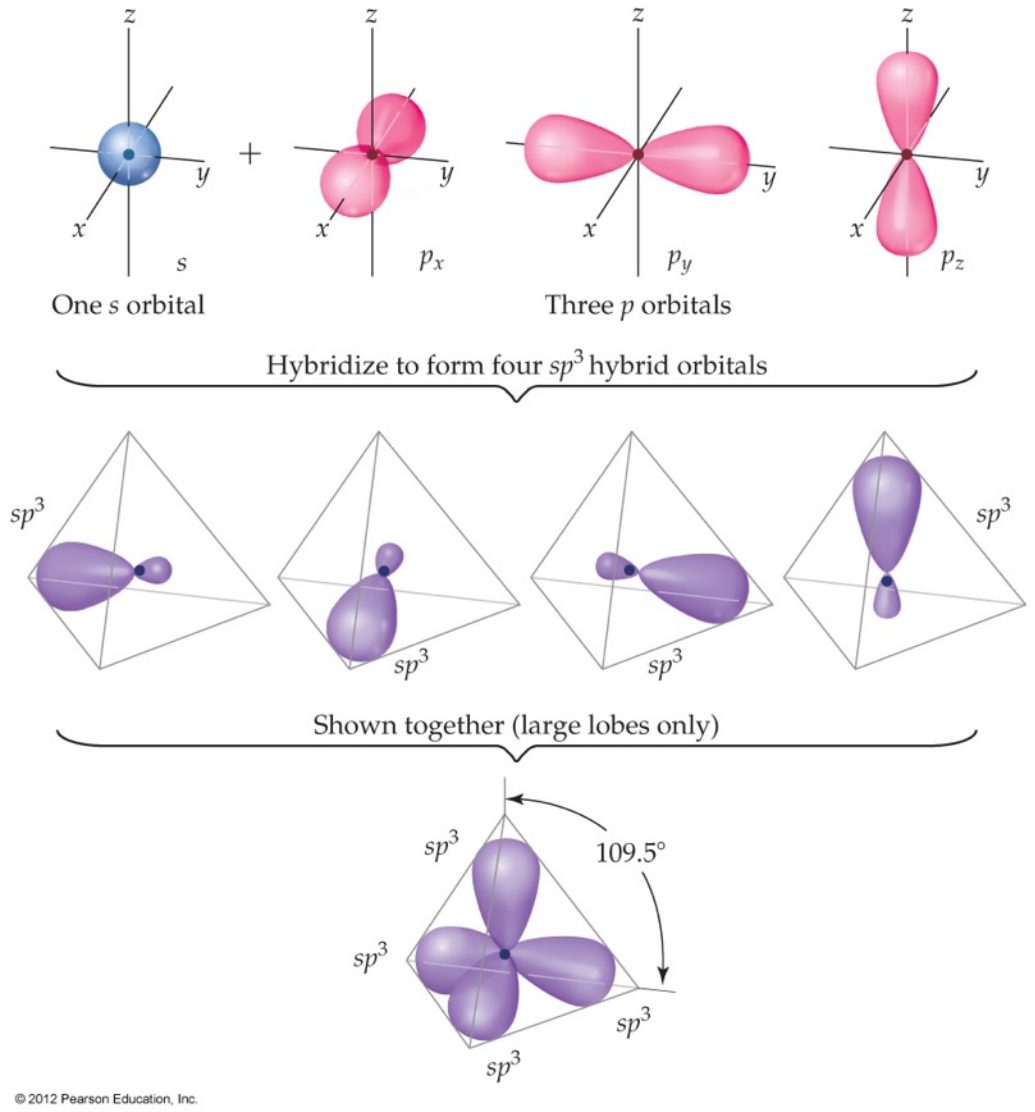
Mix together (hybridize) the 2s orbital and the three 2p orbitals

2 sp^3

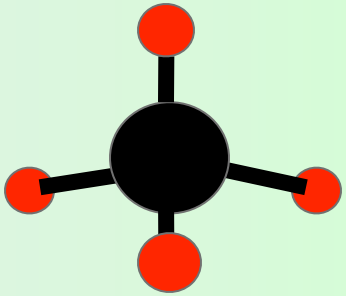


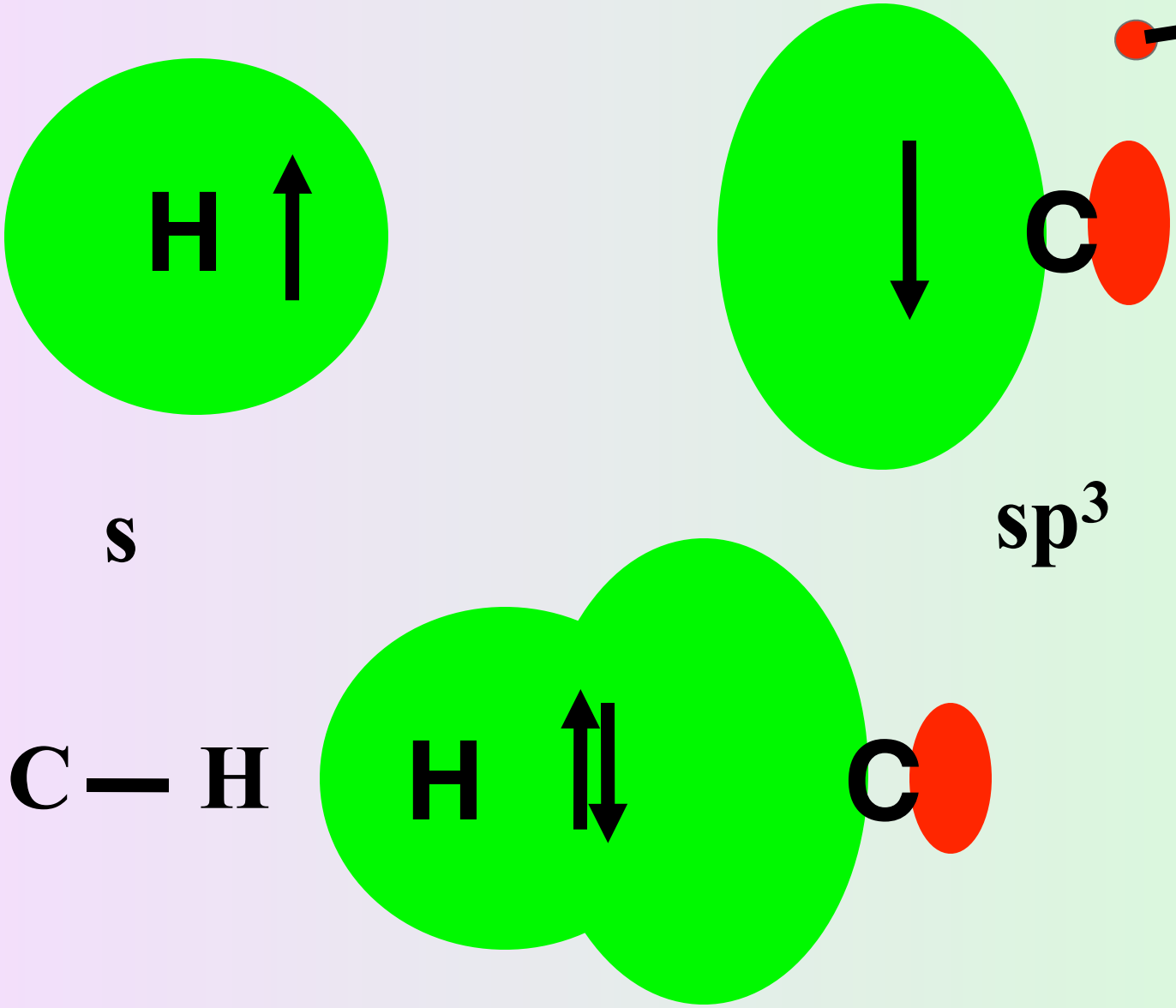
Hybrid Orbitals

With carbon, we get four degenerate sp^3 orbitals.



δ Bond in CH_4





Justification for Orbital Hybridization

The model is consistant with structure of methane

Allows for the formation of more bonds (4 rather than 2)

Bonds involving sp^3 orbitals are stronger than s-s overlap or p-p overlap

Remember

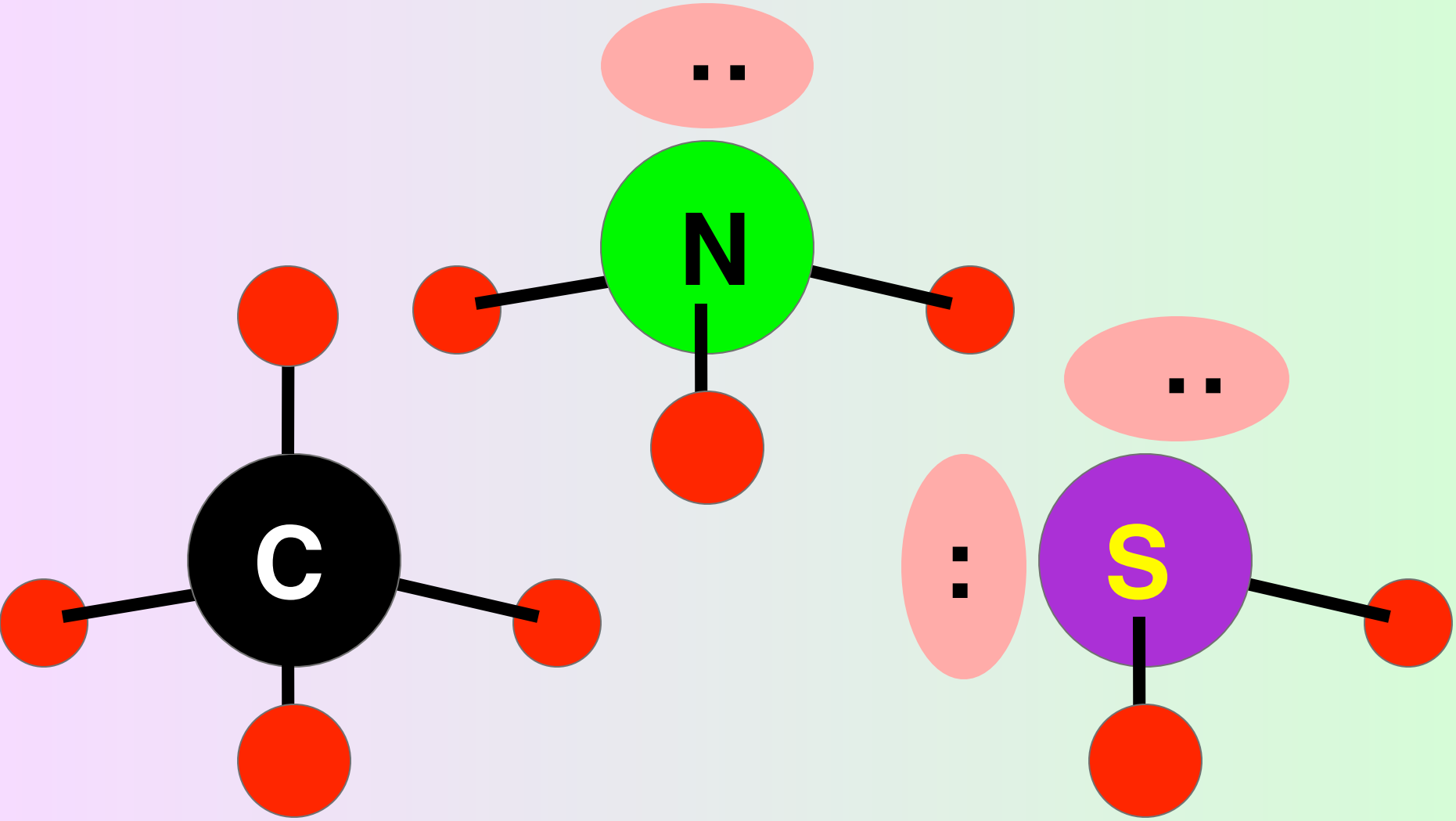
Four electron pairs

= tetrahedral arangement of those electron pairs

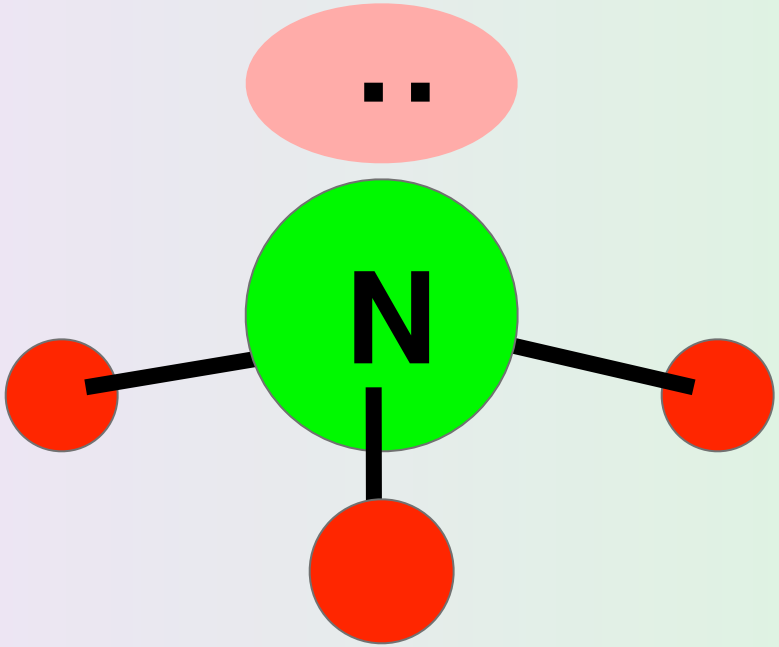
= sp^3 hybridization

Four electron pairs

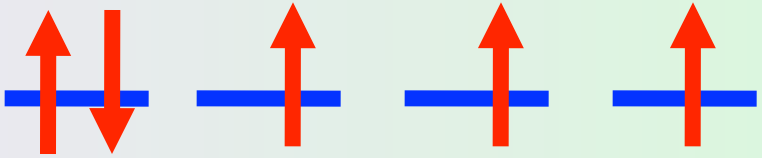
tetrahedral arrangement of electron pairs



NH_3



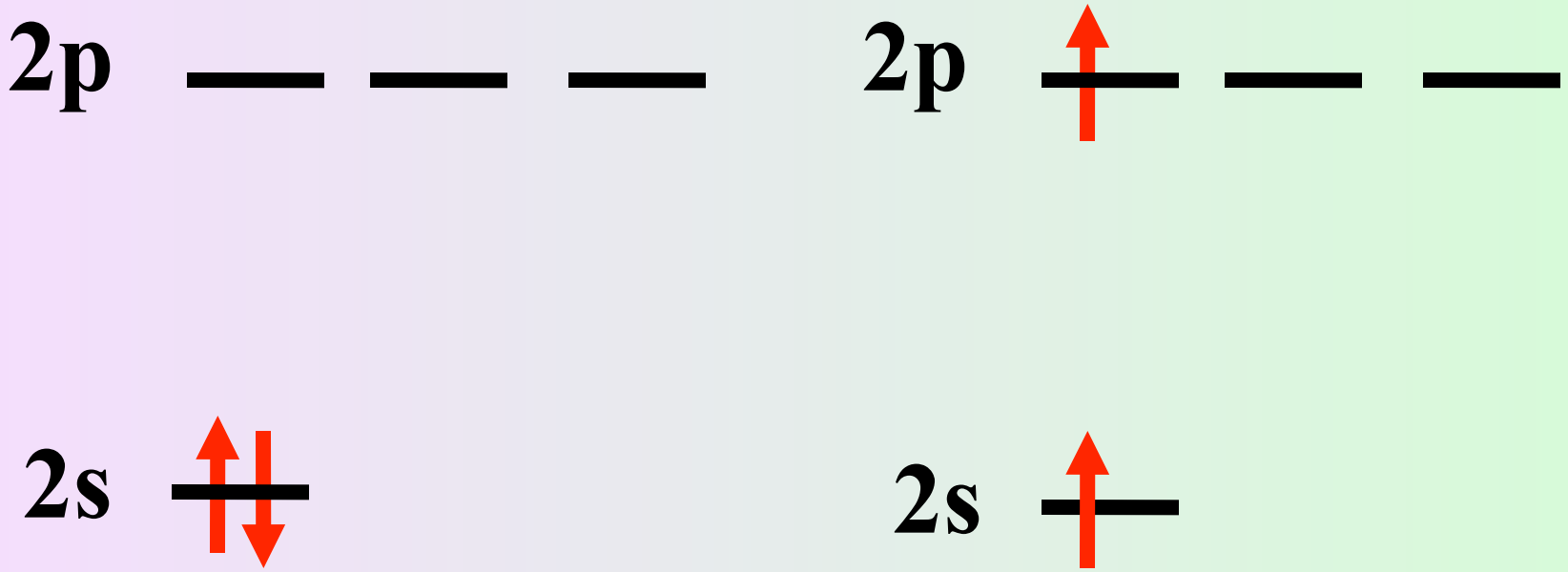
2 sp^3



sp Hybridization

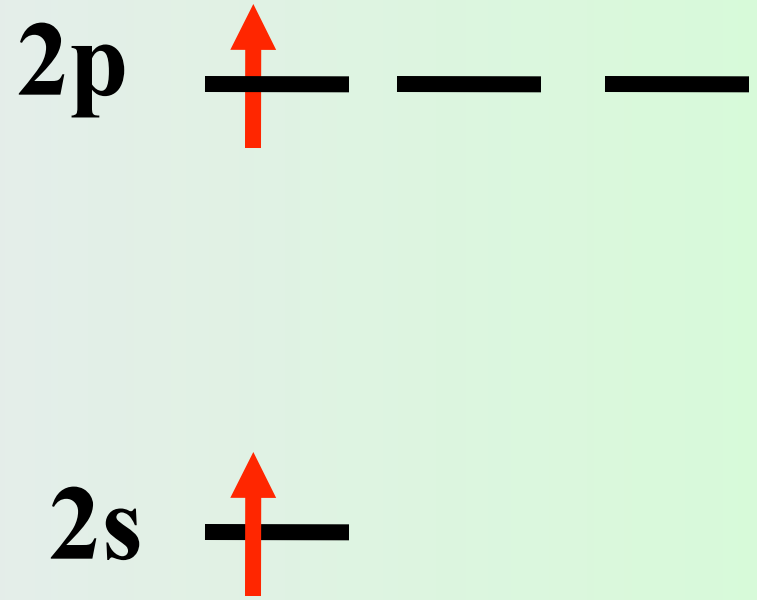
Beryllium chloride ($BeCl_2$)

Promote an electron from the 2s to the 2p orbital



Beryllium chloride ($BeCl_2$)

Mix together (hybridize) the 2s orbital and one 2p orbitals



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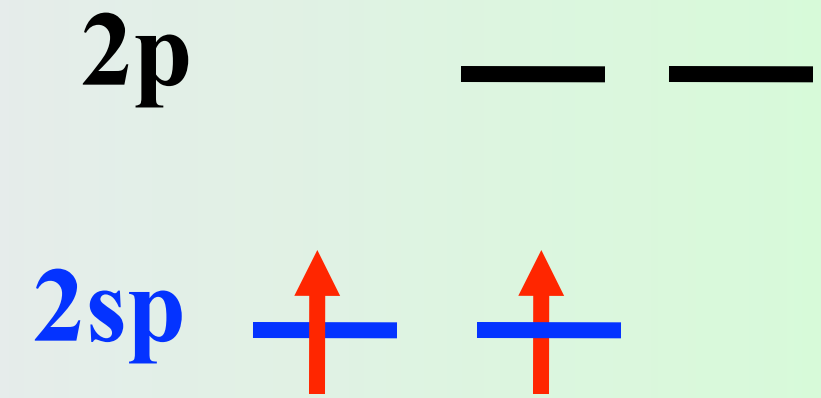
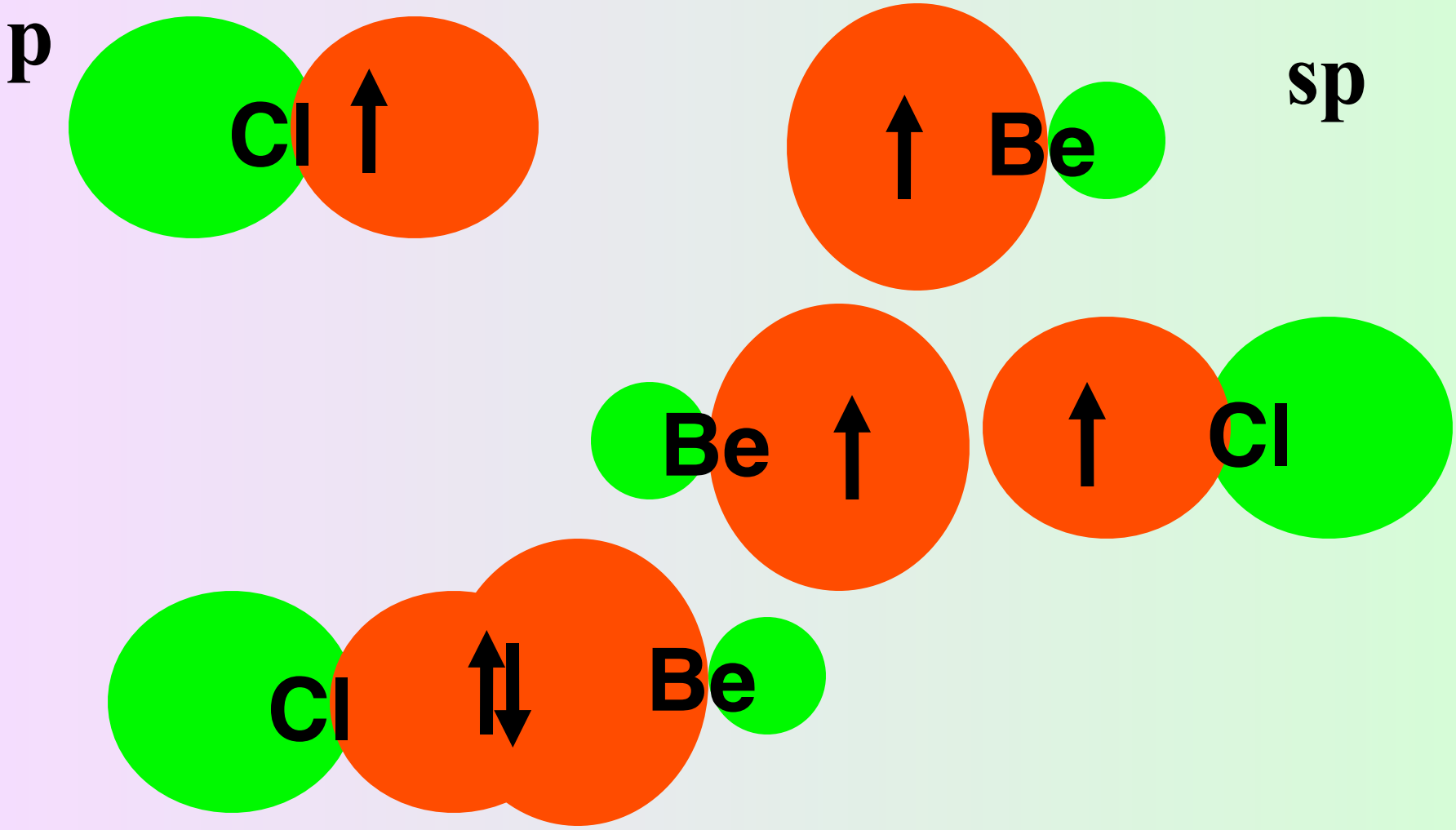


The Be — Cl δ Bond in BeCl



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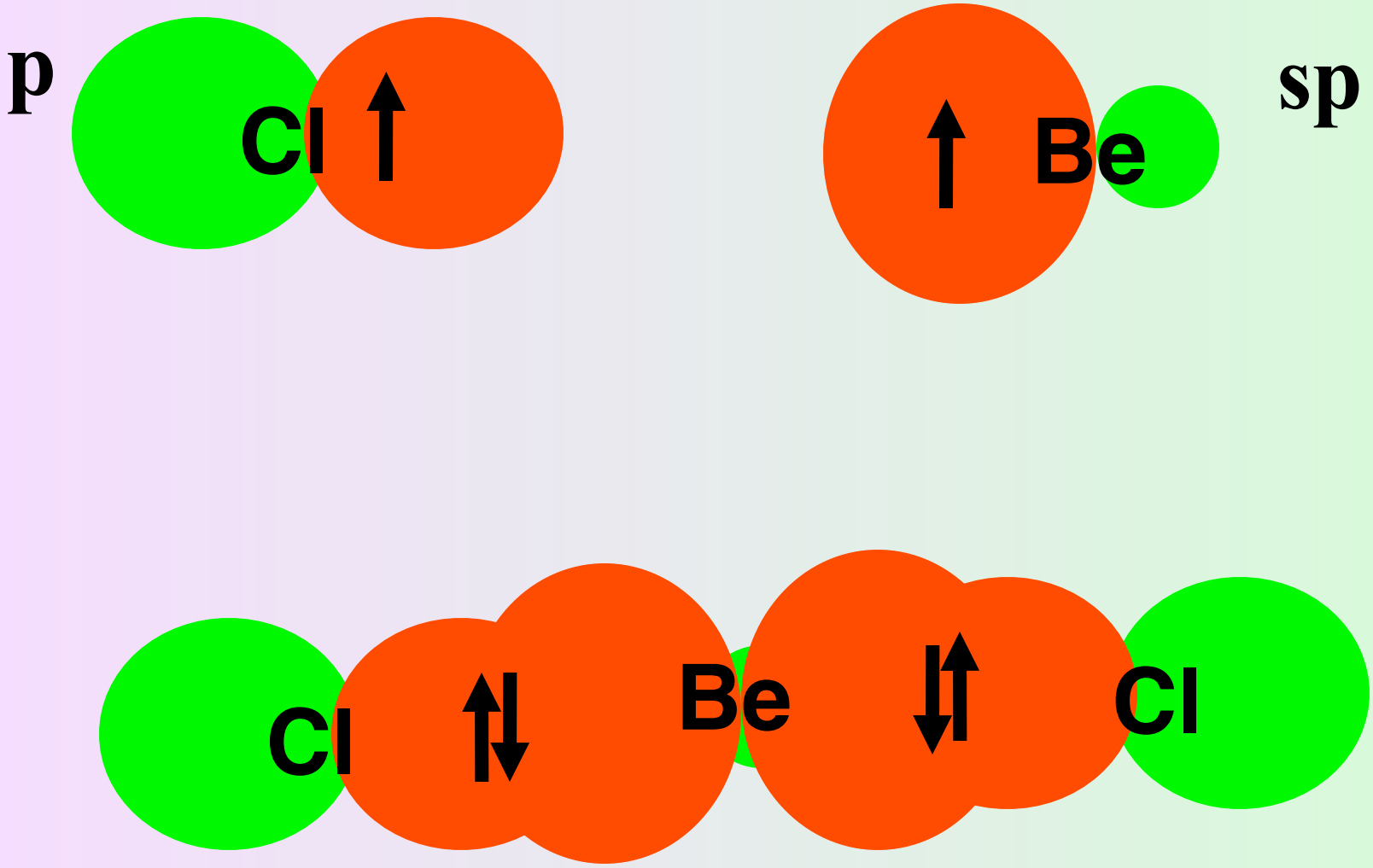
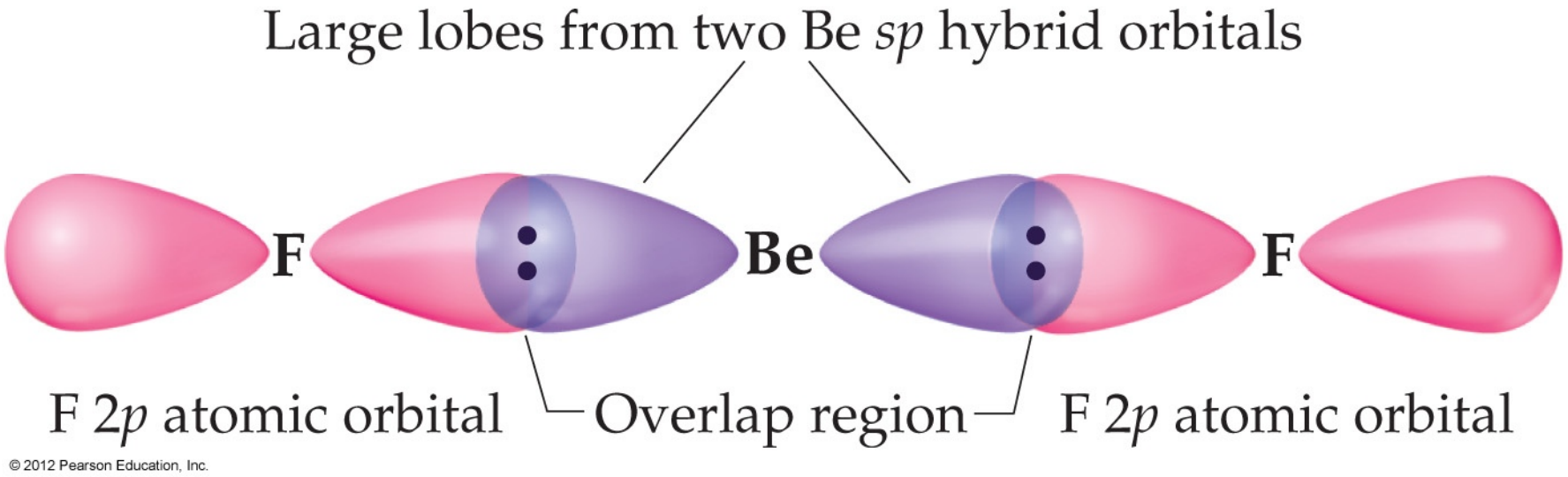


Hybrid Orbitals

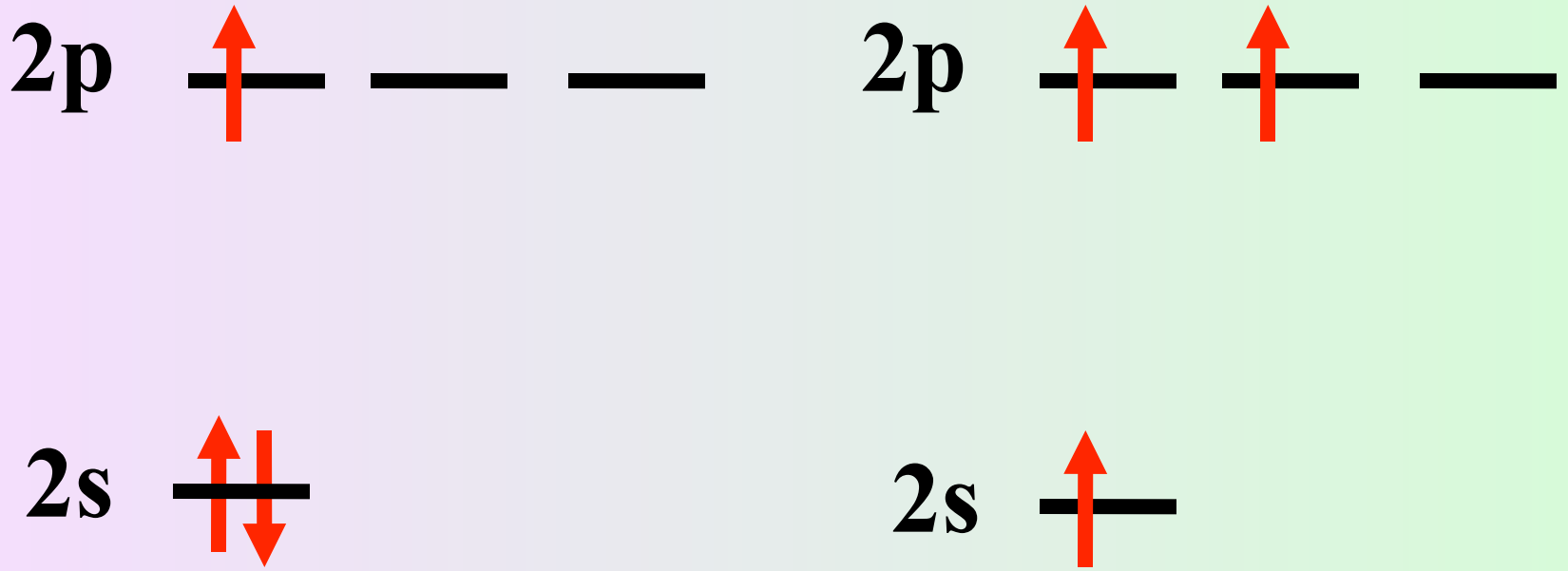
- These two degenerate orbitals would align themselves 180° from each other.
- This is consistent with the observed geometry of beryllium compounds: linear.



sp^2 Hybridization

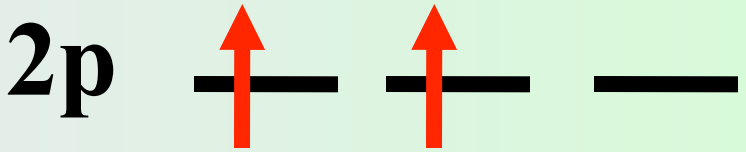
Boron trifloride

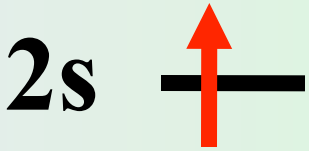
Promote an electron from the 2s to the 2p orbital



Boron trifloride

Mix together (hybridize) the 2s orbital and two 2p orbitals





Boron trifloride

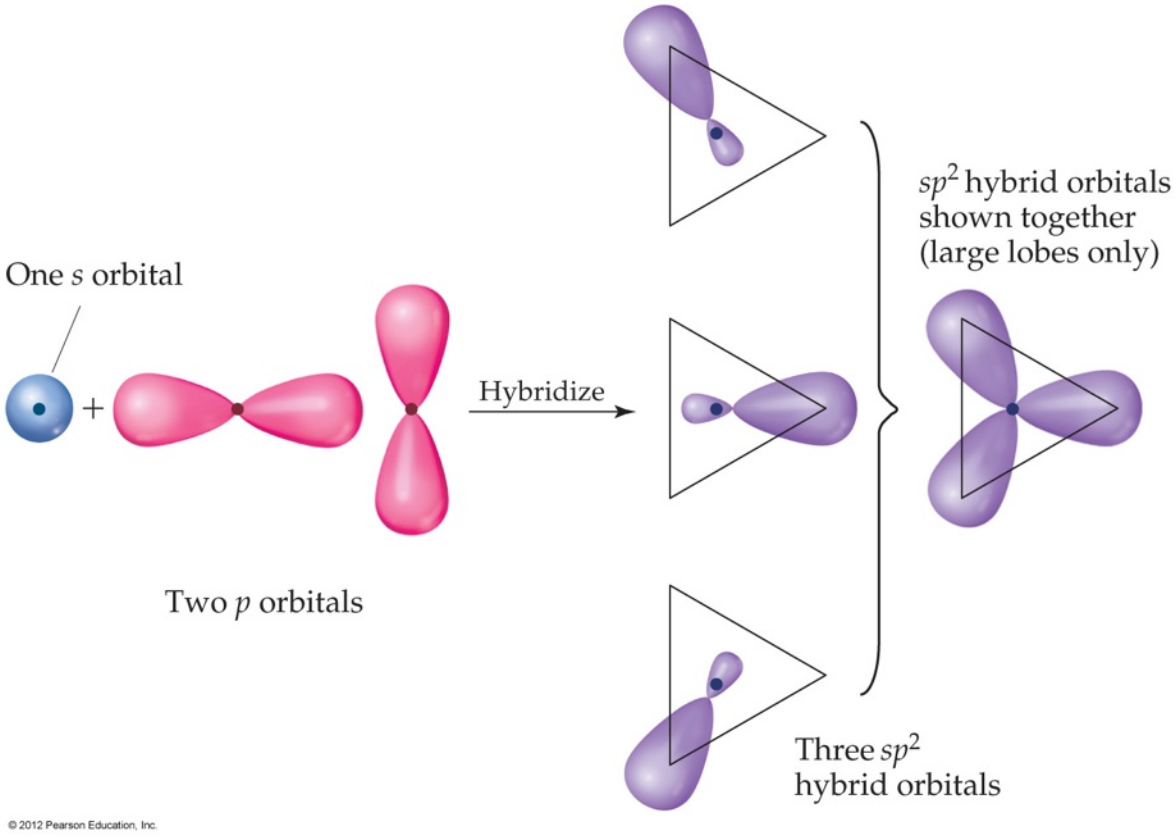
Mix together (hybridize) the 2s orbital and two 2p orbitals

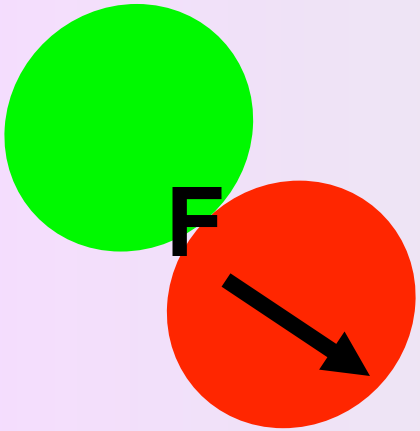
2p —

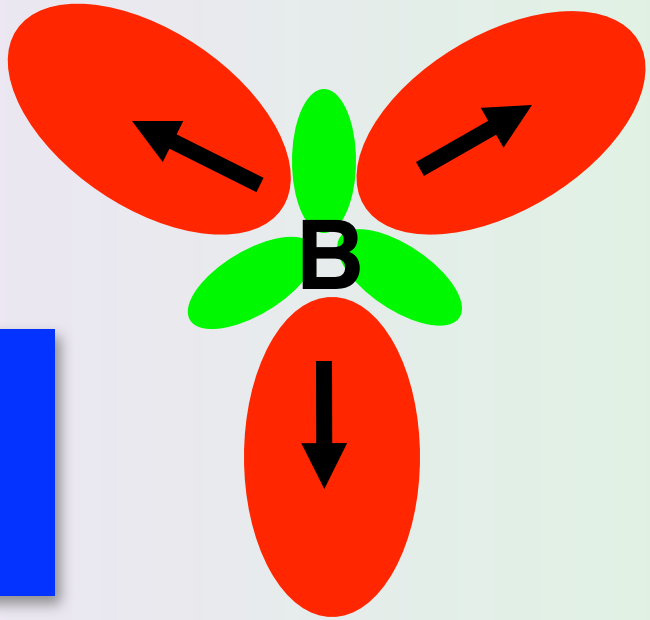
2 sp^2 ↑ ↑ ↑

Hybrid Orbitals

Using a similar model for boron leads to three degenerate sp^2 orbitals.

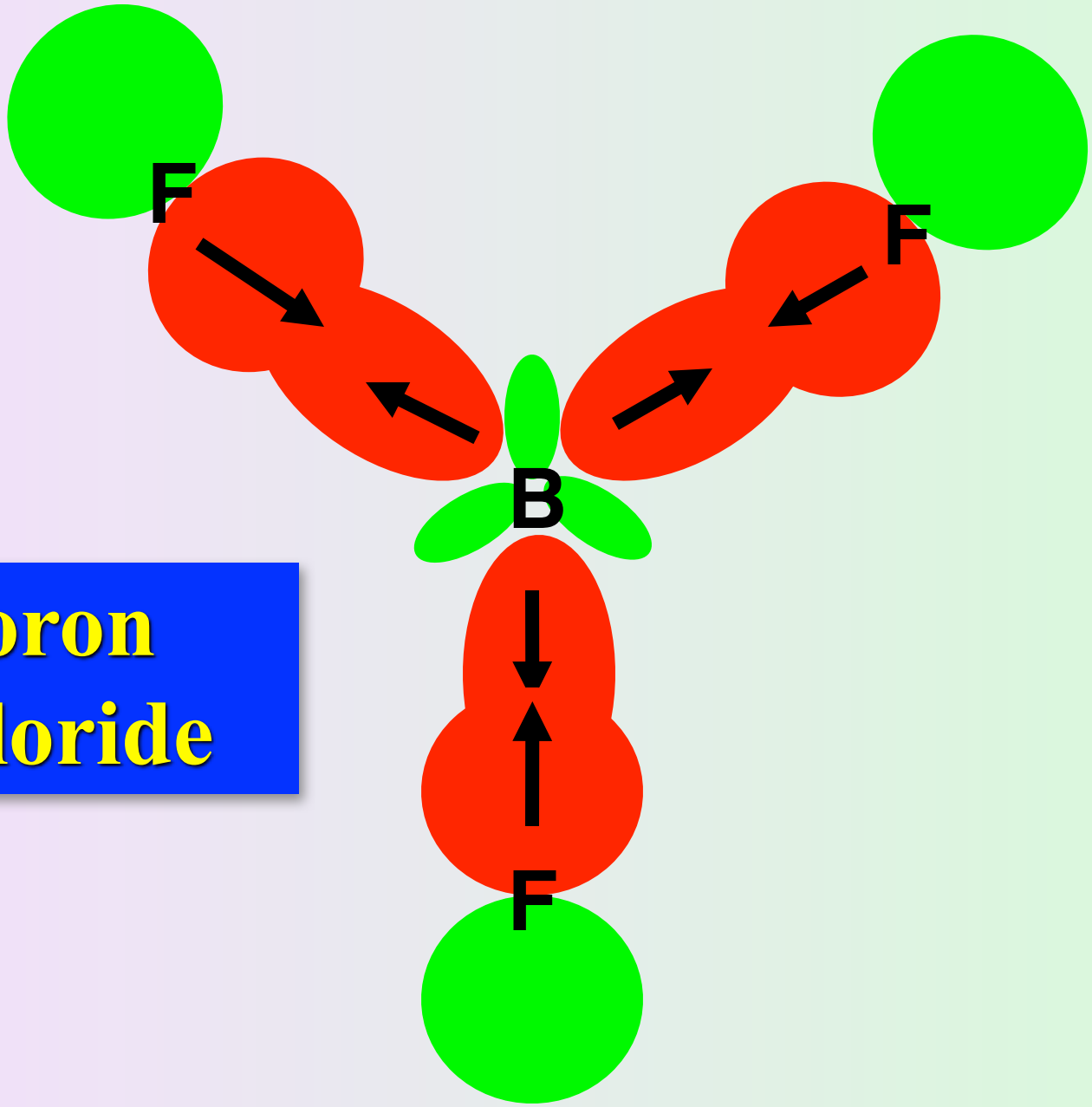






Boron trifloride

Boron trifloride



Hybridizing Atomic Orbitals

hybrid orbitals are used only for atoms in a molecule, not for isolated atoms

hybrid orbitals are different in shape from the atomic orbitals from which we derive them

number of hybrid orbitals equals number of atomic orbitals from which they were generated

hybridization permits more bonds and stronger bonds

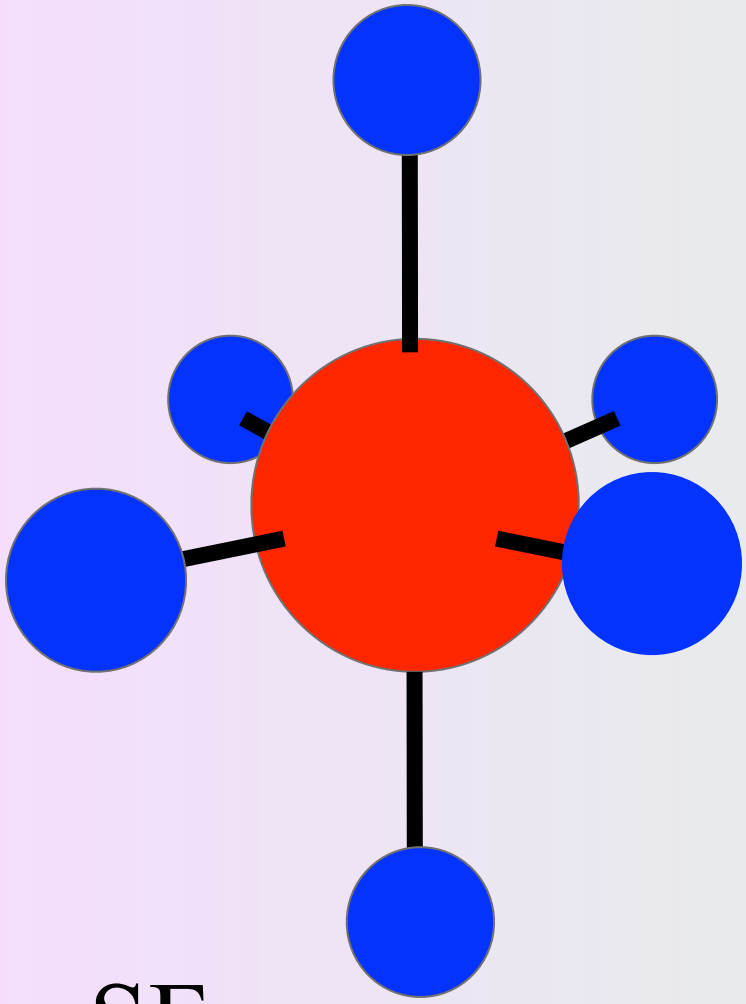
covalent bond results from overlap of half-filled orbitals

Procedure For Hybridizing Atomic Orbitals

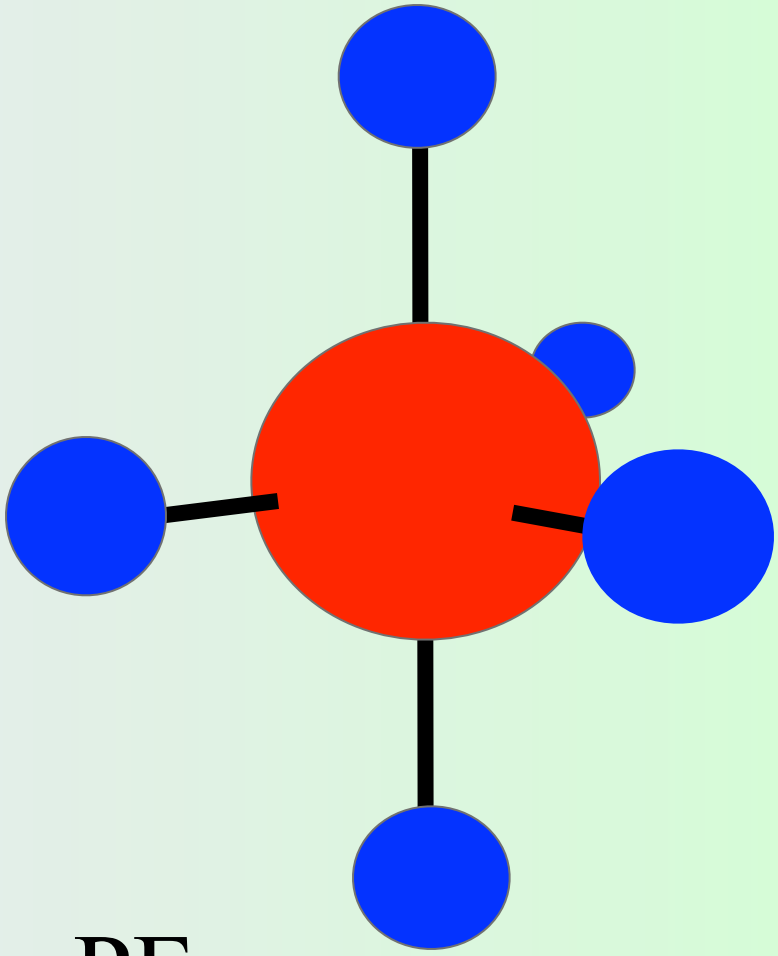
draw the Lewis structure of the molecule

predict the overall arrangement of the electron pairs using the VSEPR model

deduce the hybridization of the central atom



SF_6



PF_5

Hybridization of s, p, and d Orbitals

Beginning with the third period of the periodic table

1 3s orbital + 3 3p orbital + 1 3d orbital

gives sp^3d

Permits five electron pairs (trigonal bipyramidal)

1 3s orbital + 3 3p orbital + 2 3d orbital

gives sp^3d^2

Permits six electron pairs (octahedral)

π -Bonds

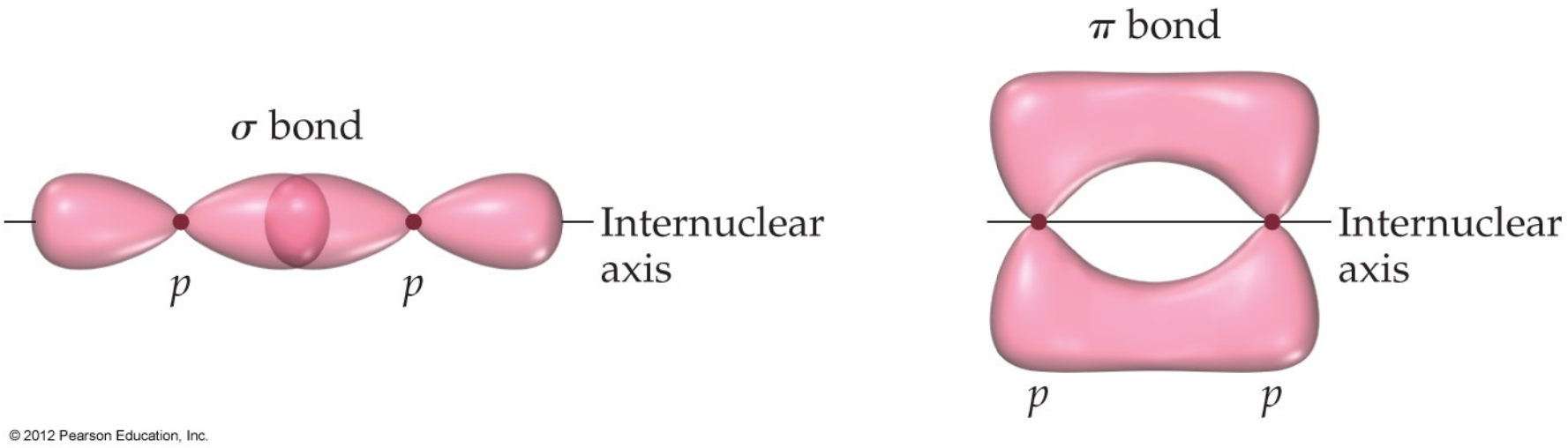
Review :Valence bond model

Electron pair can be shared when the half-filled orbital of one atom overlaps with half-filled orbital of another.

δ Bond: orbitals overlap along the internuclear axis

π Bond: side by side overlap of orbitals

Pi (π) Bonds



- Pi bonds are characterized by
  - Side-to-side overlap.
  - Electron density above and below the internuclear axis.

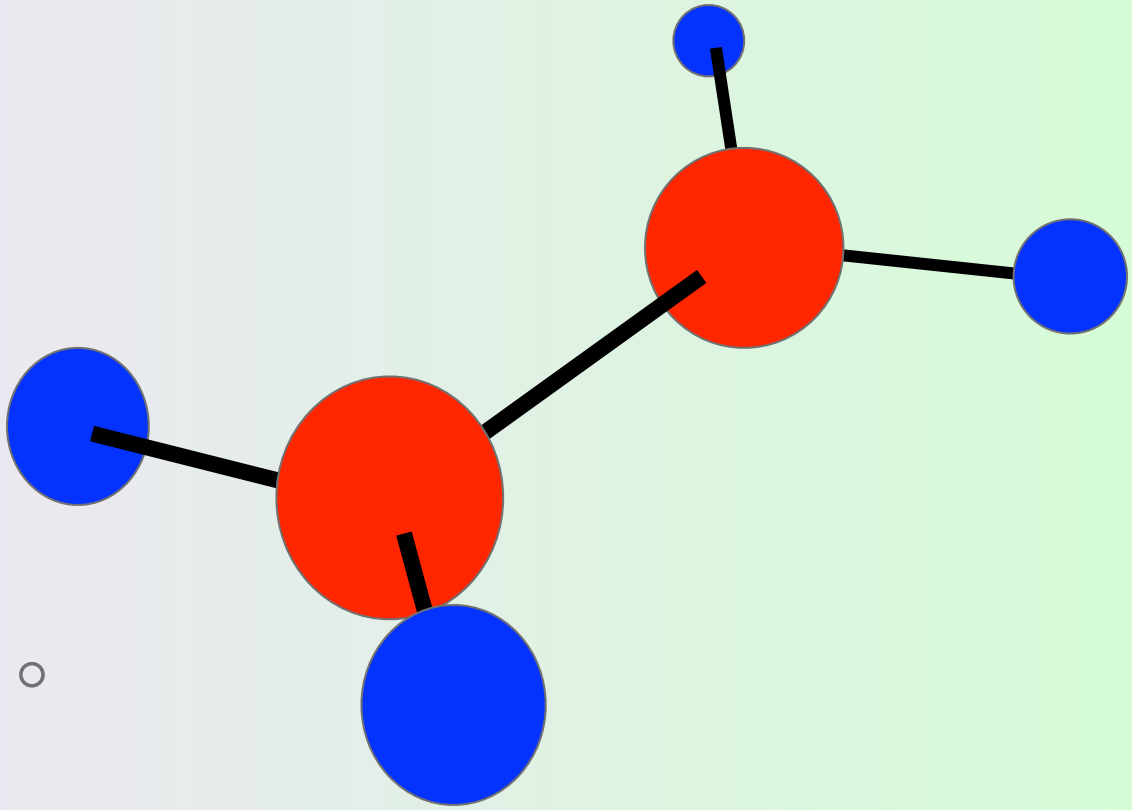
Structure of Ethylene

C_2H_4

$CH_2 = CH_2$

planar

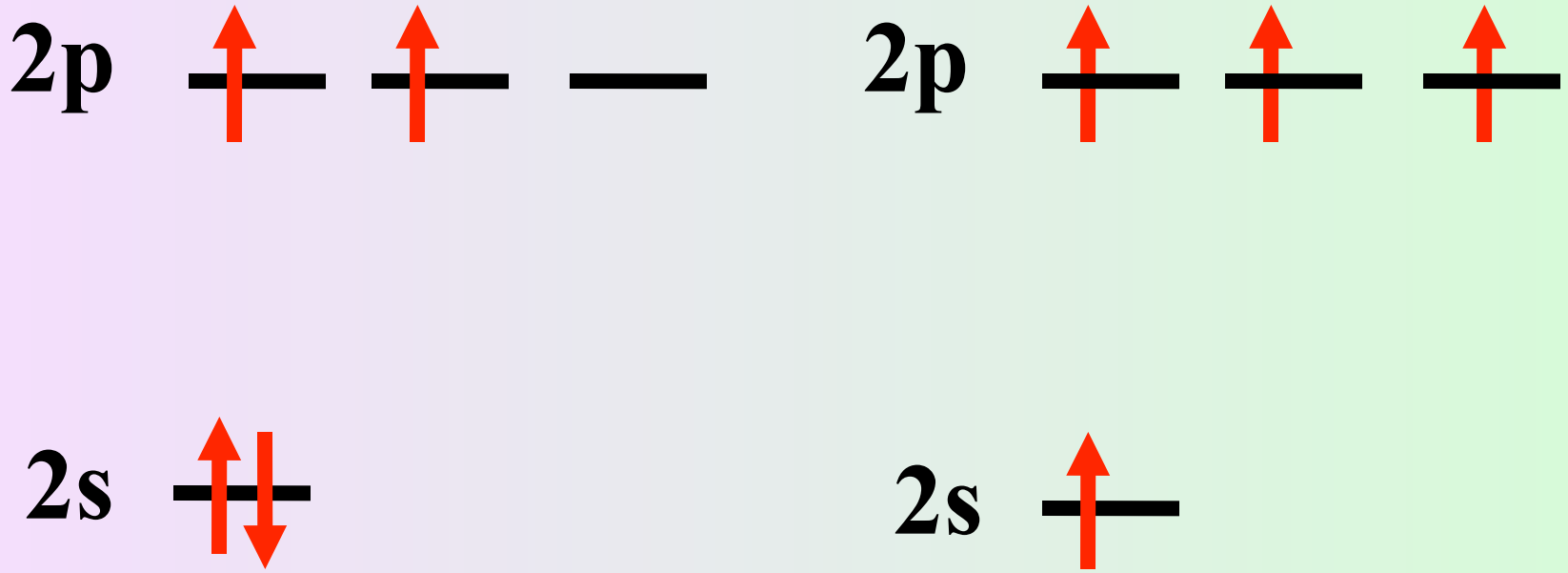
Bond angle 120 °



Requires hybridization different from sp^3

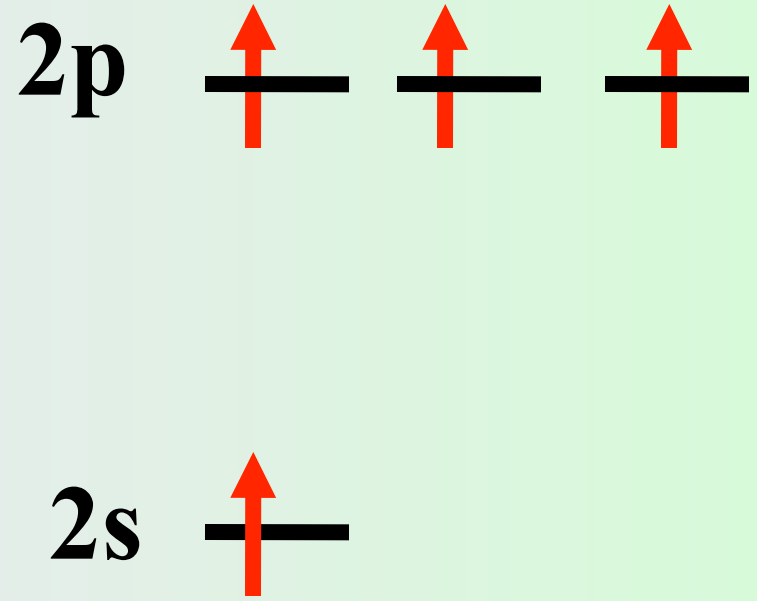
Orbital Hybridization

Promote an electron from the 2s to the 2p orbital



Orbital Hybridization

Mix together (hybridize) the 2s orbital and the two 2p orbitals



Orbital Hybridization

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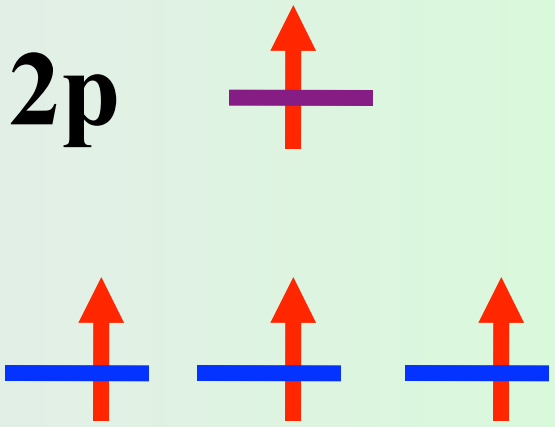
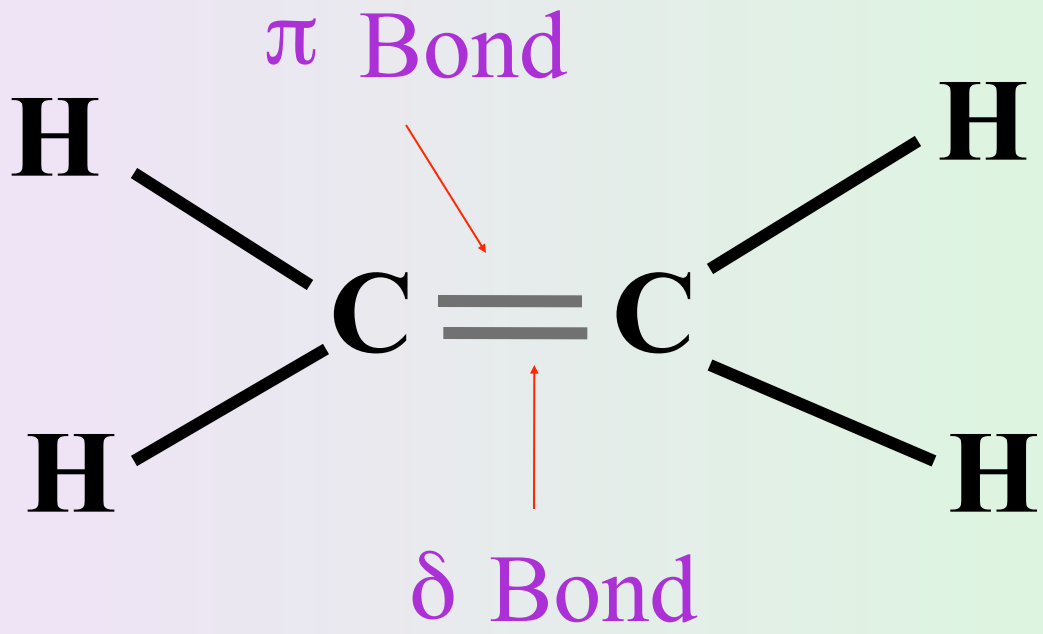
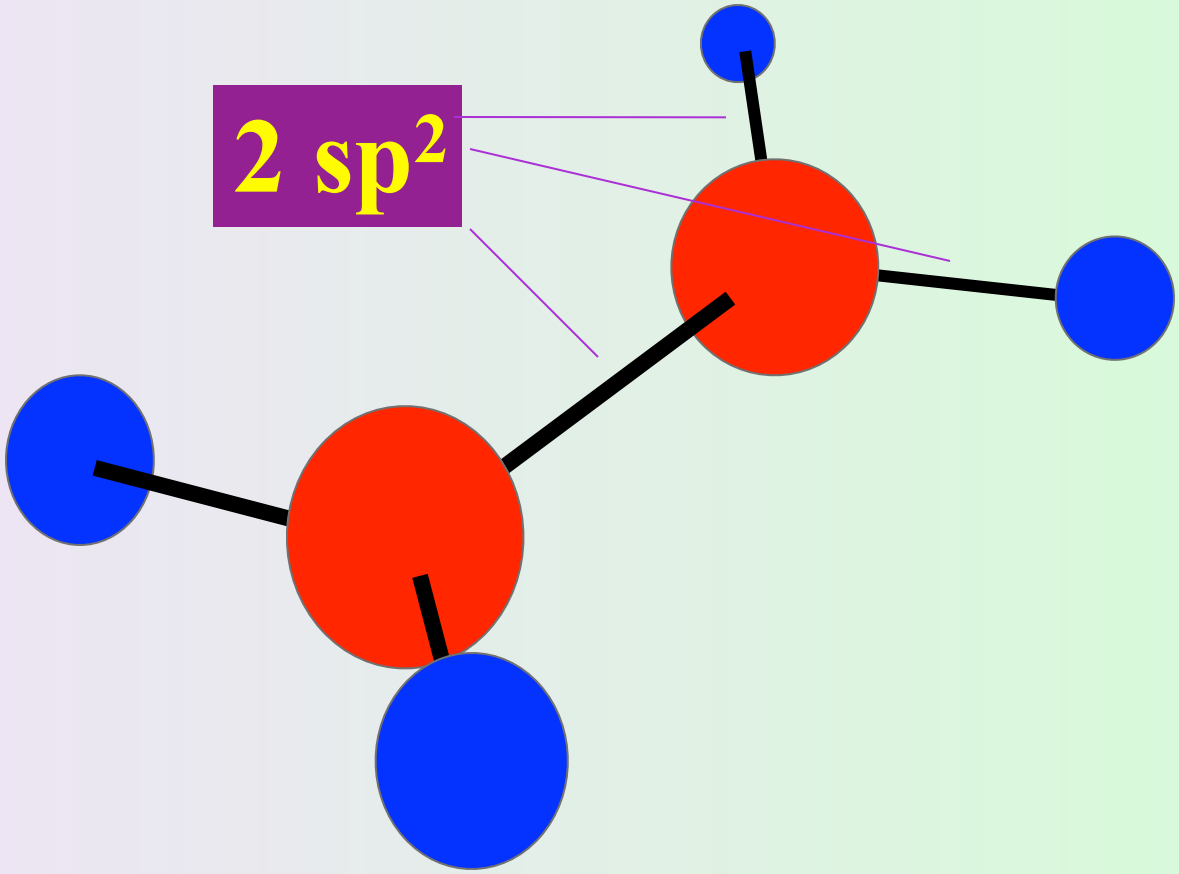


Lewis model : Ethylene

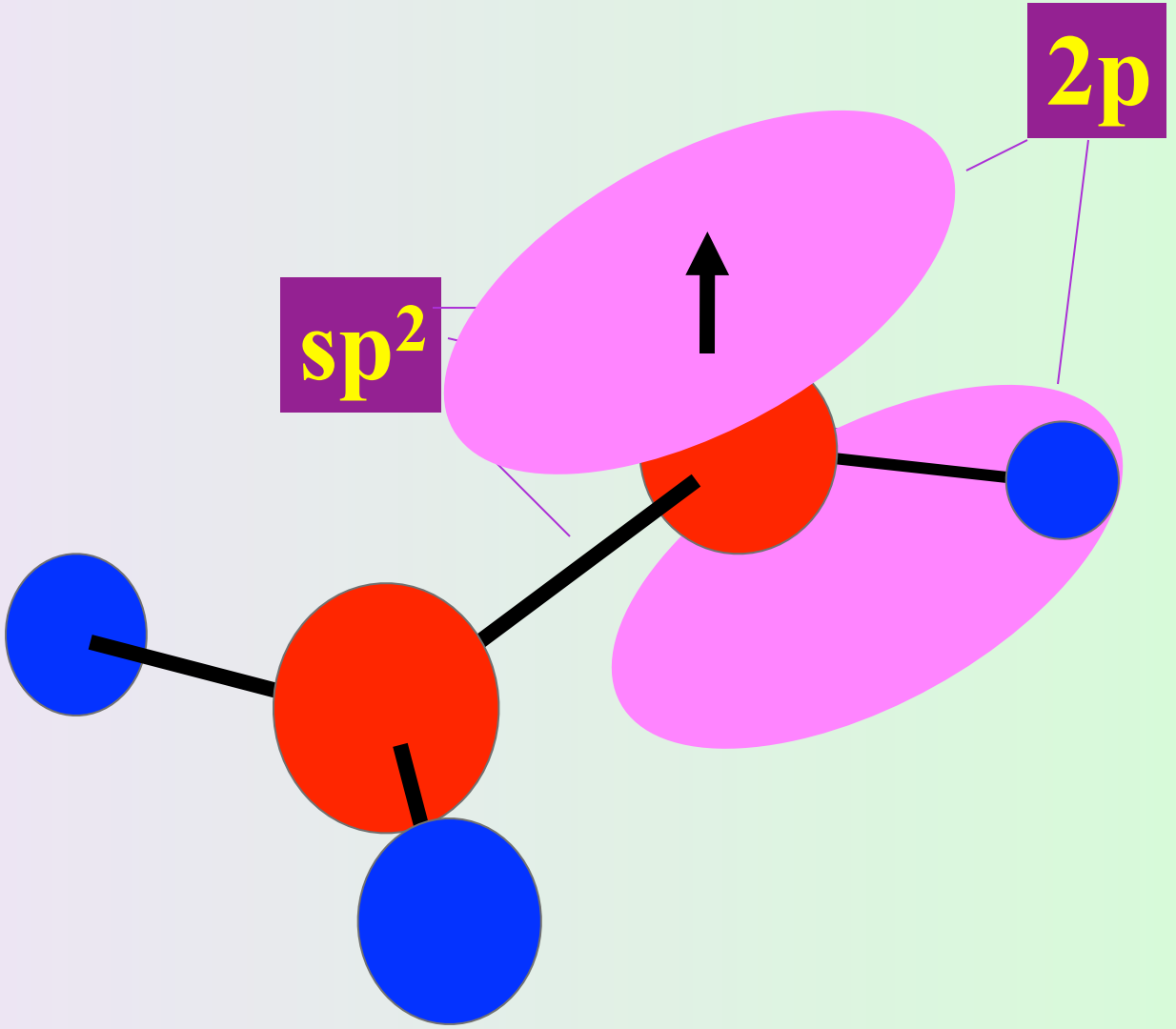


The carbon-carbon double bond of ethylene is a combination of an δ Bond and πBond

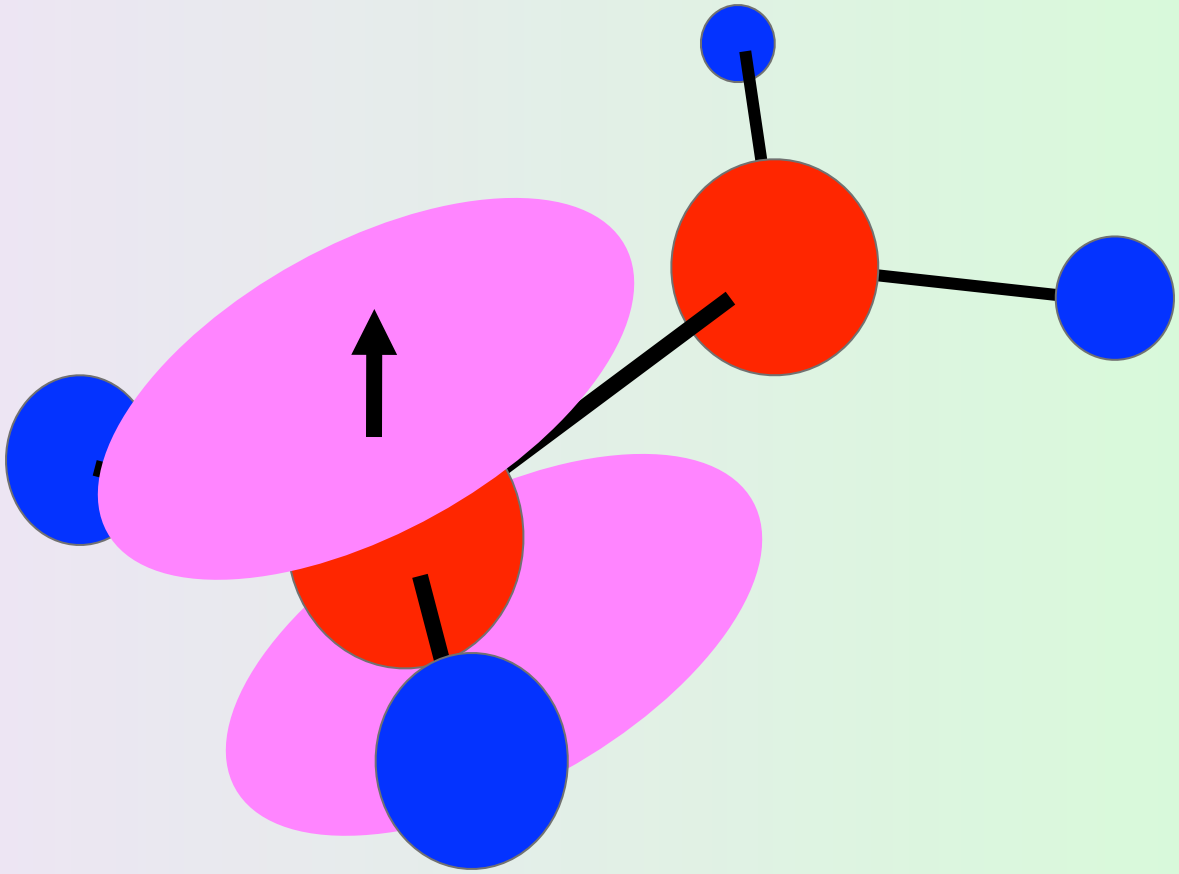
π –Bonding in Ethylene



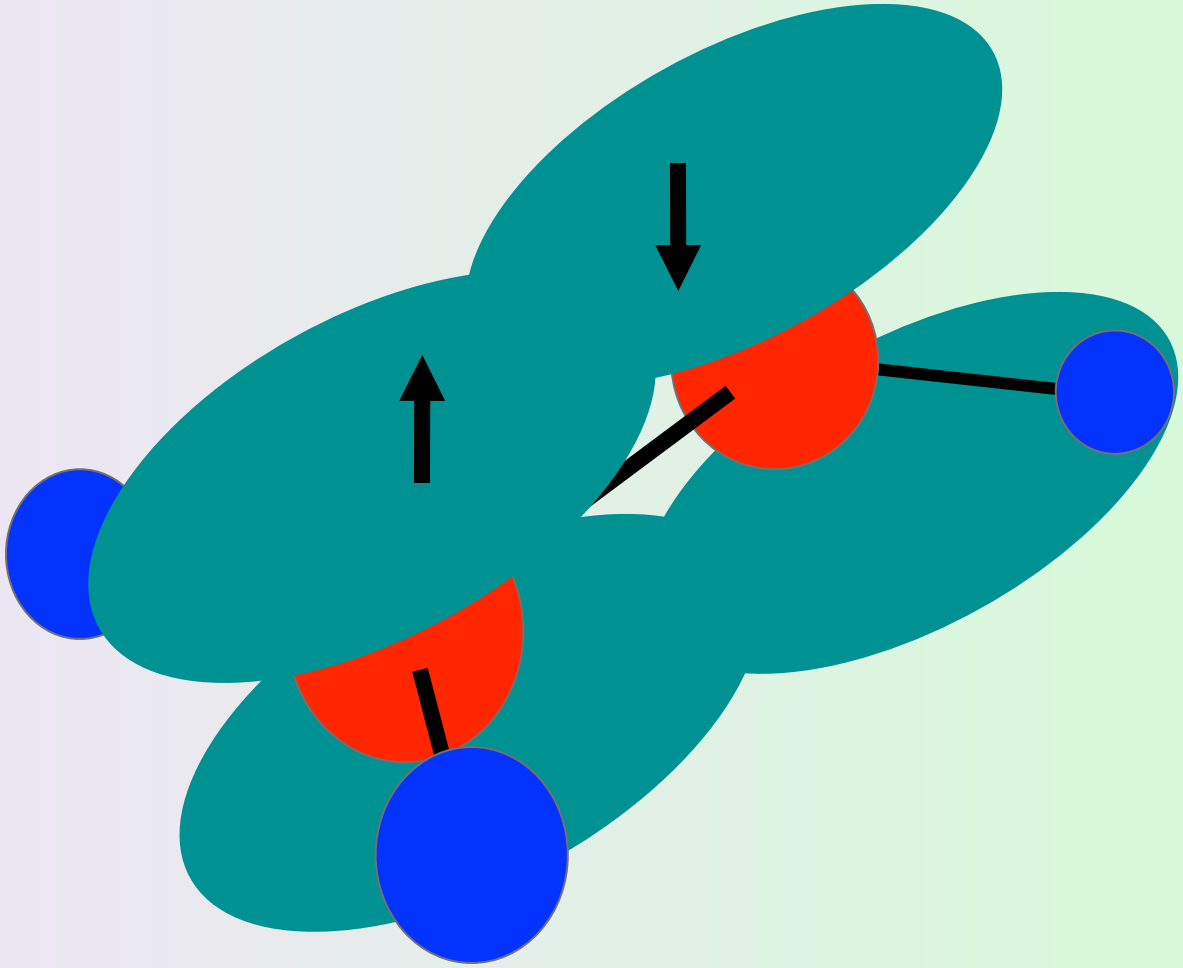
π –Bonding in Ethylene



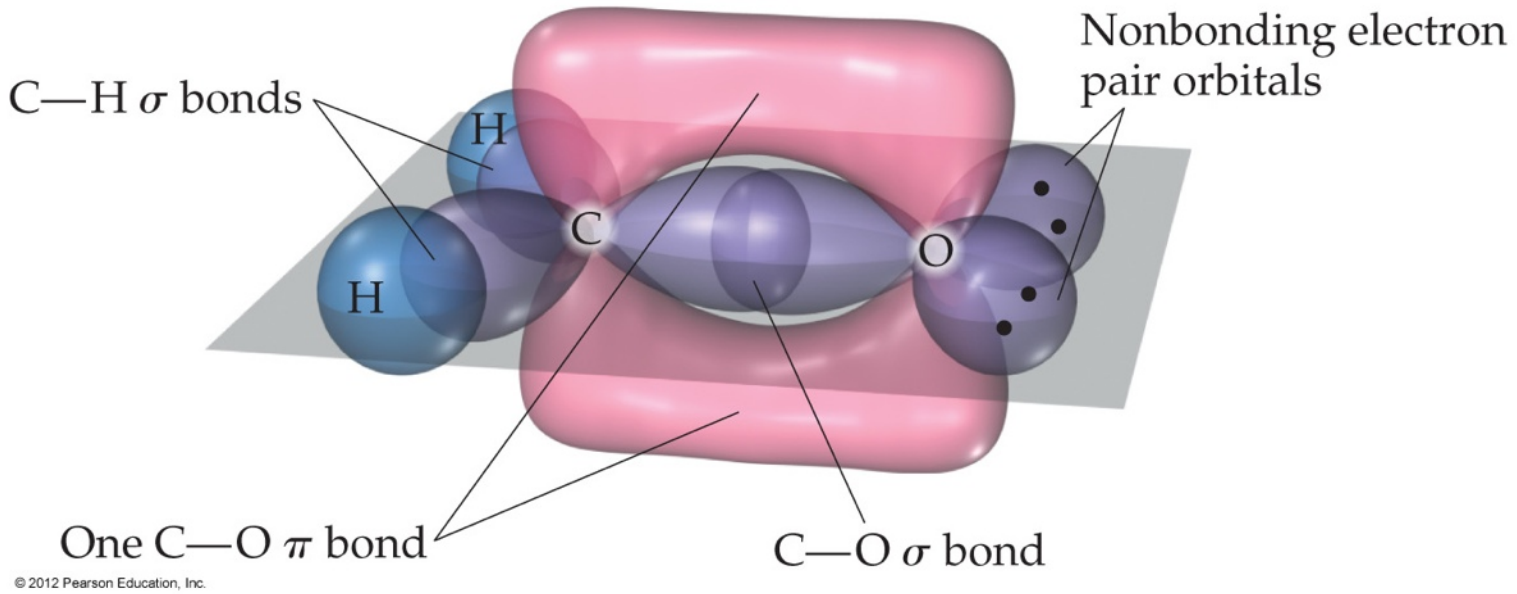
π –Bonding in Ethylene



π –Bonding in Ethylene



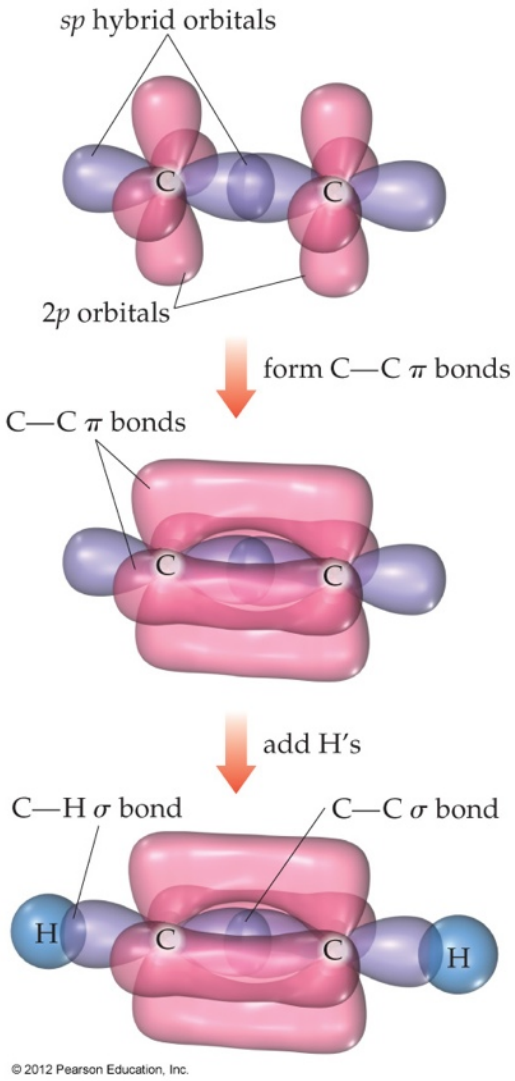
Multiple Bonds



- In a molecule like formaldehyde (shown at left), an sp^2 orbital on carbon overlaps in σ fashion with the corresponding orbital on the oxygen.
- The unhybridized *p* orbitals overlap in π fashion.

Multiple Bonds

In triple bonds, as in acetylene, two *sp* orbitals form a σ bond between the carbons, and two pairs of *p* orbitals overlap in π fashion to form the two π bonds.



Molecular Geometries and Bonding