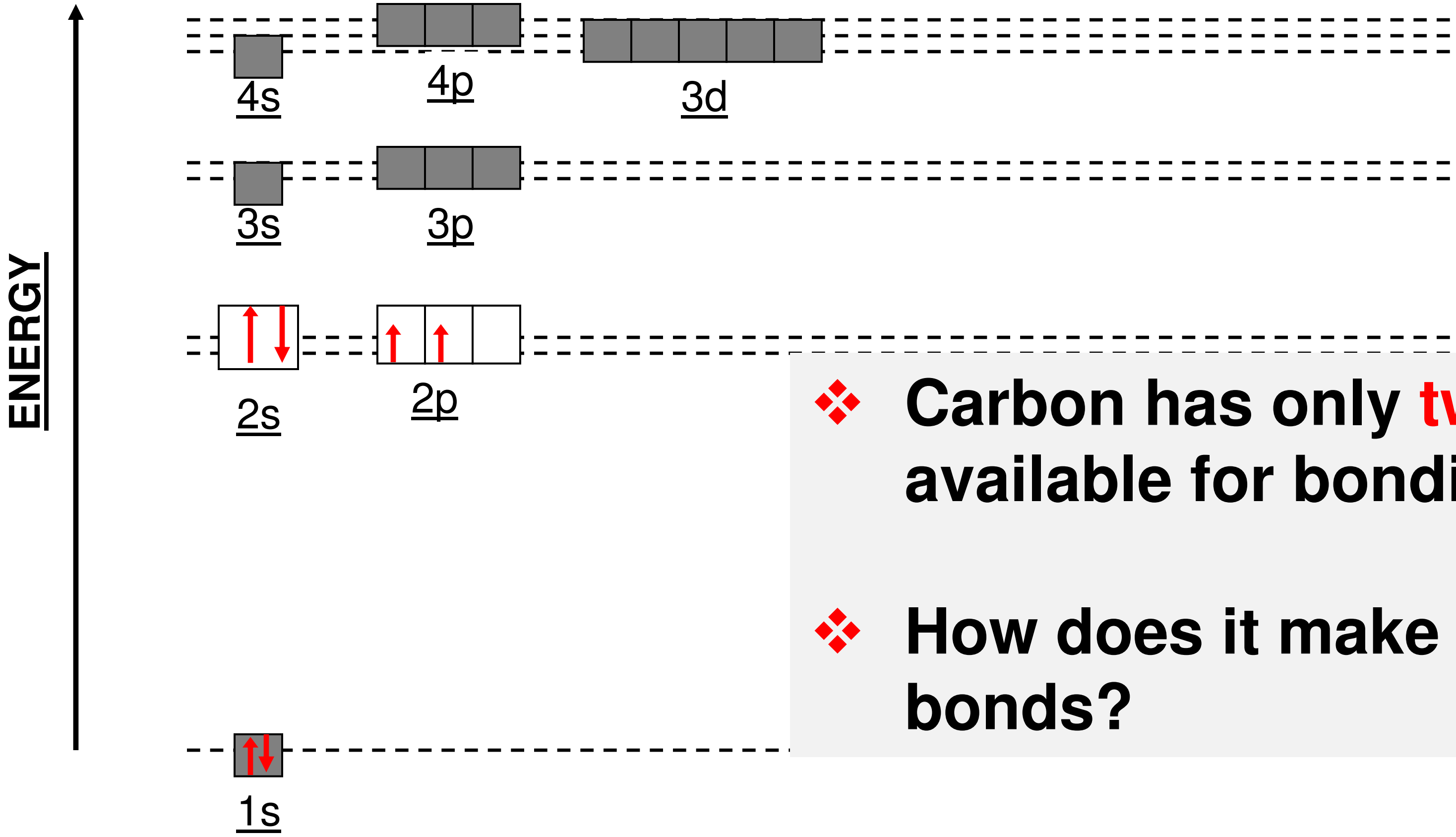
Hybridization of Atomic Orbitals

- The wave functions for the *s* and *p* atomic orbitals can be mathematically combined to form a new set of equivalent wave functions (**Linus Pauling**, **1931**).

- The mathematical process of **replacing** pure atomic orbitals with reformulated atomic orbital for bonded atoms is called **hybridization** **(hybrid orbitals)** .

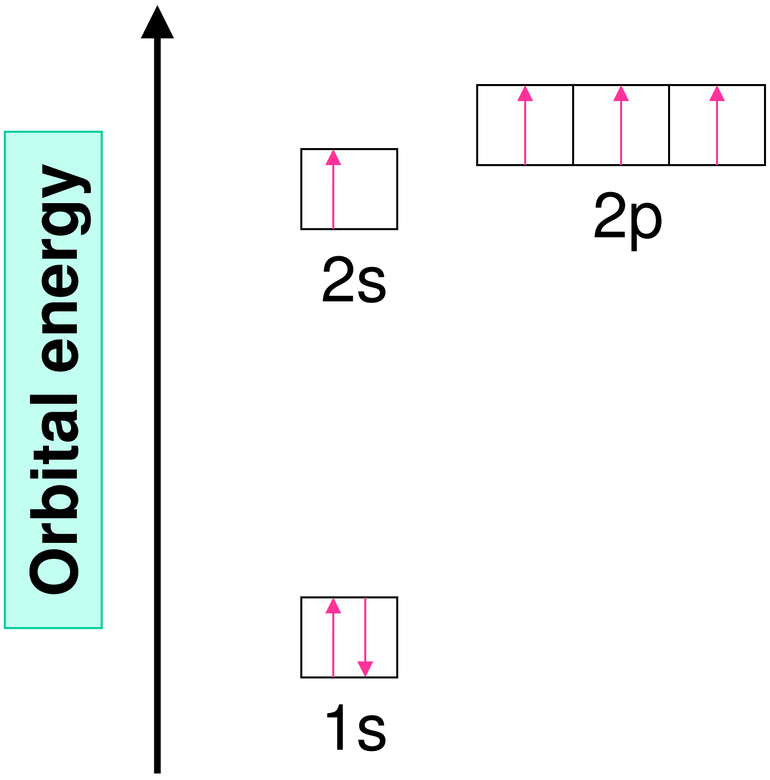
- In a hybridization scheme, the number of hybrid orbitals **equals** to the total number of atomic orbitals that are combined. The symbols identify the numbers and kinds orbitals involved.

Orbital Energy Diagram for Carbon



- Carbon has only two e^- available for bonding.
- How does it make 4 bonds?

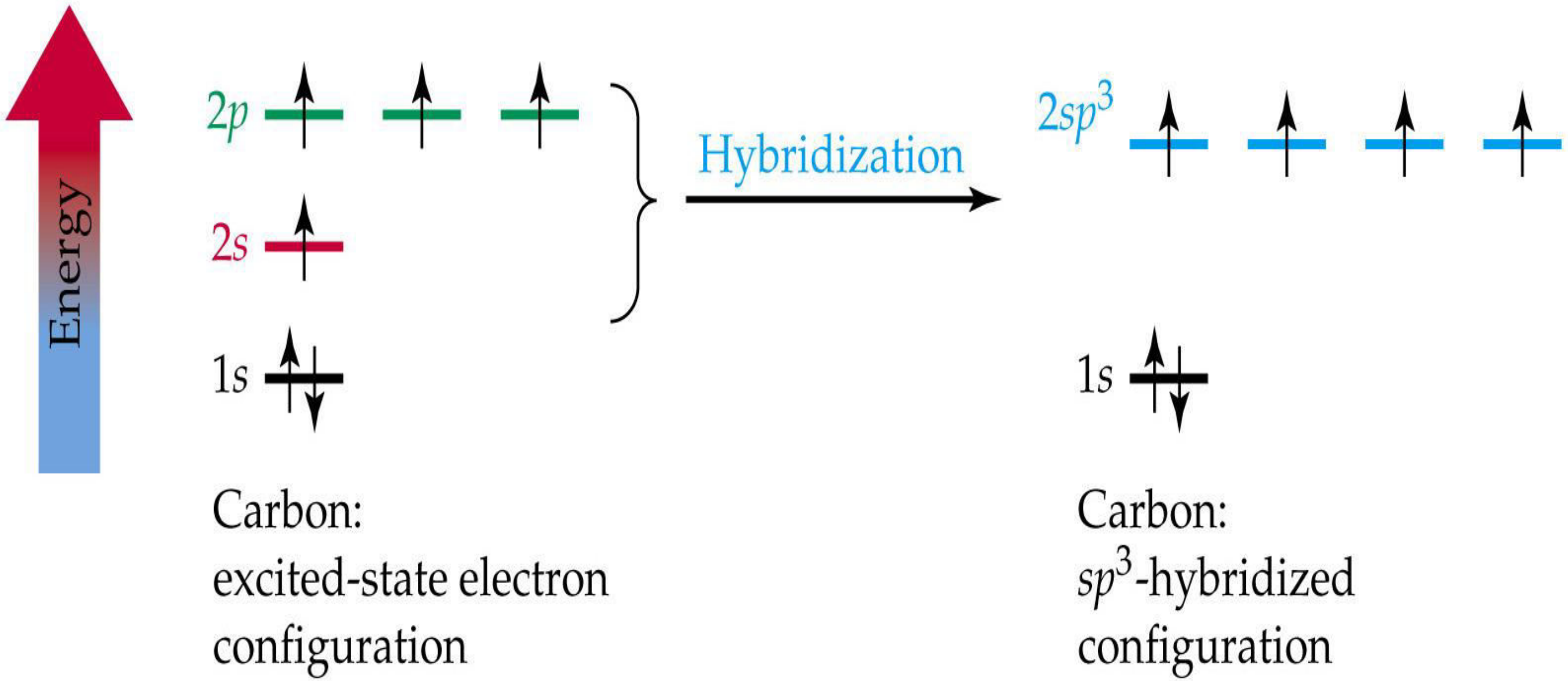
sp^3 Hybrid Orbitals

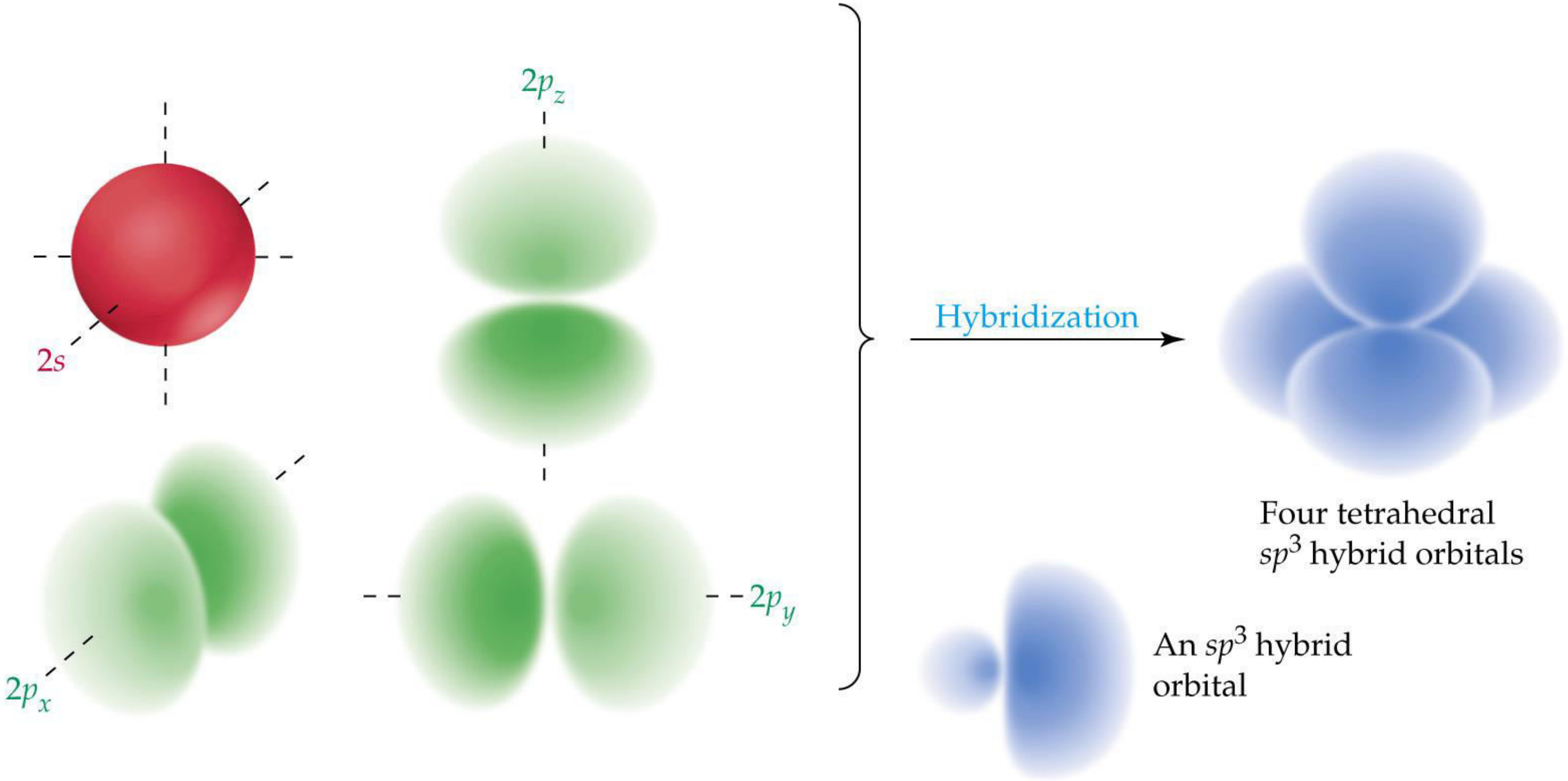


- Energy is used to promote one 2s e^- to the empty 2p orbital
- Hence, Carbon has four e^- available for bonding.
- However, the orbital containing the four e^- must first be mixed to form four orbitals with the same energy.

sp^3 signifies one s and three p orbitals are combined.

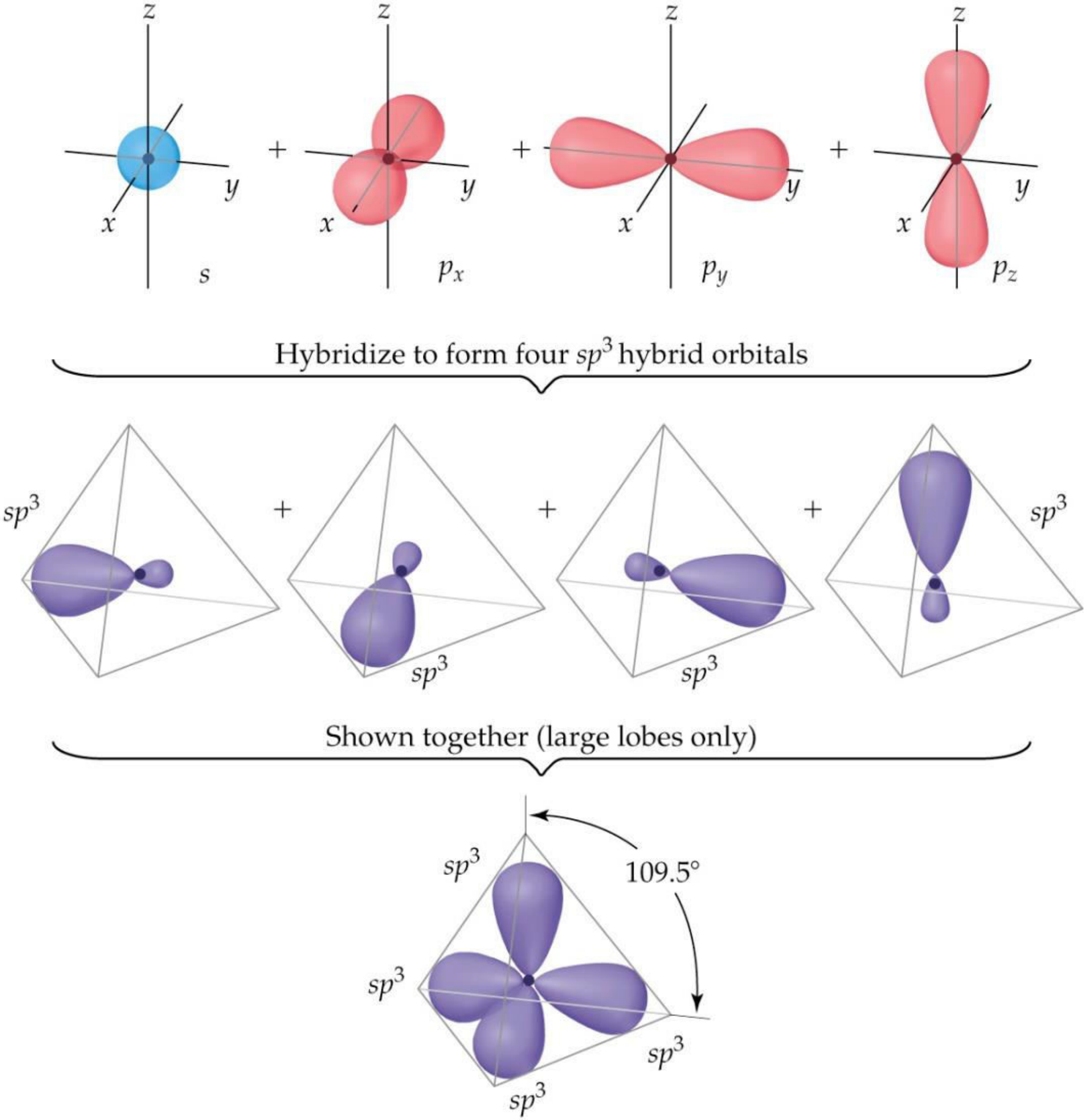
Mixing one s orbital with three p orbitals yields four **equivalent** *sp^3* hybrid orbitals.



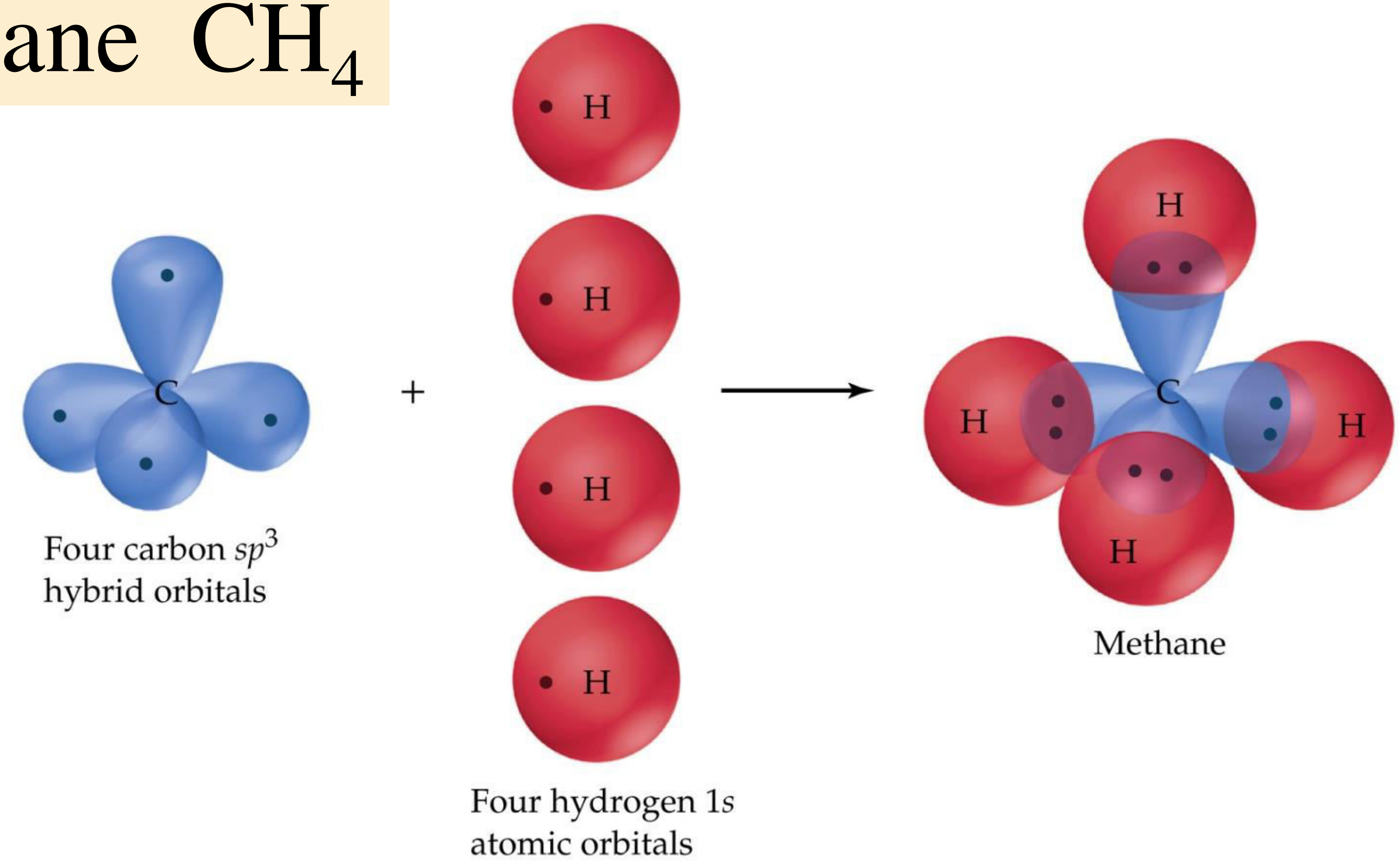


- Each sp^3 hybrid orbital has two lobes, one of which is larger than the other.
- The four large lobes are oriented toward the corners of a tetrahedron at angles of 109.5°

Native 2*s* and three *2p* atomic orbitals characteristic of a free carbon atom are combined to form a new set of four s*p*3 orbitals.



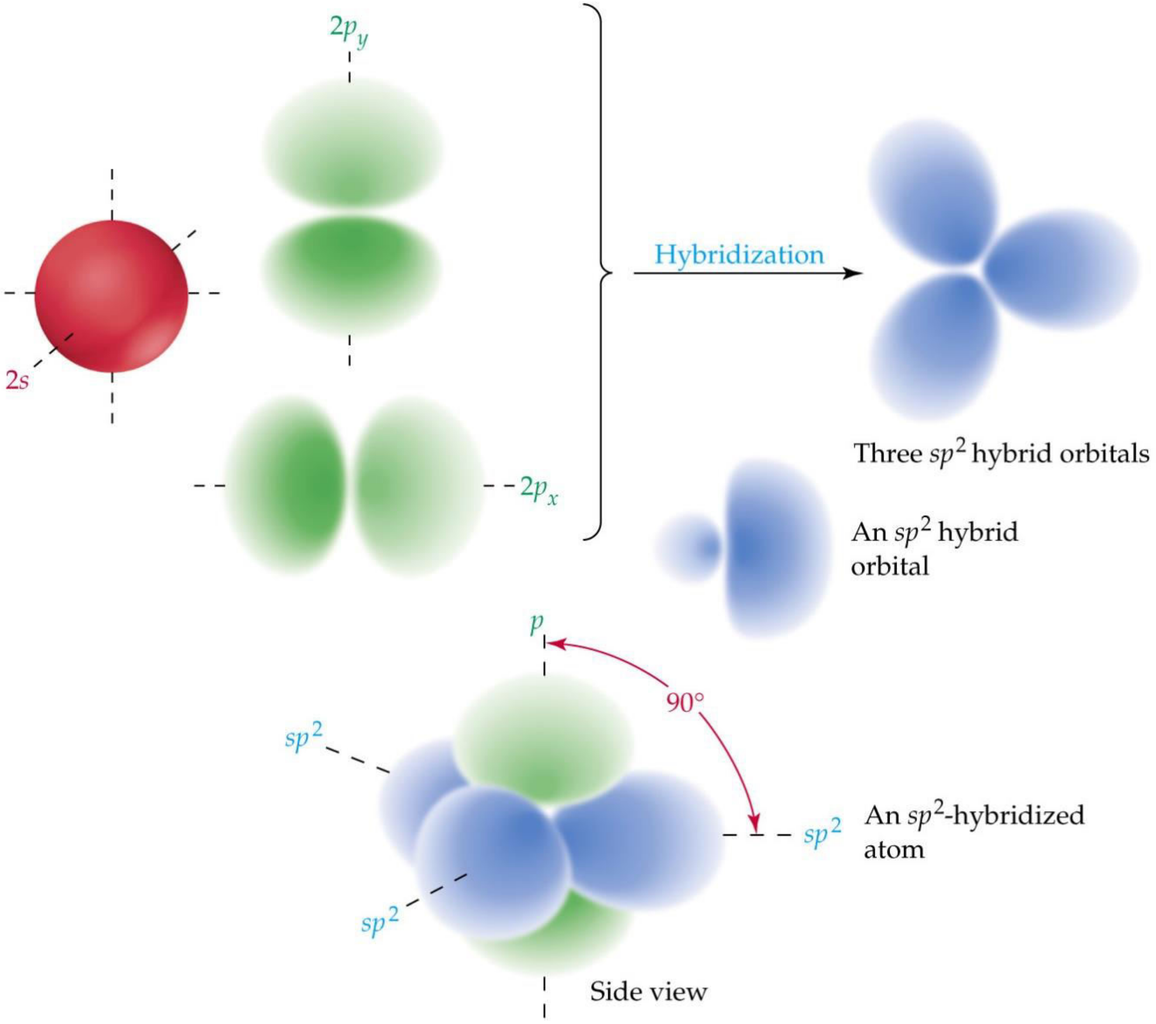
Methane CH_4



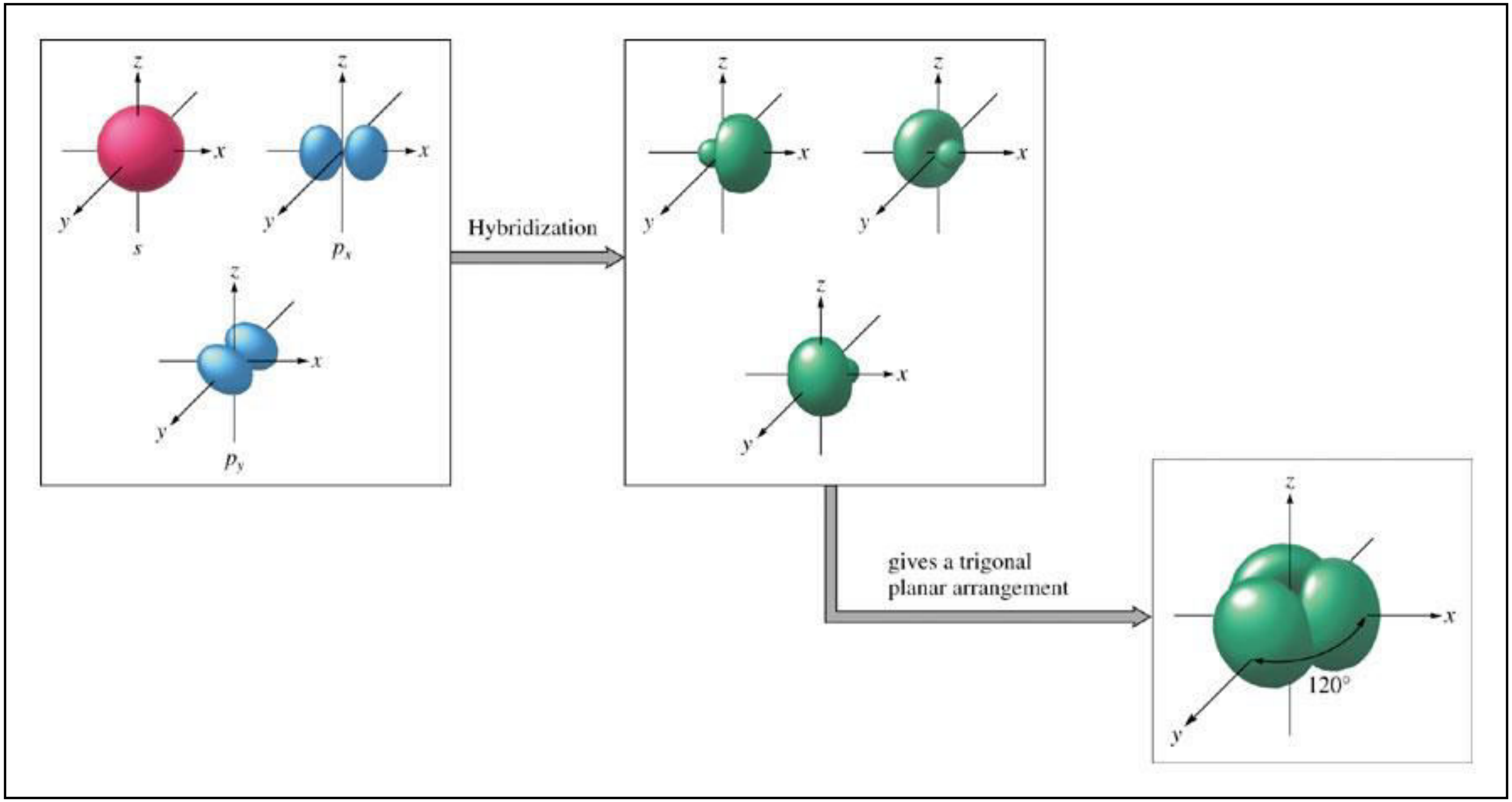
- Each of the four **C-H** bonds results from head-on (s) **overlap** of a singly occupied carbon sp^3 hybrid orbital with a singly occupied hydrogen *1s* orbital - forming a **Sigma** bonds.

sp^2 hybridization

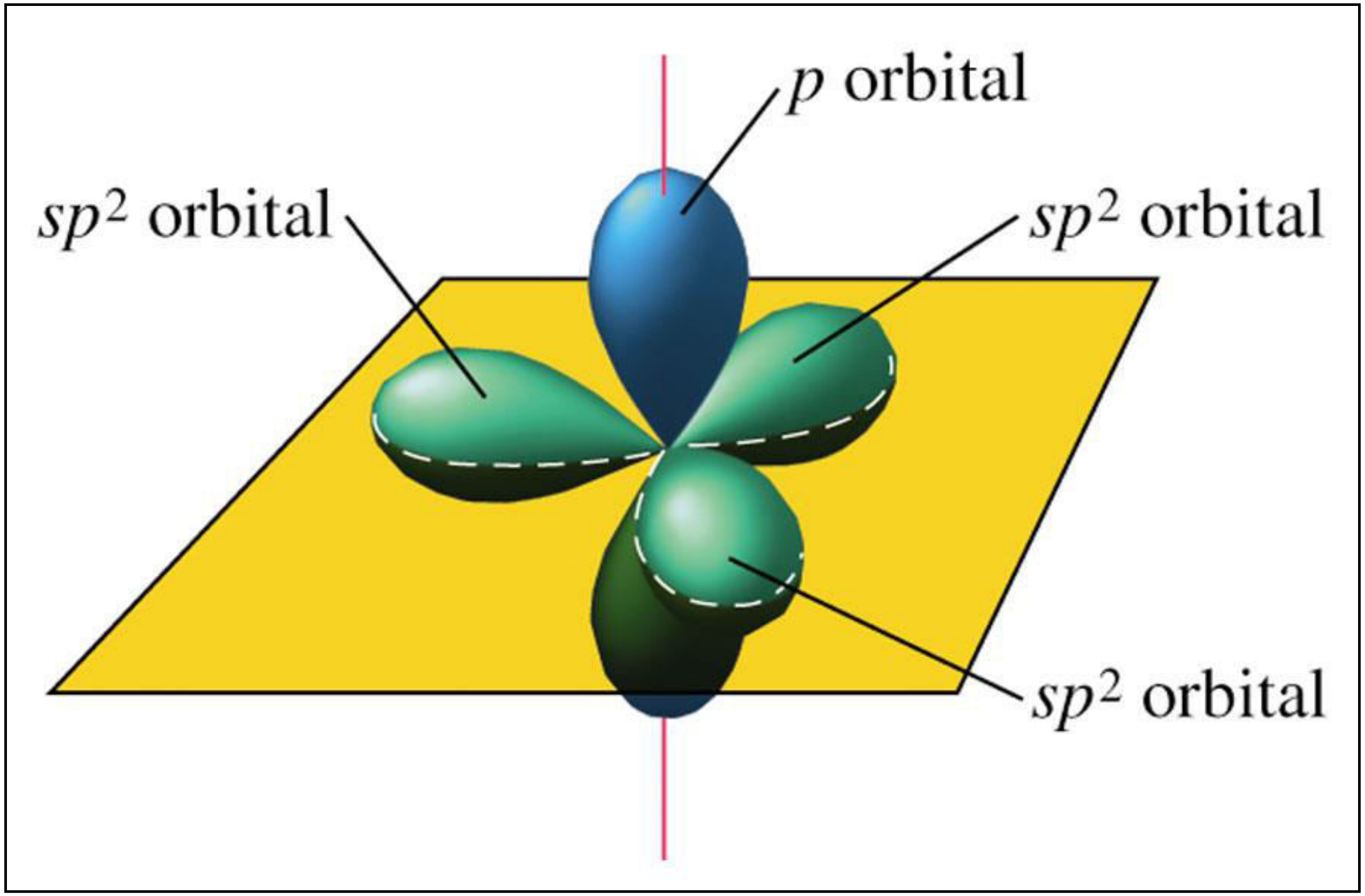
- Molecular geometry is trigonal planar, bond angle = **120°**
- sp^2 signifies one ***s*** and two *p* orbitals are combined.



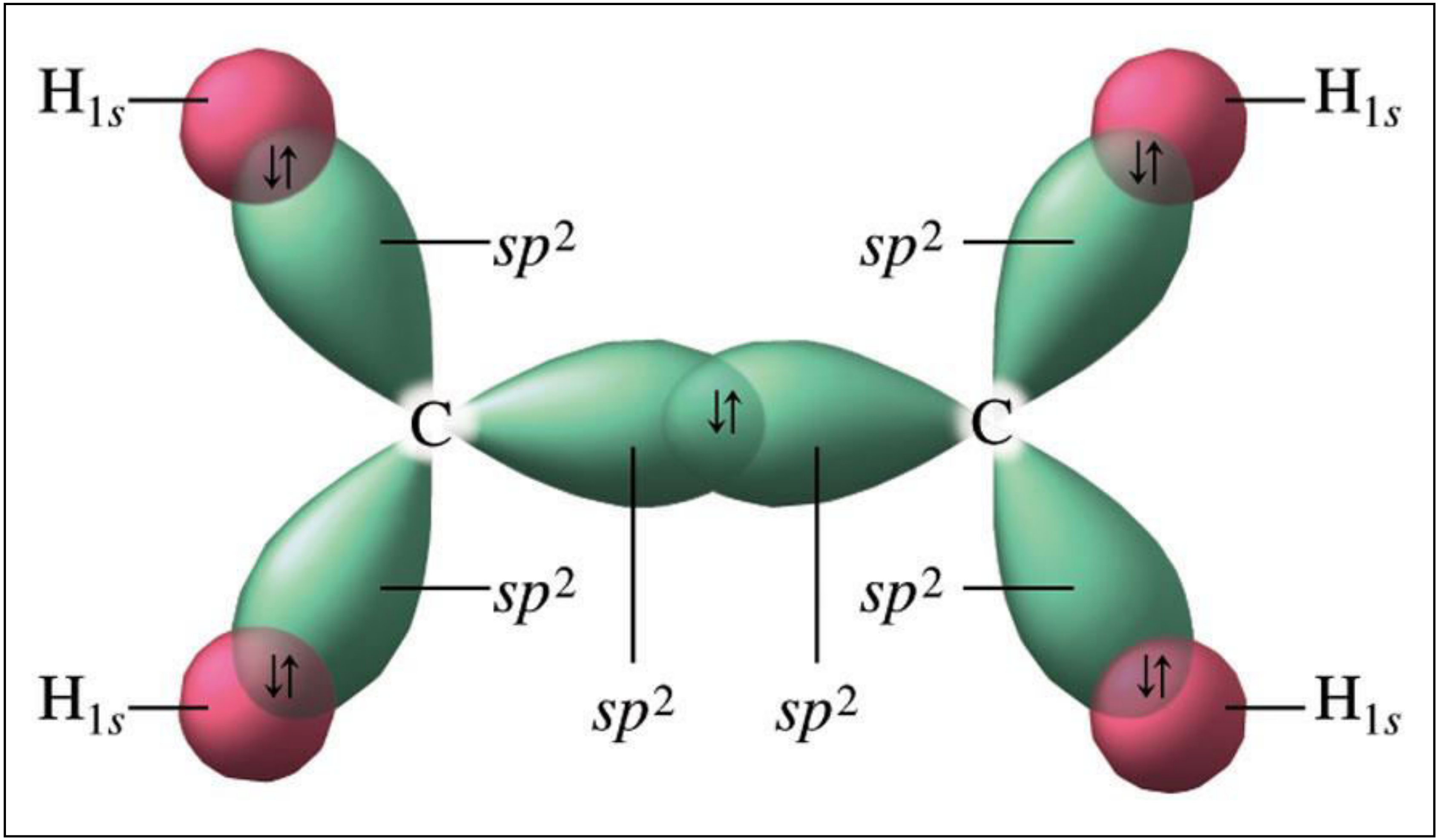
The hybridization of the *s*, p_x, and p_y atomic orbitals results in the formation of three sp^2 orbitals centered in the *xy* plane.



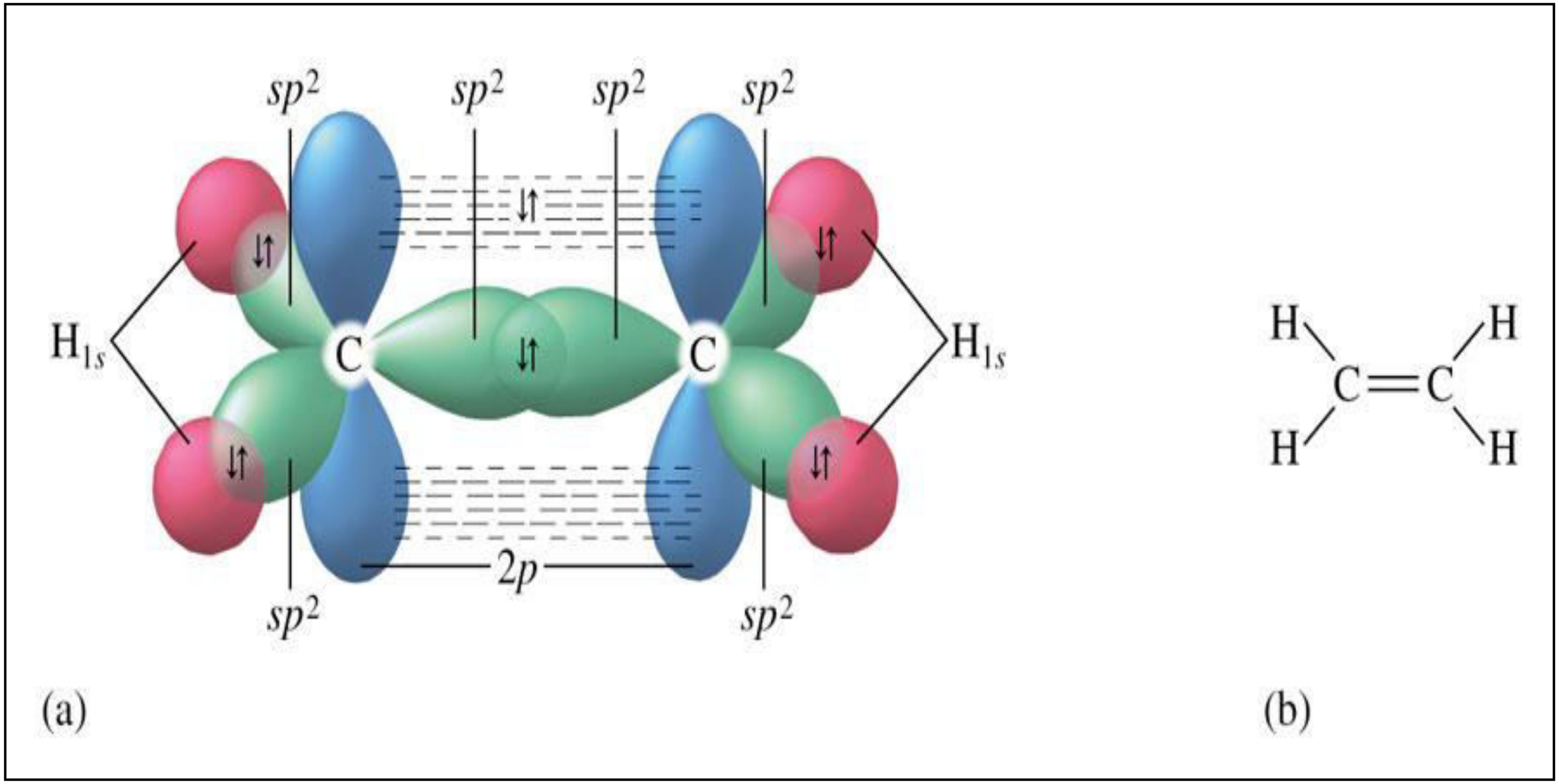
When one s and two *p* orbital are mixed to form a set of **three *sp*^{2}** orbital, **one p orbital remains unchanged** and is **perpendicular** to the plane of the hybrid orbital.



The *sigma* bonds in ethylene.

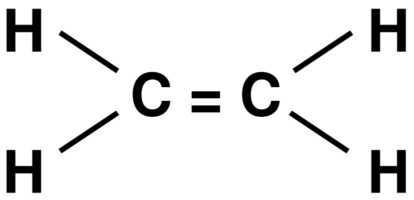


The orbitals used to form the bonds in ethylene.

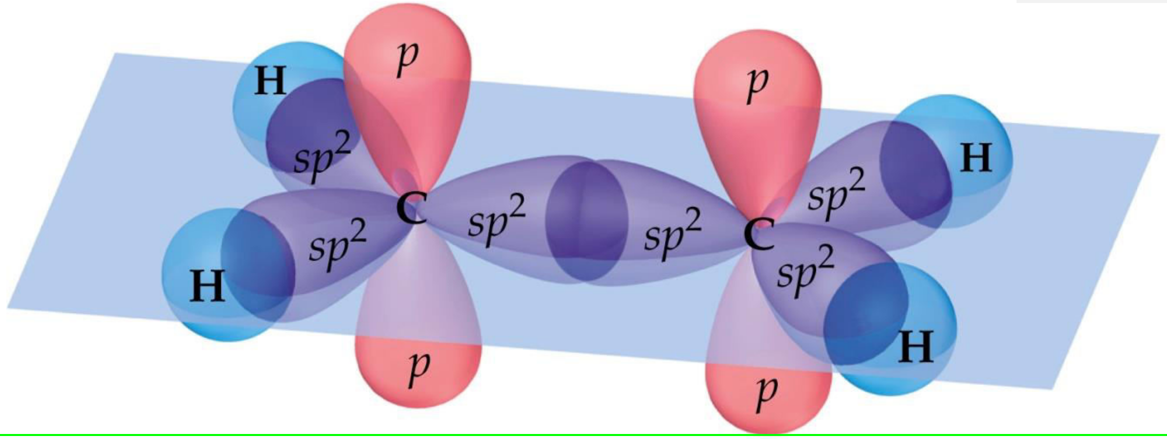


Valence Bond Theory and Double Bonds

Ethylene



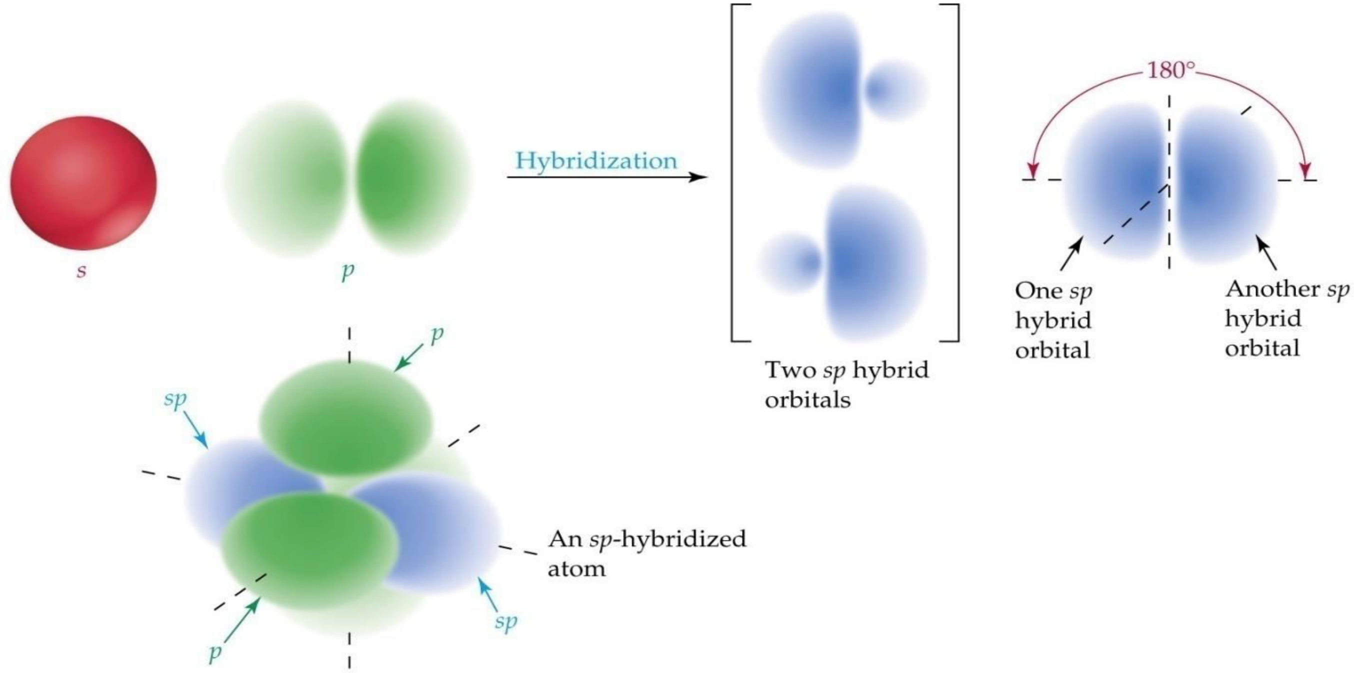
σ bonds are formed from the end-to-end overlap of orbitals.



1. Each C – H bond is a σ bond formed from the overlap of a C sp^2 orbital with the H 1s orbital.
2. One of the C – C bonds is a σ bond formed from the overlap of C sp^2 orbitals.
3. The second C – C bond is a π bond formed from the overlap of the unhybridized C 2p orbitals.

sp hybridization

$\mathrm{BeCl_2}$ which has linear molecular geometry determined experimentally.

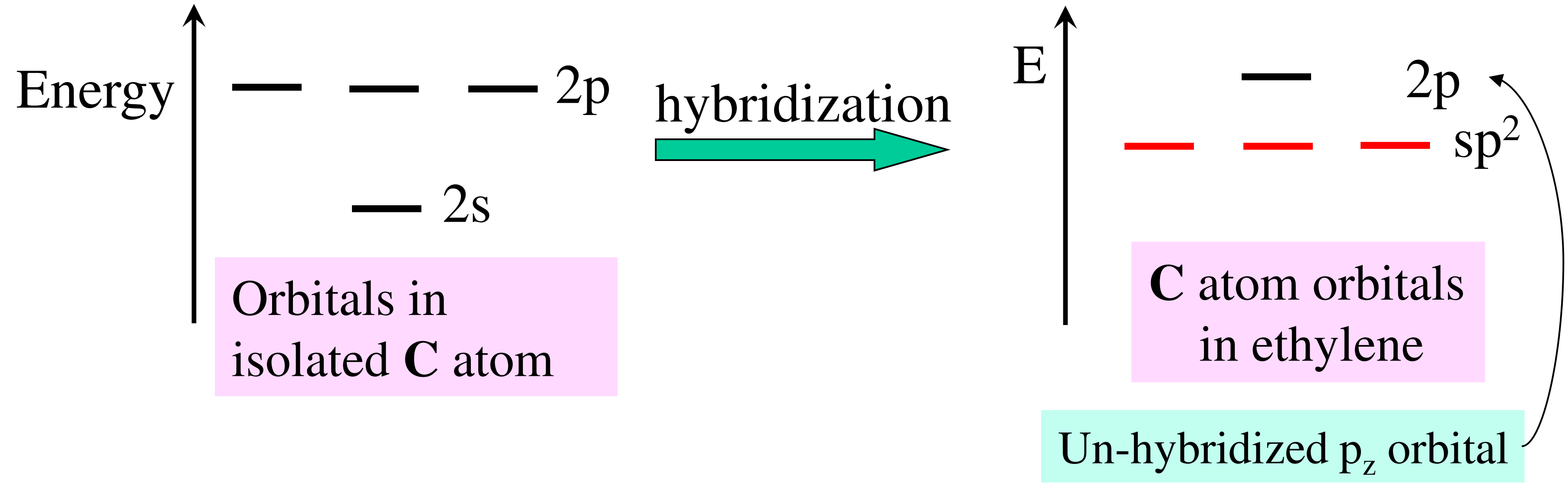


- The combination of one ***s*** and one ***p*** orbital gives two **sp** hybrid orbitals oriented **180°** apart.
- NB: Two **unhybridized p orbitals** remain and are oriented at 90° angles to the **sp** hybrids.

1 ***2s*** orbital
+
2 ***2p*** (p_x, p_y) orbitals

→ 3 ***sp²*** orbitals

→ Energy-level diagram of ***sp^2*** hybridization

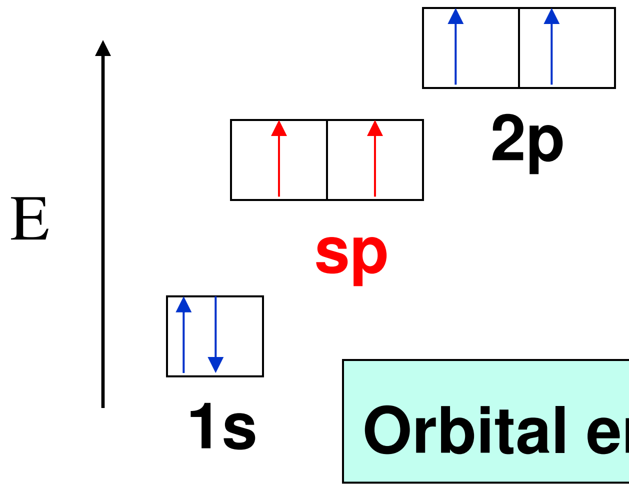


- Carbon uses the sp^2 hybridized orbitals for forming **sigma (σ)** bonds within the plane
- The remaining **$2p_z$** orbital is used for forming the **pi (π) bond**.

Note that the **double bond** consists of **one σ** and **one π** bond.

sp Hybrid Orbitals Acetylene, C_2H_2

H - C ≡ C - H ***All of the atoms of acetylene lie in a single line.***

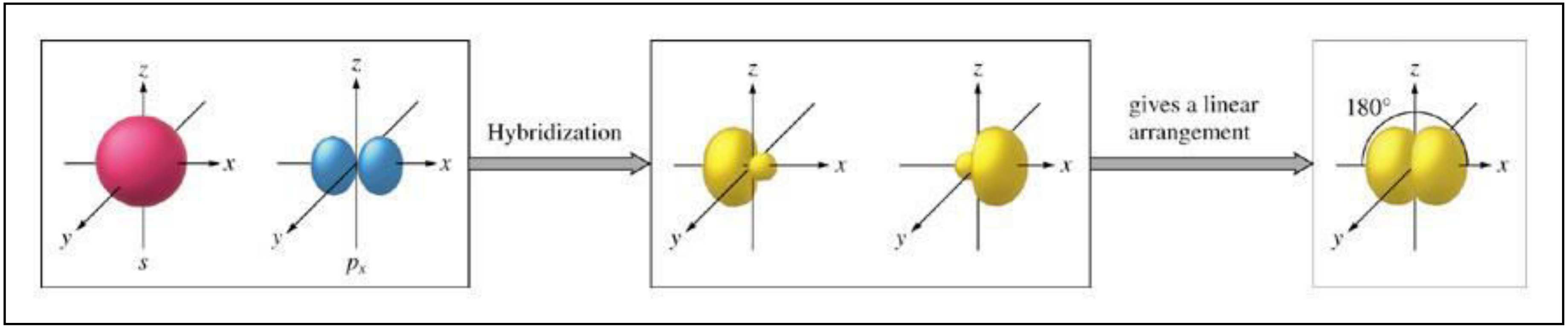


Two 2p orbitals remain unhybridized

Orbital energy diagram for C

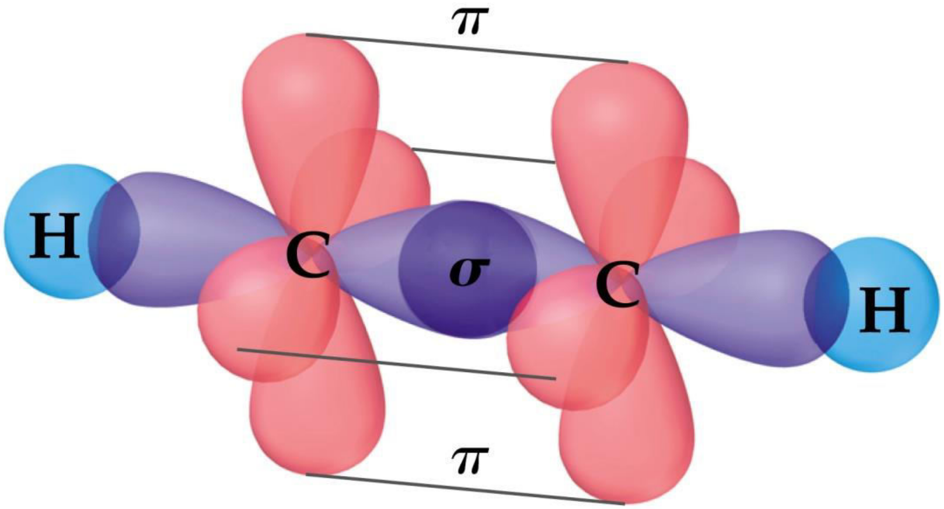
Linear VSEPR geometry → sp hybrid orbitals.

When one *s* orbital and one *p* orbital are hybridized, a set of two *sp* **HAO**s oriented at **180°** results.



Valence Bond Theory and Triple Bonds

Acetylene : H - C ≡ C - H

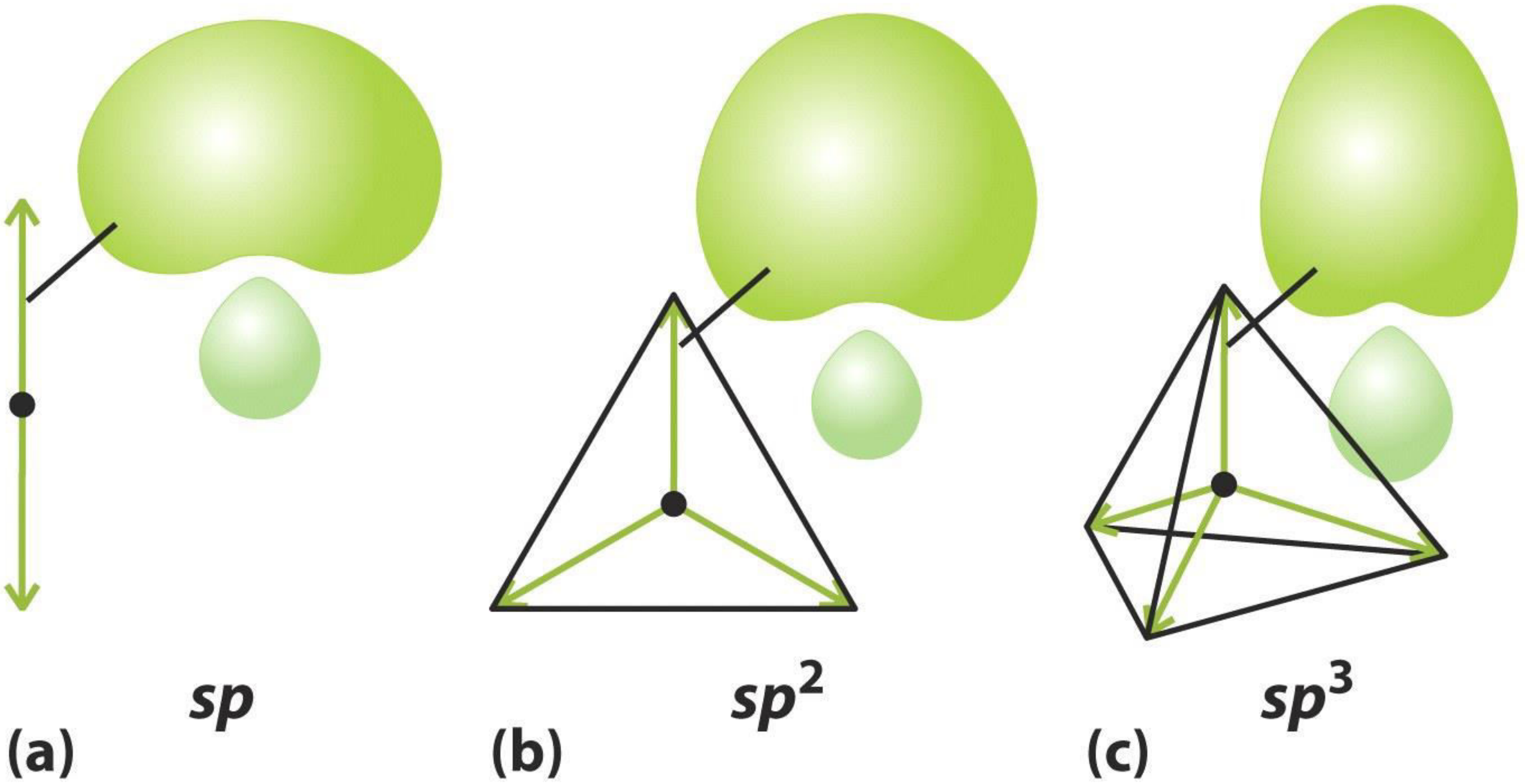


1. Each C – H bond is a σ bond formed from the overlap of a C *sp* orbital with the H 1s orbital.

2. One of the C – C bonds is a σ bond formed from the overlap of C sp orbitals.

3. The other two bonds are π bonds formed from the overlap of the C 2p orbitals.

Shapes of hybridized atomic orbitals

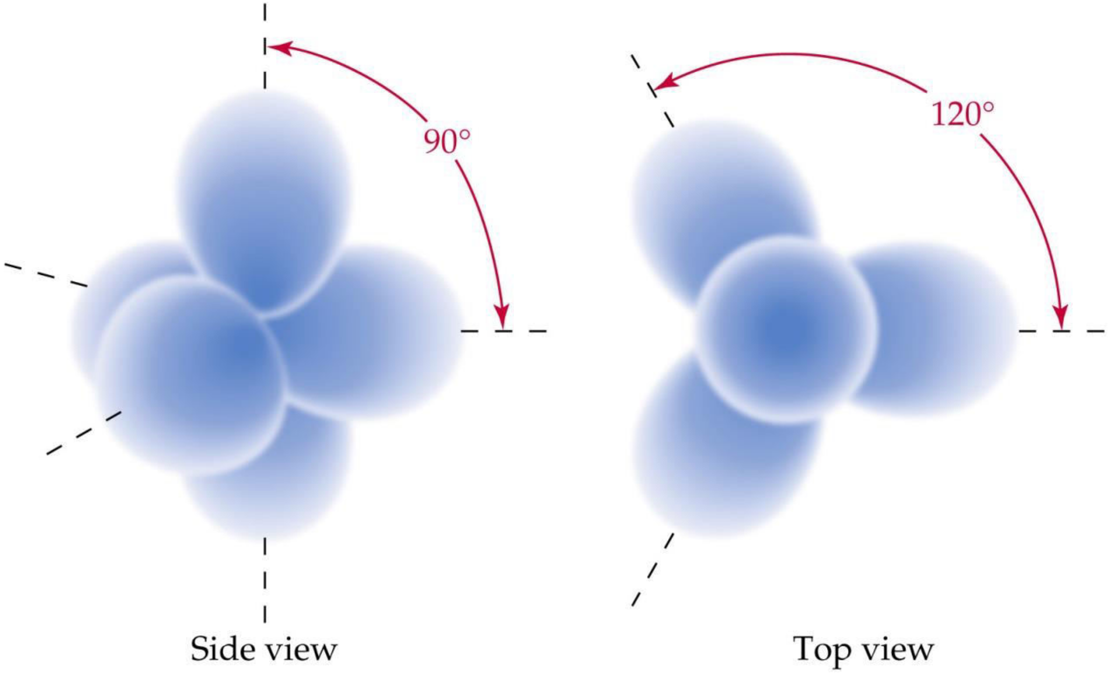


- As the percent ***S***-character increases, a hybrid orbital holds its electrons **closer** to the nucleus, and the bond becomes shorter and stronger.
- Although sp^3, sp^2 and *sp* hybrid orbitals are similar in shape, they are different in size.

sp^3d hybrid Orbitals

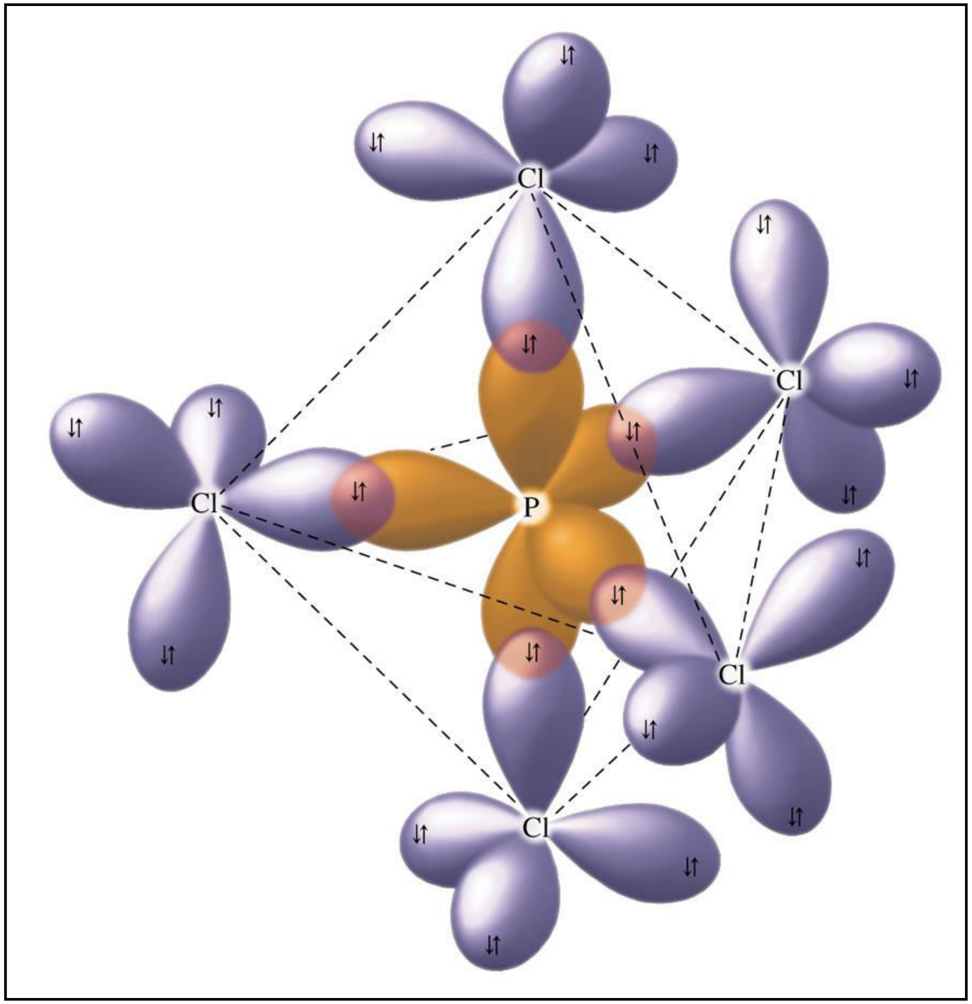
1. Hybridization scheme corresponding to the **5**- and **6**- electron-group geometries of VSEPR theory goes **beyond *s* and *p* orbitals** and traditionally this meant including ***d*** orbitals.
2. We can achieve the five half-filled orbitals and trigonal-bipyramidal molecular geometry through the hybridization of one *s*, three *p* and one *d* orbitals of valence shell into five ***sp^3d*** hybrid orbitals.

PCl_5



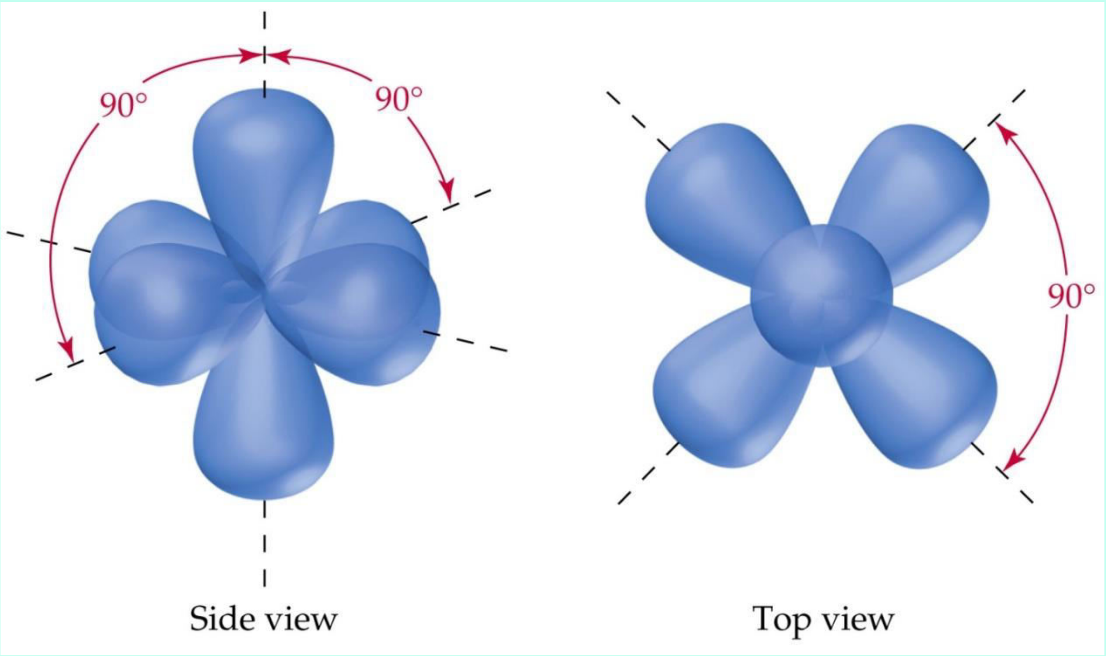
In general, when there are 5 effective pairs around an atom it uses *sp^3d* orbitals.

The orbitals used to form the bonds in the PCl_5 molecule



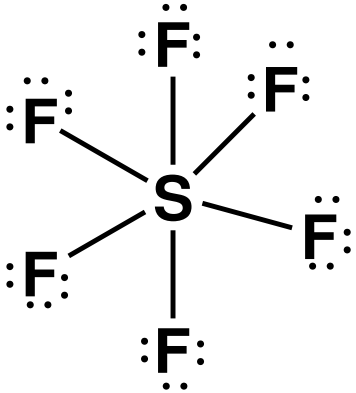
Other Examples: of sp^3d^2 Hybridization

- **48** valence electrons [Lewis structure]
- **6** effective pairs around ***S*** atoms
- VSEPR model predicts **Octahedral** geometry
- The 6 pairs lead to sp^3d^2 (d^2sp^3) hybridization of ***S*** atom, forming a set of 6 **octahedrally** oriented sp^3d^2 orbitals.



Side view

Top view



Lewis structure
Sulfur hexafluoride, **SF_6**