Physics PY4118
Physics of Semiconductor Devices

Hybrid Bonds

Why?

Orbitals?

- They explain the subsequent crystal structure

Crystal Structure?

- This is important in generating band structure
- The crystal also has interesting symmetry

Symmetry & Band Structure?

- Leads to physical properties

Hybrid Orbitals

- One might expect the number of bonds formed by an atom would equal its unpaired electrons
- Chlorine, for example, generally forms one bond as it has one unpaired electron - $1s^2 2s^2 2p^5$ [↓↑] [↓↑] [↓↑ | ↓↑ | ↓]
- Oxygen, with two unpaired electrons, usually forms two bonds - $1s^2 2s^2 2p^4$ [↓↑] [↓↑] [↓↑ | ↓ | ↓]
- However, Carbon, with only two unpaired electrons, generally forms four (4) bonds

C $(1s^2 2s^2 2p^2)$ [He] $2s^2 2p^2$ [↓↑] [↓ | ↓ |]

The four bonds come from the 2 (2s) paired electrons and the 2 (2p) unpaired electrons

Hybrid Orbitals

- Linus Pauling proposed that the valence atomic orbitals in a molecule are different from those of the isolated atoms forming the molecule
- Quantum mechanical computations show that if specific combinations of orbitals are mixed mathematically, “new” atomic orbitals are obtained
- The spatial orientation of these new orbitals lead to more “stable” bonds and are consistent with observed molecular shapes
- These new orbitals are called: ***“Hybrid Orbitals”***

Hybrid Orbitals

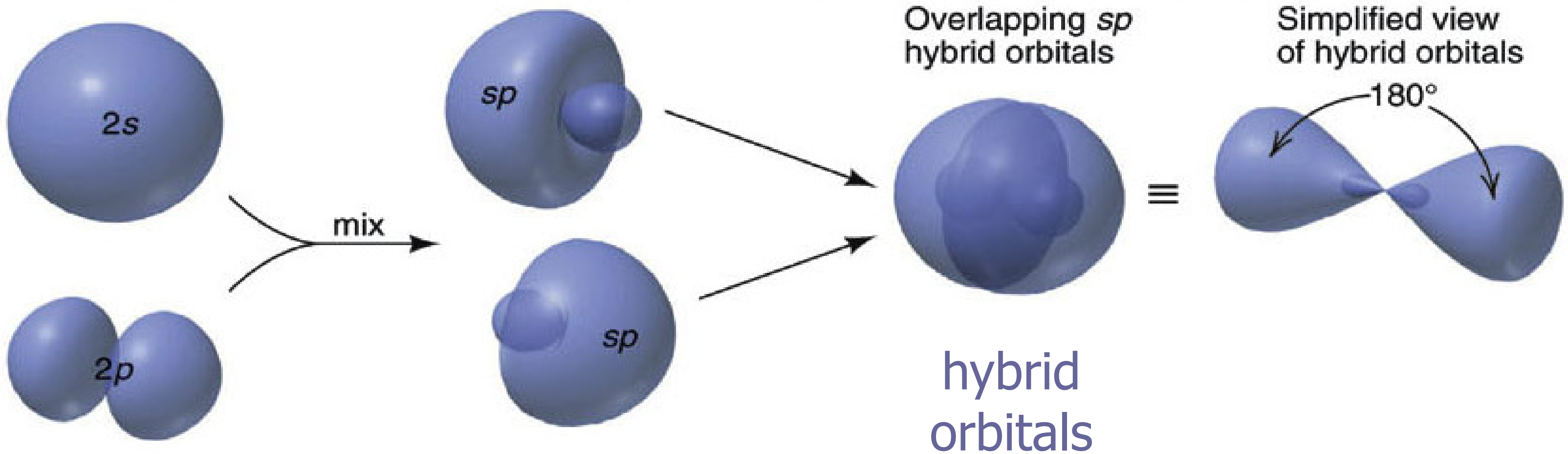
- Types of Hybrid Orbitals
  - Each type has a unique geometric arrangement
  - The hybrid type is derived from the number of s, p, d atomic orbitals used to form the Hybrid

Hybrid Orbitals (Hybridization)	Geometric Arrangements	Number of Hybrid Orbitals Formed by Central Atom	Example
sp	Linear	2	Be in BeF_2
sp^2	Trigonal planar	3	B in BF_3
sp^3	Tetrahedral	4	C in CH_4

sp Hybrid Orbitals

- SP Hybridization
  - 2 electron groups surround central atom
  - Linear shape, 180° apart
  - VB theory proposes the mixing of two nonequivalent orbitals, one "s" and one "p", to form two equivalent "sp" hybrid orbitals
  - Orientation of hybrid orbitals extend electron density in the bonding direction
  - Minimizes repulsions between electrons
  - Both shape and orientation maximize overlap between the atoms

“sp” Hybrid Orbitals



hybrid orbitals

Ex: $BeCl_2$

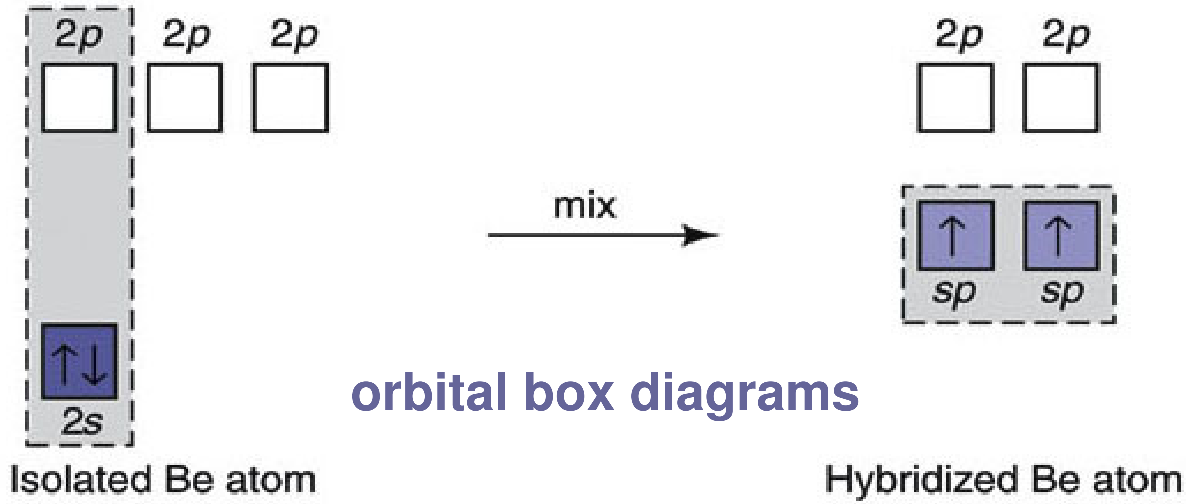
The Be-Cl bonds in $BeCl_2$ are neither spherical (s orbitals) nor dumbbell (p orbitals)

The Be-Cl bonds have a hybrid shape

In the Beryllium atom the 2s orbital and one of the 2p orbitals mix to form 2 sp hybrid orbitals

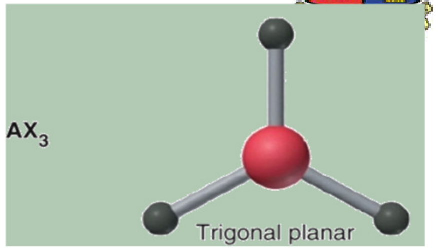
Each Be Hybrid sp orbital overlaps a Chlorine 3p orbital in $BeCl_2$

Beryllium Hybrid Orbital Diagram



orbital box diagrams

"sp^2" Hybridization



- sp^2 - Trigonal Planar geometry
- (Central atom bonded to three ligands)
- The three bonds have equivalent hybridized shapes
- The sp^2 hybridized orbitals are formed from:

1 "s" orbital and 2 "p" orbitals

Note: Of the 4 orbitals available (1 s & 3 p) only the s orbital and 2 of the p orbitals are used to form hybrid orbitals

Note: Unlike electron configuration notation, hybrid orbital notation uses superscripts for the *number of atomic orbitals* of a given type that are mixed, NOT for the number of electrons in the orbital, thus,

sp^2 (3 orbitals), sp^3 (4 orbitals)

“sp^2” Hybridization

BF_3

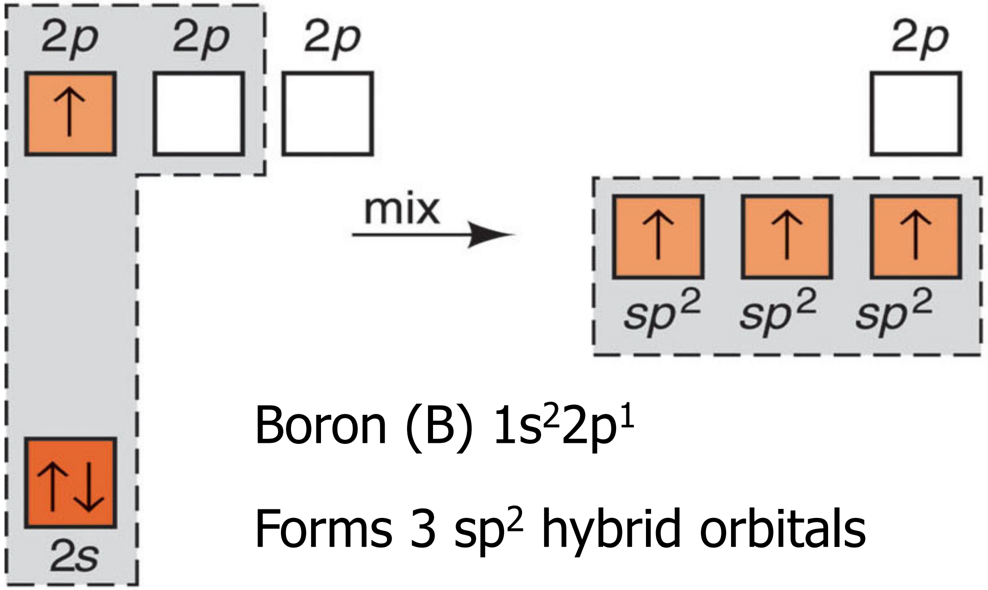
The 3 B-F bonds are neither spherical nor dumbell shaped

They are all of identical shape

In Boron, the “2s” orbital and two of the “2p” orbitals mix to form 3 sp^2 hybrid orbitals, each containing one of the 3 total valence electrons

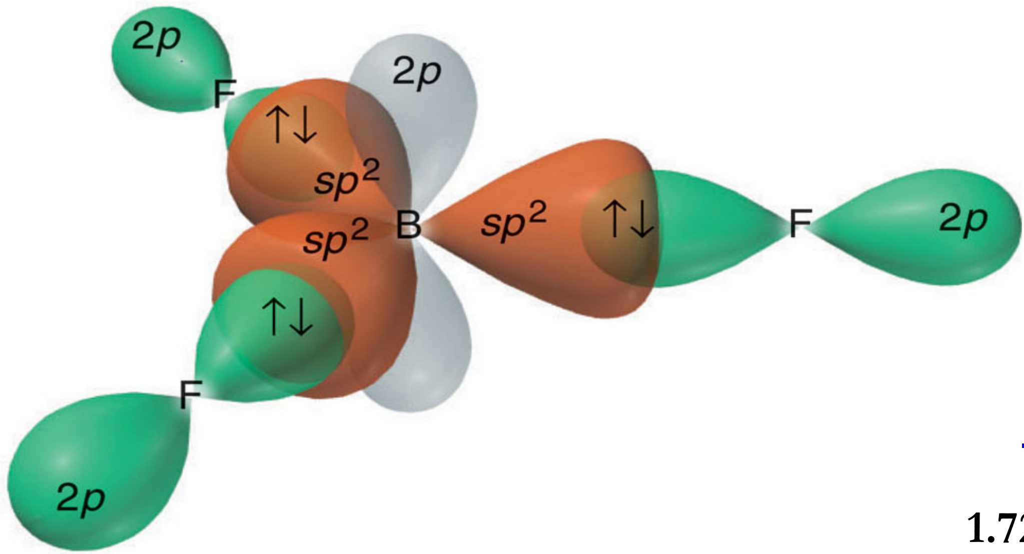
Each of the Boron hybrid sp^2 orbitals overlaps with a 2p orbital of a Fluorine atom

Hybrid Orbital Diagram

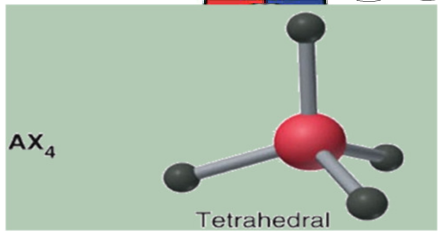


Boron (B) $1s^2 2p^1$

Forms 3 sp^2 hybrid orbitals



sp^3 Hybrid Orbitals

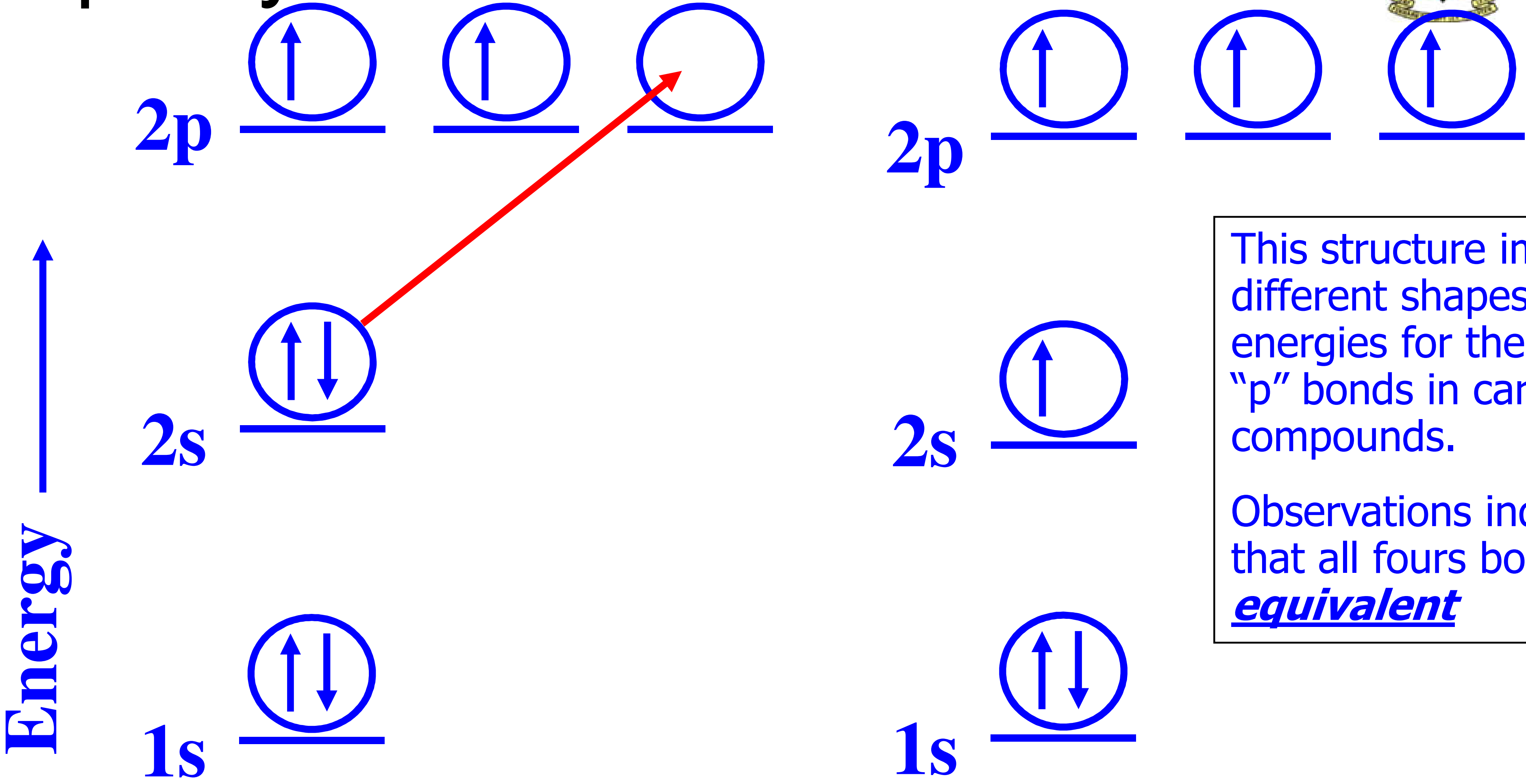


- sp^3 (4 bonds, thus, Tetrahedral geometry)
- The sp^3 hybridized orbitals are formed from:

  1 "s" orbital and 3 "p" orbitals

- Example"
  - Carbon is the basis for "Organic Chemistry"
  - Carbon is in group 4 of the Periodic Chart and has 4 valence electrons – $2s^2 2p^2$
  - The hybridization of these 4 electrons is critical in the formation of the many millions of organic compounds and as the basis of life as we know it

sp^3 Hybrid Orbitals

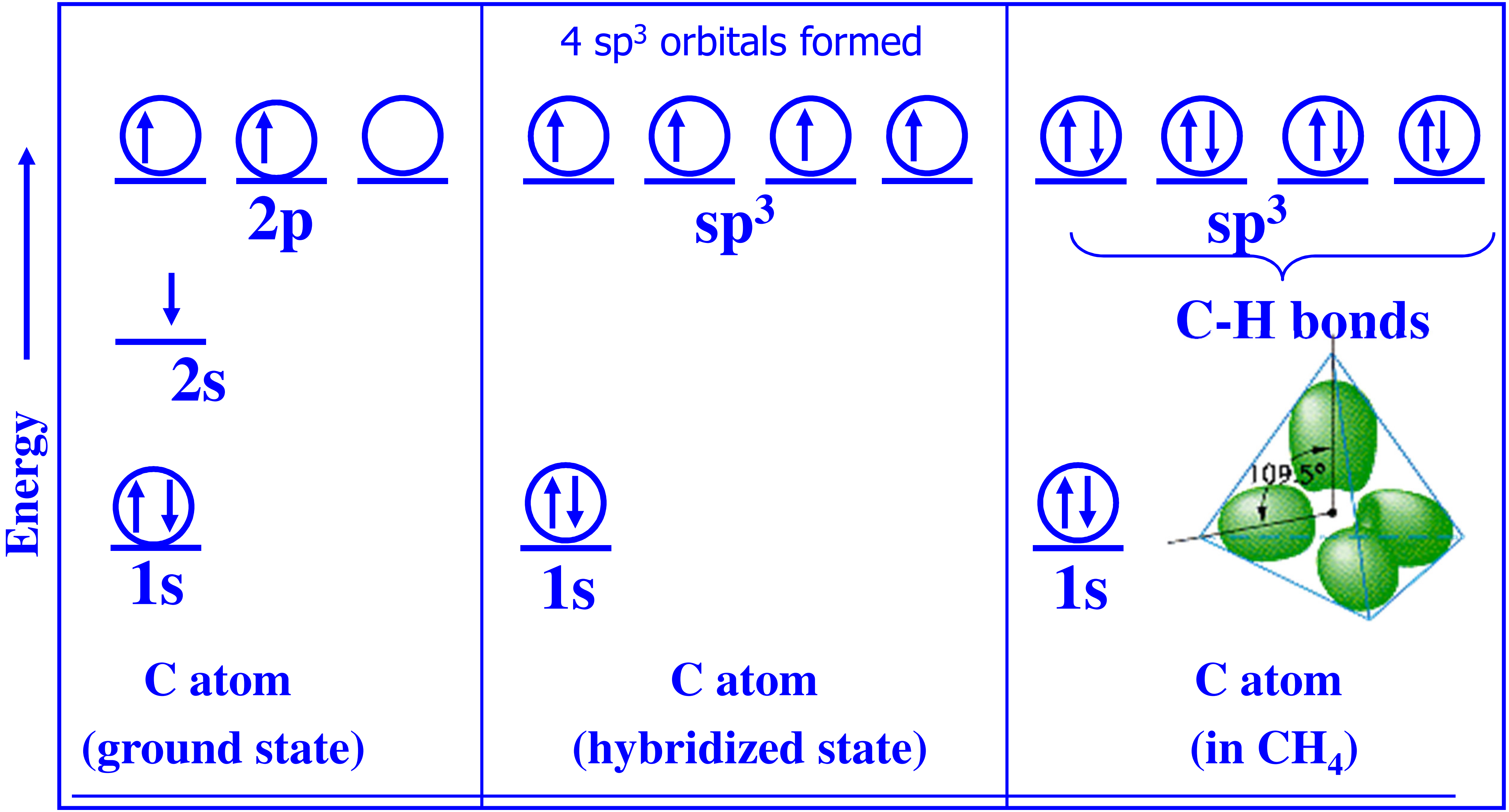


This structure implies different shapes and energies for the "s" and "p" bonds in carbon compounds.

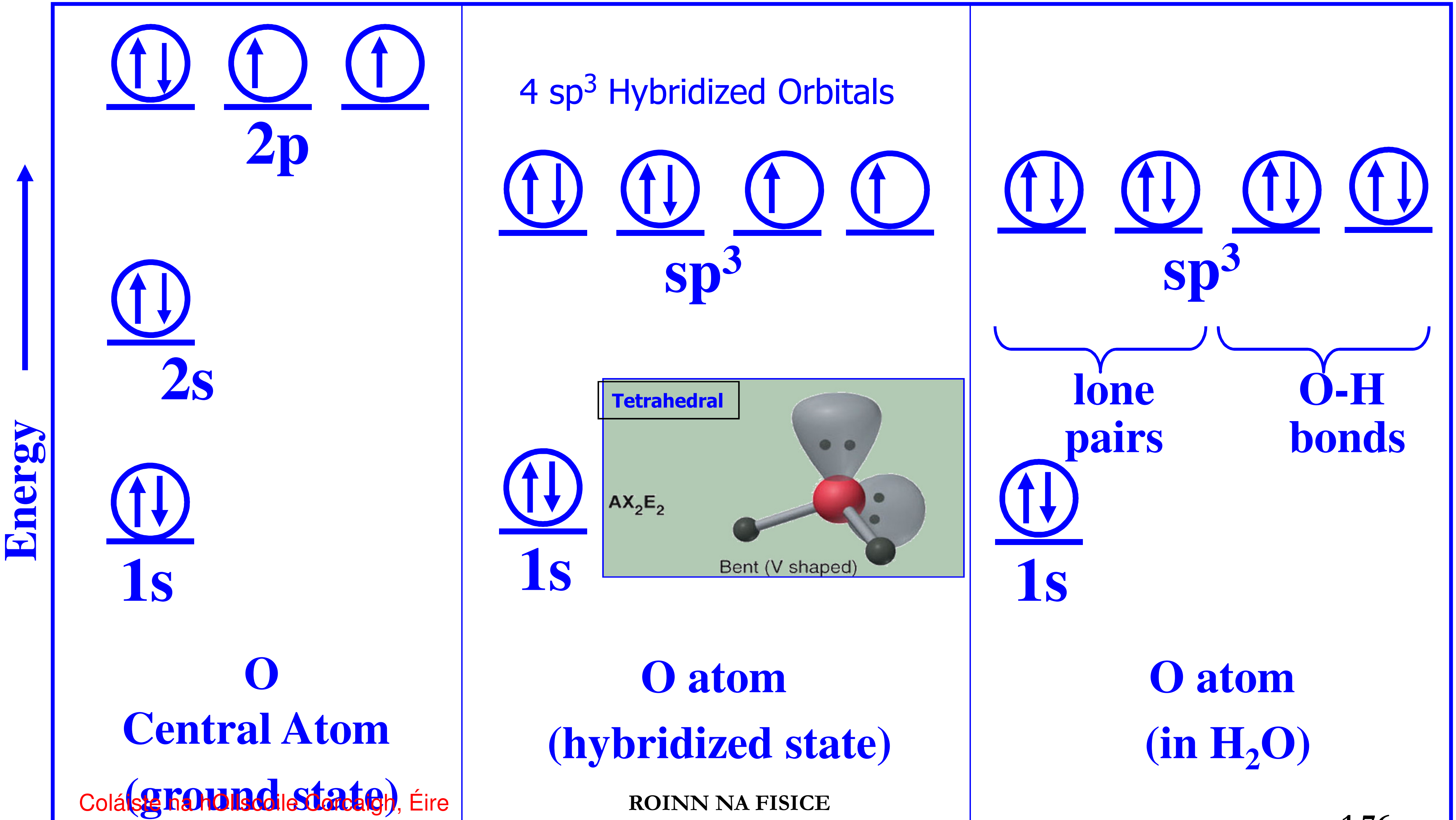
Observations indicate that all fours bonds are ***equivalent***

C atom (ground state) C atom (promoted)

Hybridization of Carbon in CH_4

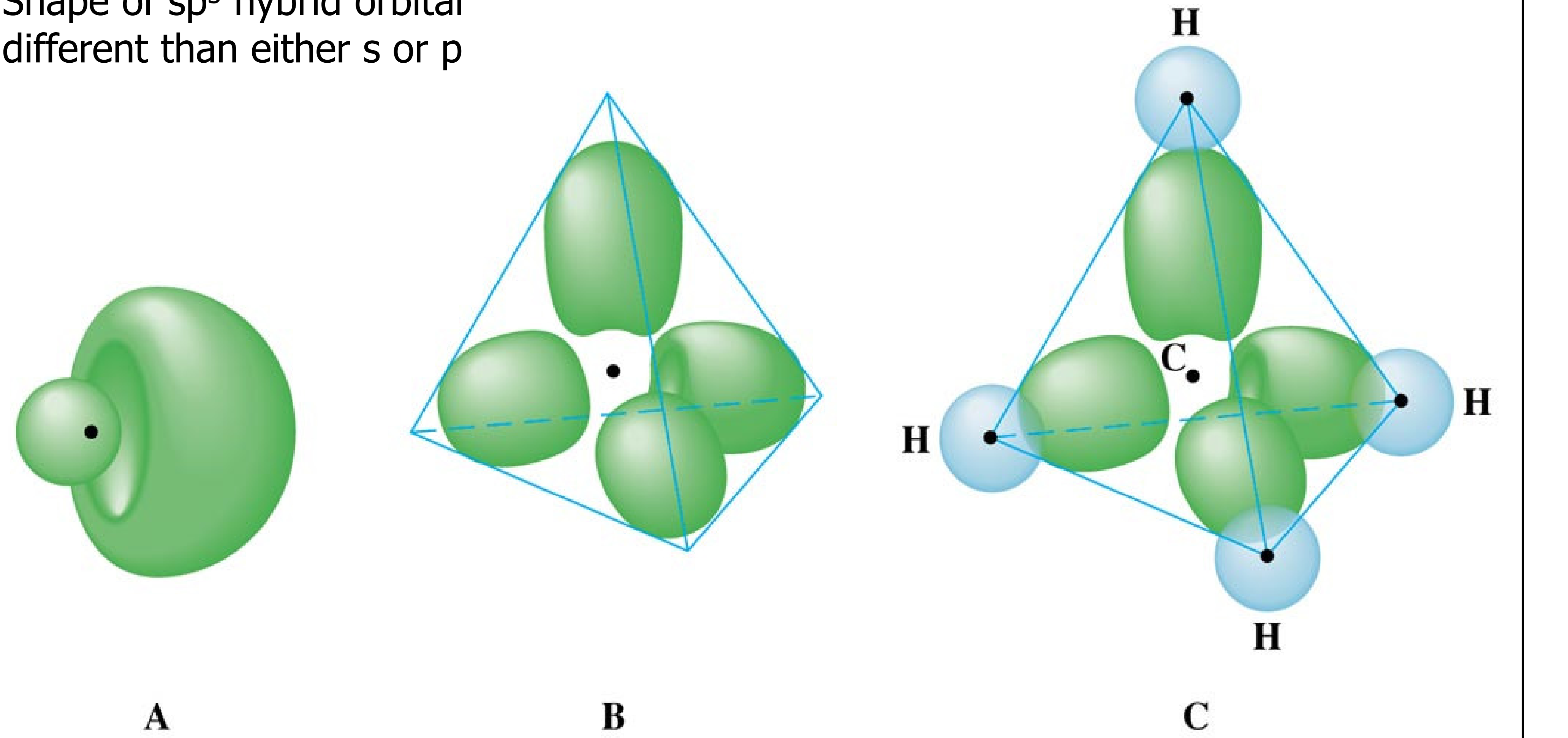


Oxygen Atom Bonding in H_2O



Spatial Arrangement of sp^3 Hybrid Orbitals

Shape of sp^3 hybrid orbital different than either s or p



sp^3 orbitals - details

- 1. $sp^3 = \frac{1}{2} s - \frac{1}{2} p_x - \frac{1}{2} p_y + \frac{1}{2} p_z$
- 2. $sp^3 = \frac{1}{2} s - \frac{1}{2} p_x + \frac{1}{2} p_y - \frac{1}{2} p_z$
- 3. $sp^3 = \frac{1}{2} s + \frac{1}{2} p_x - \frac{1}{2} p_y - \frac{1}{2} p_z$
- 4. $sp^3 = \frac{1}{2} s + \frac{1}{2} p_x + \frac{1}{2} p_y + \frac{1}{2} p_z$

Linear Combination of Atomic Orbitals

Scalar product:

$$(n.sp^3; m.sp^3) = 0$$

Hybridization visualisation

- http://www.mhhe.com/physsci/chemistry/essentialchemistry/flash/hybrv18.swf