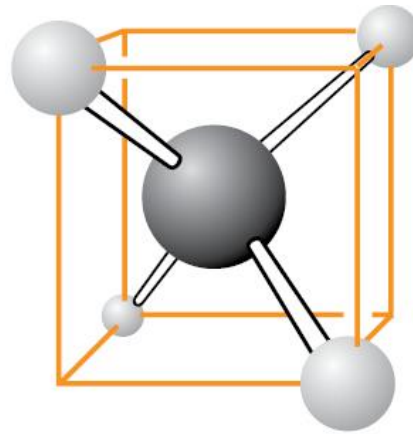


## *Bonding in Organic Molecules and Reactivity*

- ✓ Valence Bond Theory (VBT): Hybrid atomic orbitals, Resonance
  - ✓ Molecular Orbital Theory (MOT): Molecular orbitals
- 
- Organic chemists like to use the concept of hybridization and resonance whenever possible
  - Molecular Orbital Theory is more sophisticated and more precise
  - However, *in many instances a better picture of bonding is described by combining the hybrid approach with delocalized MO approach*

## *Hybrid Atomic Orbitals (VBT-Valence Bond Theory)*

- ✓ As  $\text{CH}_4$  is tetrahedral, we should construct some new orbitals on the carbon that point towards the corners of a tetrahedron
- ✓ The important thing is that we are combining the AOs from the same atom, in contrast to when MOs are formed where we combine AOs from different atoms



a molecule of methane  
enclosed in a cube

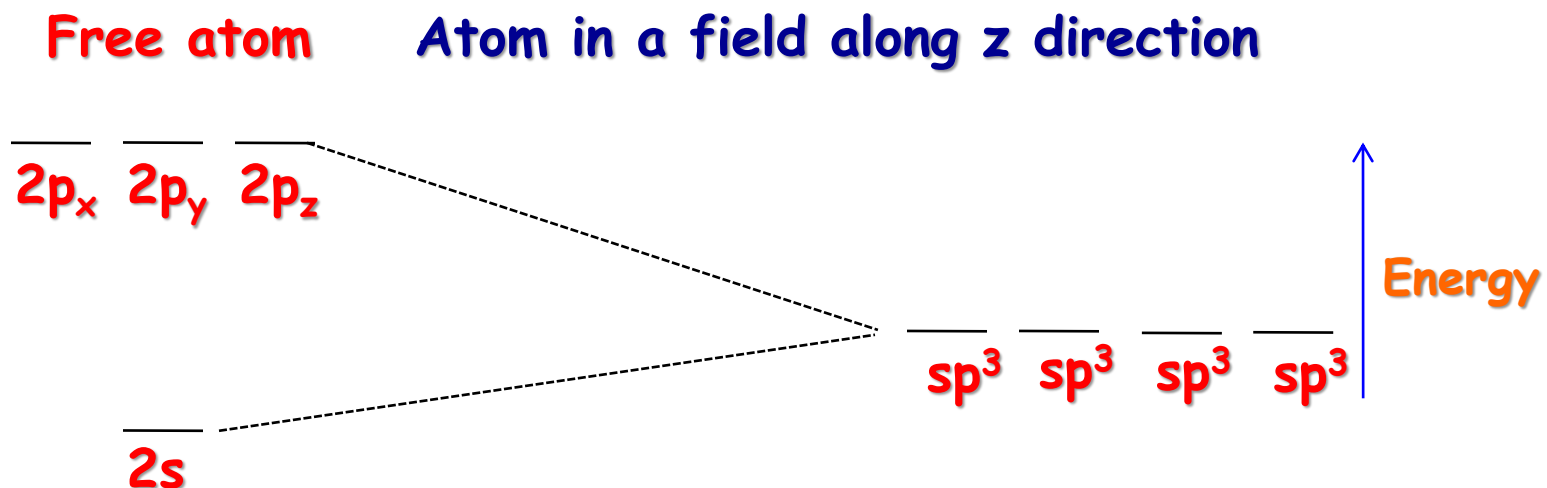
Hybrid AOs: Linear Combination of S and P  $\rightarrow$  lowering of energy



Linus Pauling, ~1930

## Hybrid (1e) Orbitals

- Linear combination of atomic orbital's within an atom leading to more effective bonding situation



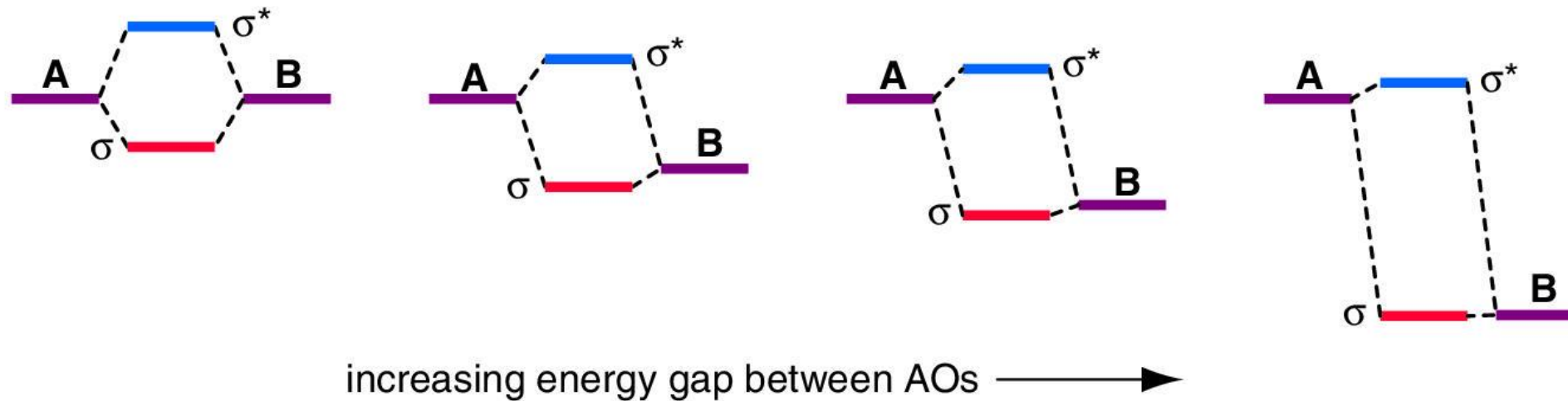
- Hybridization is a VBT concept. Use of experimental information
- All hybrid orbitals are equivalent

## The case for Hybrid Orbitals

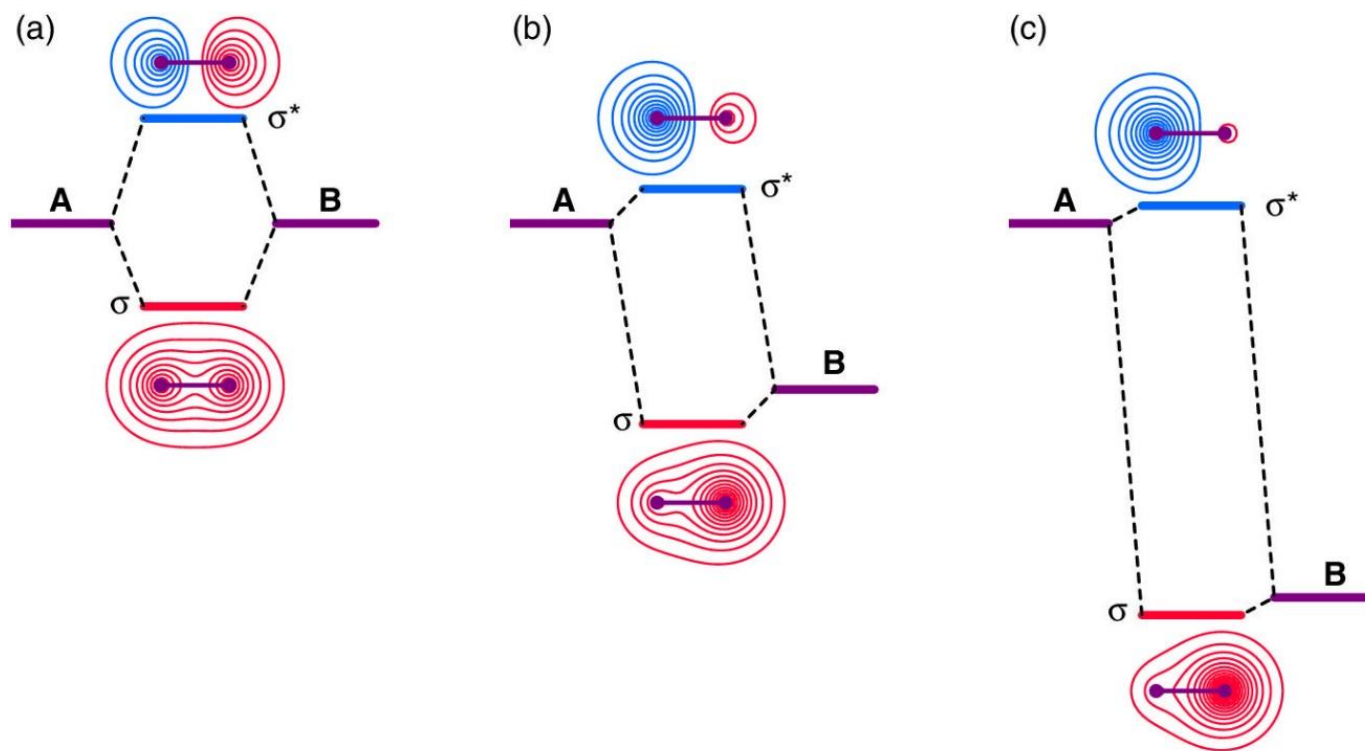
- ✓ It is convenient to use a particular set of functions  $\psi$  (which we call *hybrid orbitals*) that are constructed by combining the atomic  $s$ ,  $p$ ,  $d$ , and  $f$  functions that are already familiar to us.
- ✓ You should understand that *hybridization is not a physical phenomenon*; it is merely a *mathematical operation* that combines the atomic orbitals we are familiar with in such a way that the new (hybrid) orbitals possess the geometric and other properties that are reasonably consistent with what we observe in a wide range (but certainly not in all) molecules
- ✓ In other words, hybrid orbitals are abstractions that describe reality fairly well in certain classes of molecules (and fortunately, in much of the very large class of organic substances) and are therefore a useful means of organizing a large body of chemical knowledge...

# Molecular Orbitals

- ✓ Energy match and contribution from different AOs



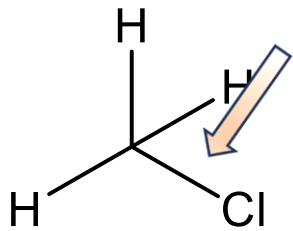
- ✓ When AOs are closely matched in energy, the bonding and anti-bonding MOs lie significantly above and below the AOs
- ✓ The bonding MO lies closer in energy to that of the lower energy AO
- ✓ The anti-bonding MO lies closer in energy to that of the higher energy AO



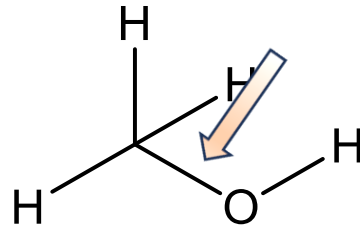
- ✓ Contribution to the bonding MO from the lower energy AO increases, while from the higher energy AO decreases
- ✓ Contribution to the anti-bonding MO from the higher energy AO increases, while from the lower energy AO decreases

# Reactivity in Organic Molecules

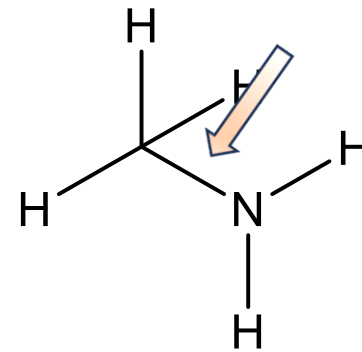
- ✓ Hydrocarbons are typically unreactive
- ✓ The reactivity in organic compounds arises from C-X (heteroatom) bonds
- ✓ The electronegativity difference between C and X atoms brings a change in the MOs compared to C-C bonds



*Halide*

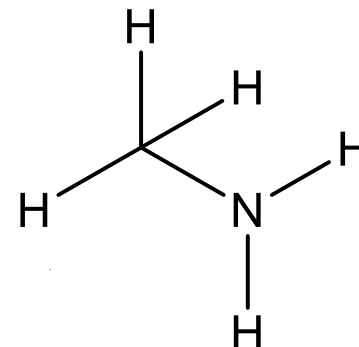
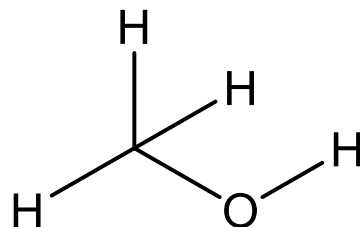
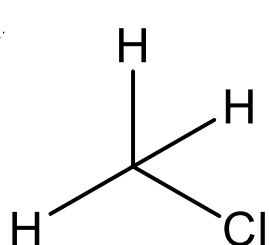


*Alcohol*



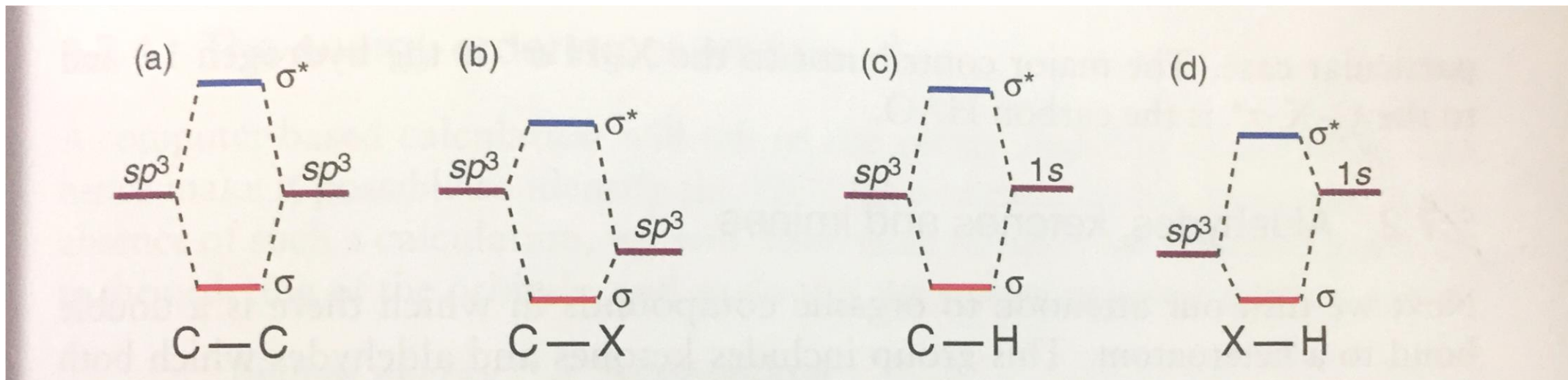
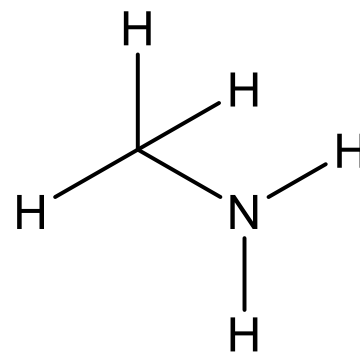
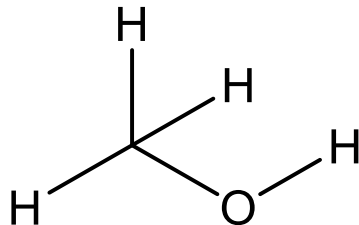
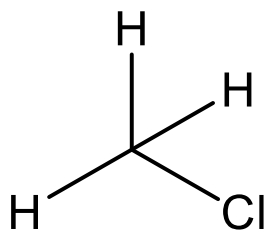
*Amine*

## Halides, Alcohols and Amines



- ✓  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{OH}$  and  $\text{CH}_3\text{NH}_2$ : 3 very common organic molecules
- ✓ The arrangement of atoms around the carbon is close to tetrahedral:  $\text{sp}^3$  hybridized
- ✓ We will also assume the heteroatom (Cl, O and N) are also  $\text{sp}^3$  hybridized
- ✓ In all the molecules, the HOMO is essentially one of the heteroatom hybrid atomic orbitals not involved in bonding
- ✓ LUMO are  $\sigma^*$  antibonding MOs associated with C-H, X-H and C-X bonds.





✓  $\sigma^*$  (C-X) is lower in energy than the  $\sigma^*$  (C-C)

✓  $\sigma^*$  (X-H) is lower in energy than the  $\sigma^*$  (C-H)

- ✓ In case of the attack of a nucleophile, the electrons will be initially donated to the  $\sigma^*$  orbital
- ✓ Between C-C and C-X bond, a nucleophile would prefer to react with C-X bond since it has a lower energy  $\sigma^*$