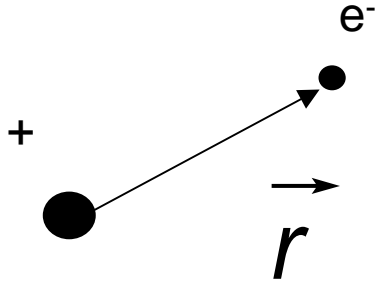


# Structures of atoms and molecules

# Atomic structure



$$p(\vec{r}) = [\psi(\vec{r})]^2$$

According to quantum mechanics, the probability of an electron being at a certain spot is given by the square of the wavefunction. The wavefunction and energy are found by solving Schrödinger's equation,

$$H\psi = E\psi.$$

# Finding the wavefunctions and energy levels for an atom

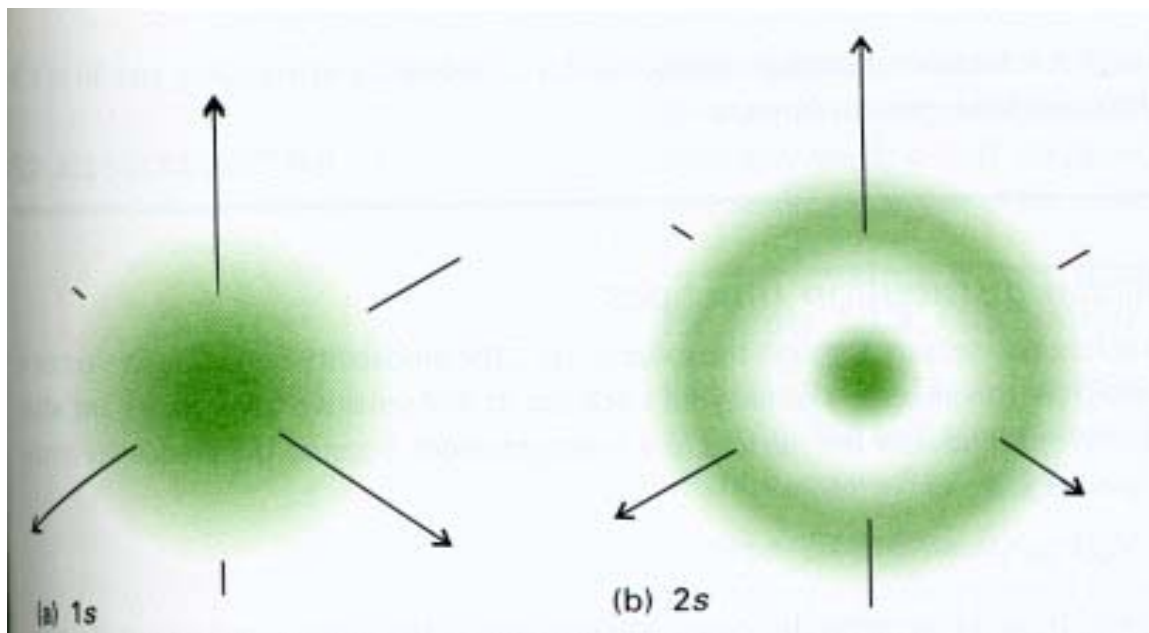
We must solve Schrödinger's equation.

$$H\psi(\vec{r}) = E\psi(\vec{r})$$
$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r}$$

The probability of an electron being at a site  $\vec{r}$  is

$$p(\vec{r}) = \psi^2(\vec{r})$$

# Atomic orbitals

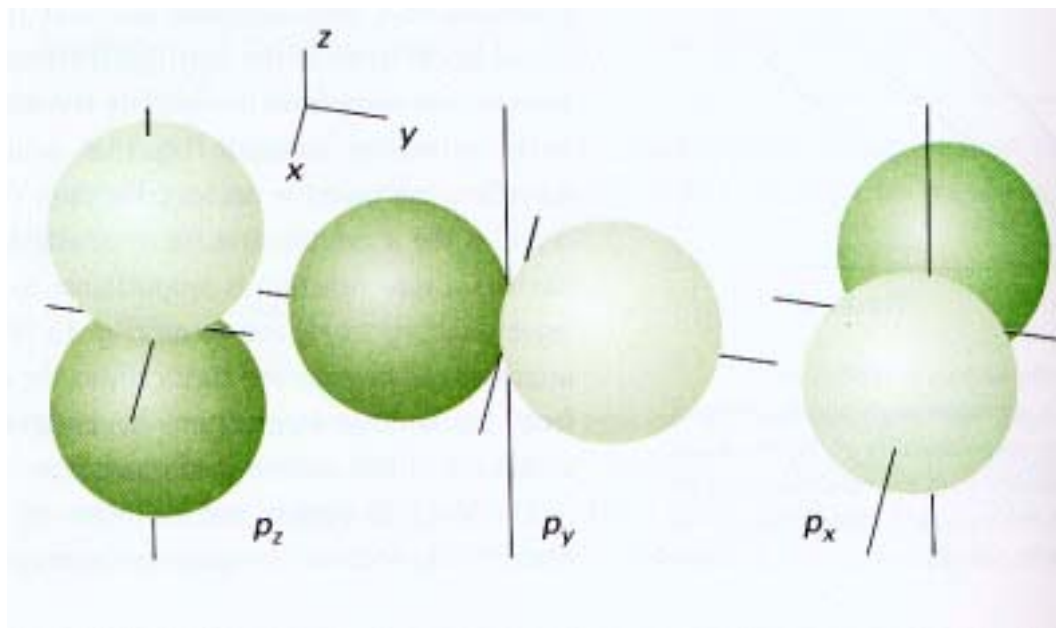


These plots show the 1s and 2s wavefunction.

Orbitals are defined as the region where the electrons are 90 % likely to be found.

s orbitals are radially symmetric.

# p orbitals

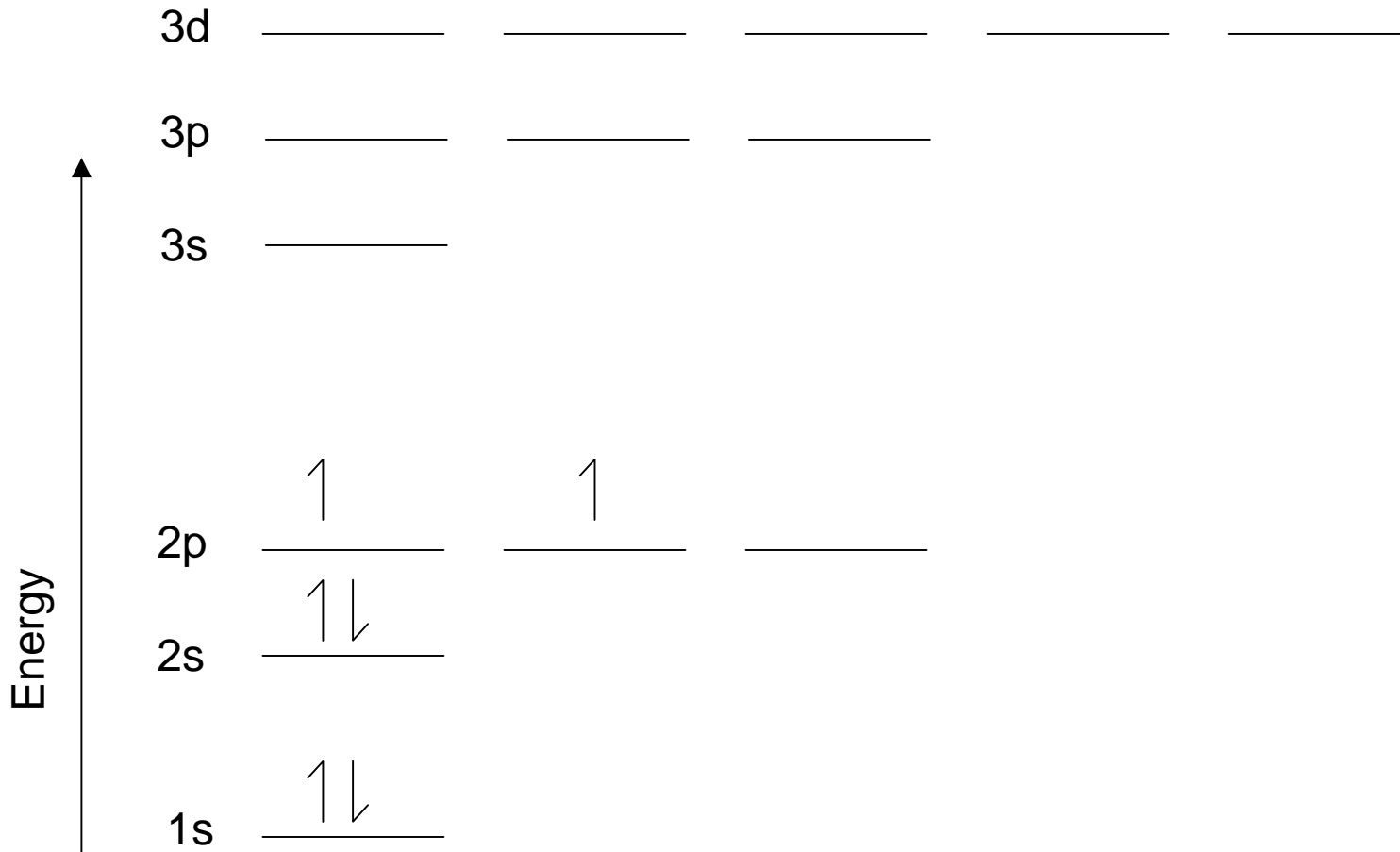


p orbitals have a positive lobe (light color) and a negative lobe (dark green).

Remember that the probability of an electron occupying a certain spot is the square of the wavefunction. Thus, the electron is equally likely to be in either lobe of the p orbital.

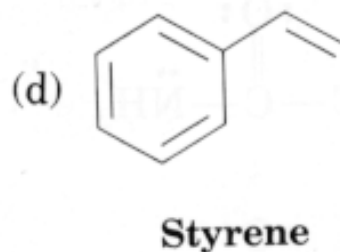
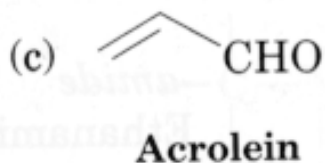
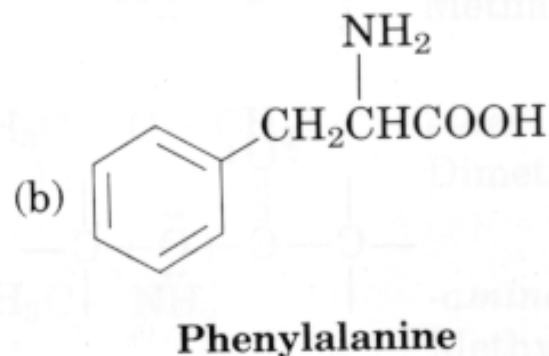
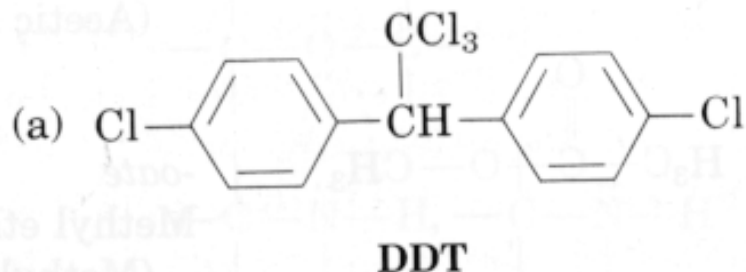
The p wavefunctions are not radially symmetric.

# Atomic energy levels



- The energy levels are discrete.
- Each level can take a spin up and a spin down electron.
- Carbon has six electrons. They occupy the levels as shown above.

# What are organic materials and why are they special?



- Organic materials contain carbon.
- Carbon has 4 valence electrons and can form single, double or triple bonds.
- An almost infinite number of materials with a wide range of properties can be made with carbon and the elements that bond to it.

# Why are bonds so important?

## Characteristics of the bond

Strength/ energy

Polarity

Size and directionality

Rigidity

Localization of electrons

## Material Property

Strength, stiffness, melting temperature  
chemical stability, absorption and emission  
spectra

Melting temperature, solubility

The shape of the molecule affects almost all  
properties

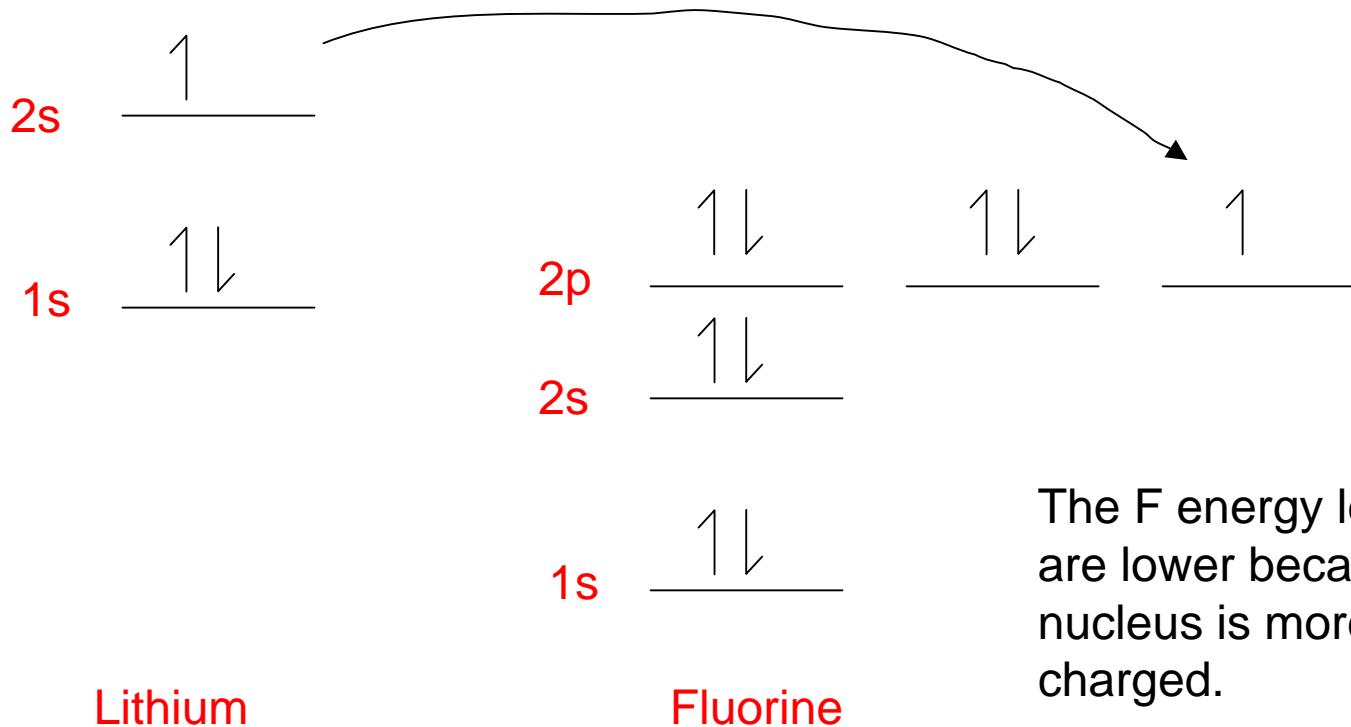
Stiffness or viscosity

Conductivity

**Understanding bonds is crucial for understanding any material.**



# Ionic bonds

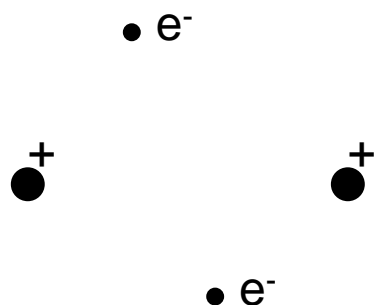


The F energy levels are lower because the F nucleus is more positively charged.

The one electron in the 2s level of Li sits in a high energy level. Adding one more electron to fluorine doesn't cost much energy. Li gives its electron to F. The positive Li cation forms an ionic bond with the negatively charged F anion.

General principle: atoms bond in such a way that they have completely full and completely empty energy shells.

## A more general approach to bonding



$$H\psi = E\psi$$

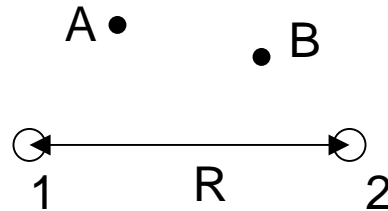
How do we find the wavefunctions of the electrons in a molecule?

We assume that the core electrons have the same wavefunctions they would have in an atom.

We cannot exactly solve Schrödinger's equation for the valence electrons.  
We must make an approximation.

We assume that the molecular orbital is a linear combination of atomic orbitals.  
The atomic orbitals are found by solving Schrödinger's equation for the atom.

# Finding the wavefunctions and energy levels of a molecule



We still need to solve Schrödinger's equation.

$$H = -\frac{\hbar^2}{2m_A} \nabla^2 - \frac{\hbar^2}{2m_B} \nabla^2 + V + \frac{e^2}{4\pi\epsilon_0 R}$$

kinetic energy

nuclear repulsion

$$V = -\frac{Ze^2}{4\pi\epsilon_0} \left( \frac{1}{r_{A1}} + \frac{1}{r_{A2}} + \frac{1}{r_{B1}} + \frac{1}{r_{B2}} \right) + \frac{e^2}{4\pi\epsilon_0 r_{AB}}$$

electron-nucleus interactions

electron repulsion

## Calculating the energy levels

$$E = \int \psi^* H \psi d\vec{r}$$

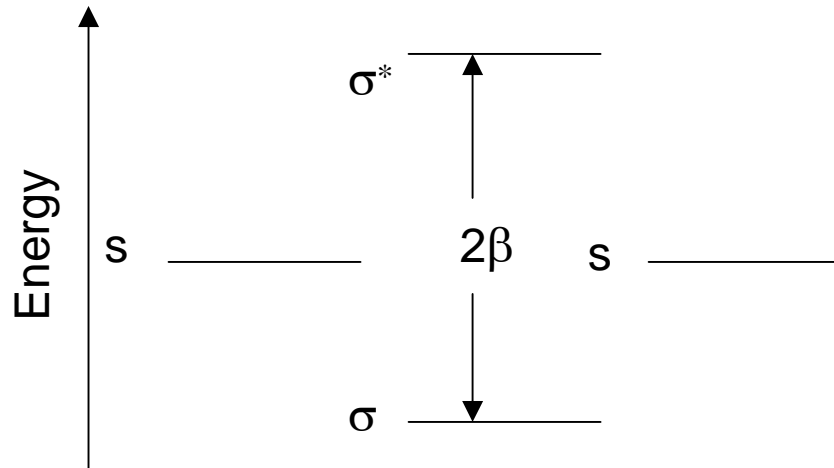
(Normalization factors have been ignored.)

$$= \int \psi_A^* H \psi_A d\vec{r} \pm \int \psi_A^* H \psi_B d\vec{r} = \alpha \pm \beta$$

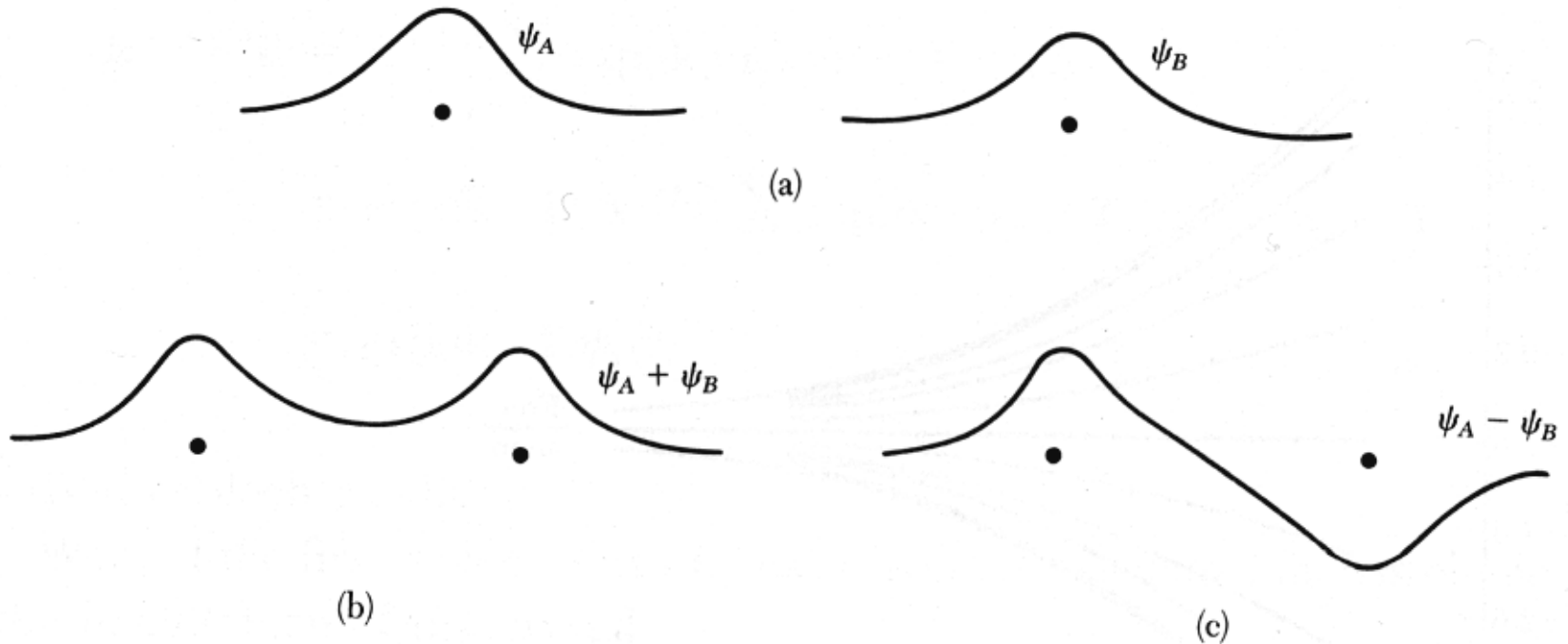
$$\alpha = \int \psi_A^* H \psi_A d\vec{r} = \text{Coulomb integral}$$

$$\beta = \int \psi_A^* H \psi_B d\vec{r} = \text{resonance integral}$$

Atomic s orbitals overlap to form radially symmetric  $\sigma$  and  $\sigma^*$  molecular orbitals

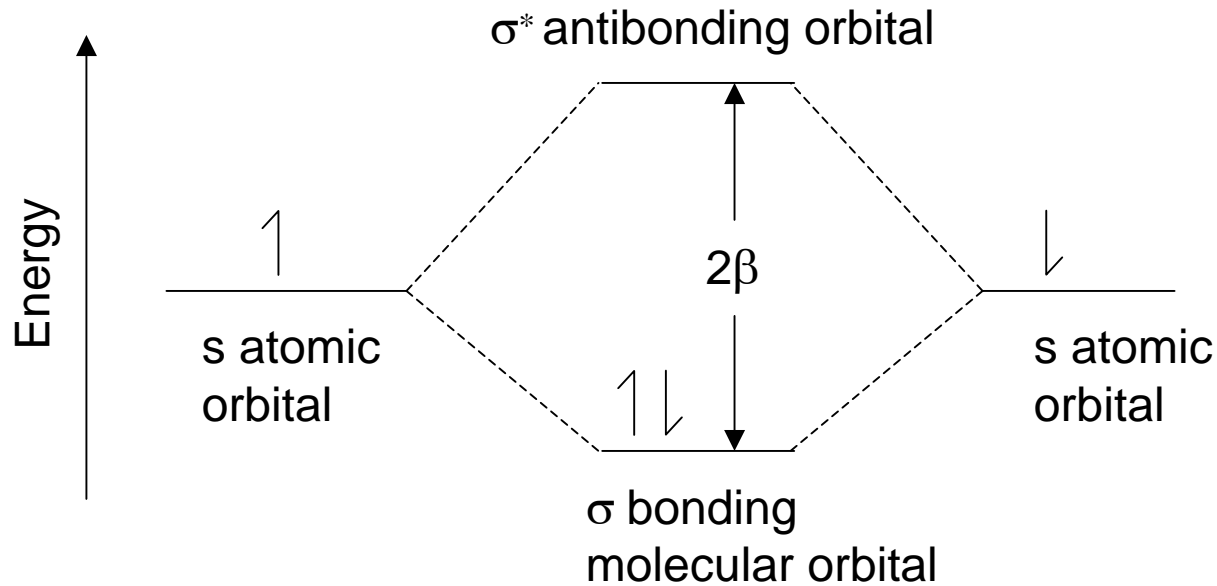


# Bonding and antibonding orbitals



When two atoms are far apart, the wavefunctions of electrons are just those of individual atoms. When the atoms approach, we can get approximate molecular orbitals by taking linear combinations of atomic orbitals. The symmetric wavefunction lowers the energy by increasing the electron density between the two nuclei. The antisymmetric wavefunction raises the energy by reducing the electron density between the nuclei.

# Energy levels

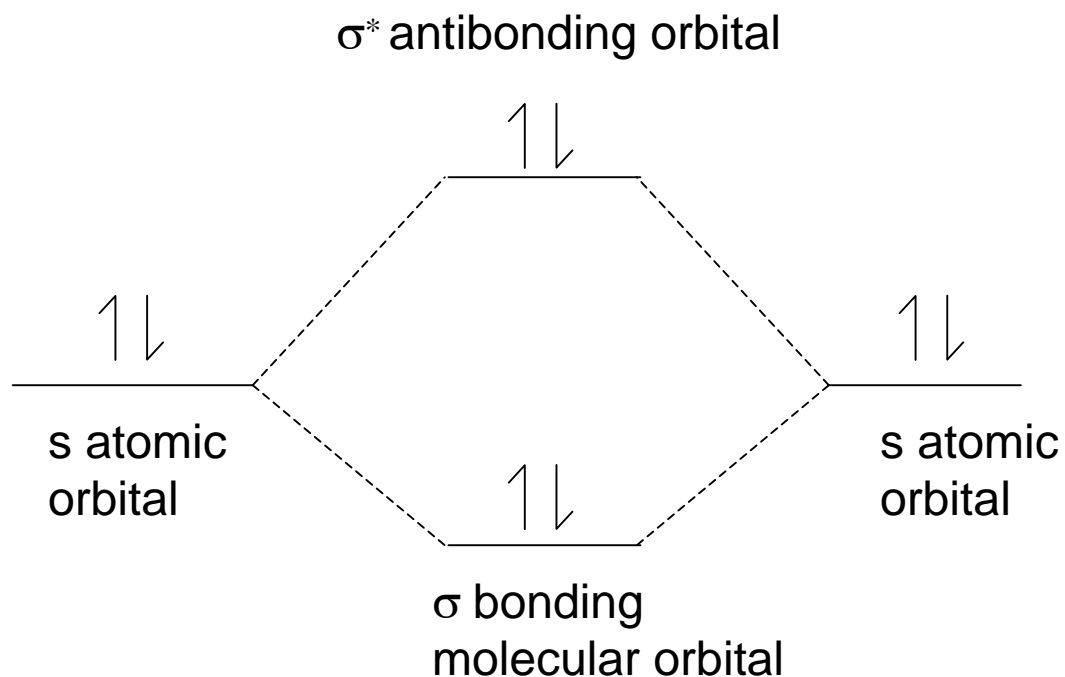


The splitting between the bonding ( $\sigma$ ) orbital and the antibonding ( $\sigma^*$ ) orbital depends on the Coulomb interaction between the electrons and the nuclei.

$$\beta = \int \psi_A^* H \psi_B d\vec{r}$$

The bond is stable because the two electrons occupy a lower energy in the bonding orbitals than they would have in the individual atomic orbitals.

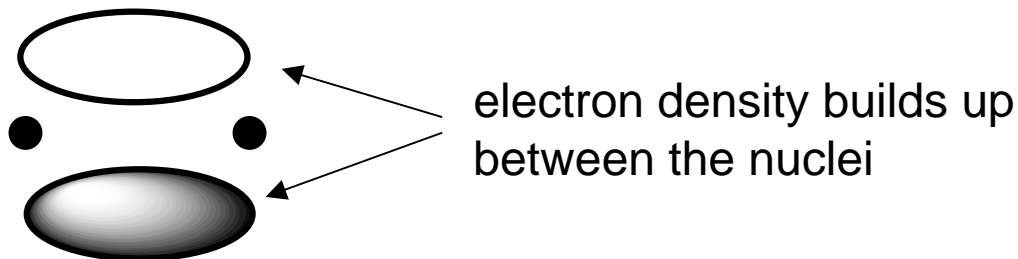
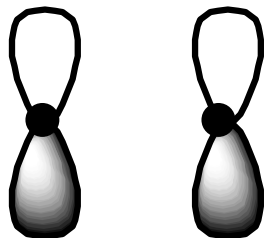
# Why don't helium atoms bind to each other?



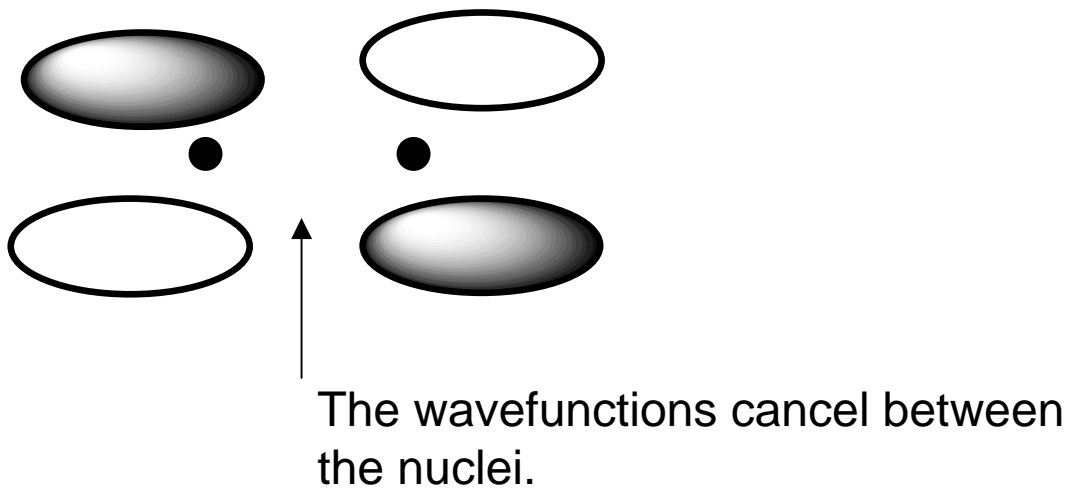
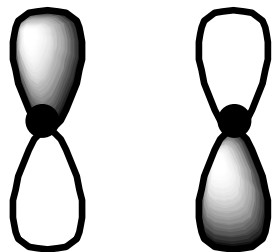
The energy cost for placing two electrons in the  $\sigma^*$  orbital is slightly greater than the energy savings of placing two electrons in the  $\sigma$  orbital. Energy is increased if the atoms are close to each other.

# $\pi$ bonds

Bonding combination of p orbitals ( $\pi$ )

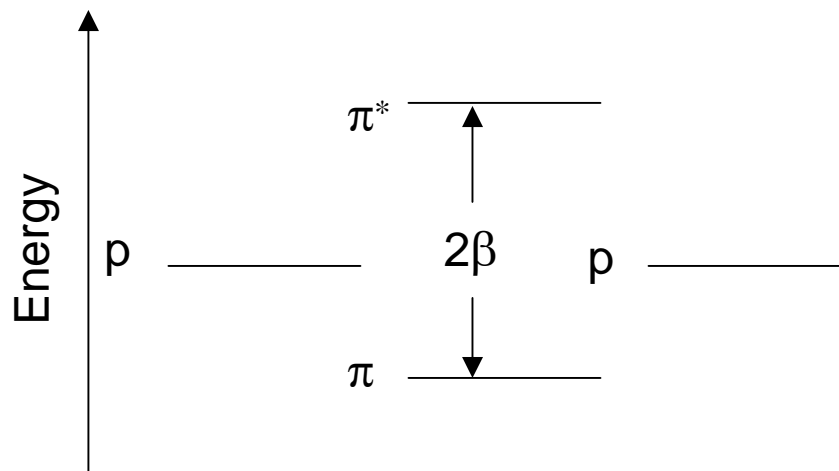


Antibonding combination of p orbitals ( $\pi^*$ )





## $\pi$ energy levels



$$\beta = \int \psi_A^* H \psi_B d\vec{r}$$

The  $\pi$ – $\pi^*$  gap is usually much smaller than the  $\sigma$ – $\sigma^*$  gap because the p orbitals don't build up electron density right between the nuclei.

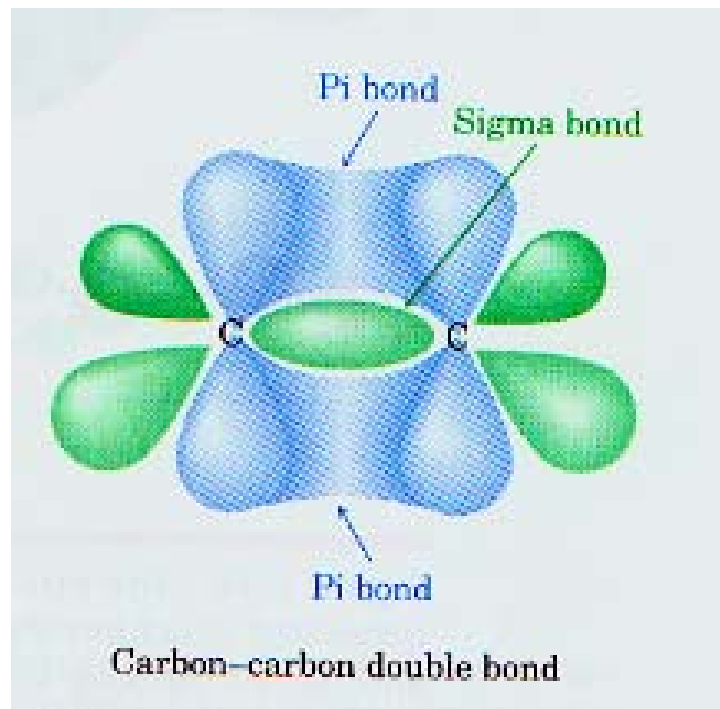
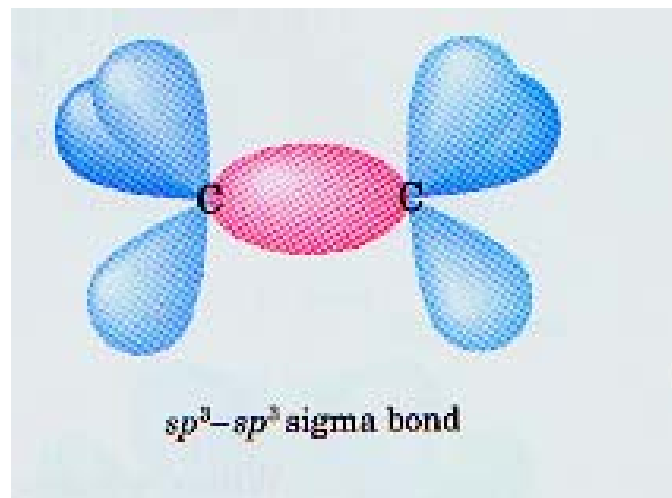
Since  $\pi$  bonds aren't as strong as  $\sigma$  bonds, they tend to be more reactive.

# Bond stiffness

Atomic s orbitals overlap to form radially symmetric  $\sigma$  and  $\sigma^*$  molecular orbitals. Molecules can rotate at the site of a  $\sigma$  bond.

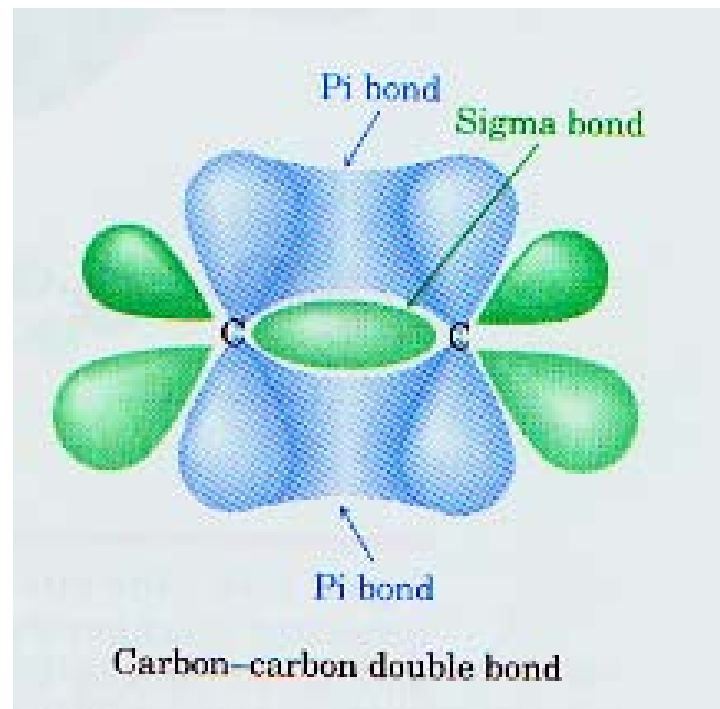
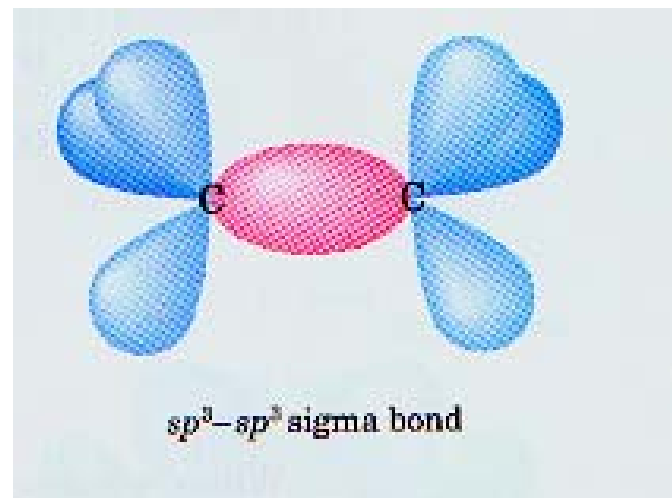
The molecule is not completely free to rotate because the other parts of the molecule repel each other.

$\pi$  bonds are not radially symmetric. They are stiff because the overlap of the p orbitals is disrupted if the molecule is twisted.

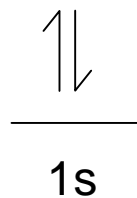
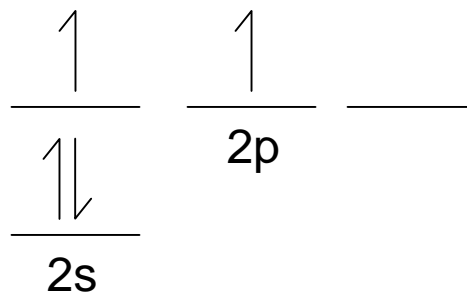


# Polarizability

The electrons in  $\pi$  bonds are more polarizable (easily distorted by an electric field) than those in  $\sigma$  bonds because they are farther from the nuclei and not held as tightly.

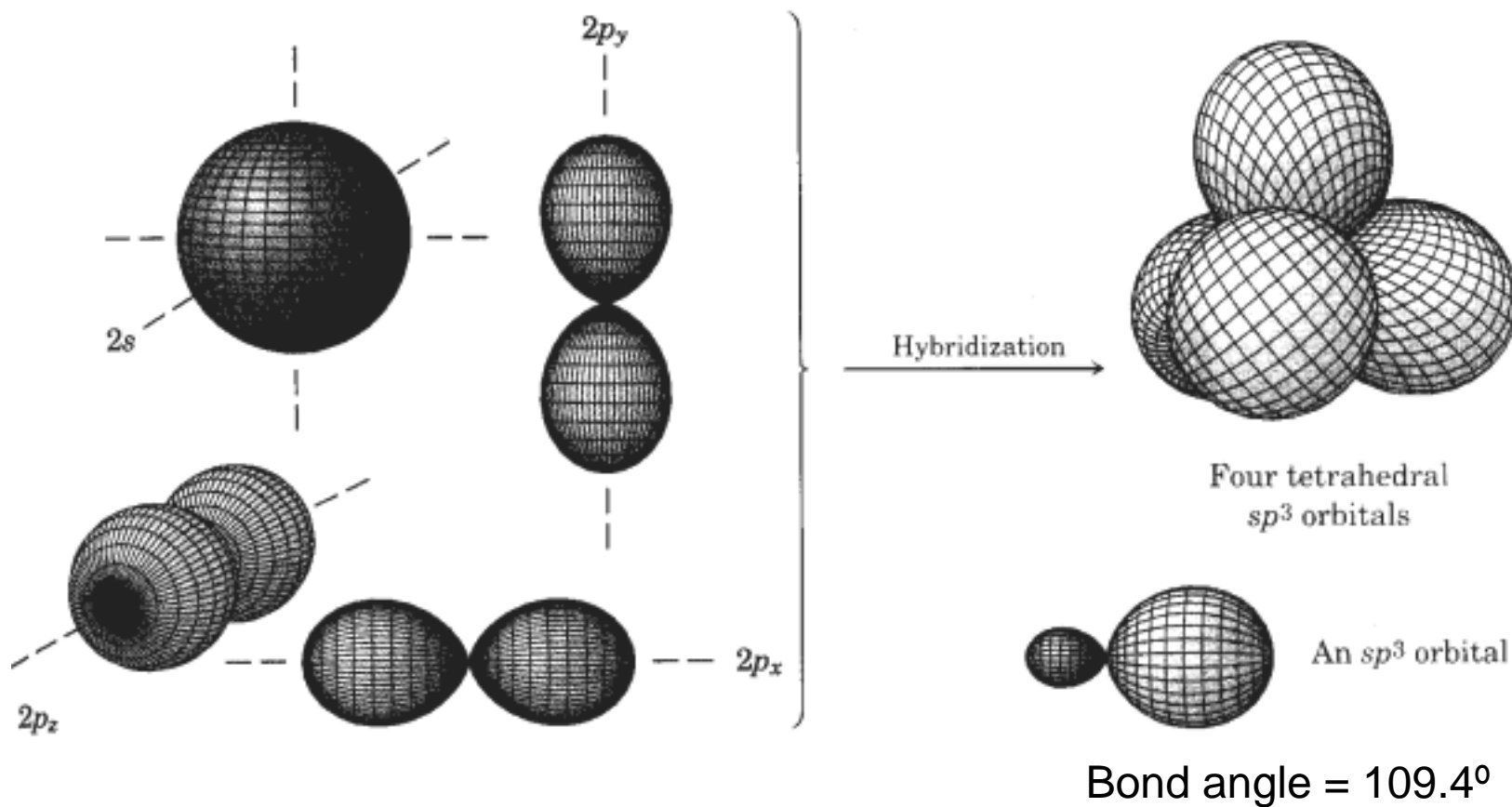


What type of bonds does carbon form with itself?



e.g. Carbon

# sp<sup>3</sup> hybridization



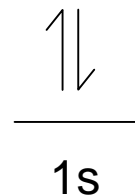
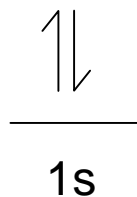
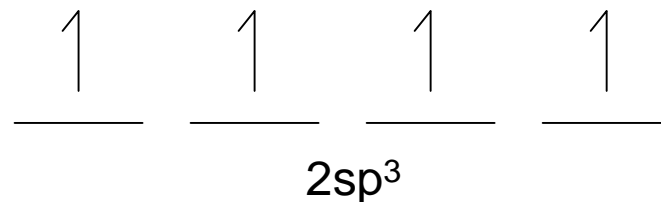
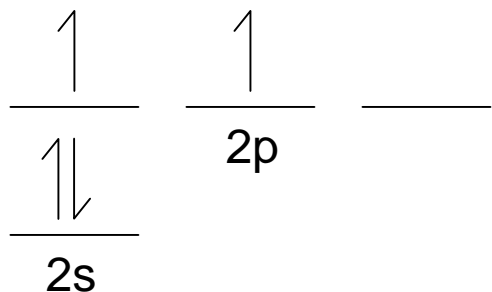
$$h_1 = s + p_x + p_y + p_z$$

$$h_3 = s - p_x + p_y - p_z$$

$$h_2 = s - p_x - p_y + p_z$$

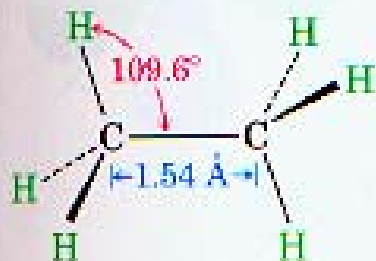
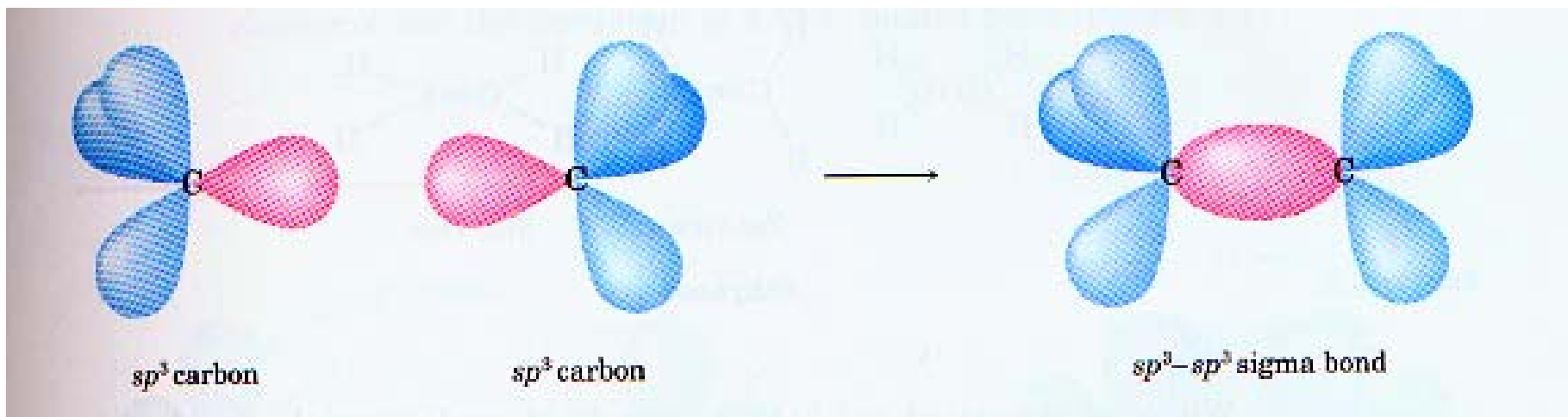
$$h_4 = s + p_x - p_y - p_z$$

## Energy levels of hybridized orbitals



By combining the s and 3 p orbitals to form 4  $sp^3$  orbitals, carbon has four unpaired electrons and can form four bonds.

# Ethane ( $\text{C}_2\text{H}_6$ )

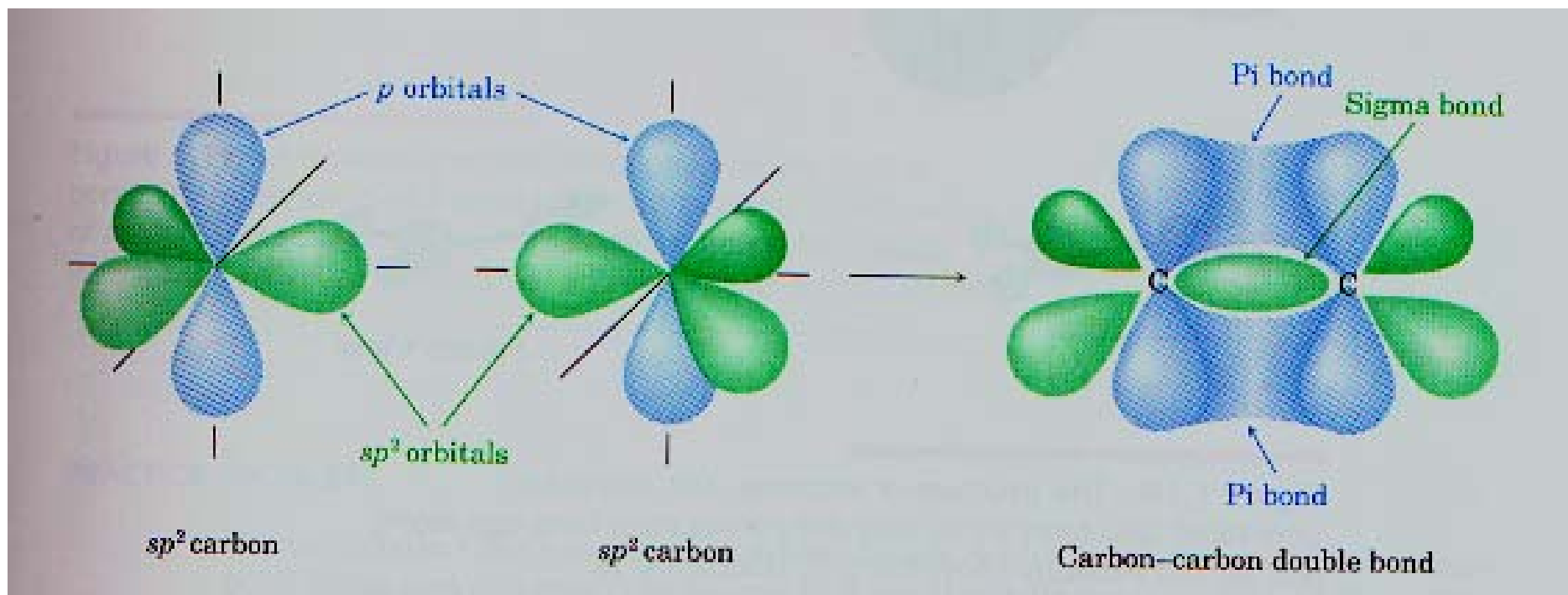
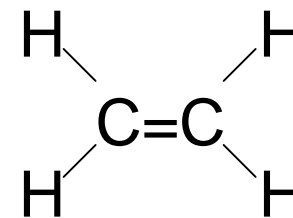


Dashed line - into the board  
Wedged line- out of the board

Remember that a carbon-carbon bond is  $1.5 \text{ \AA}$  long. This will be helpful for estimating the size of molecules.

$\sigma$  and  $\pi$  bonds

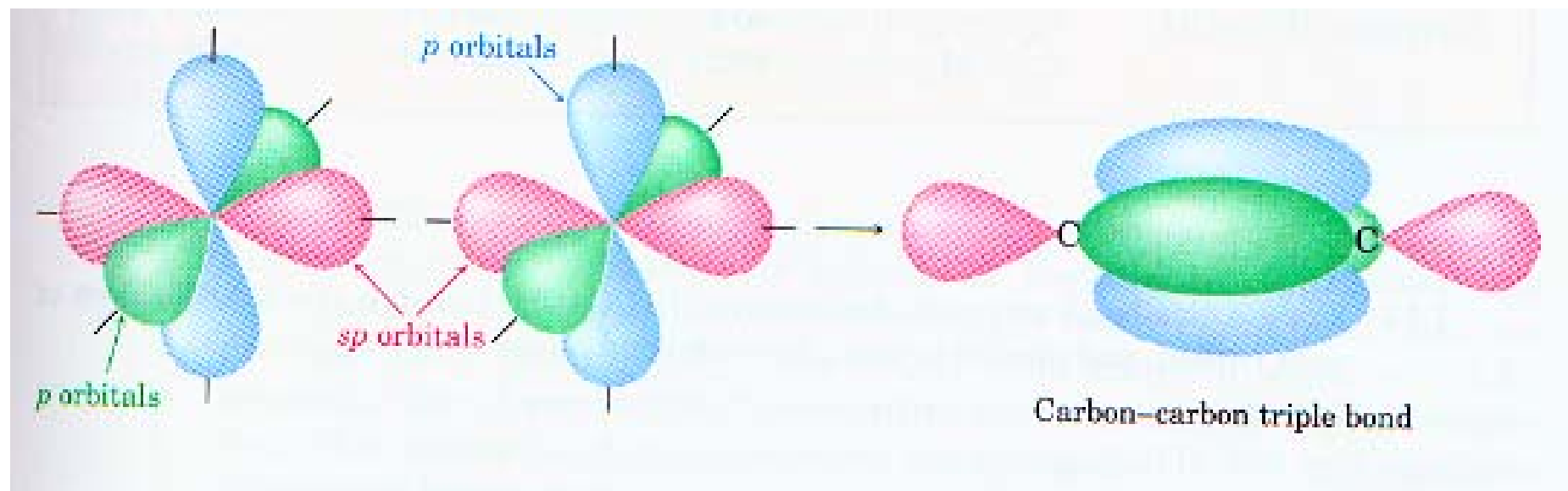
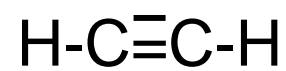
ethylene



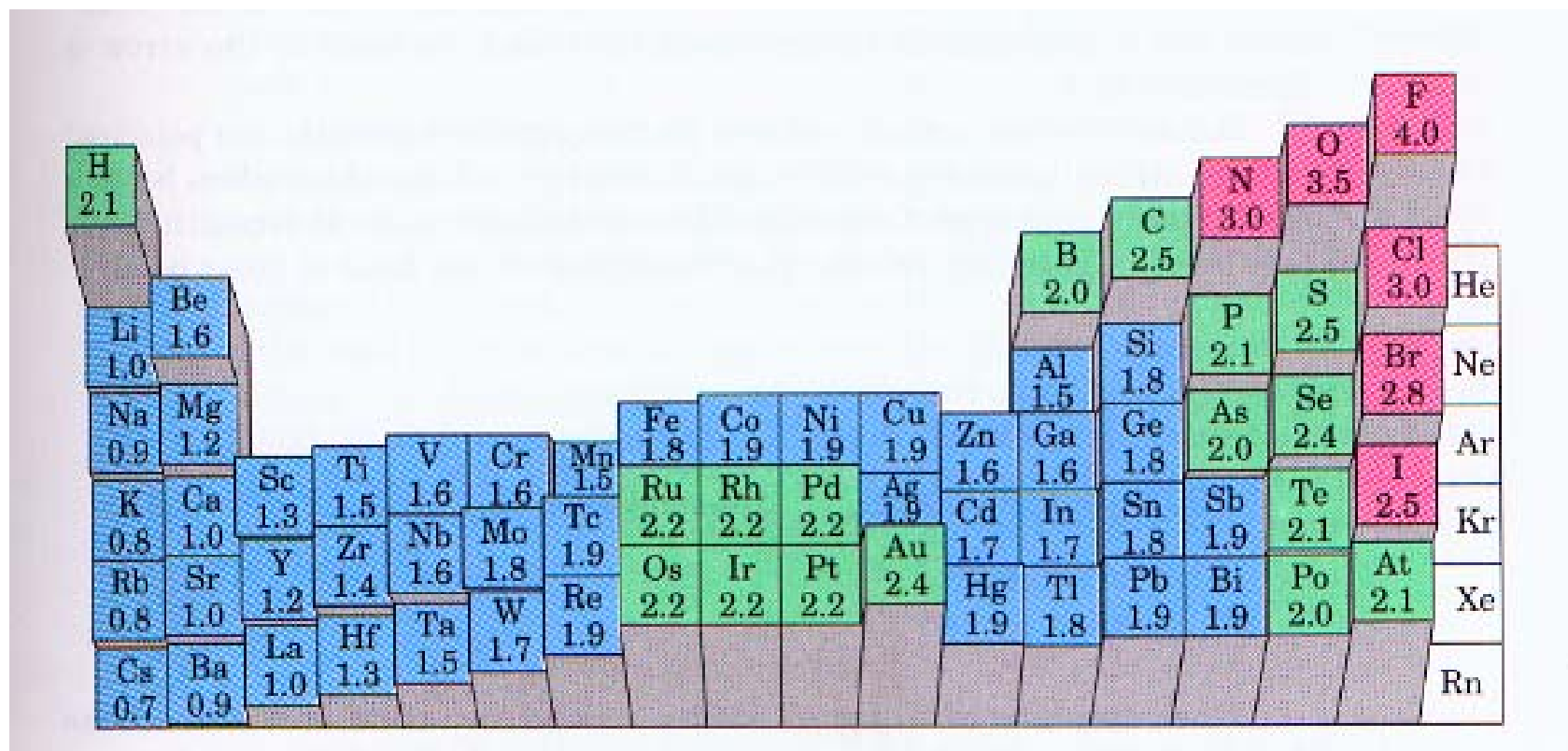
The bond angles are approximately  $120^\circ$ .



Acetylene



# Electronegativity of the elements



Electronegativity measures the ability of an element to attract electrons in a covalent bond.

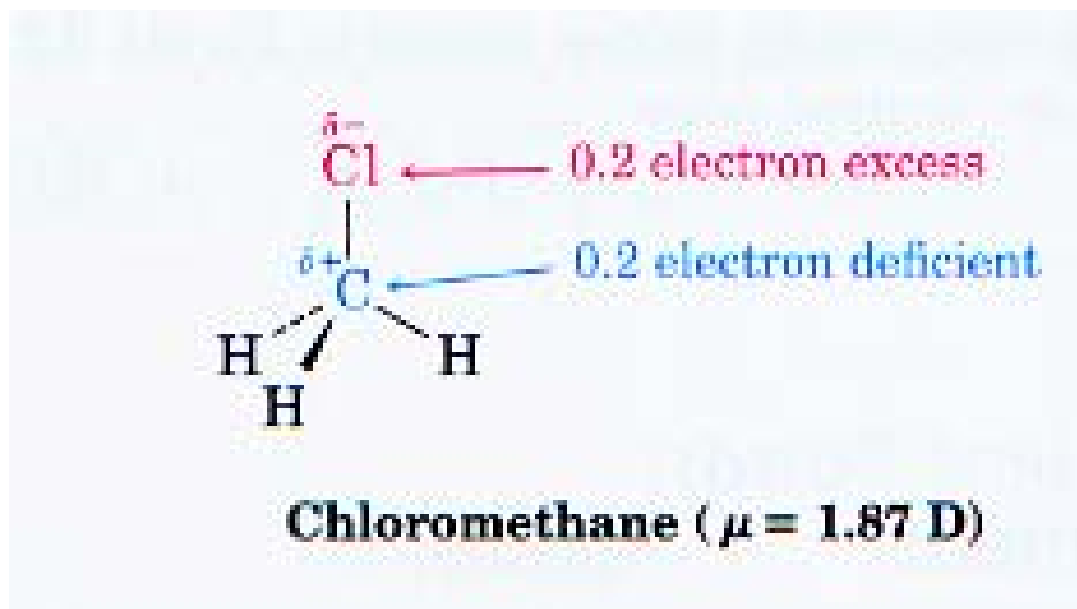
# Dipole moment

$$\mu = q \times r$$

$$1 \text{ Debye} = 3.336 \times 10^{-30} \text{ Coulomb-meter}$$

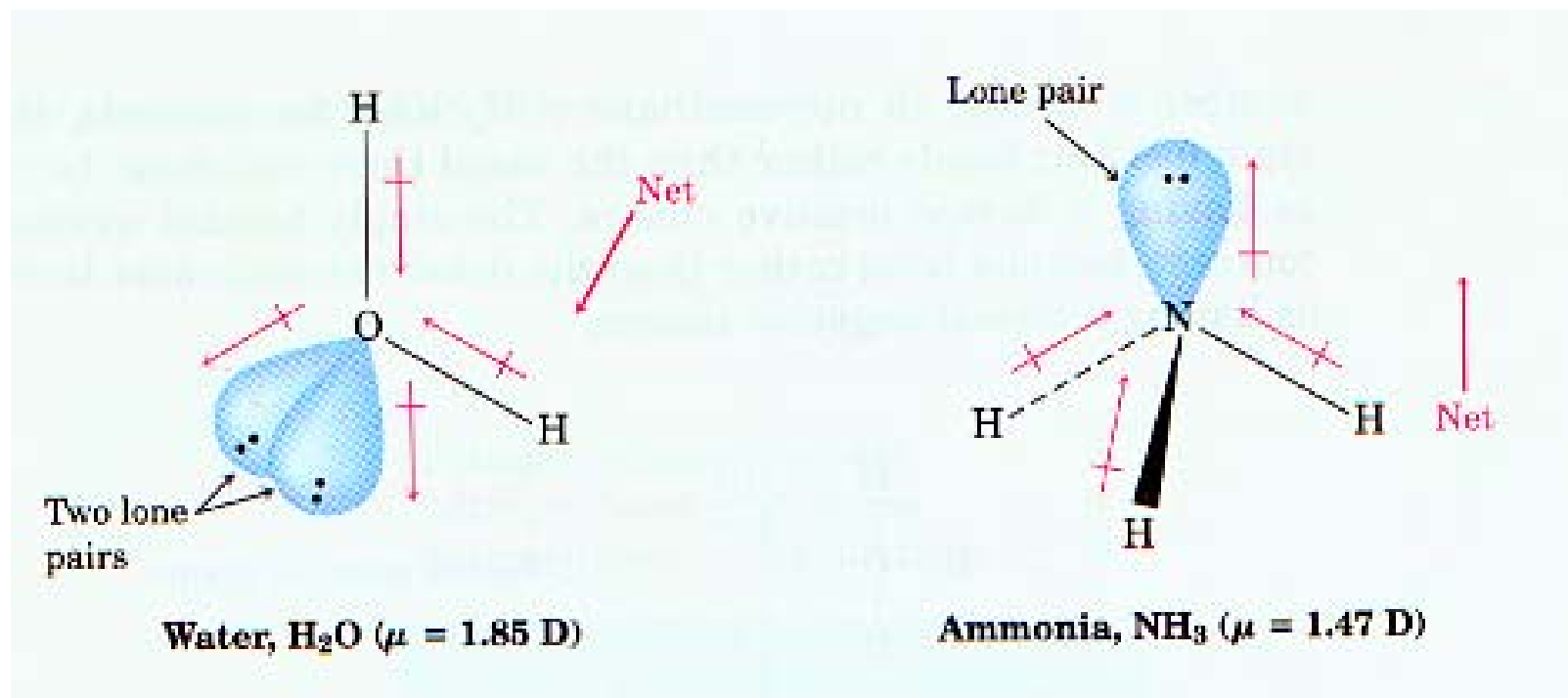
If one proton and one electron are separated by 1 Å, then

$$\mu = (1.6 \times 10^{-19} \text{ C})(10^{-10} \text{ m}) = 4.8 \text{ D.}$$



$$r = 1.78 \text{ Å}$$

## Dipole moments add as vectors



# Band structure of conjugated polymers



When there are many p electrons, the  $\pi$  energy levels become very close to each other and we say that there are energy bands. The gap between the  $\pi$  and  $\pi^*$  levels in the band gap of the semiconductor.



The band gaps of conjugated polymers are in the range of 1 to 3 eV.

# Formation and propagation of solitons



Event 1: Two gray dopant molecule accept an electron from the polymer.

Event 2: The unpaired electrons migrate towards each other and pair up to form a double bond.

Event 3: The positively charged solitons move in an electric field.

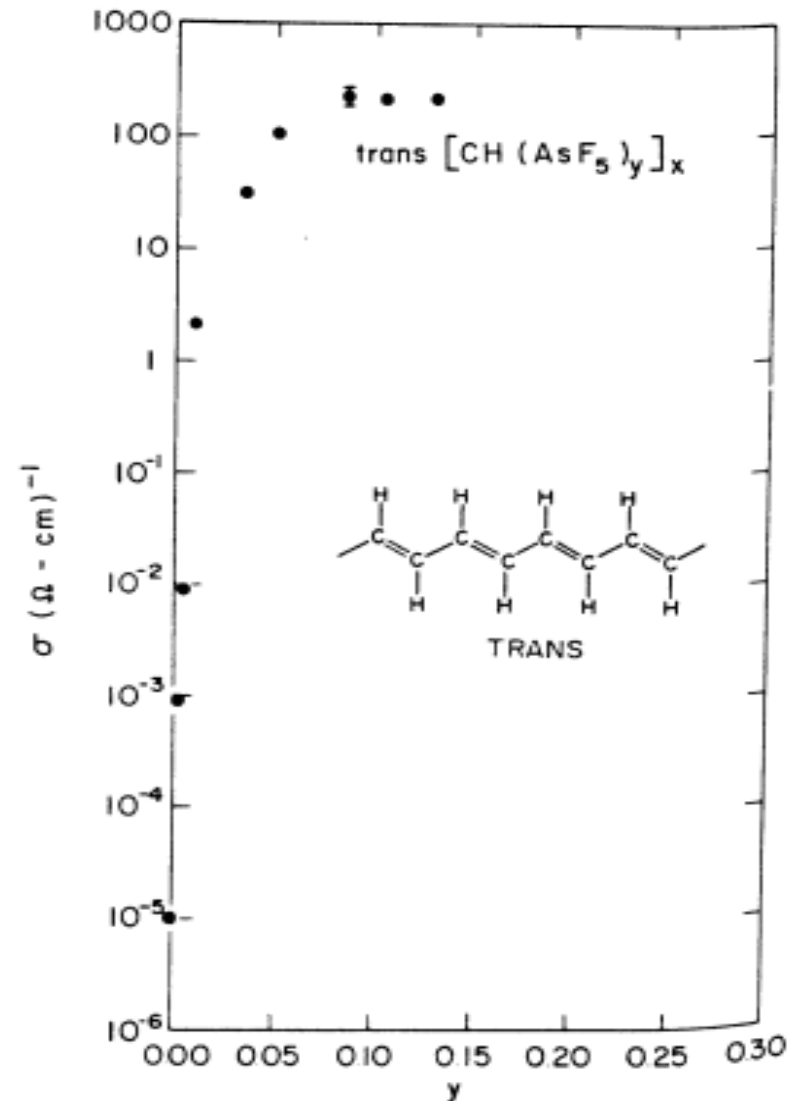
The additional doping molecules that come at the end signify what happens when the polymer is further doped.

This movie can be viewed at <http://www.nobel.se/chemistry/laureates/2000/press.html>

# Electrical conductivity of $trans\text{-(CH)}_x$ as a function of $(\text{AsF}_5)$ dopant concentration

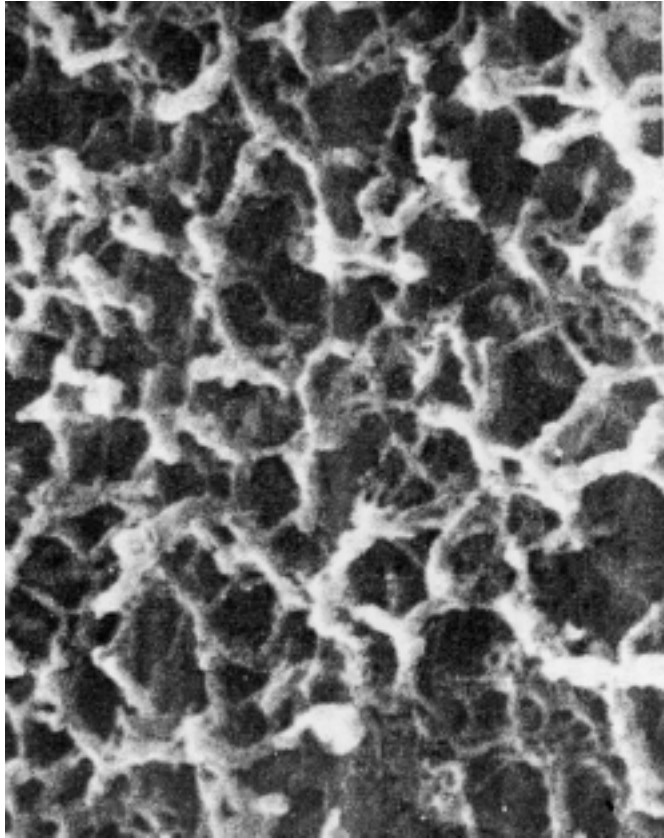
For comparison, the conductivity of copper is  $10^6 (\text{Ohm-cm})^{-1}$ .

In 2000, Heeger, MacDiarmid and Shirakawa won the Nobel Prize in Chemistry for this experiment and their development of the science and technology of conjugated polymers.

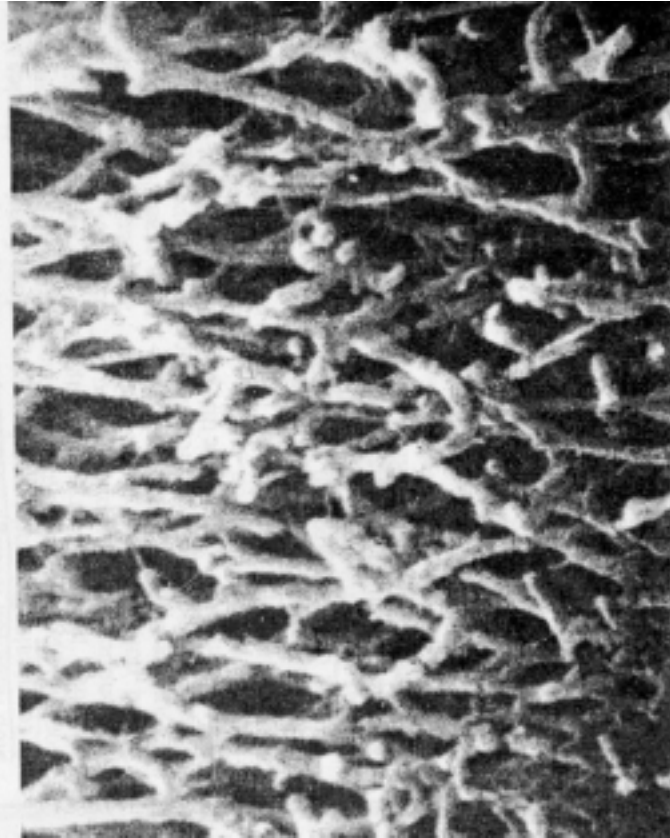


# How conductive can polymers be?

Unstretched



Stretched



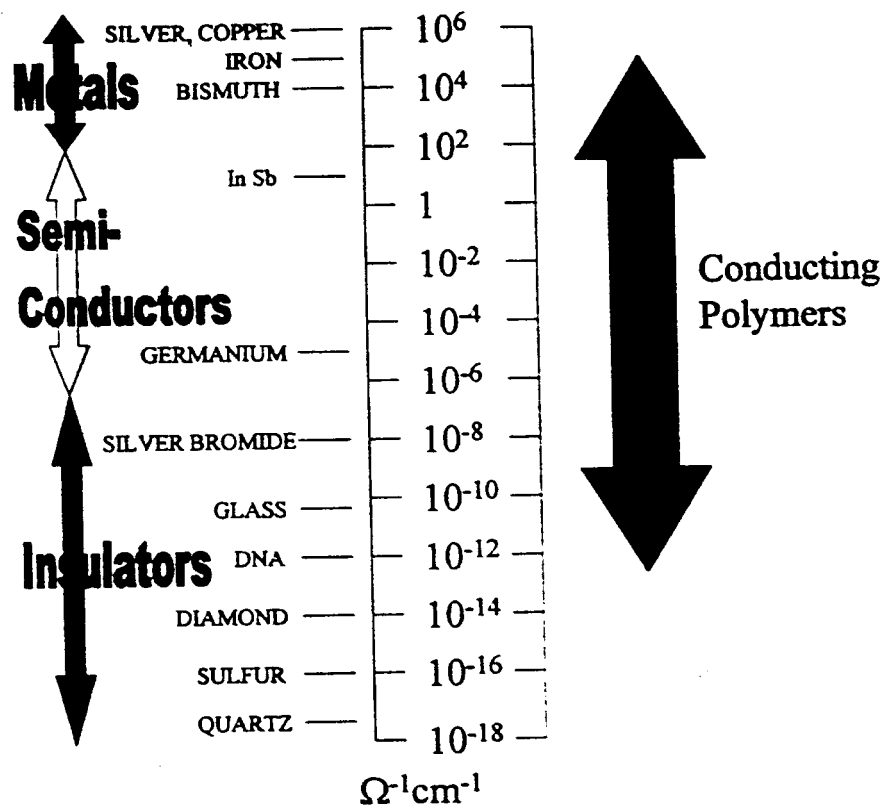
Stretching polyacetylene aligns the chains and improves conductivity. Each fiber shown here consists of about 1,500 polymer chains. A goal of molecular electronics is to use individual polymer chains.



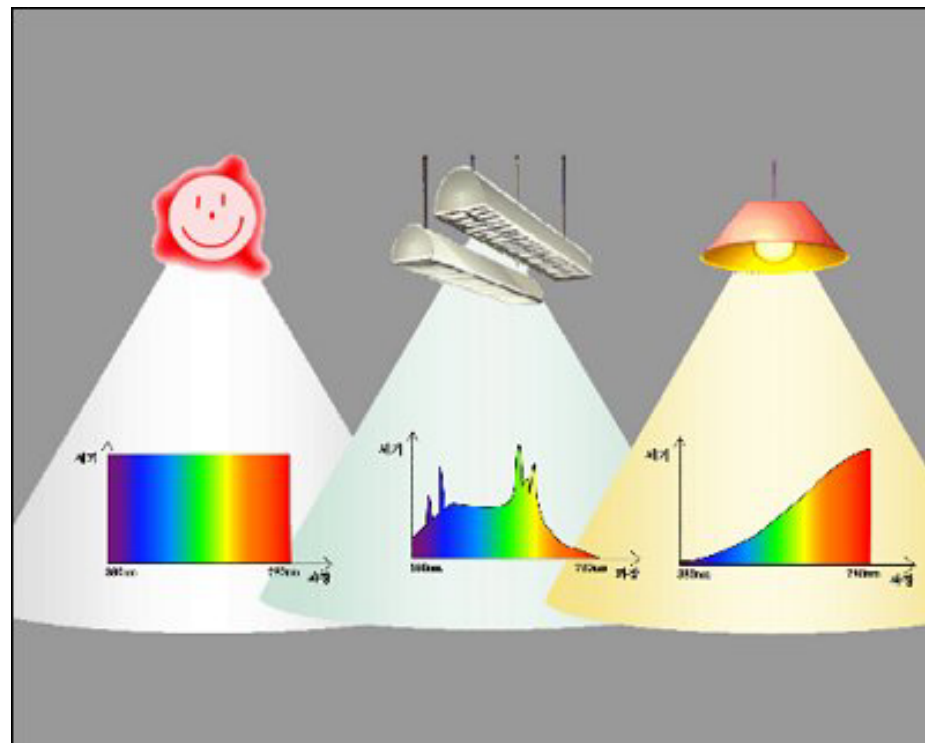
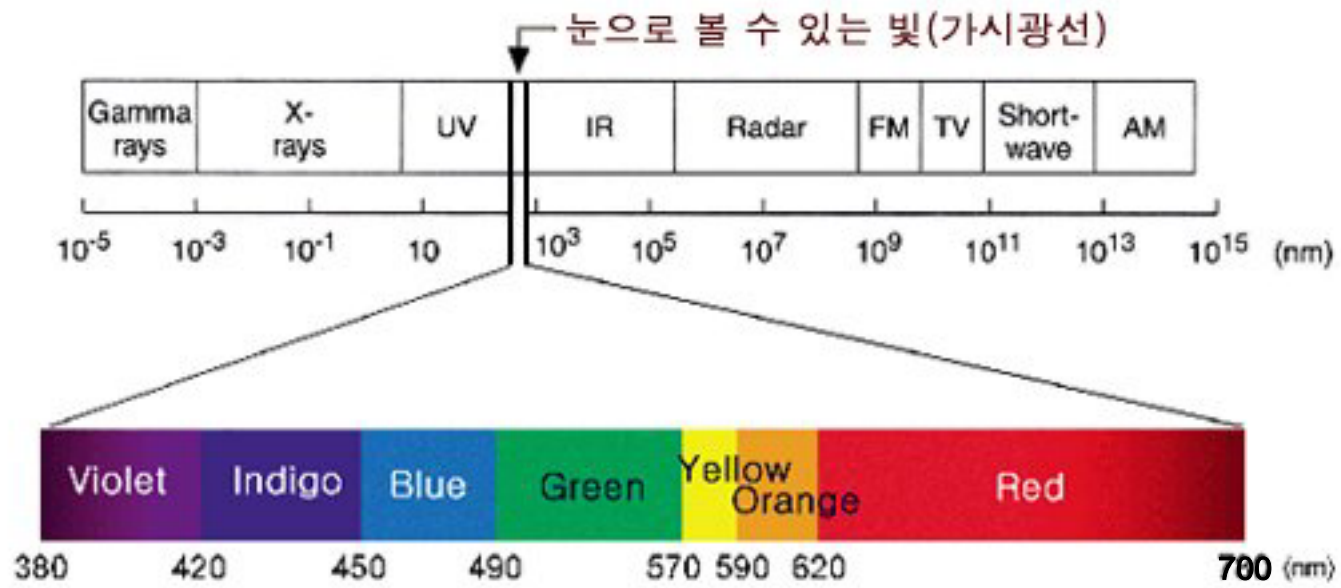
# Comparison of conjugated polymers to other materials

Stretch-aligning polyacetylene and removing chemical defects has increased the conductivity to  $10^5 \text{ Ohm}^{-1}\text{cm}^{-1}$ . Further improvements are expected.

## Electrical Conductivity

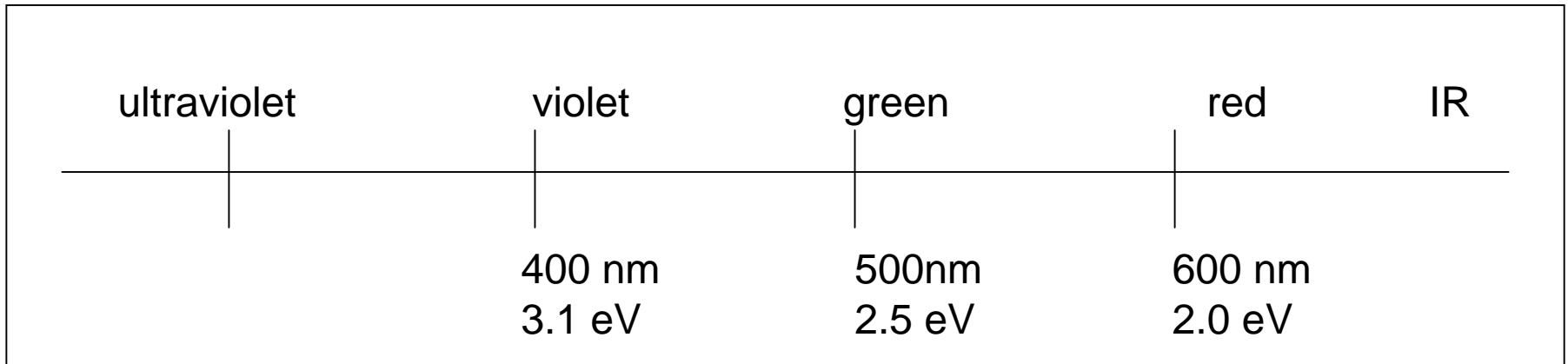


Full range of electrical conductivity:  
INSULATOR to METAL.

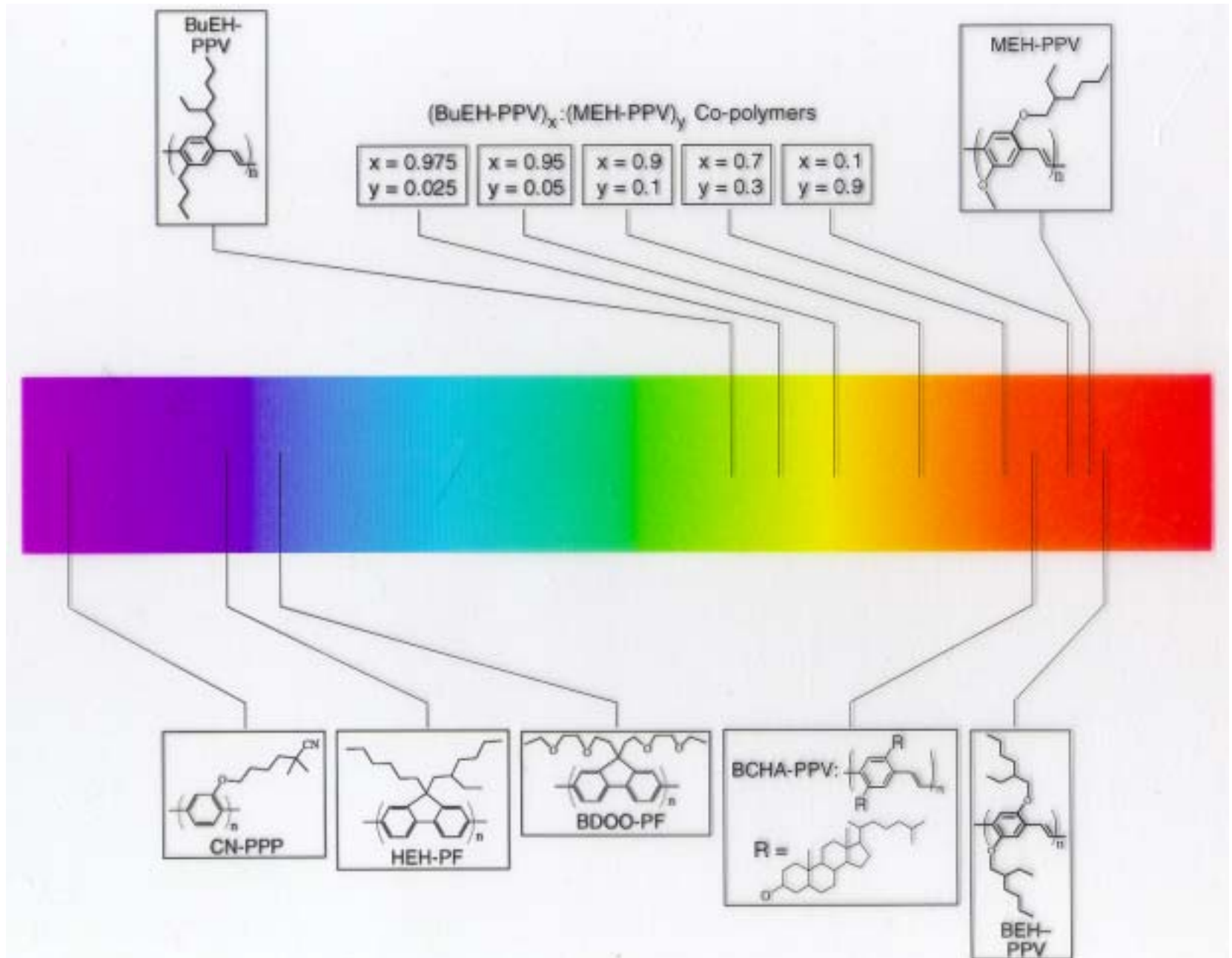


# Why some organic materials are colored

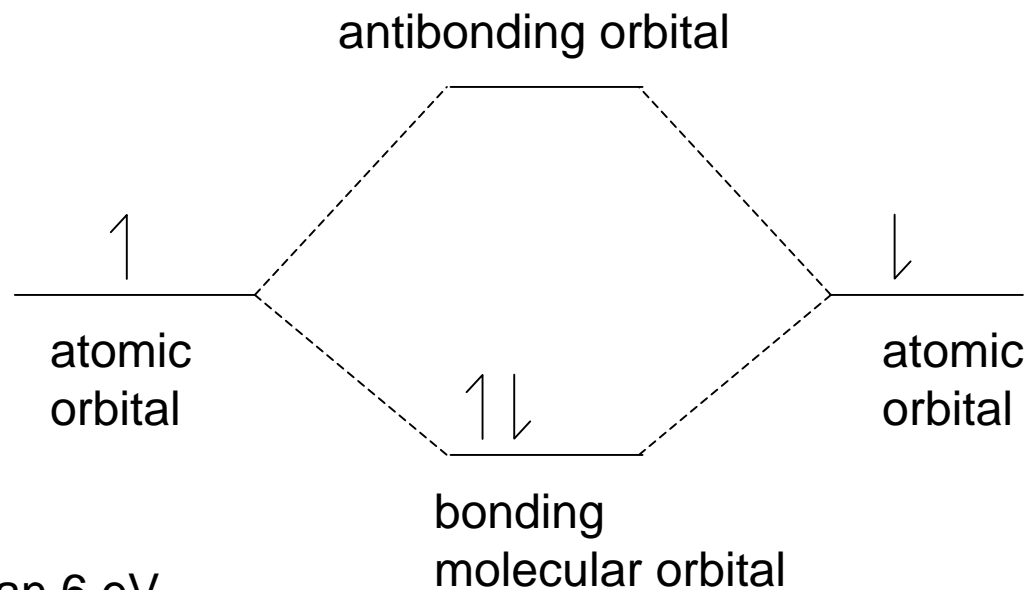
- Most plastics have band gaps greater than 3 eV. Consequently, they do not absorb any photons in the visible spectrum.
- Conjugated dyes and polymers have bandgaps in the 1 -3 eV range, so they absorb visible photons and appear colored.
- Most colored plastics have dyes blended in them. The dye, not the plastic, is responsible for the color.



# Examples of conjugated polymers with a range of band gaps



# Absorption and emission spectra



The  $\sigma-\sigma^*$  gap is usually greater than 6 eV.

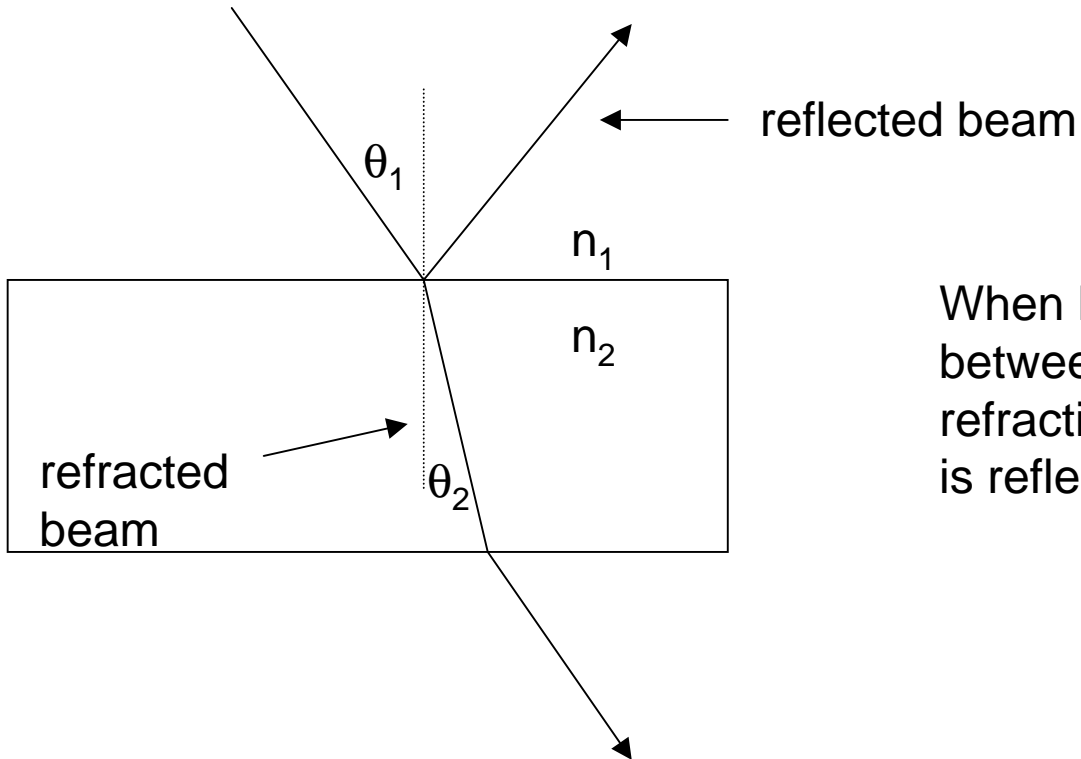
The  $\pi-\pi^*$  gap is typically 1-4 eV.

The visible region of the spectrum is 2-3 eV.

Many materials with double bonds absorb in the visible region of the spectrum and appear colored.

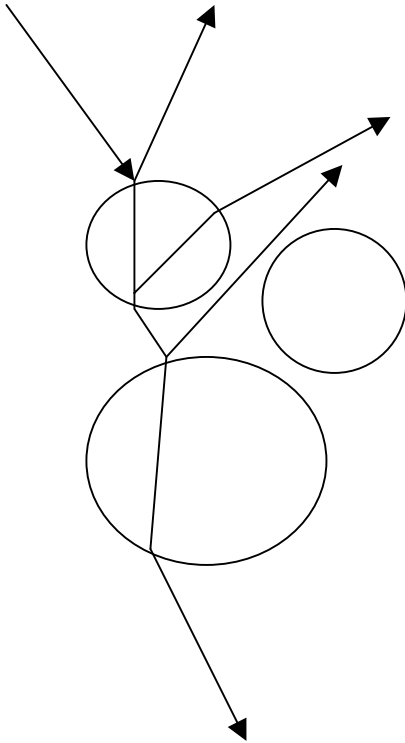
Organic materials with nothing but single bonds tend to be transparent, unless they scatter light, in which case they appear white.

# Reflection and refraction



When light encounters a boundary between two regions with different refractive indices, part of the beam is reflected and part is refracted.

# Scattering



If the refractive index in a material varies, light gets reflected and refracted into random directions.

In this example, the circular regions have a higher index than the surrounding region.

Milk looks white because it has lots of fat particles that scatter all of the different wavelengths of light into random directions.

## Three classifications

**Transparent** - Light passes through. Images can be seen with little distortion.

**Translucent** - Light passes through, but is scattered so much that images can not be seen.

**Opaque** - Light does not pass through. It is either absorbed or severely scattered.



# What do the optical properties tell us about the structure of a material?

If a material is **transparent**, then it must have a large energy gap since it is not absorbing the light and it must be homogenous since it is not scattering the light. The material is probably completely crystalline or completely amorphous.

If a material is **translucent**, then it must have spatial variations in its refractive index. It is likely that the material is partially crystalline and partially amorphous or that it has two different components that are not fully mixed. The fluctuations in refractive index must occur on a length scale that is on the same order as the wavelength of the light. If the fluctuations occur at the nanometer length scale, the light will just sense the average refractive index.

If a material is **opaque**, it either absorbs all of the light or has very large fluctuations in refractive index.



발 산

지 각



(가)



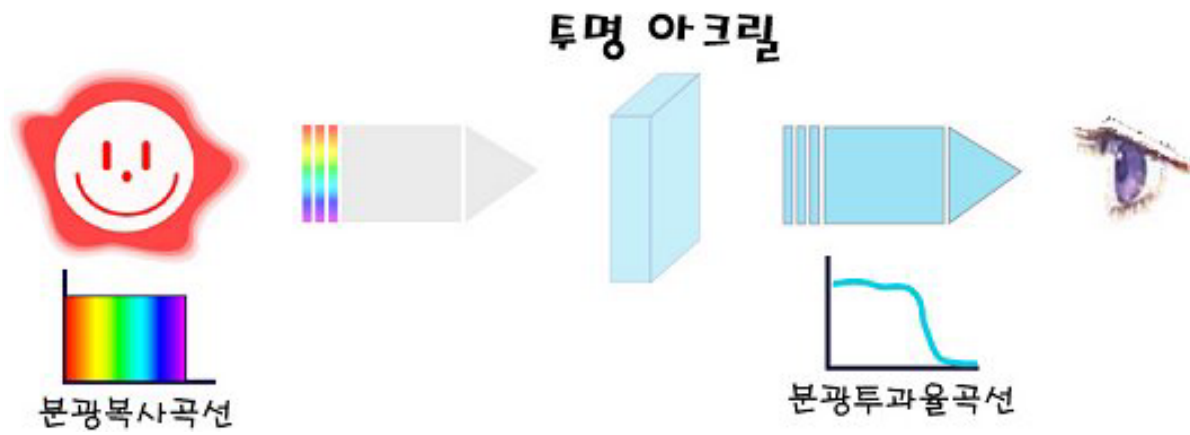
반 사

지 각



(나)

색의 정의에 대한 개념도 (가) 반사체가 없는 경우의 색 (나) 반사체가 있는 경우의 색



### 3 (three attributions of color)

(色相, hue)

- (wavelength)
- , , , , ,

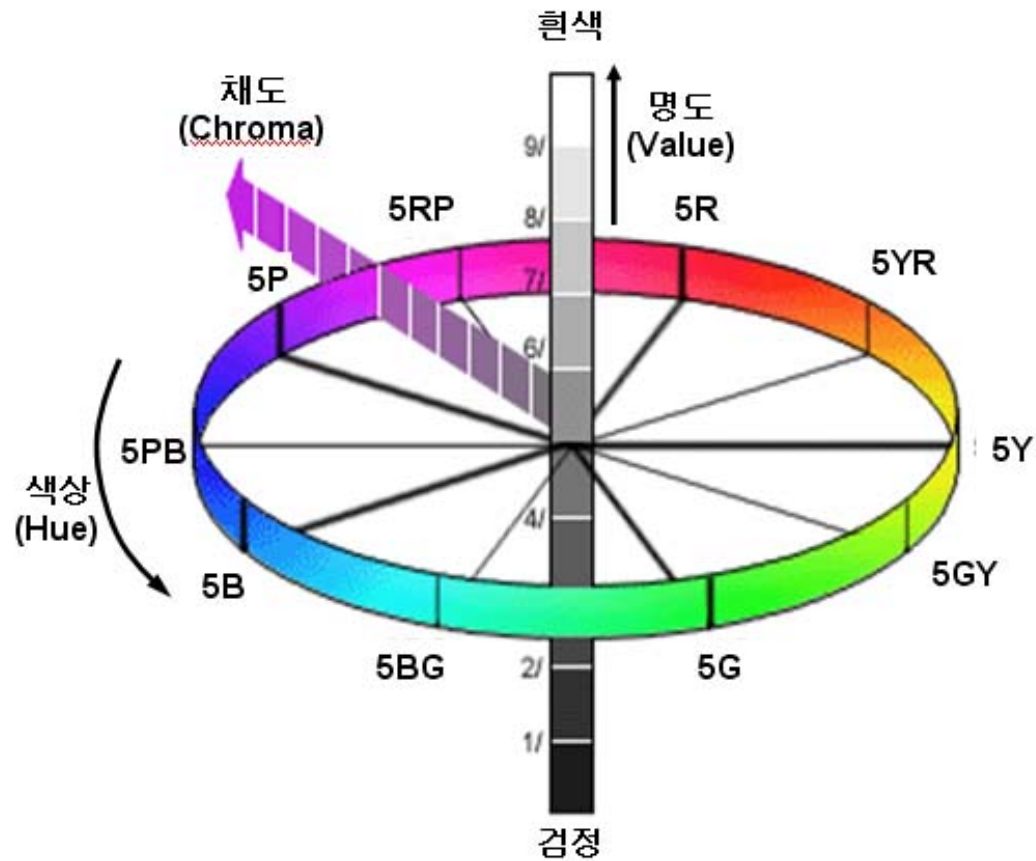
(明度, lightness)

- 
- 3 가
- value

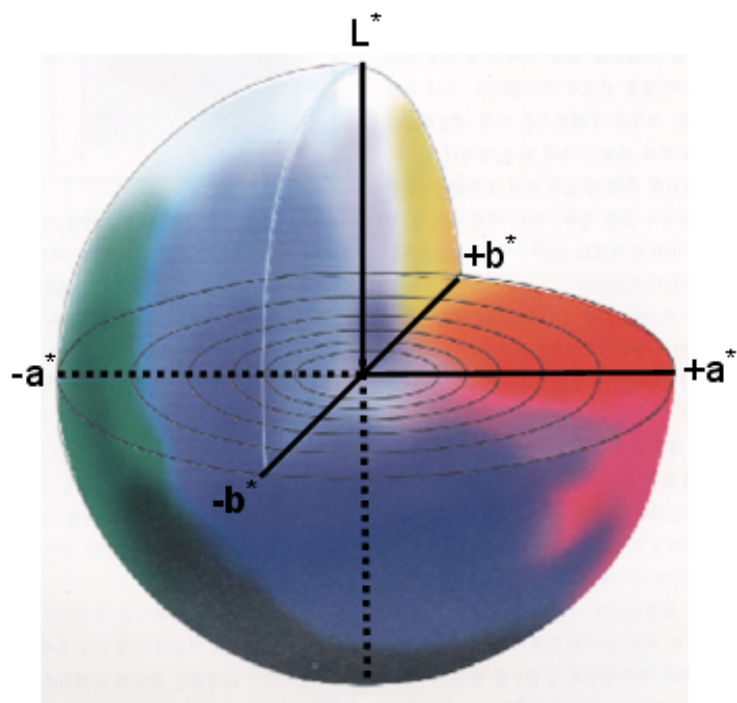
(彩度, chroma)

- ,
- ,

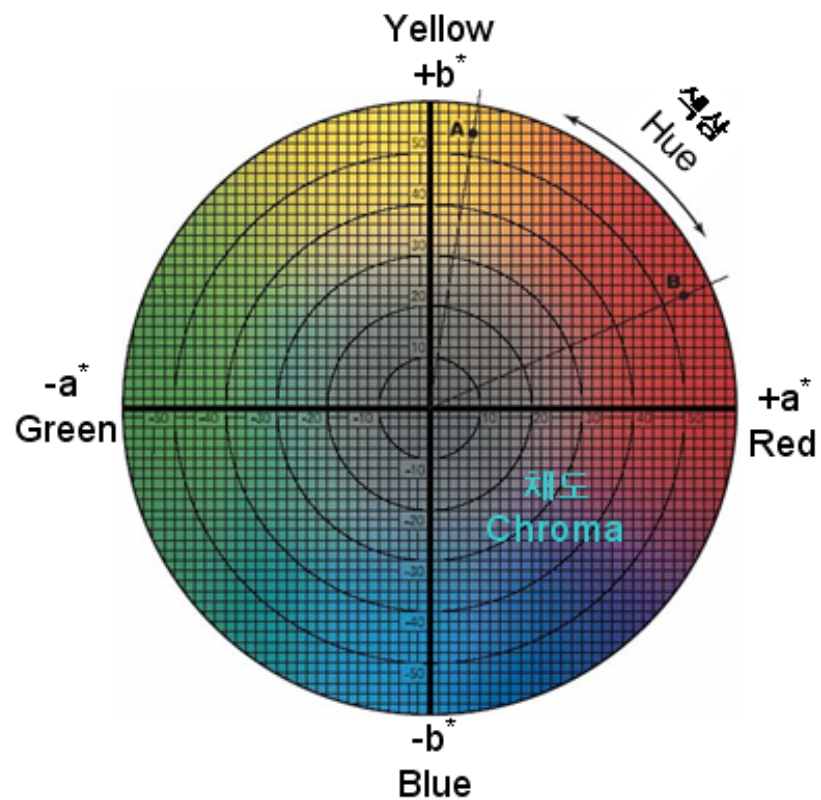
# Munsell Color System



Munsell



(가)



(나)

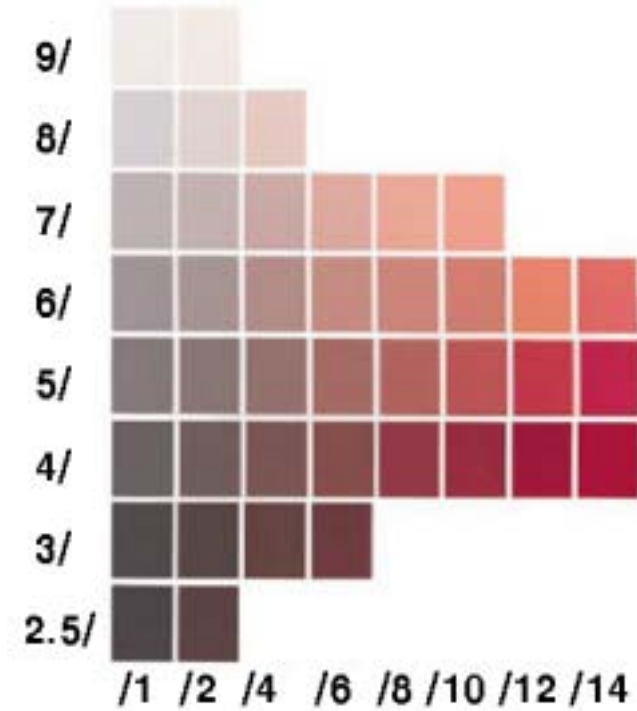
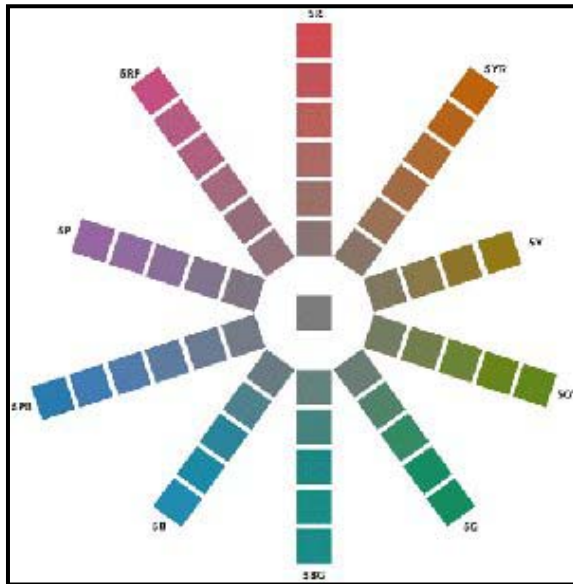
CIE 1976  $L^*a^*b^*$  (CIELAB)

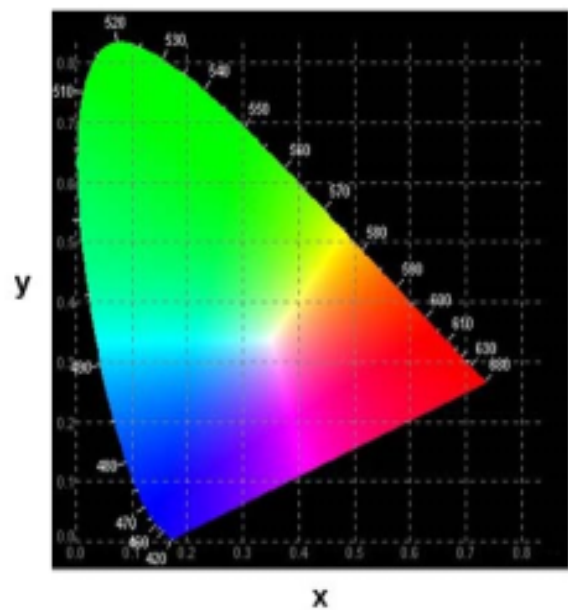


(色相, hue)

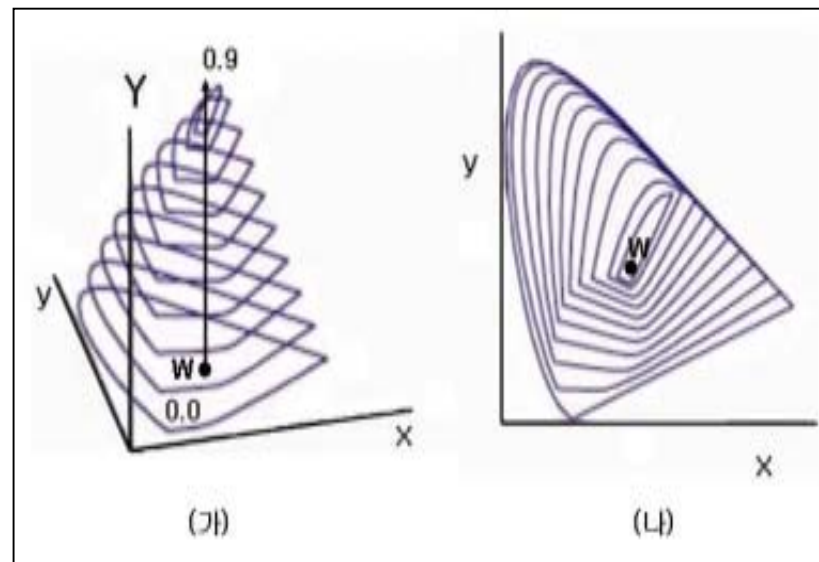
(明度, lightness)

(彩度, chroma)





**x y**  
(chromaticity diagram)



(가) **x y Y**

(나) **x y Y**