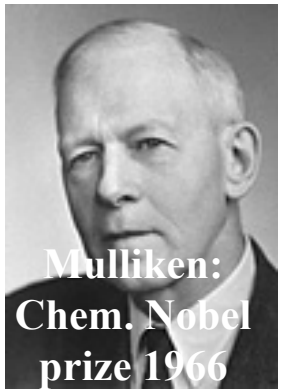
Heteronuclear Diatomic Molecules

⇒ **Polar bond: Electron distribution is not symmetric, e.g., $H^{\delta+}F^{\delta-}$**

Electronegativity χ = power of an atom to draw electrons to itself

$$|\chi_A - \chi_B| = 0.102 \times \sqrt{\frac{\Delta E}{kJmol}}; \quad \text{with } \Delta E = E(AB) - \frac{1}{2}\left(E(AA) + E(BB)\right)$$

Bond dissociation energies

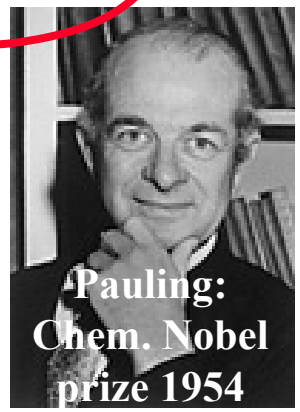


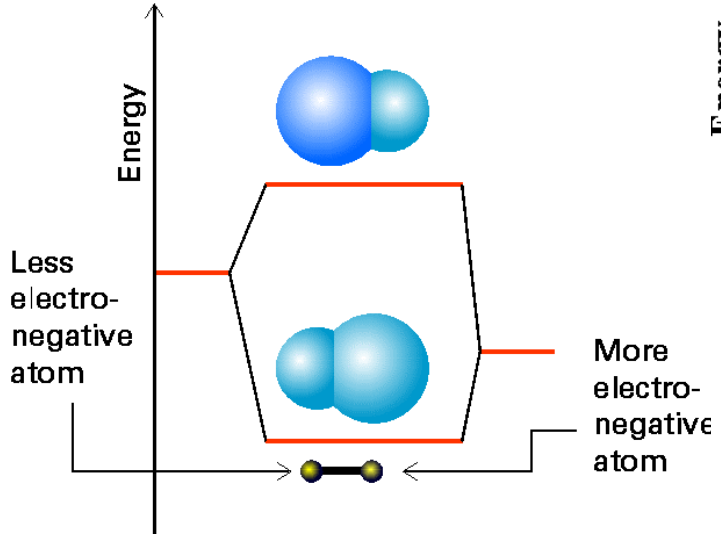
$$\chi = \frac{1}{2}(I + E_{ea})$$

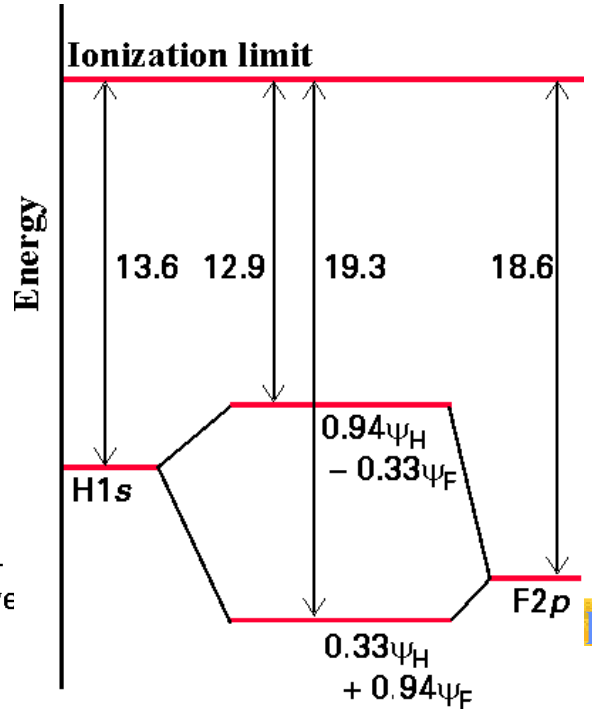
ionization energy

electron affinity

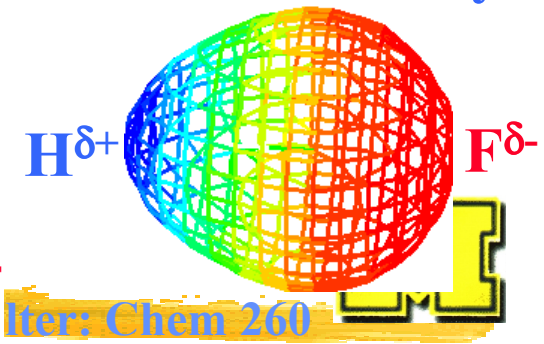
$$\Psi = c_H \Psi_H + c_F \Psi_F; \; c_F > c_H$$







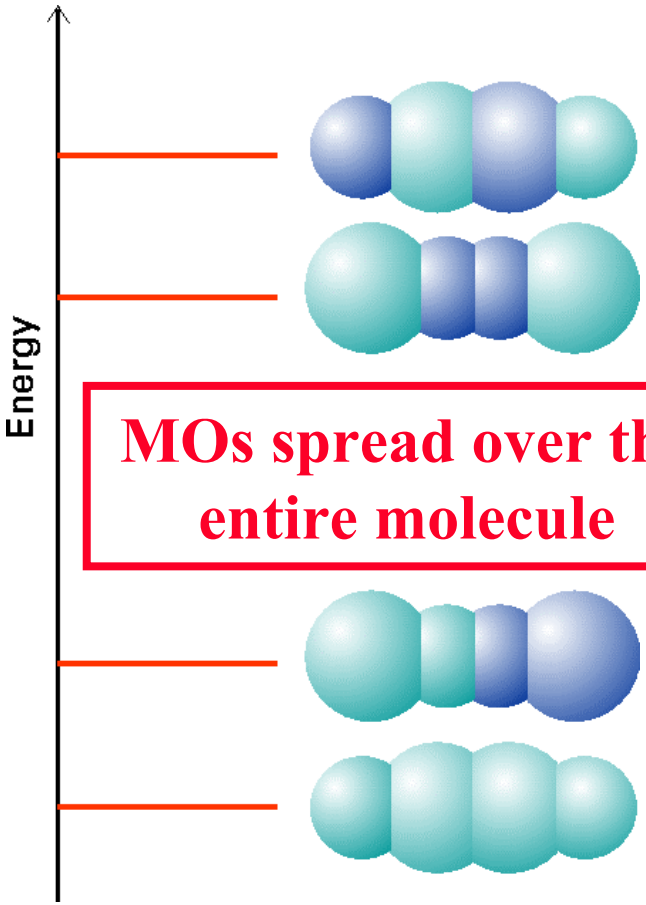
Electron density:



Polyatomic Molecules

LCAO-MOs of four atoms in a row:

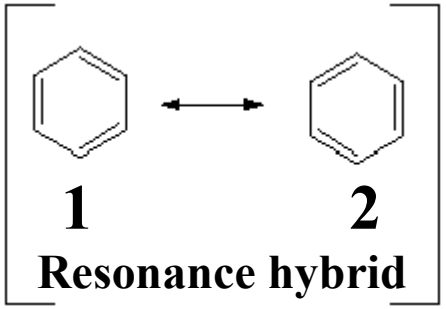
$$\Psi = c_A \Psi_A + c_B \Psi_B + c_C \Psi_C + c_D \Psi_D$$



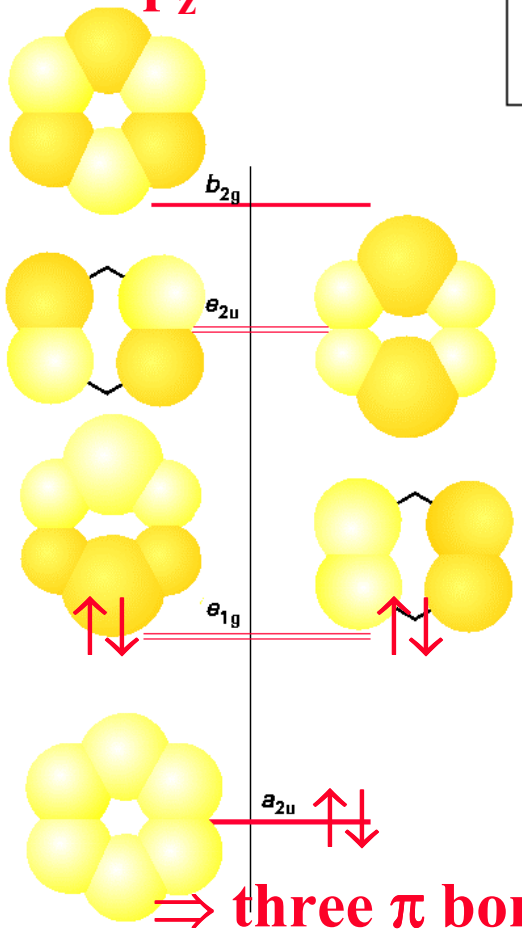
MOs spread over the entire molecule

shading = signs of AOs combined

C_6H_6: benzene



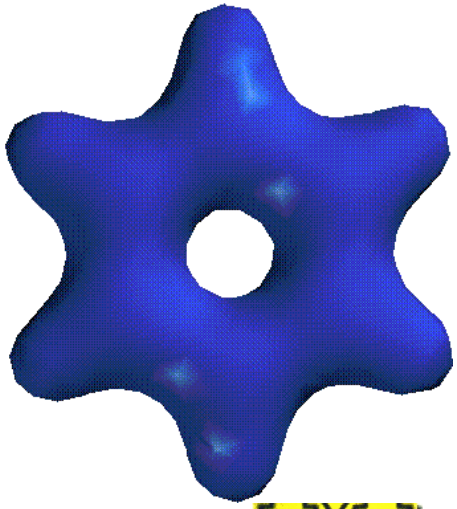
Six p_z orbitals:



$\Rightarrow$ three π bonds

Electron density:

A donut!



hem 260

Chemical Bonds are Only Part of the Story: Cohesion of Molecules

Atkins, Chapter 16

Example 1: Ion-ion interactions

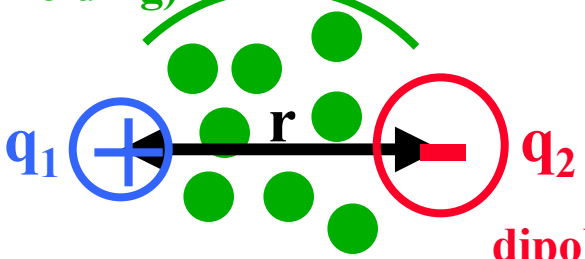
$\Rightarrow V < 0$ (attractive) for unlike charges q_1, q_2

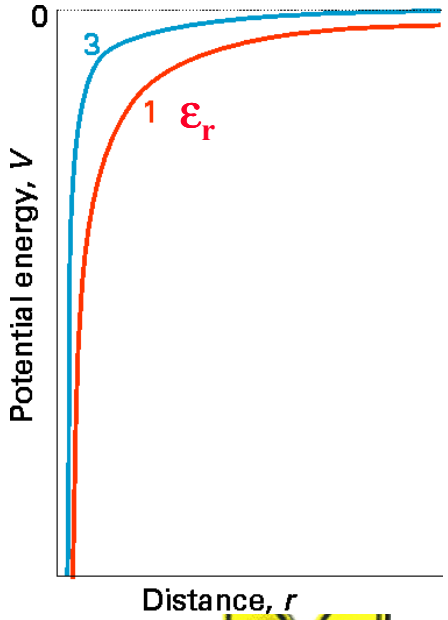
$$V = \frac{q_1 q_2}{4\pi\varepsilon_r\varepsilon_0 r}$$

vacuum permittivity

relative permittivity (shielding)

Coulomb: 1736-1806

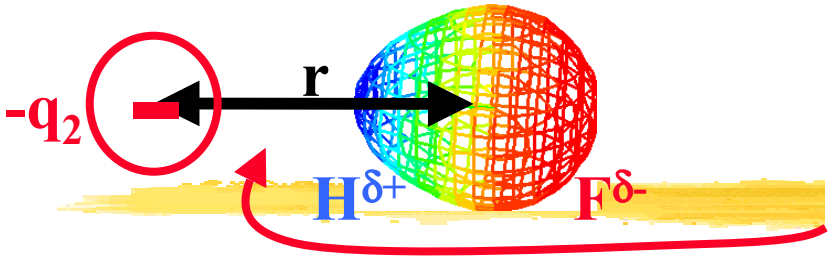




dipole moment

Example 2: Ion-dipole interactions

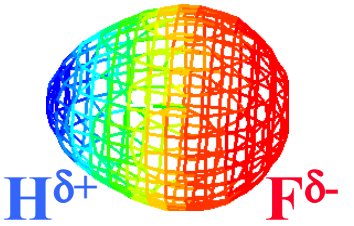
$$V = -\frac{\mu_1 q_2}{4\pi\varepsilon_r\varepsilon_0 r^2}$$

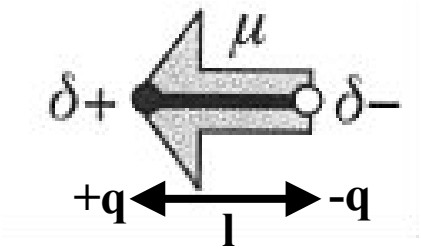


attractive for this orientation

less long-range

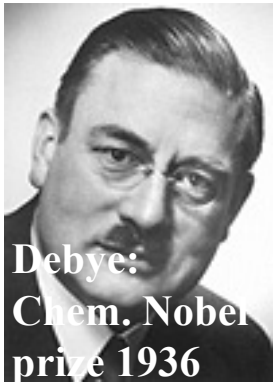
Electric Dipole Moments



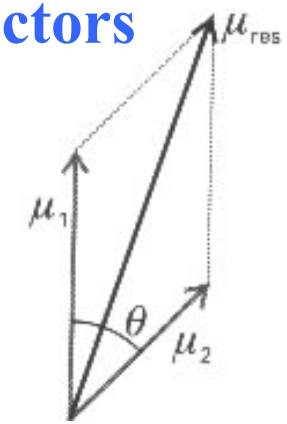


$$\mu = ql$$

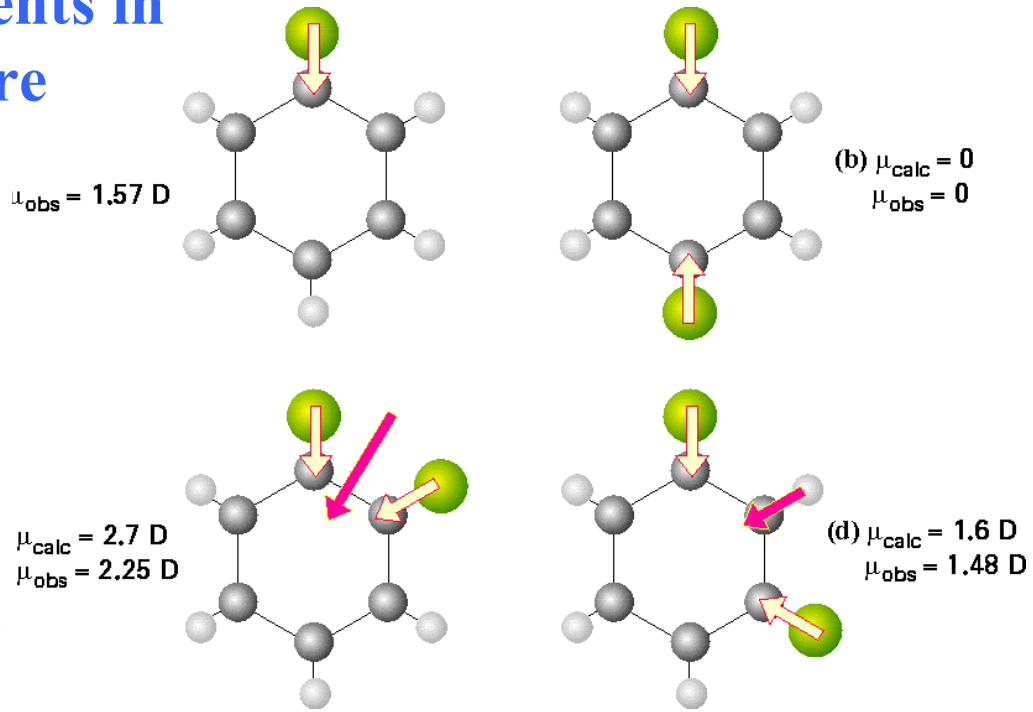
[Cm;
1 D(ebye) =
3.34 x10^{-30}Cm]



Dipole moments in a molecule are additive as vectors

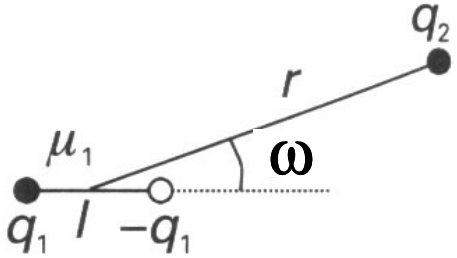


E.g., dichlorobenzenes:



$$\mu_{total} = \sqrt{\mu_1^{\,2} + \mu_2^{\,2} + 2\mu_1\mu_2\cos\theta}$$

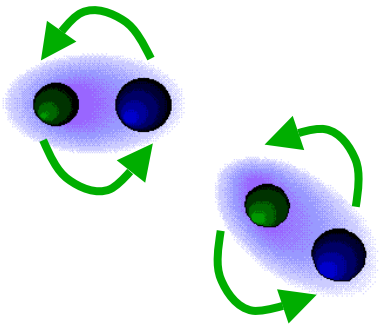
⇒ **Example 2: Ion-dipole interactions**

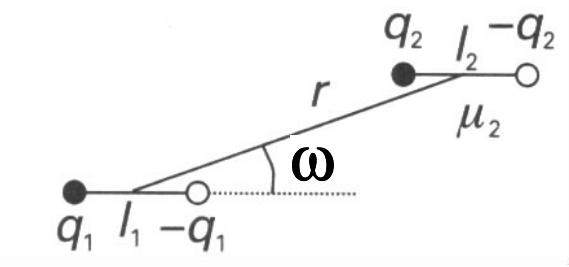


$$V = -\frac{\mu_1 q_2 \cos\omega}{4\pi\varepsilon_r\varepsilon_0 r^2}$$

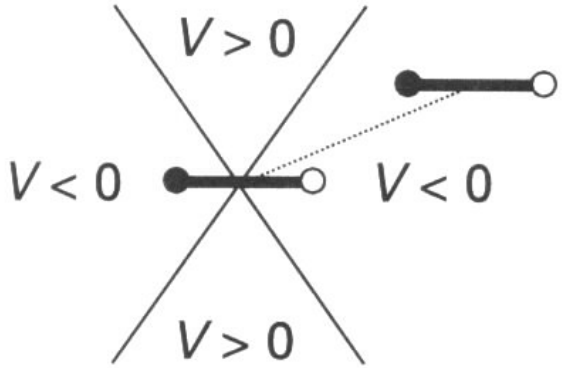
Dipole-Dipole Interactions

Example 3: Dipole-dipole interactions





$$V = \frac{\mu_1\mu_2(1-3\cos^2\omega)}{4\pi\varepsilon_r\varepsilon_0 r^3}$$



if the dipoles are fixed

in solution: rotation

but attractive orientations are favored ⇒

$$V = -\frac{2}{3}\frac{\mu_1^2\mu_2^2}{(4\pi\varepsilon_r\varepsilon_0)^2 r^6}\frac{1}{kT}$$

attractive

even less long-range

Example 4: Dispersion interactions

Induced dipoles

London formula

polarizabilities

$$V = -\frac{3}{2}\frac{\alpha_1\alpha_2}{(4\pi\varepsilon_r\varepsilon_0)^2 r^6}\frac{I_A I_B}{I_A + I_B}$$