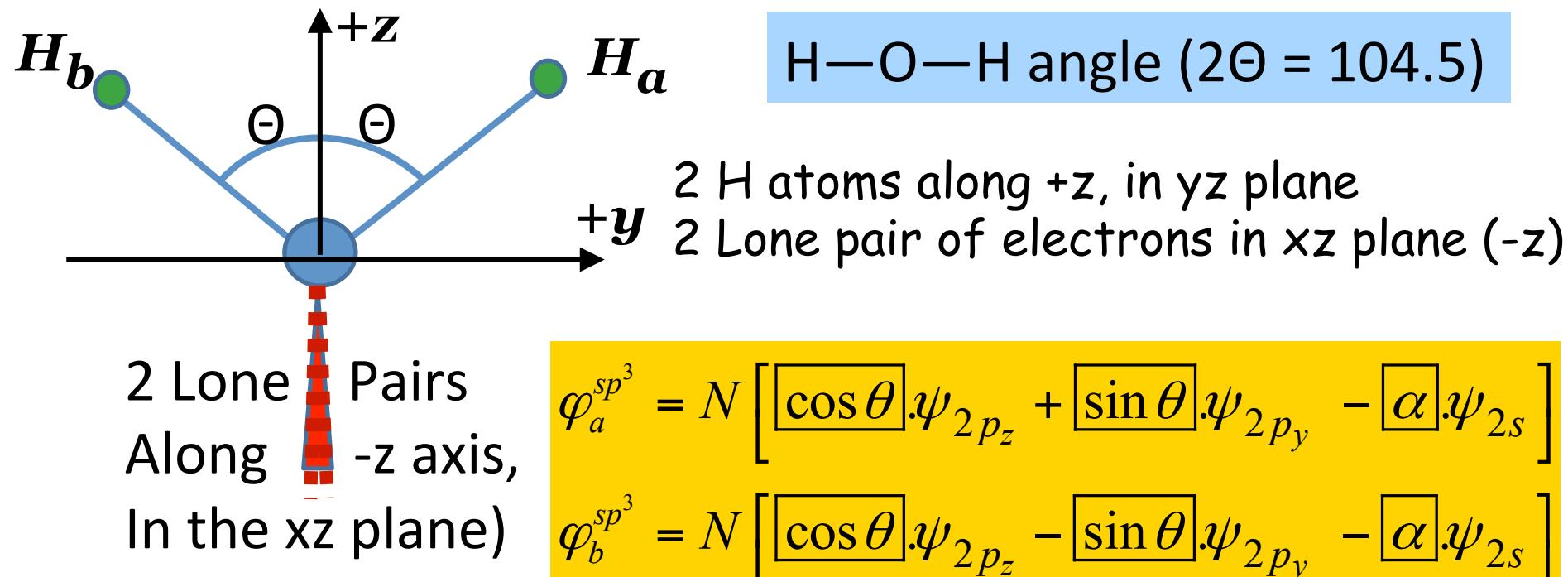
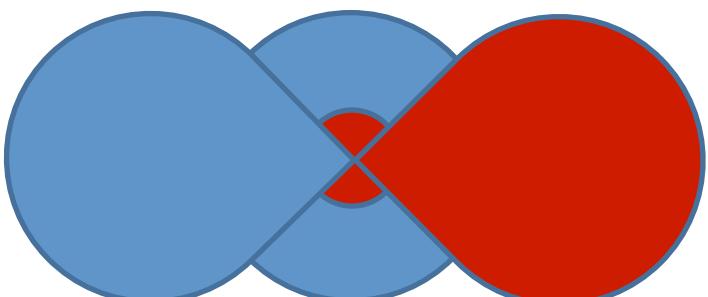


Non-equivalent Hybrid Orbitals: H₂O



Why take a negative sign of coefficient for 2s?



Will end up with a “-” sign on each hybrid orbital; which have to form MO with 1s of H (with + sign)

Coefficients of 2 Hybrid Orbitals involved in bonding with H(1s)

Hybrid orbitals are Orthogonal: $0 = \int \varphi_a^{sp^3} \cdot \varphi_b^{sp^3} d\tau = \langle \varphi_a^{sp^3} | \varphi_b^{sp^3} \rangle$

$$= N^2 \left\langle \left[\cos \theta \psi_{2p_z} + \sin \theta \psi_{2p_y} - [\alpha] \psi_{2s} \right] \middle| \left[\cos \theta \psi_{2p_z} - \sin \theta \psi_{2p_y} - [\alpha] \psi_{2s} \right] \right\rangle$$
$$0 = N^2 \left[\cos^2 \theta \langle \psi_{2p_z} | \psi_{2p_z} \rangle - \sin^2 \theta \langle \psi_{2p_y} | \psi_{2p_y} \rangle + \alpha^2 \langle \psi_{2s} | \psi_{2s} \rangle \right]$$

$$N^2 [\cos^2 \theta - \sin^2 \theta + \alpha^2] = N^2 [\cos 2\theta + \alpha^2] = 0$$
$$\rightarrow \boxed{\cos 2\theta = -\alpha^2 \rightarrow 180^\circ \geq 2\theta \geq 90^\circ} \text{ (Consistent!)}$$

In H_2O , H – O – H angle: $2\theta = 104.5^\circ \rightarrow \theta = 52.25^\circ$

$$\varphi_a^{sp^3} = N \left[\boxed{0.61} \psi_{2p_z} + \boxed{0.79} \psi_{2p_y} - \boxed{0.50} \psi_{2s} \right]$$

$$\varphi_b^{sp^3} = N \left[\boxed{0.61} \psi_{2p_z} - \boxed{0.79} \psi_{2p_y} - \boxed{0.50} \psi_{2s} \right]$$

Normalize each bonding-hybrids to obtain correct coefficients

$$\text{Normalize} \rightarrow 1 = \int \varphi_a^{sp^3} \cdot \varphi_a^{sp^3} d\tau = \left\langle \varphi_a^{sp^3} \middle| \varphi_a^{sp^3} \right\rangle$$

$$1 = N^2 \left[(0.61)^2 \left\langle \psi_{2p_z} \middle| \psi_{2p_z} \right\rangle + (0.79)^2 \left\langle \psi_{2p_y} \middle| \psi_{2p_y} \right\rangle + (0.50)^2 \left\langle \psi_{2s} \middle| \psi_{2s} \right\rangle \right]$$

$$N^2 = 1 / \left[(0.61)^2 + (0.79)^2 + (0.50)^2 \right] \rightarrow N = 0.89$$

$$\varphi_a^{sp^3} = 0.55\psi_{2p_z} + 0.71\psi_{2p_y} - 0.45\psi_{2s}$$

$$\varphi_b^{sp^3} = 0.55\psi_{2p_z} - 0.71\psi_{2p_y} - 0.45\psi_{2s}$$

% P character: $(0.55)^2 + (0.71)^2 = 0.80$ (80%)

% S character = $(-0.45)^2 = 0.2$ (20%)

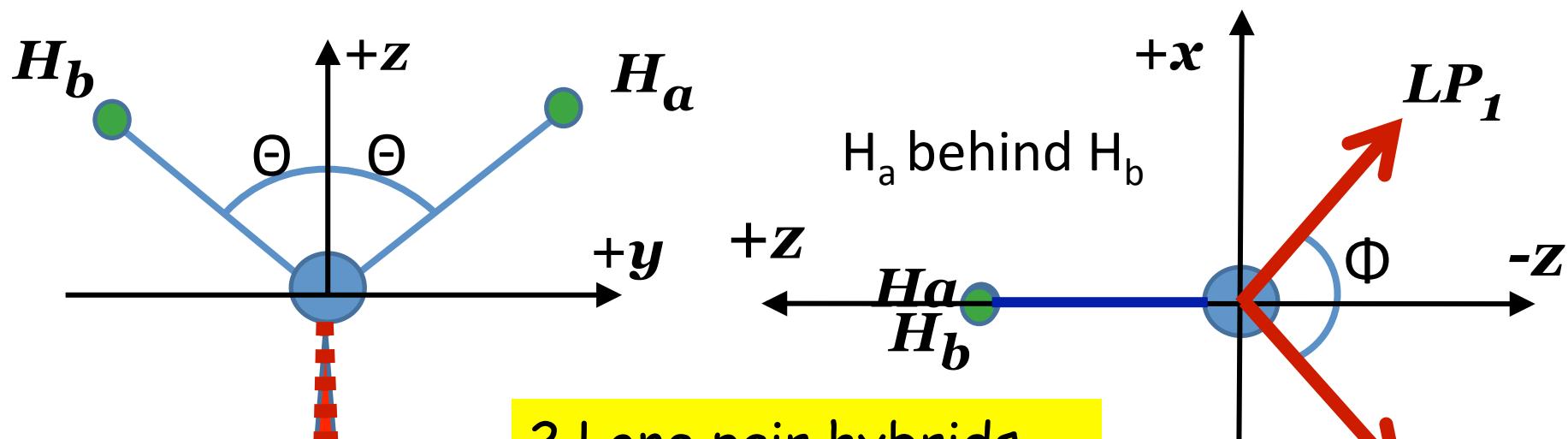
→ more like SP4 , rather than SP3

What happens to the lone pairs of electrons?

Lone-pair hybrid orbitals will have different coefficients!

$$\varphi_{lp1}^{sp^3} = d_1.\psi_{2p_z} + d_2.\psi_{2p_y} + d_3.\psi_{2s} + d_4.\psi_{2p_x}$$

$$\varphi_{lp2}^{sp^3} = d_5.\psi_{2p_z} + d_6.\psi_{2p_y} + d_7.\psi_{2s} + d_8.\psi_{2p_x}$$



2 Lone pair hybrids
along negative z axis
and in xz plane - No
contribution from p_y

Lone-pair hybrid orbitals will have different coefficients!

$$\varphi_{lp1}^{sp^3} = d_1.\psi_{2p_z} + d_2.\psi_{2p_y} + d_3.\psi_{2s} + d_4.\psi_{2p_x}$$

$$\varphi_{lp2}^{sp^3} = d_5.\psi_{2p_z} + d_6.\psi_{2p_y} + d_7.\psi_{2s} + d_8.\psi_{2p_x}$$

Because lone-pairs are directed along x-z plane: $d_2=d_6=0$

$$\varphi_{lp1}^{sp^3} = d_1.\psi_{2p_z} + 0.\psi_{2p_y} + d_3.\psi_{2s} + d_4.\psi_{2p_x}$$

$$\varphi_{lp2}^{sp^3} = d_5.\psi_{2p_z} + 0.\psi_{2p_y} + d_7.\psi_{2s} + d_8.\psi_{2p_x}$$

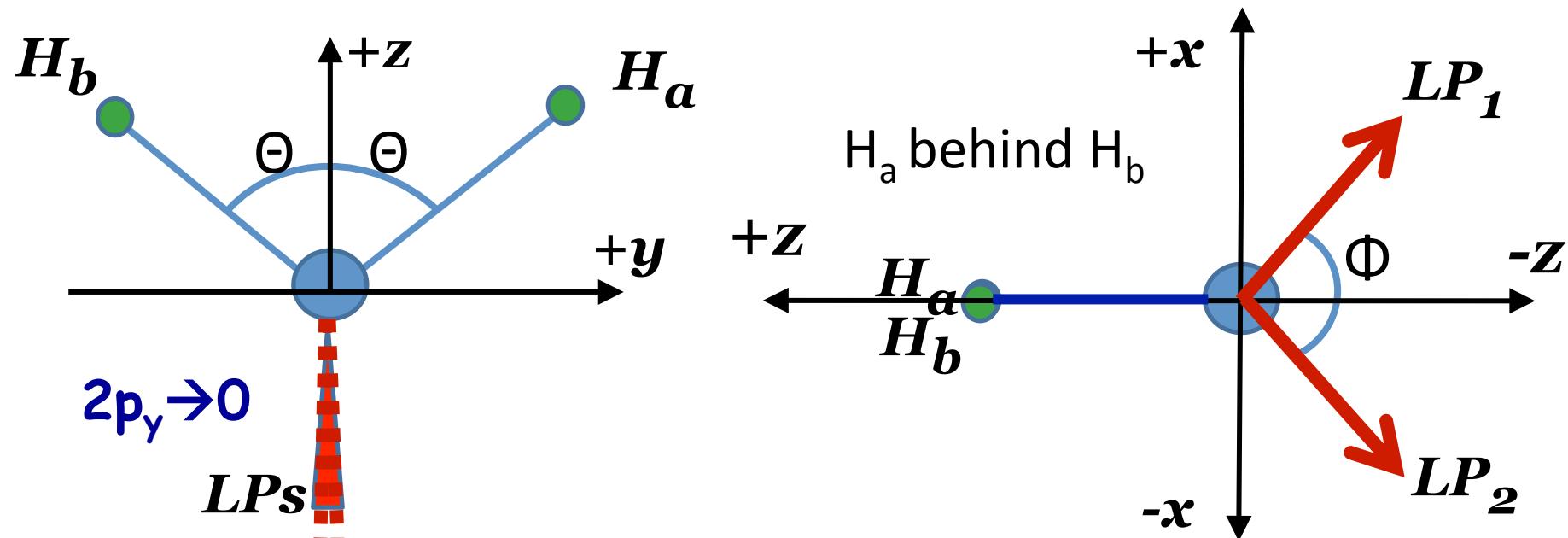
Others' contributions (using symmetry)

S : Same for both LP hybrid orbitals: $d_3 = d_7$

$2p_z$: Same for both LP hybrids: $d_5 = d_1$

$2p_x$: Same magnitude, opposite in sign: $d_8 = -d_4$

Use symmetry to equate coefficients



$$2p_z \rightarrow d5 = d1$$

$$S \rightarrow d3 = d7 \quad 2p_x \rightarrow d8 = -d4$$

$$\varphi_{lp1}^{sp^3} = d_1 \psi_{2p_z} + 0 \psi_{2p_y} + d_3 \psi_{2s} + d_4 \psi_{2p_x}$$

$$\varphi_{lp2}^{sp^3} = d_1 \psi_{2p_z} + 0 \psi_{2p_y} + d_3 \psi_{2s} - d_4 \psi_{2p_x}$$

Total contributions of s , p_x , p_y , p_z is unity considering all four hybrids

For 2 lone-pair hybrid orbitals:

$$\varphi_{lp1}^{sp^3} = d_1 \psi_{2p_z} + 0 \psi_{2p_y} + d_3 \psi_{2s} + d_4 \psi_{2p_x}$$

$$\varphi_{lp2}^{sp^3} = d_1 \psi_{2p_z} + 0 \psi_{2p_y} + d_3 \psi_{2s} - d_4 \psi_{2p_x}$$

For bonded hybrid orbitals:

$$\varphi_a^{sp^3} = 0.55 \psi_{2p_z} + 0.71 \psi_{2p_y} - 0.45 \psi_{2s} + 0 \psi_{2p_x}$$

$$\varphi_b^{sp^3} = 0.55 \psi_{2p_z} - 0.71 \psi_{2p_y} - 0.45 \psi_{2s} + 0 \psi_{2p_x}$$

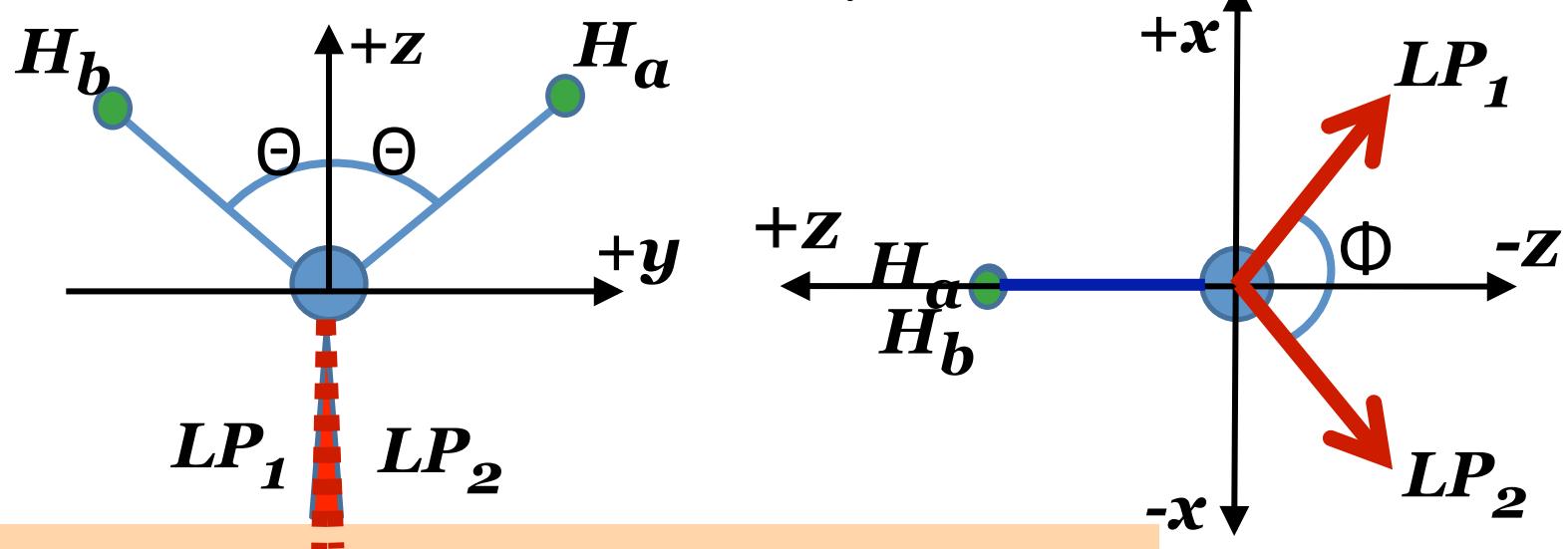
For $2p_z$ $d_1^2 + d_1^2 + (0.55)^2 + (0.55)^2 = 1 \rightarrow d_1 = \pm 0.45$

For $2p_y$ $(0)^2 + (0)^2 + (0.71)^2 + (0.71)^2 = 1$ (*done before*)

For $2s$ $d_3^2 + d_3^2 + (0.45)^2 + (0.45)^2 = 1 \rightarrow d_3 = \pm 0.55$

For $2p_x$ $d_4^2 + d_4^2 + (0)^2 + (0)^2 = 1 \rightarrow d_4 = \pm 0.71$

Different s-/p- character for the two classes of hybrids in H₂O



$$\varphi_{lp1}^{sp^3} = -0.45\psi_{2p_z} - 0.55\psi_{2s} + 0.71\psi_{2p_x}$$

$$\varphi_{lp2}^{sp^3} = -0.45\psi_{2p_z} - 0.55\psi_{2s} - 0.71\psi_{2p_x}$$

S → (0.55)² → 30%

P → 100 - 30 → 70%

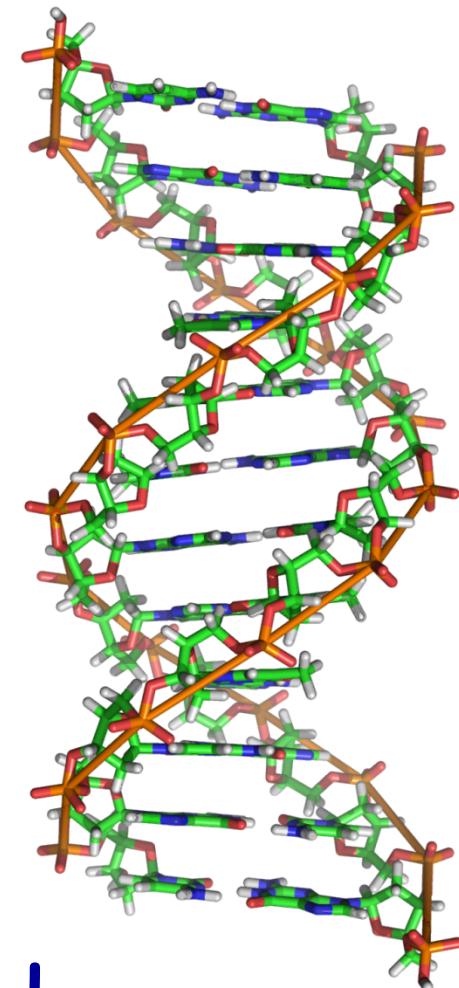
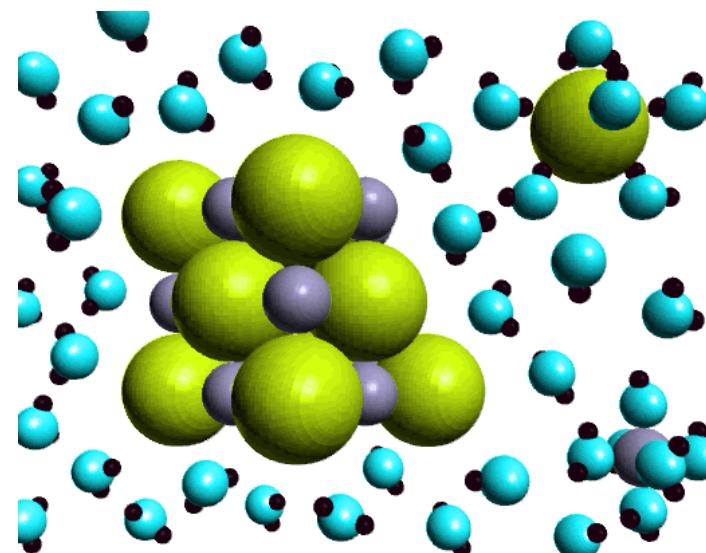
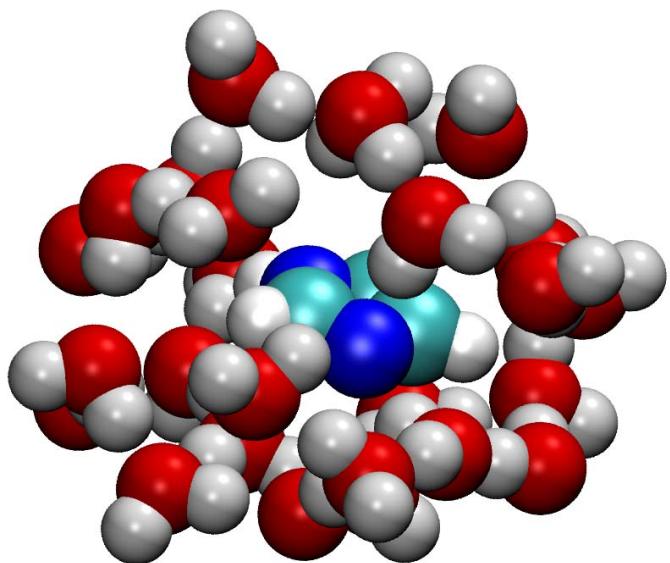
$$\varphi_a^{sp^3} = 0.55\psi_{2p_z} + 0.71\psi_{2p_y} - 0.45\psi_{2s} + 0\psi_{2p_x}$$

$$\varphi_b^{sp^3} = 0.55\psi_{2p_z} - 0.71\psi_{2p_y} - 0.45\psi_{2s} + 0\psi_{2p_x}$$

S → 20%

P → 80%

Intermolecular Forces



Forces that bind individual non-reacting molecules in gases/liquids

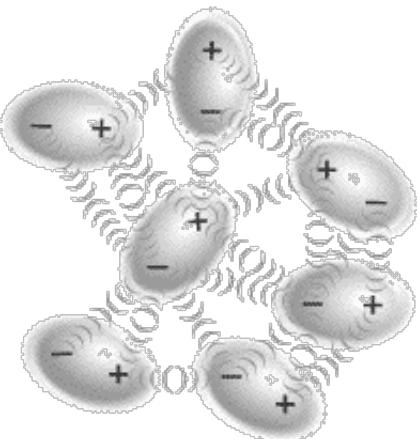
Intra- and Inter-molecular Forces

H_2 molecule: 2 nuclei; 2 electrons : $H_{H_2} \sim -\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{\hbar^2}{2m_e} \nabla_2^2 + V,$

$$V = -\frac{(q_1 e)(q_2 e)}{r_{1A}} - \frac{(q_1 e)(q_2 e)}{r_{1B}} - \frac{(q_1 e)(q_2 e)}{r_{2A}} - \frac{(q_1 e)(q_2 e)}{r_{2B}} + \frac{(q_1 e)(q_2 e)}{R_{AB}} + \frac{e^2}{r_{12}}$$

||||((((()))))) attraction

))))))))))(((((repulsion



$$V(r) = \frac{(q_1 e)(q_2 e)}{4\pi\epsilon_0 r} \quad F(r) = \frac{(q_1 e)(q_2 e)}{4\pi\epsilon_0 r^2}$$

Intermolecular forces are typically much weaker than forces that bind electrons and atoms within a molecule → does not disrupt molecular electronic structure significantly (except for certain special cases!)

Intermolecular Forces

Intramolecular forces hold atoms together in a molecule.

Intermolecular forces are attractive/repulsive forces between molecules.

Intermolecular vs Intramolecular

- 41 kJ to vaporize 1 mole of water (inter)
- 930 kJ to break all O-H bonds in 1 mole of water (intra)

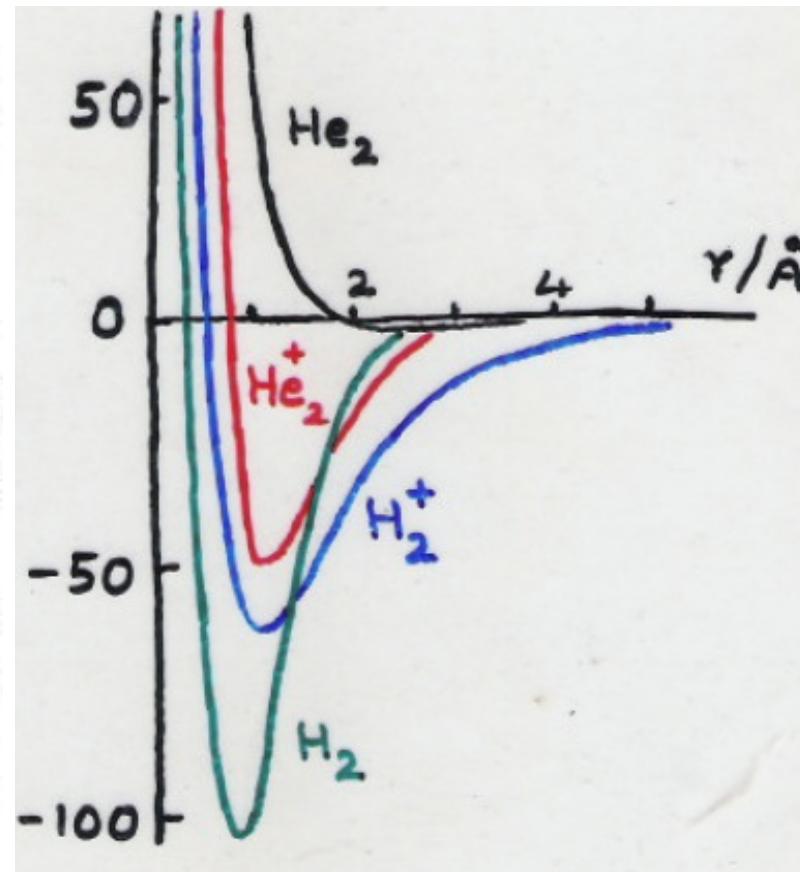
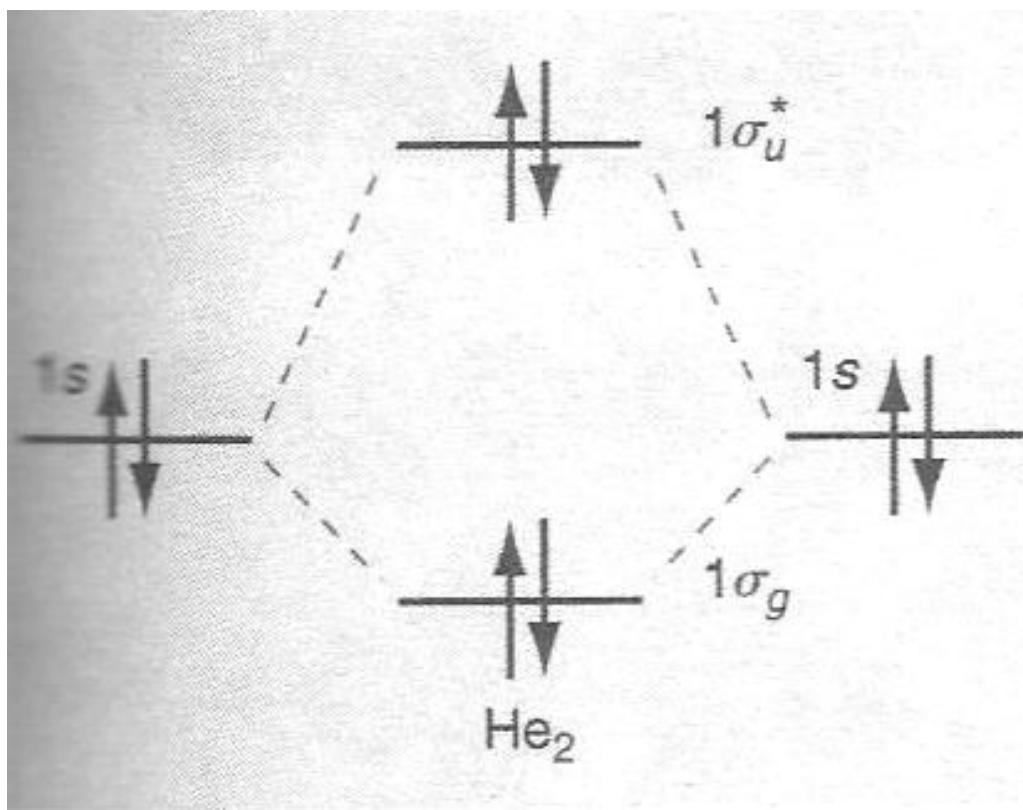
A qualitative “Measure” of intermolecular force

boiling point

melting point

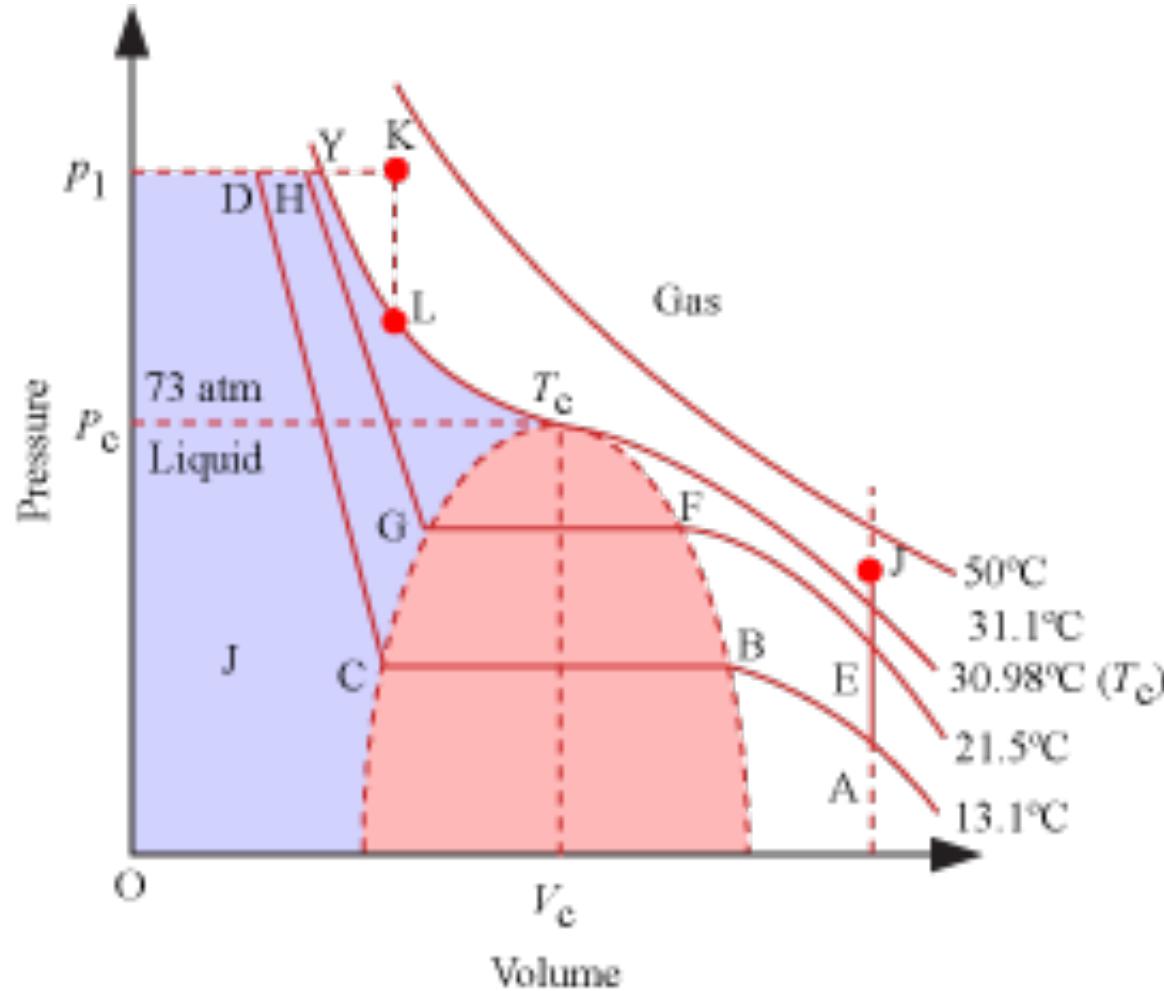
No Phase change without intermolecular forces

He_2 : PE Curve shows a minimum



Species	Number of electrons	Ground-state electron configuration	Bond order	Bond length/pm	Binding energy/kJ·mol ⁻¹
H_2^+	1	$(\sigma_g 1s)^1$	1/2	106	268
H_2	2	$(\sigma_g 1s)^2$	1	74	457
He_2^+	3	$(\sigma_g 1s)^2 (\sigma_u 1s)^1$	1/2	108	241
He_2	4	$(\sigma_g 1s)^2 (\sigma_u 1s)^2$	0	≈ 600	$\ll 1$

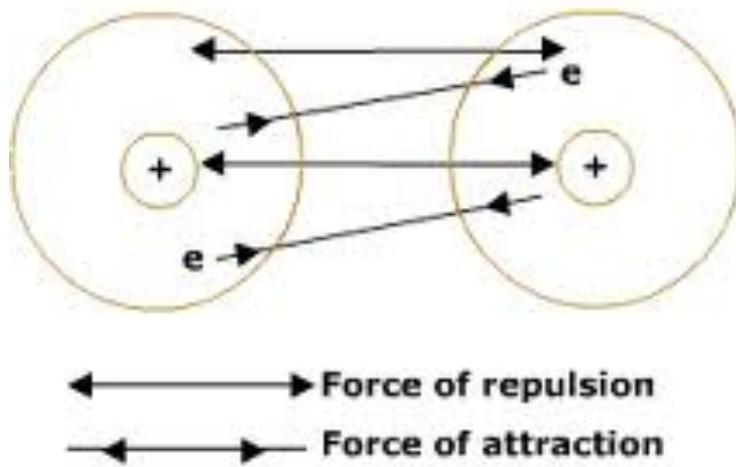
All gases can be liquified !



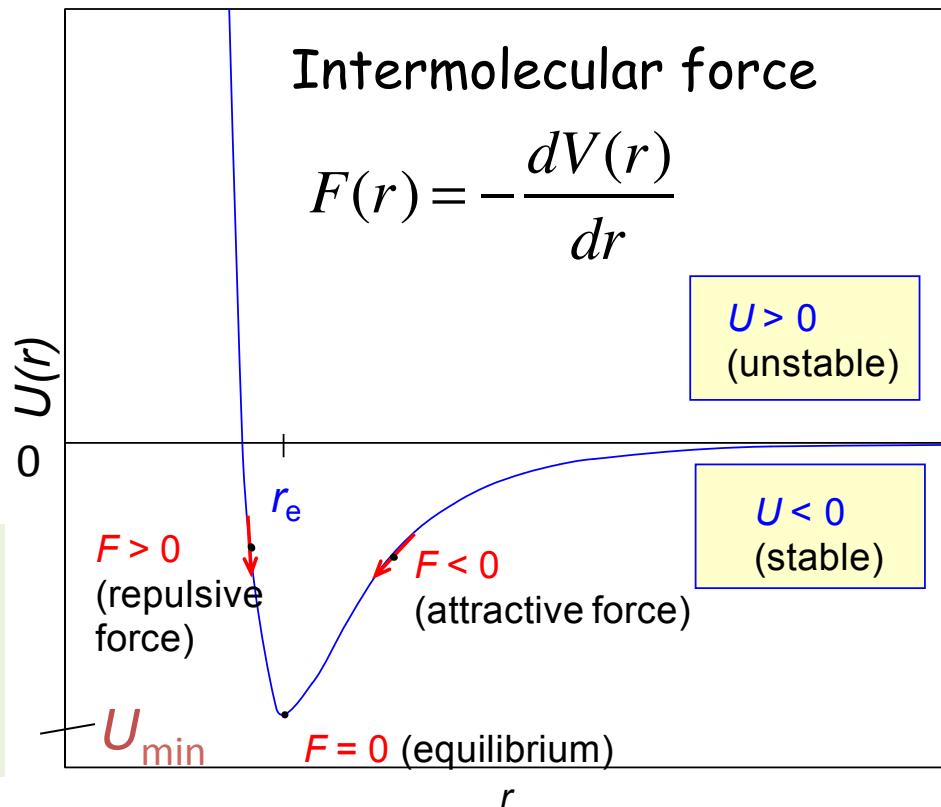
Real gases are not ideal, even though they can sometimes behave as one! NOT just points with no volume!

Intermolecular-interactions EXISTS between gaseous atoms!

Interaction potentials: Short range - Repulsive; Long range - attractive!



Two stable atoms/molecules
Which do not form chemical
bonds also interact → weak!



1. Much weaker than chemical bonds (Typically few $k_B T$)
2. Schrodinger Equation is almost impossible to solve

Some important considerations !

- Instead of particles and interparticle forces → molecules and Intermolecular Forces (IMFs),
(some interactions applicable to atoms as well)
- In the discussion of Intermolecular Forces (origins and distance dependence), refer to intermolecular potential energy function, $U(r)$, not force $F(r)$.
- Need to separate interaction energies in terms of pair-wise potentials – neglect more than two-body interactions; i.e., assume total energy of interaction is the sum of pairwise potential energies

Molecules consist of negative charge density around a set of nuclei!

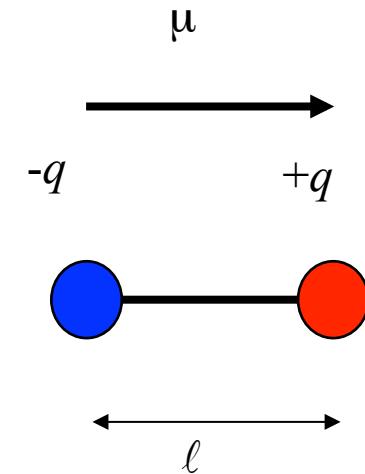
Monopole - Point charge (or ions)

Dipole - Two point charges separated by a distance d

Quadrupole - Three point charges separated from each other

$$\overset{\mu}{\mu} = qr \quad (1 \text{ Debye} = 4.8 \times 10^{-18} \text{ esu.cm})$$

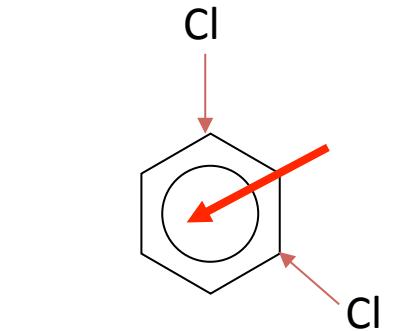
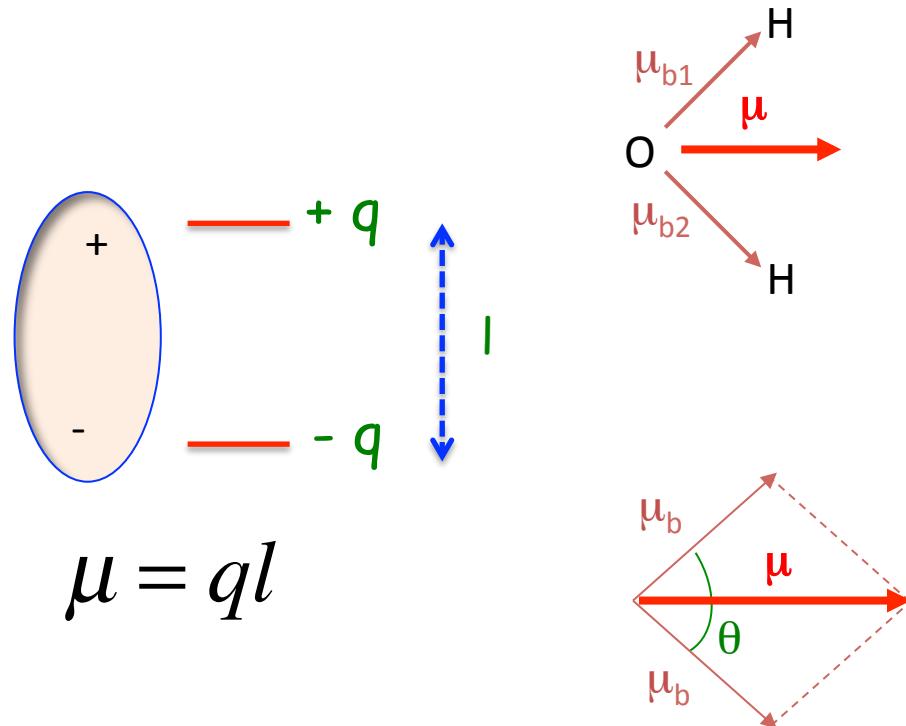
$$\overset{\mu}{\mu} = \sum_i q_i r_i$$



Charge Distribution

$$\overset{\mu}{\mu} = \int r(x, y, z) \sigma(x, y, z) dx dy dz$$

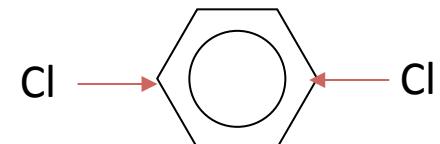
Dipole moment - Vector! For polymatatomic molecules?



$$\mu = 2\mu_b \cos\left(\frac{\theta}{2}\right)$$

Note: the direction of
The arrows should be reversed:
In chemistry, dipole moment
Direction Is from positive to negative!

$\text{O}=\text{C}=\text{O}$



Induced Dipole in presence of an electric field: Polarizability

$$\mu = \alpha E; \quad \alpha \rightarrow \text{Polarizability (molecular property)}$$

$$\alpha(E) = \alpha_0 E + \beta E + \gamma E$$

$$\mu = \alpha_0 E + \beta E + \gamma E$$

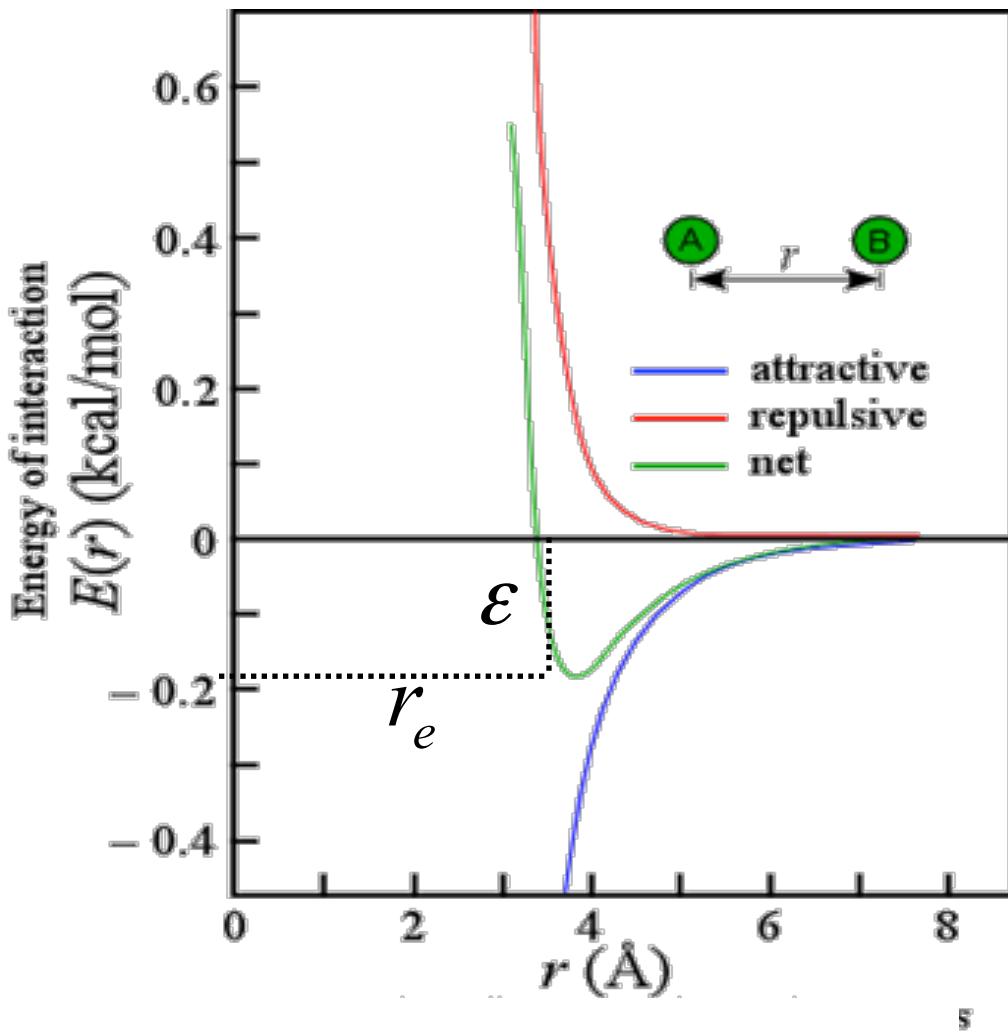
$\beta \rightarrow$ Hyperpolarizability; $\gamma \rightarrow$ 2nd order hyperpolarizability

Induced dipole moment in a atom or molecule due to the polarization of charge distribution

$\alpha \rightarrow$ Measure of the extent to which a charge distribution around an atom or a molecule can be distorted in presence on an uniform electric field (due to ion, another dipole)

Loosely relate polarizability to volume \rightarrow units of volume!

Nature of intermolecular potential



Lennard-Jones Potential

$$V_{LJ} = \epsilon \left[\left(\frac{r_e}{r} \right)^{12} - 2 \left(\frac{r_e}{r} \right)^6 \right]$$

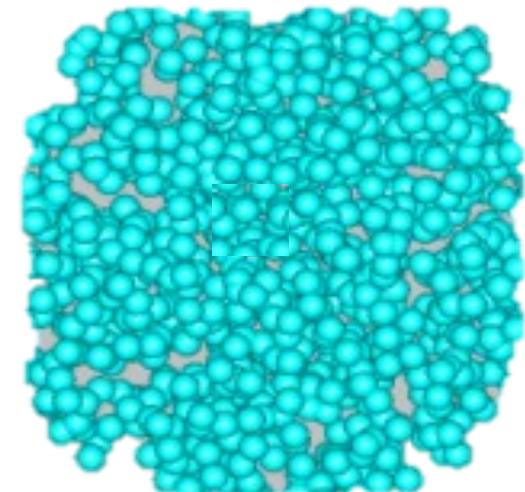
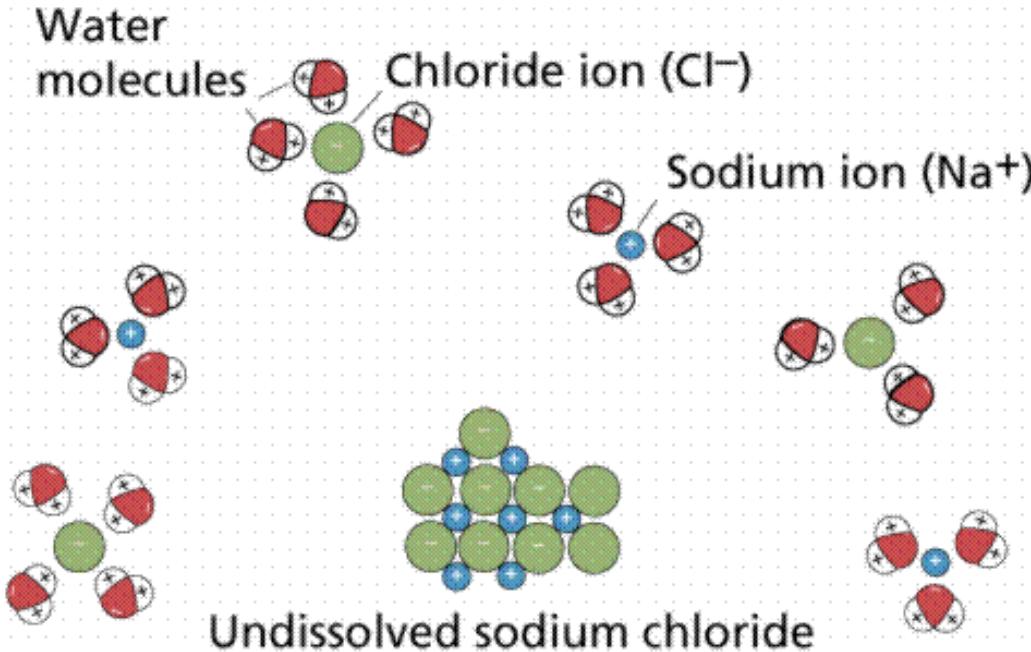
What are the intermolecular interactions that contribute to the total potential energy between two species?

Sum of the pairwise potential energy of interaction

Magnitudes of force vary depending on the type of interaction

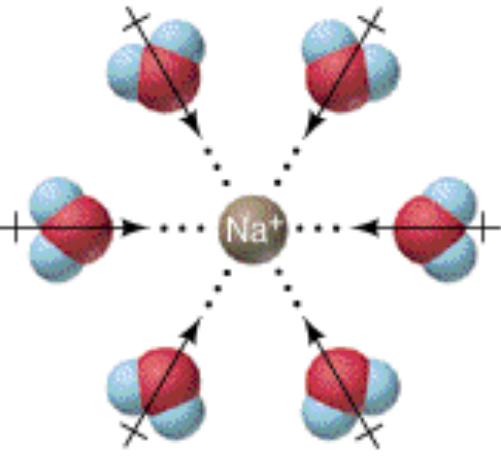
Ions in Electrolyte – Charges involve strong force!

Liquid Helium- Weakest interactions

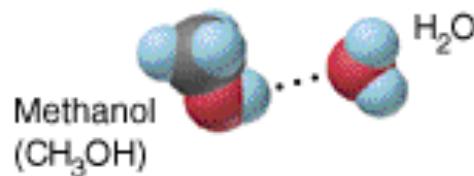


Energy spectrum of intermolecular interactions

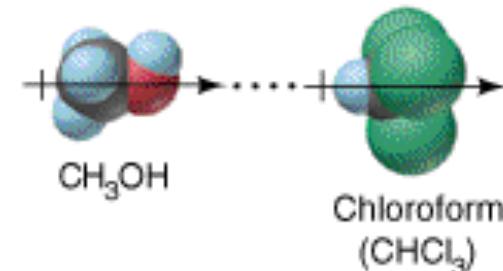
Various categories of intermolecular interactions (forces)



Ion-dipole

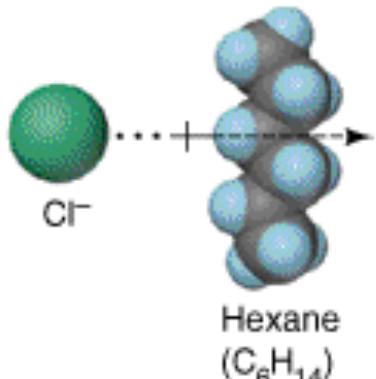


H bond



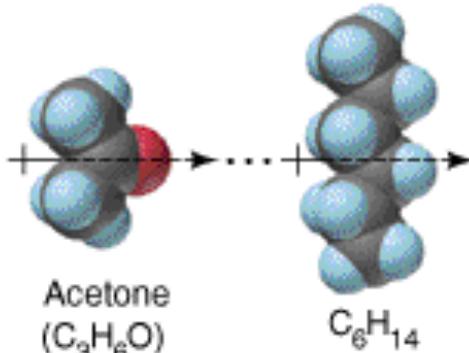
CHCl_3

Dipole-dipole



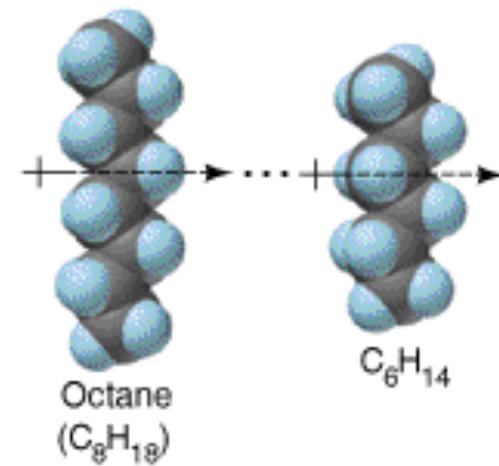
C_6H_{14}

Ion-induced dipole



$\text{C}_3\text{H}_6\text{O}$

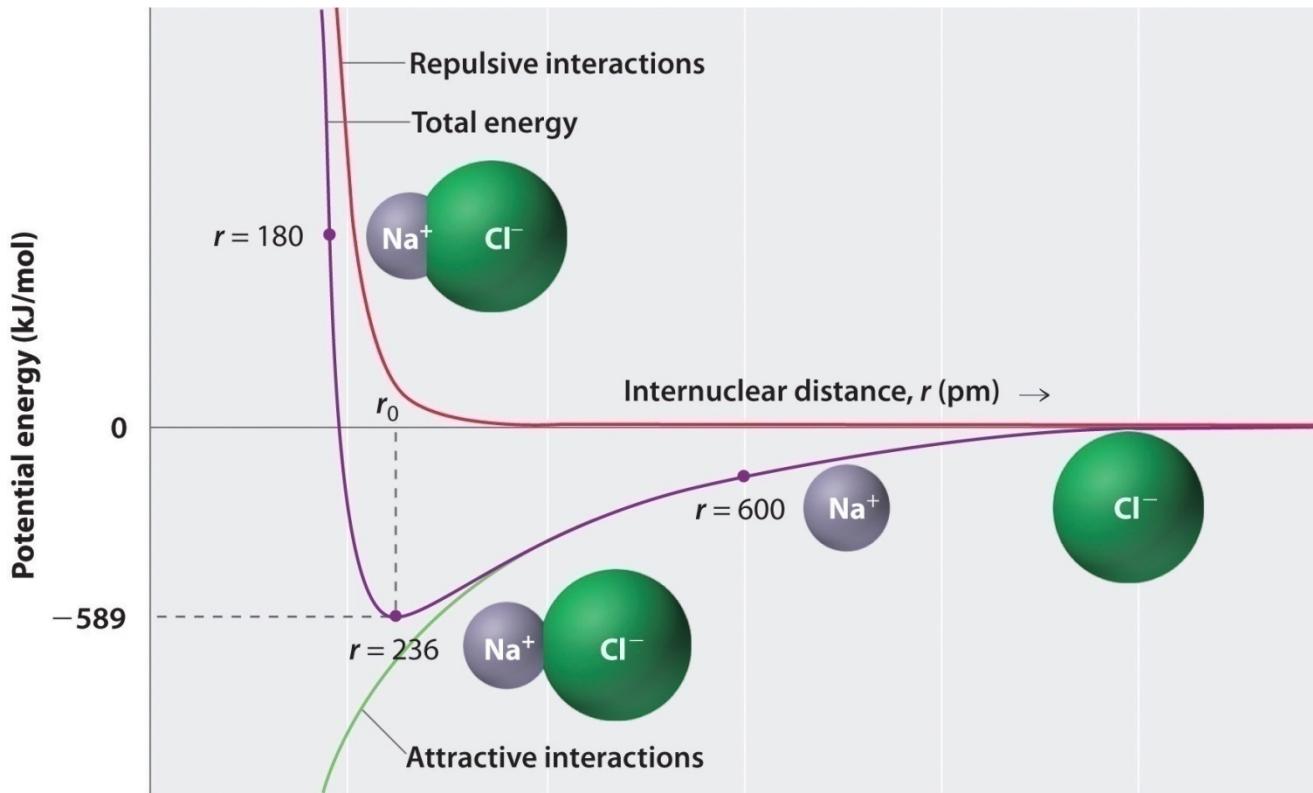
Dipole-induced dipole



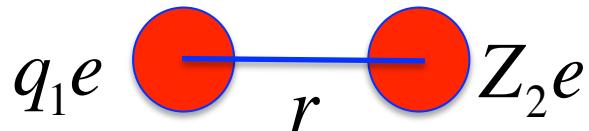
C_8H_{18}

Dispersion

Ion-Ion Interaction for Charged molecules: Coulomb Potential

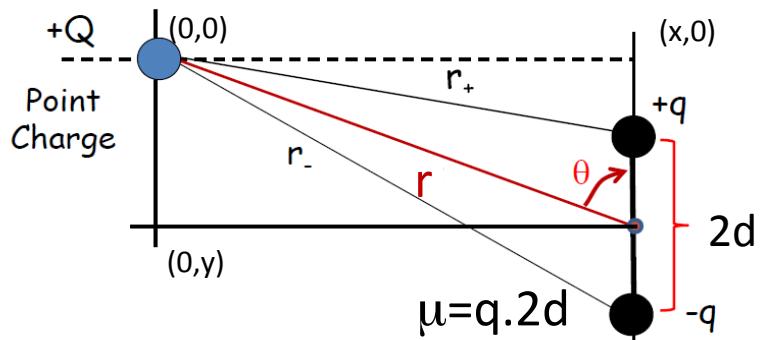
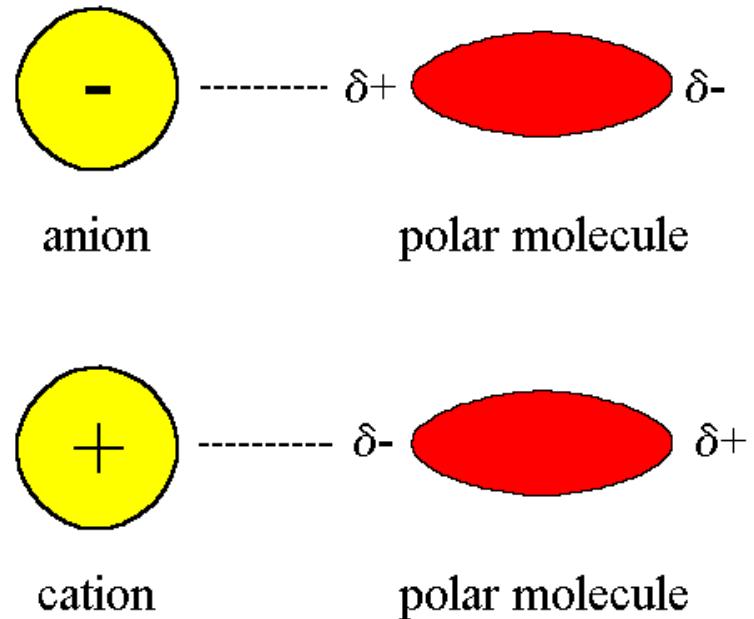
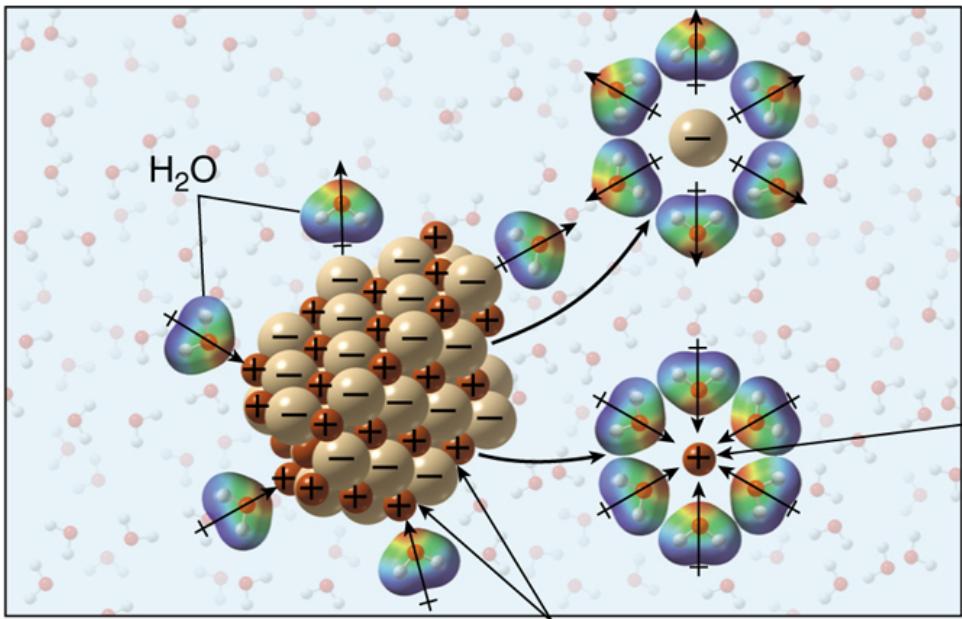


Interaction via Coulomb potential



$$V(r) = \frac{(q_1 e)(q_2 e)}{4\pi\epsilon_0 r}$$

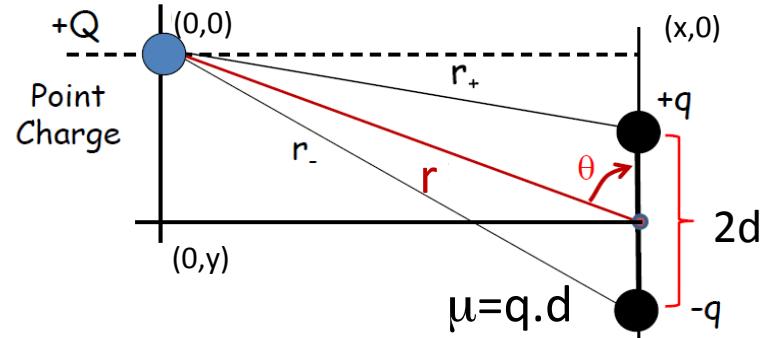
Monopole (Ion)-dipole interaction



$$V(r, \theta)_{ion-dipole} = \vec{\mu}_j \cdot \vec{E} = \frac{\vec{\mu}_j \cdot q_i \cos\theta}{r^2}$$

Ion - Dipole Interaction

$$V = \frac{1}{4\pi\epsilon_0} \cdot Q \cdot \left(\frac{q}{r_+} - \frac{q}{r_-} \right)$$



$$r_-^2 = x^2 + (y + d)^2$$

$$\frac{1}{r_-} = \left[x^2 + (y + d)^2 \right]^{-1/2} = \left[x^2 + y^2 + d^2 + 2yd \right]^{-1/2} = \left[r^2 + d^2 + 2yd \right]^{-1/2}$$

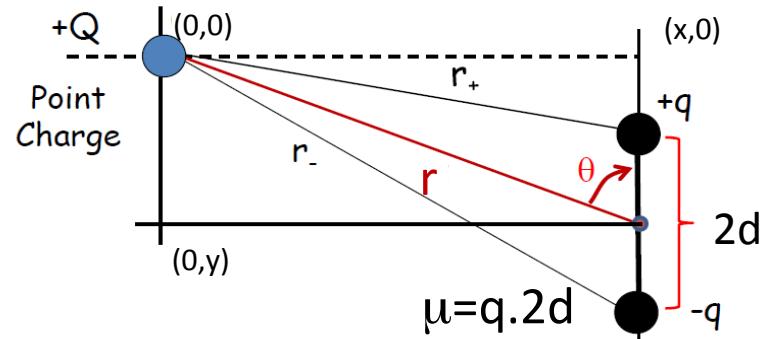
$$\frac{1}{r_-} = \frac{1}{r} \left[1 + \left(\frac{d}{r} \right)^2 + \frac{2yd}{r^2} \right]^{-1/2} \approx \frac{1}{r} \left[1 + \frac{2yd}{r^2} \right]^{-1/2} \quad r \gg 2d$$

$$\frac{1}{r_-} = \frac{1}{r} \left[1 - \frac{yd}{r^2} \right]$$

$$\frac{1}{r_+} = \frac{1}{r} \left[1 + \frac{yd}{r^2} \right]$$

Ion - Dipole Interaction

$$V = \frac{1}{4\pi\epsilon_0} \cdot Q \cdot q \left(\frac{1}{r_+} - \frac{1}{r_-} \right)$$



$$\frac{1}{r_-} = \frac{1}{r} \left[1 - \frac{yd}{r^2} \right] \quad \frac{1}{r_+} = \frac{1}{r} \left[1 + \frac{yd}{r^2} \right]$$

$$\left(\frac{1}{r_+} - \frac{1}{r_-} \right) = \frac{1}{r} \left[1 + \frac{yd}{r^2} \right] - \frac{1}{r} \left[1 - \frac{yd}{r^2} \right] = \frac{2yd}{r^3}$$

$$V = \frac{1}{4\pi\epsilon_0} \cdot Q \cdot q \cdot \frac{2yd}{r^3} = \frac{1}{4\pi\epsilon_0} \cdot \frac{Q \cdot q \cdot 2d}{r^2} \cdot \frac{y}{r} = \frac{1}{4\pi\epsilon_0} \cdot \frac{Q\mu}{r^2} \cdot \cos\theta$$

Monopole-dipole interaction

$$V(r, \theta)_{ion-dipole} = \vec{\mu}_j \cdot \vec{E} = \frac{\vec{\mu}_j q_i \cos\theta}{r^2}$$

Simple average over all θ : $\int_0^\pi \cos\theta \sin\theta d\theta = \int_0^\pi \cos\theta d(\cos\theta) = 0$

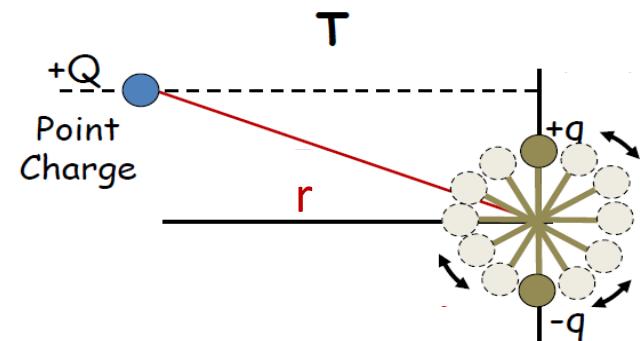
$$\langle V(r, \theta)_{ion-dipole} \rangle = 0 !!!$$

Are all orientations equally probable?

No! Orientations with lower energy are slightly favored!

Dictated by Boltzmann Distribution

$$P(Orientation) \sim \exp\left(-\frac{V(r, \theta)}{k_B T}\right)$$



Need to calculate the average over all orientations weighted by Boltzmann factor \rightarrow Boltzman Average!

Boltzmann Average over all orientations

$$\left\langle V(r,\theta)_{ion-dip} \right\rangle_{BA} = \left\langle \frac{\vec{u}_j q_i \cos\theta}{r^2} \cdot \exp\left(-\frac{V(r,\theta)}{k_B T}\right) \right\rangle = \frac{\vec{u}_j q_i}{r^2} \cdot \left\langle \cos\theta \exp\left(-\frac{V(r,\theta)}{k_B T}\right) \right\rangle$$

Analytically difficult, numerically easy!

Assume: $V(r,\theta) \ll k_B T \rightarrow$ interaction energy between monopole and dipole is small compared to the thermal energy ($k_B T$)

expand exponential function $\exp(-x) = 1 - x + \frac{x^2}{2!} - \dots \approx 1 - x$

$$\begin{aligned} \left\langle \cos\theta \exp\left(-\frac{V(r,\theta)}{k_B T}\right) \right\rangle &\approx \left\langle \cos\theta \left(1 - \frac{V(r,\theta)}{k_B T}\right) \right\rangle \\ &= \langle \cos\theta \rangle - \left\langle \cos\theta \frac{V(r,\theta)}{k_B T} \right\rangle = - \left\langle \frac{V(r,\theta) \cos\theta}{k_B T} \right\rangle \end{aligned}$$

Orientation-Averaged potential for ion-dipole interactions

$$\begin{aligned}\left\langle V(r,\theta)_{ion-dipole} \right\rangle_{Boltzman} &= \frac{\vec{\mu}_j q_i}{r^2} \times \left\{ - \left\langle V(r,\theta) \times \frac{\cos\theta}{k_B T} \right\rangle \right\} \\ &= - \frac{\vec{\mu}_j q_i}{r^2} \times \left\langle \frac{\vec{\mu}_j q_i \cos\theta}{r^2} \times \frac{\cos\theta}{k_B T} \right\rangle\end{aligned}$$

$$\left\langle V(r,\theta)_{ion-dipole} \right\rangle_{Boltzman} = - \left(\frac{\vec{\mu}_j q_i}{r^2} \right)^2 \times \frac{1}{k_B T} \times \left\langle \cos^2\theta \right\rangle$$

$$\left\langle \cos^2\theta \right\rangle = \int_0^\pi \cos^2\theta \sin\theta d\theta = \int_0^\pi \cos^2\theta [d(\cos\theta)] = \left. \frac{\cos^3\theta}{3} \right|_0^\pi = -\frac{2}{3} \neq 0$$

$$\left\langle V(r)_{ion-dipole} \right\rangle_{Boltzman} \sim \frac{1}{3k_B T} \frac{\left(\vec{\mu}_j q_i \right)^2}{r^4} \sim \frac{const.}{r^4}$$