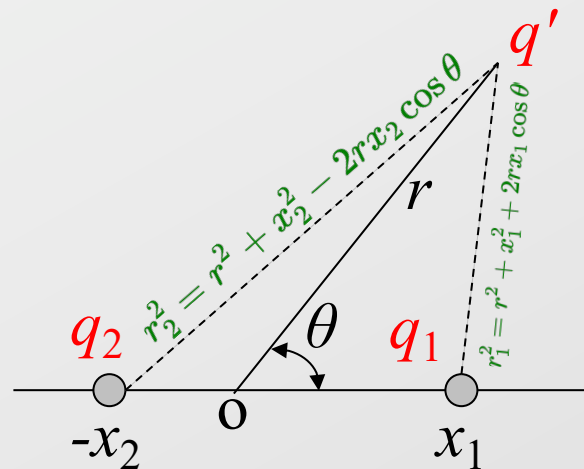# Lecture 17
Electrostatics, Part 2

electric potential and field; polarization; van der Waals forces

Prof. David A. Kofke
CE 500 – Modeling Potential-Energy Surfaces
Department of Chemical & Biological Engineering
University at Buffalo

University at Buffalo
The State University of New York

Multipole moments quantify the most important features of a charge distribution

$$E_{\text{el}} = \frac{q'(q_1 + q_2)}{r} + \frac{q'(q_2 x_2 - q_1 x_1)}{r^2} \cos\theta$$

charge   dipole

quadrupole

$$+ \frac{q'(q_1 x_1^2 + q_2 x_2^2)}{r^3} \frac{1}{4}(1 + 3\cos 2\theta) + \mathcal{O}\left(\frac{1}{r}\right)^4$$

$$E_{\text{el}} = \frac{q'Q}{r} + \frac{q'\mu}{r^2}\cos\theta + \frac{q'\Theta}{r^3}\frac{1}{4}(1 + 3\cos 2\theta) + \ldots$$
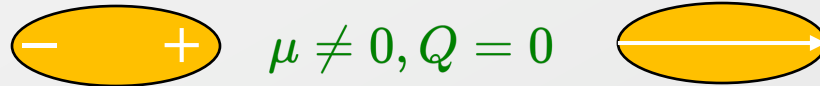

q'

q_2 $r_2^2 = r^2 + x_2^2 - 2rx_2\cos\theta$

r $r_1^2 = r^2 + x_1^2 + 2rx_1\cos\theta$

θ q_1

$-x_2$ o x_1

- The electrostatic moments are

  - *Charge* $q = q_1 + q_2$

  - *Dipole* $\mu = q_2 x_2 - q_1 x_1$

  - *Quadrupole* $\Theta = q_1 x_1^2 + q_2 x_2^2$

2

Next would be octupole

Energies for interaction of multipoles with each other are available

- Pure dipole

$\mu \neq 0, Q = 0$

Note: opposite arrow conventions are used too

- Pure quadrupole
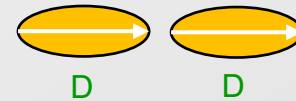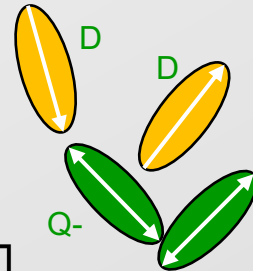
$\mu = 0, Q > 0$

$\mu = 0, Q < 0$

$$u_{dd} = -\frac{\mu_1 \mu_2}{r^3}\left[3(\hat{\mu}_1 \cdot \hat{\mathbf{r}})(\hat{\mu}_2 \cdot \hat{\mathbf{r}}) - (\hat{\mu}_1 \cdot \hat{\mu}_2)\right]$$
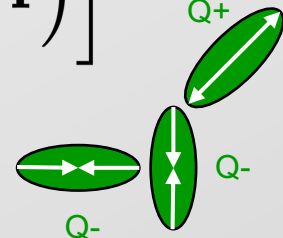
Energetically favorable arrangements

$$u_{dQ} = \frac{3}{2}\frac{\mu_1 Q_2}{r^4}\left[(\hat{\mu}_1 \cdot \hat{\mathbf{r}})\left(5\left(\hat{Q}_2 \cdot \hat{\mathbf{r}}\right)^2 - 1\right) - 2(\hat{\mu}_1 \cdot \hat{\mu}_2)\left(\hat{Q}_2 \cdot \hat{\mathbf{r}}\right)\right]$$

Axially symmetric quadrupoles

$$u_{QQ} = \frac{3}{4}\frac{Q_1 Q_2}{r^5}\left[1 - 5c_1^2 - 5c_2^2 + 2c_{12}^2 + 35c_1^2 c_2^2 - 20c_1 c_2 c_{12}\right]$$

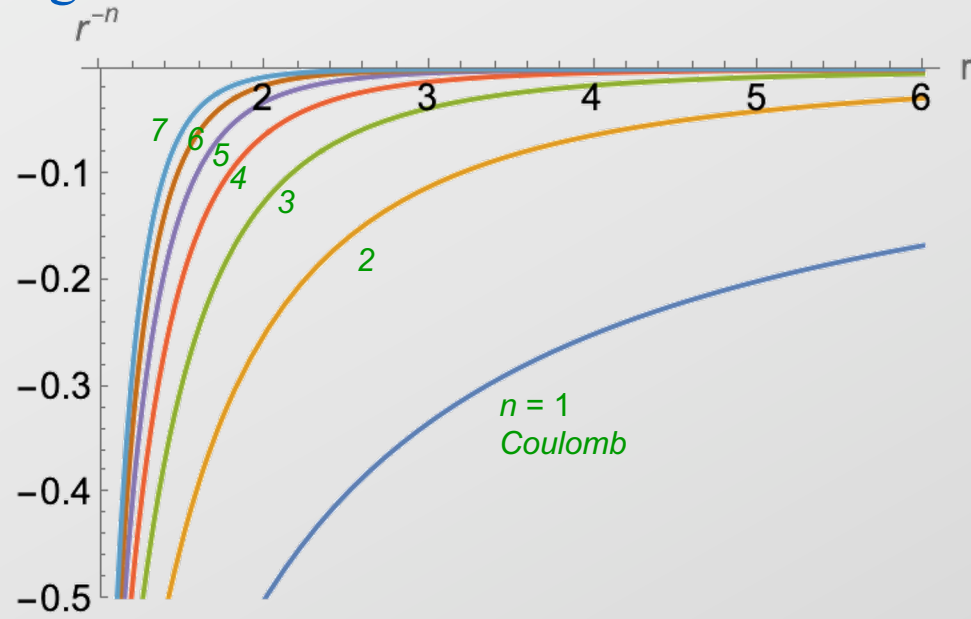- Can model electrostatics as point dipole, etc. rather than charges

3

- Coulomb interaction is very long ranged!

  – Integral over all contributions diverges, except for cancellation of positive and negative contributions

$$\int_1^\infty \frac{1}{r} 4\pi r^2 dr$$

Decay rates for multipole interactions

	charge Q	dipole μ	quadrupole Θ	octupole Ξ
Q	R^{-1}	R^{-2}	R^{-3}	R^{-4}
μ	R^{-2}	R^{-3}	R^{-4}	R^{-5}
Θ	R^{-3}	R^{-4}	R^{-5}	R^{-6}
Ξ	R^{-4}	R^{-5}	R^{-6}	R^{-7}

F. Jensen

4

Simple orientation average of dipole energy is zero; Boltzmann-weighted average is not
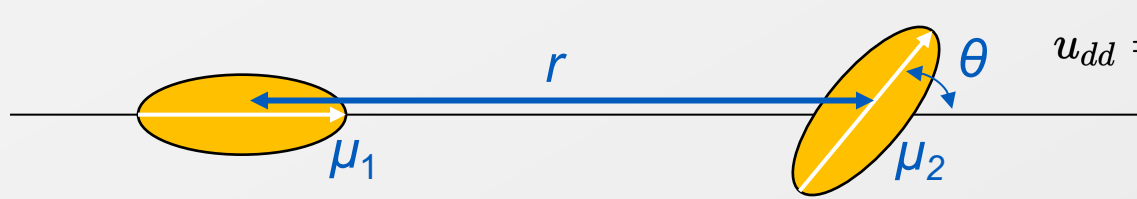
$$u_{dd} = -\frac{\mu_1 \mu_2}{r^3}\left[3(\hat{\mu}_1 \cdot \hat{\mathbf{r}})(\hat{\mu}_2 \cdot \hat{\mathbf{r}}) - (\hat{\mu}_1 \cdot \hat{\mu}_2)\right]$$

r^{-3} decay

$$\langle u_{dd} \rangle = \int_0^\pi u_{dd}(\theta)\sin(\theta)d\theta = 0$$

Unweighted average

```
Integrate[uμμ[{x, 0, 0}, μ1 {Cos[theta], Sin[theta], 0}, μ2 {1, 0, 0}] Sin[theta], {theta, 0, Pi}]

0
```

Boltzmann-weighted average

```
boltzAvg = Integrate[u12[r, theta, μ1, μ2] Exp[−u12[r,theta,μ1,μ2]/kT] Sin[theta], {theta, 0, Pi}] / Integrate[Exp[−u12[r,theta,μ1,μ2]/kT] Sin[theta], {theta, 0, Pi}];

Series[boltzAvg, {r, Infinity, 8}]
```

$$-\frac{4\left(\mu1^2\,\mu2^2\right)}{3\,kT\,r^6} + O\left[\frac{1}{r}\right]^9$$

$$\langle u_{dd} \rangle_{\text{Boltz}} = \frac{\int_0^\pi u_{dd}(\theta)e^{-u_{dd}(\theta)/k_B T}\sin(\theta)d\theta}{\int_0^\pi e^{-u_{dd}(\theta)/k_B T}\sin(\theta)d\theta} \sim -\frac{4}{3}\frac{\mu_1^2 \mu_2^2}{k_B T}\frac{1}{r^6}$$

r^{-6} decay

5

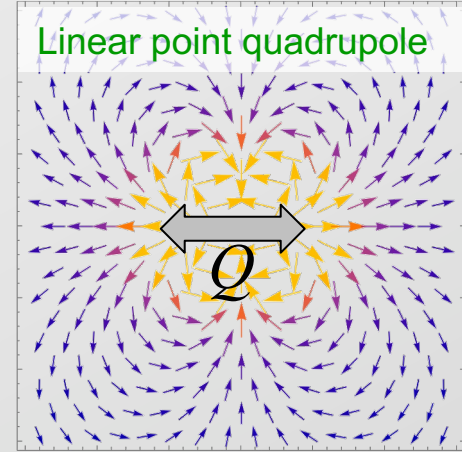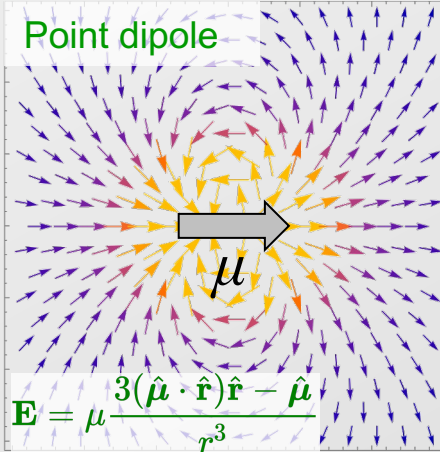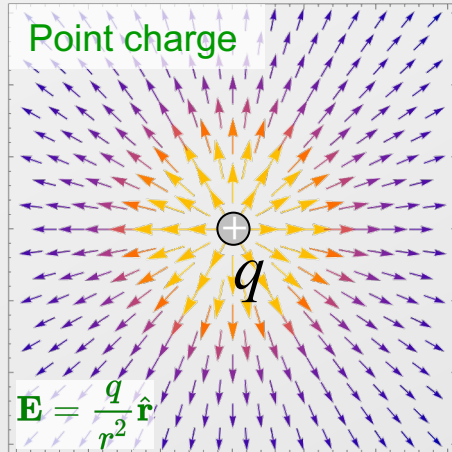# A molecule's electron distribution can change with its conformation, and by other molecules

- The charge distribution on a molecule, A, creates an electric field that can change the charge distribution on another molecule, B

- The change in B's charge distribution can affect how it interacts with a third molecule, C

- Polarization is an important source of 3-body and higher-order contributions to the energy
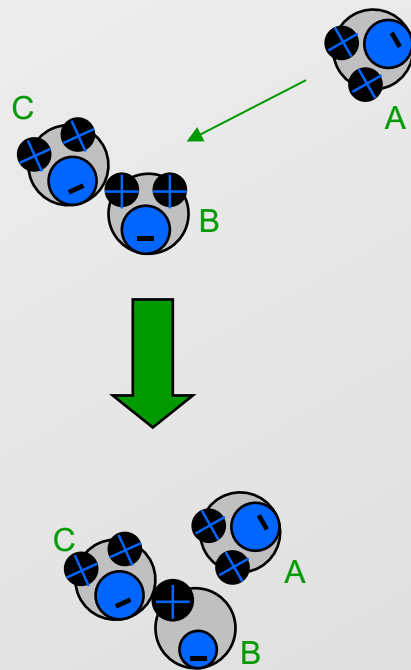
Distortion of charge density is result of interaction with electric field

- Electric potential ϕ yields energy of a charge q: $u = \phi(\mathbf{r})q$

- Electric field is gradient of potential: $\mathbf{E}(\mathbf{r}) = -\nabla\phi(\mathbf{r})$

  ϕ [=] volts

  – It provides the force on a charge q: $\mathbf{F} = \mathbf{E}q$

- Electric moments give rise to electric fields

Point charge

$\mathbf{E} = \dfrac{q}{r^2}\hat{\mathbf{r}}$

q

Point dipole

$\mathbf{E} = \mu\dfrac{3(\hat{\boldsymbol{\mu}} \cdot \hat{\mathbf{r}})\hat{\mathbf{r}} - \hat{\boldsymbol{\mu}}}{r^3}$

μ

Linear point quadrupole

Q

Dipole field is derived as sum of two opposite point-charge fields, slightly displaced

+ charge at (½,0)
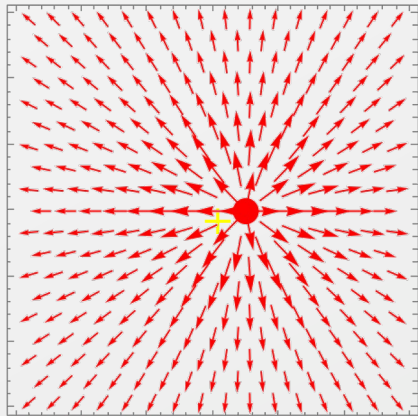
− charge at (0,0)
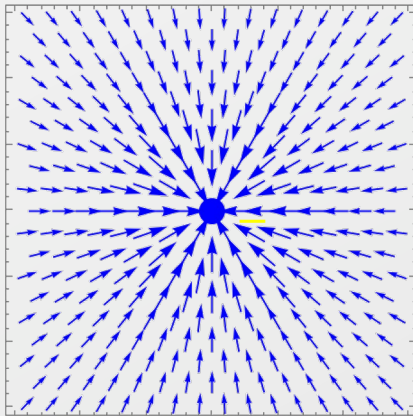
superimpose
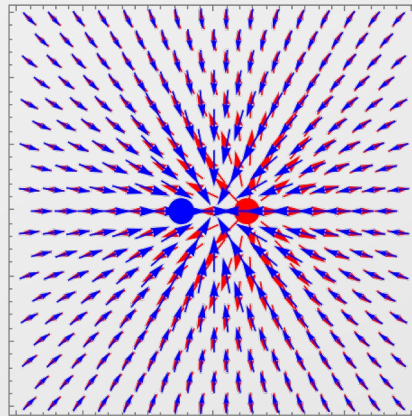
sum
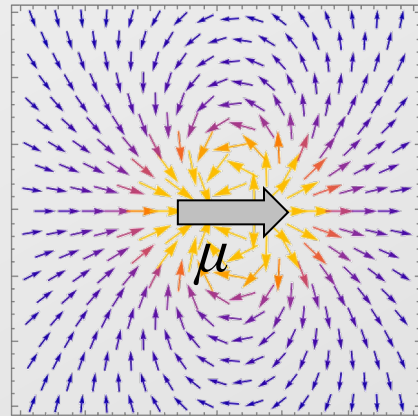
$$E_+ = \frac{\hat{\mathbf{r}}}{r^2} = \frac{((x - \frac{1}{2}, y)}{((x - \frac{1}{2})^2 + y^2)^{3/2}}$$

$$E_- = \frac{-(x, y)}{(x^2 + y^2)^{3/2}}$$

$$E_+ + E_-$$

- Electric field of *dipole* given as derivative of *point-charge* field

$$\mathbf{E}_{\text{dipole}} = \frac{E(\frac{1}{2}) - E(0)}{\frac{1}{2} - 0} \rightarrow \frac{\partial \mathbf{E}}{\partial x}$$

(−) due to negative charge

Same for electric potential:

$$\phi_{\text{dipole}}(\mathbf{r}) = \frac{\partial \phi_{\text{pt chrg}}}{\partial x} = q \frac{\partial (1/r)}{\partial x}$$

8

Multipole-moment potential and electric field can be given in terms of point-charge derivatives

- Rank-1 polytensors for moments and derivatives

$$\mathbf{M}_A = \left(Q^A, \mu_x^A, \mu_y^A, \mu_z^A, \Theta_{xx}^A, \Theta_{xy}^A, \Theta_{xz}^A, \Theta_{yy}^A, \Theta_{yz}^A, \Theta_{zz}^A, \dots \right)^{\mathrm{T}}$$

$$\mathbf{T}^{(1)} = \left(1 \quad \frac{\partial}{\partial x_A} \quad \frac{\partial}{\partial y_A} \quad \frac{\partial}{\partial z_A} \quad \frac{\partial^2}{\partial x_A^2} \quad \frac{\partial^2}{\partial x_A \partial y_A} \quad \frac{\partial^2}{\partial x_A \partial z_A} \quad \frac{\partial^2}{\partial y_A \partial x_A} \quad \frac{\partial^2}{\partial y_A^2} \quad \frac{\partial^2}{\partial y_A \partial z_A} \quad \frac{\partial^2}{\partial z_A \partial x_A} \quad \frac{\partial^2}{\partial z_A \partial y_A} \quad \frac{\partial^2}{\partial z_A^2} \quad \dots \right) \frac{1}{r}$$

$$= \left(\frac{1}{r} \quad -\frac{x}{r^3} \quad -\frac{y}{r^3} \quad -\frac{z}{r^3} \quad -\frac{-2x^2+y^2+z^2}{r^5} \quad \frac{3xy}{r^5} \quad \frac{3xz}{r^5} \quad \frac{3xy}{r^5} \quad -\frac{x^2-2y^2+z^2}{r^5} \quad \frac{3yz}{r^5} \quad \frac{3xz}{r^5} \quad \frac{3yz}{r^5} \quad -\frac{x^2+y^2-2z^2}{r^5} \right)$$

- Gradient of electric potential ϕ gives electric field $\mathbf{E}$

$$\phi = \mathbf{T}^{(1)} \mathbf{M}_A$$

$$\mathbf{E} = \nabla \phi$$

$$= \left(\nabla \mathbf{T}^{(1)} \right) \mathbf{M}_A = \begin{pmatrix} \frac{\partial \mathbf{T}^{(1)}}{\partial x_B} \\ \frac{\partial \mathbf{T}^{(1)}}{\partial y_B} \\ \frac{\partial \mathbf{T}^{(1)}}{\partial z_B} \end{pmatrix} \mathbf{M}_A = \begin{pmatrix} \frac{x_{AB}}{r_{AB}^3} & \frac{r_{AB}^2 - 3x_{AB}^2}{r_{AB}^5} & -\frac{3x_{AB}y_{AB}}{r_{AB}^5} & -\frac{3x_{AB}z_{AB}}{r_{AB}^5} & \dots \\ \frac{y_{AB}}{r_{AB}^3} & -\frac{3x_{AB}y_{AB}}{r_{AB}^5} & \frac{r_{AB}^2 - 3y_{AB}^2}{r_{AB}^5} & -\frac{3y_{AB}z_{AB}}{r_{AB}^5} & \dots \\ \frac{z_{AB}}{r_{AB}^3} & -\frac{3x_{AB}z_{AB}}{r_{AB}^5} & -\frac{3y_{AB}z_{AB}}{r_{AB}^5} & \frac{r_{AB}^2 - 3z_{AB}^2}{r_{AB}^5} & \dots \end{pmatrix} \mathbf{M}_A$$

$\mathbf{T}_{\text{dipole}}^{(2)}$

Same as

$$\mathbf{E} = \mu \frac{3(\hat{\boldsymbol{\mu}} \cdot \hat{\mathbf{r}})\hat{\mathbf{r}} - \hat{\boldsymbol{\mu}}}{r^3}$$

9

- Electric moment vector (polytensor)   Interaction energy

$$\mathbf{M}_A = \left(Q^A, \mu_x^A, \mu_y^A, \mu_z^A, \Theta_{xx}^A, \Theta_{xy}^A, \Theta_{xz}^A, \Theta_{yy}^A, \Theta_{yz}^A, \Theta_{zz}^A, \dots \right)^{\mathrm{T}}$$

$$U_{AB} = \mathbf{M}_B^T \mathbf{T}^{(2)} \mathbf{M}_A$$

- Derivative matrix (rank-2 polytensor)

E.g., dipole-dipole special case

$$\mathbf{T}^{(2)} = \begin{pmatrix} 1 & \frac{\partial}{\partial x_B} & \frac{\partial}{\partial y_B} & \frac{\partial}{\partial z_B} & \cdots \\ \frac{\partial}{\partial x_A} & \frac{\partial^2}{\partial x_A \partial x_B} & \frac{\partial^2}{\partial x_A \partial y_B} & \frac{\partial^2}{\partial x_A \partial z_B} & \cdots \\ \frac{\partial}{\partial y_A} & \frac{\partial^2}{\partial y_A \partial x_B} & \frac{\partial^2}{\partial y_A \partial y_B} & \frac{\partial^2}{\partial y_A \partial z_B} & \cdots \\ \frac{\partial}{\partial z_A} & \frac{\partial^2}{\partial z_A \partial x_B} & \frac{\partial^2}{\partial z_A \partial y_B} & \frac{\partial^2}{\partial z_A \partial z_B} & \cdots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix} \frac{1}{r}$$

$$\mathbf{T}^{(2)}_{\mathrm{dipole}} = \begin{pmatrix} \frac{\partial^2}{\partial x_A \partial x_B} & \frac{\partial^2}{\partial x_A \partial y_B} & \frac{\partial^2}{\partial x_A \partial z_B} \\ \frac{\partial^2}{\partial y_A \partial x_B} & \frac{\partial^2}{\partial y_A \partial y_B} & \frac{\partial^2}{\partial y_A \partial z_B} \\ \frac{\partial^2}{\partial z_A \partial x_B} & \frac{\partial^2}{\partial z_A \partial y_B} & \frac{\partial^2}{\partial z_A \partial z_B} \end{pmatrix} \frac{1}{r}$$

$$= \frac{1}{r^5} \begin{pmatrix} r^2 - 3x^2 & -3xy & -3xz \\ -3xy & r^2 - 3y^2 & -3yz \\ -3xz & -3yz & r^2 - 3z^2 \end{pmatrix}$$

$x_B - x_A$

$$r = \sqrt{(x_B - x_A)^2 + (y_B - y_A)^2 + (z_B - z_A)^2}$$

Polarizability tensor quantifies how easily a molecule's charge distribution can be changed

- Induced dipole moment

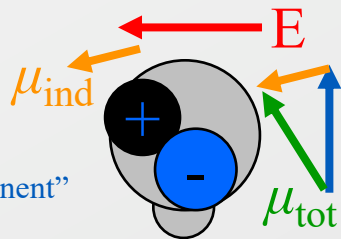Could also do induced quadrupole, etc.

$$\boldsymbol{\mu}_{\text{ind}} = \boldsymbol{\alpha} \cdot \mathbf{E}$$

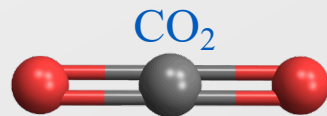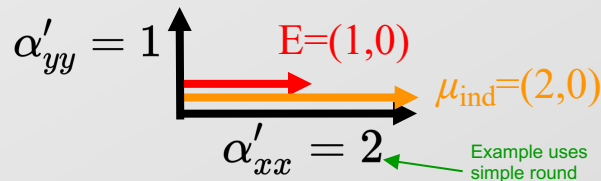$$\boldsymbol{\alpha} = \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix}$$

Induced dipole moment in *x* direction due to electric field in *z* direction

No electric field

E

μ_{ind}

μ_{tot}

"permanent" μ dipole moment

CO_2

$\alpha'_{xx} = 4.5\text{Å}^3, \quad \alpha'_{yy} = \alpha'_{zz} = 2.2\text{Å}^3$

Field parallel to a principal axis: μ_{ind} parallel to field

$\alpha'_{yy} = 1$

E=(1,0)

μ_{ind}=(2,0)

$\alpha'_{xx} = 2$

Example uses simple round numbers

- Diagonalize $\boldsymbol{\alpha}$ and find principal axes

$$\boldsymbol{\alpha}' = \begin{pmatrix} \alpha'_{xx} & 0 & 0 \\ 0 & \alpha'_{yy} & 0 \\ 0 & 0 & \alpha'_{zz} \end{pmatrix}$$

Field not parallel to a principal axis: μ_{ind} not parallel to field

$\alpha'_{yy} = 1$

E=(1,1)

μ_{ind}=(2,1)

$\alpha'_{xx} = 2$

11

- Imagine inducing a dipole by moving a point charge reversibly along x
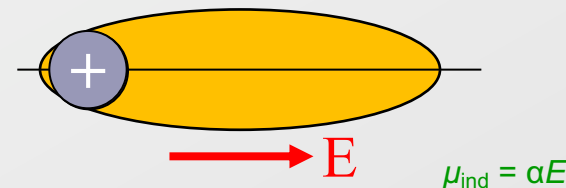
$\mu_{\text{ind}} = \alpha E$

- Differential work: $dW = Fdx = (qE)dx = Ed\mu$

- Use $d\mu_{\text{ind}} = \alpha\, dE$ and integrate: $W = \int_0^E Ed(\alpha E) = \frac{1}{2}\alpha E^2 = \frac{1}{2\alpha}\mu_{\text{ind}}^2$

- Energy of induced dipole in field: $-\mu_{\text{ind}}\, E = -\alpha\, E^2$

- Net energy of induced dipole: $-\alpha E^2 + \frac{1}{2}\alpha E^2 = -\frac{1}{2}\alpha E^2$

- More generally: $u_{\text{ind}} = -\frac{1}{2}\boldsymbol{\alpha} : \mathbf{EE} = -\frac{1}{2}\mathbf{E} \cdot \boldsymbol{\alpha} \cdot \mathbf{E}$

A variety of approaches can be used to model polarization

- Fluctuating charge (FQ)
  - Charges change but don't move
  - Limits on direction in which response can be made (e.g., out of plane)

- Drude oscillator (DO)
  - Charges move, but don't change
  - More interaction sites to process

- Point dipole (PD)
  - Strength and direction of dipole responds to field
  - Can model anisotropic polarizability
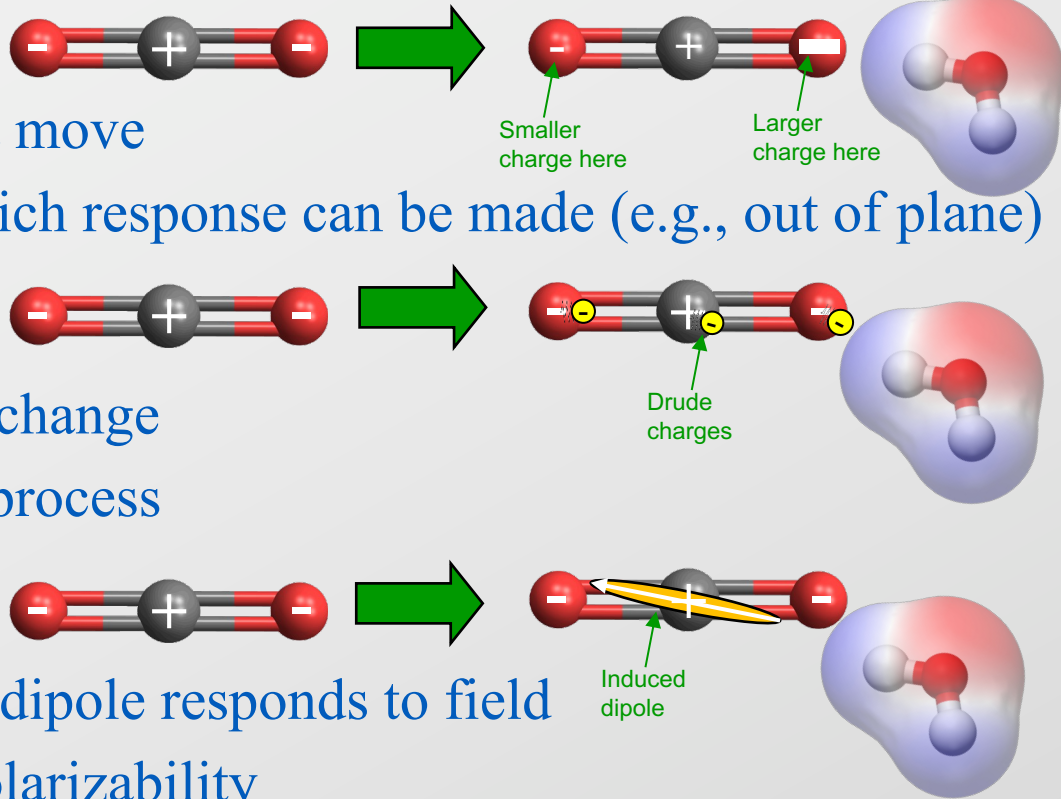
In principle, induced electrostatic features need to be converged to self-consistency

- A direct solution is possible

$$\boldsymbol{\mu}_{\text{ind}} = \boldsymbol{\alpha}\mathbf{E}_{\text{tot}} = \boldsymbol{\alpha}(\mathbf{E}_{\text{static}} + \mathbf{E}_{\text{ind}}) = \boldsymbol{\alpha}(\mathbf{E}_{\text{static}} + \mathbf{T}_{\text{dipole}}^{(2)}\boldsymbol{\mu}_{\text{ind}})$$

$$\boldsymbol{\mu}_{\text{ind}} = \left(\boldsymbol{\alpha}^{-1} - \mathbf{T}_{\text{dipole}}^{(2)}\right)^{-1}\mathbf{E}_{\text{static}} \equiv \mathbf{R}\mathbf{E}_{\text{static}} \qquad u = -\tfrac{1}{2}\boldsymbol{\alpha}^{-1} : \boldsymbol{\mu}_{\text{ind}}\boldsymbol{\mu}_{\text{ind}}$$

(need to double check this)

- But the matrices are very large, $3N \times 3N$

  - *E.g., for N = 3*

$$T_{AB}^{(2)} = \frac{1}{r_{AB}^5}\begin{pmatrix} r_{AB}^2 - 3x_{AB}^2 & -3x_{AB}y_{AB} & -3x_{AB}z_{AB} \\ -3x_{AB}y_{AB} & r_{AB}^2 - 3y_{AB}^2 & -3y_{AB}z_{AB} \\ -3x_{AB}z_{AB} & -3y_{AB}z_{AB} & r_{AB}^2 - 3z_{AB}^2 \end{pmatrix}$$

$$\boldsymbol{\alpha} = \begin{pmatrix} \boldsymbol{\alpha}_A & (0)_{3\times 3} & (0) \\ (0) & \boldsymbol{\alpha}_B & (0) \\ (0) & (0) & \boldsymbol{\alpha}_C \end{pmatrix} \quad \mathbf{T}_{\text{dipole}}^{(2)} = \begin{pmatrix} (0)_{3\times 3} & \mathbf{T}_{AB}^{(2)} & \mathbf{T}_{AC}^{(2)} \\ \mathbf{T}_{BA}^{(2)} & (0) & \mathbf{T}_{BC}^{(2)} \\ \mathbf{T}_{CA}^{(2)} & \mathbf{T}_{CB}^{(2)} & (0) \end{pmatrix} \quad \boldsymbol{\mu}_{\text{ind}} = \begin{pmatrix} \mu_{A,x} \\ \mu_{A,y} \\ \mu_{A,z} \\ \mu_{B,x} \\ \vdots \\ \mu_{C,z} \end{pmatrix} \quad \boldsymbol{E}_{\text{static}} = \begin{pmatrix} E_{A,x}^{\text{static}} \\ E_{A,y}^{\text{static}} \\ E_{A,z}^{\text{static}} \\ E_{B,x}^{\text{static}} \\ \vdots \\ E_{C,z}^{\text{static}} \end{pmatrix}$$

- Usually iteration is used instead

14

Electrostatics for some simple molecules

Images not to scale!
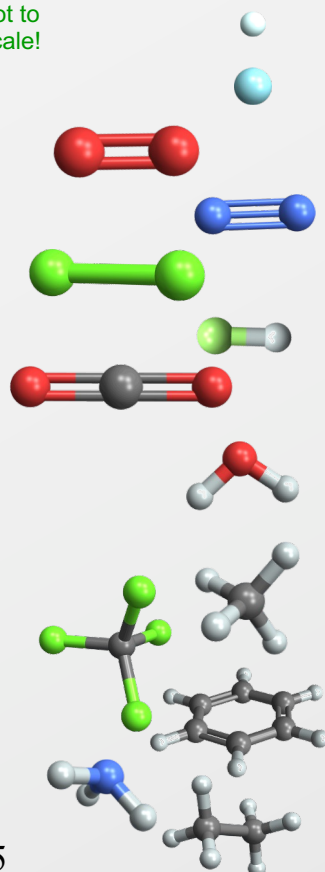
Molecule	μ, Debye	Q, B	α, A^3
He	0	0	0.206
Ar	0	0	1.642
O_2	0	-0.4	1.48
N_2	0	→ -1.4	1.7
Cl_2	0	4.2	4.6
HF	→ 1.8	2.6	→ 0.8
CO_2	0	→ -4.3	2.9
H_2O	→ 1.85	+1.97 (xx) -1.89 (yy) -0.08 (zz)	1.5 (xx) 1.43 (yy) 1.45 (zz)
CH_4	0	0	2.6
CCl_4	0	0	→ 11.2
C_6H_6	0	→ -9.5	→ 10.6
NH_3	1.5	-2.3	2.22
C_2H_6	0	-1.2	4.4

Short-range repulsion is due to exchange and Coulomb effects

- Approach of molecules causes distortion of electron clouds, as they avoid each other due to Pauli exclusion
  - This increases the energy of the pair
  - Also, shifted electron clouds attract nuclei in a direction that pulls molecules apart

- Theory provides little guidance on form of model
  - Total repulsion energy drops quickly (exponentially) with separation
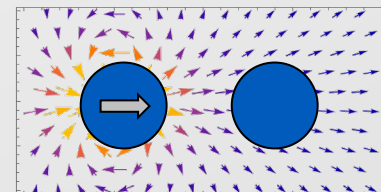 - Not expressible in terms of properties of individual atoms
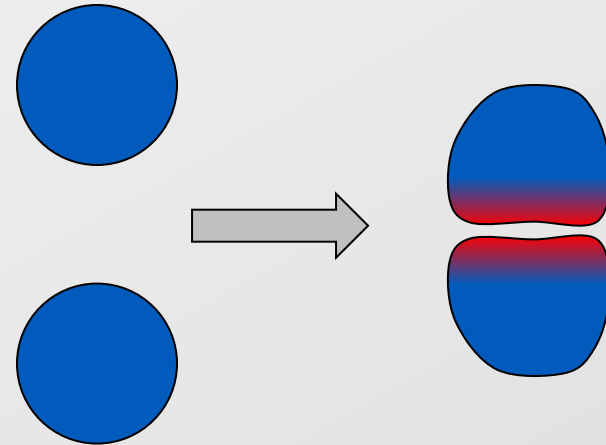
Long-range attraction is due to coordinated dipole (and higher) fluctuations

- Consider two neutral atoms
  - Too separated for exchange or charge overlap

- Electrons constantly moving
  - Atom-1 fluctuation makes instantaneous dipole

- This creates an electric field about atom 2
  - Field: $E \sim \mu_1 r^{-3}$ $\mathbf{E} = \mu \dfrac{3(\hat{\boldsymbol{\mu}} \cdot \hat{\mathbf{r}})\hat{\mathbf{r}} - \hat{\boldsymbol{\mu}}}{r^3}$

- Field induces dipole in atom 2
  - Induction: $\mu_{\text{ind}} = \alpha_2 E$

- Net energy of induced dipole   Induced-μ/E-field interaction, minus work to make dipole
  - Dispersion energy: $u_{\text{disp}} \sim -\frac{1}{2}\alpha_2 E^2 \sim -\frac{1}{2}\alpha_2 \mu_1^2 r^{-6} \sim -\alpha_2 \langle \mu_1^2 \rangle r^{-6} \sim -\alpha_2 \alpha_1 r^{-6}$

time average

Long-range attraction is due to coordinated dipole (and higher) fluctuations

- London dispersion energy decays as r^{-6}
  - "dispersion" has to do with polarizability and diffraction of light

- Hartree-Fock is unable to exhibit this behavior
  - Lack of correlation in model
  - Basic DFT also fails to accommodate this effect

Theoretical results have been developed for multibody dispersion, but are rarely used

- Axilrod-Teller

  - consider response of atoms 2 and 3 to fluctuation in dipole moment of atom 1

  - average over all fluctuations in 1

  $$E_3(1,2,3) = \frac{3}{2} E_0 \frac{\alpha_1 \alpha_2 \alpha_3}{r_{12}^3 r_{13}^3 r_{23}^3} (3 \cos \theta_1 \cos \theta_2 \cos \theta_3 + 1)$$

  - this is rarely, if ever, used in practice
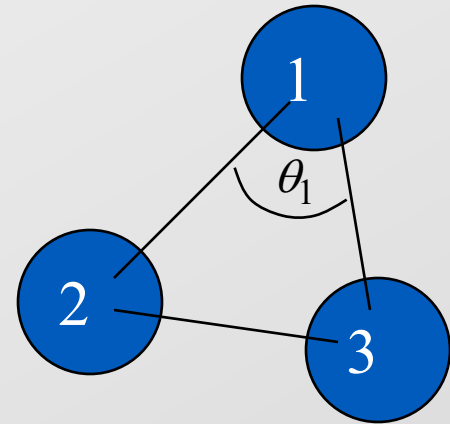
Van der Waals energy is the term used to describe repulsion + dispersion interactions

- Two popular approaches to model repulsion
  - Inverse power $U_{vdW}^{rep} \sim \dfrac{A}{r^n}$ Exponential $U_{vdW}^{rep} \sim Ae^{-Br}$

    typically $n \sim 9 - 12$ 2 parameters
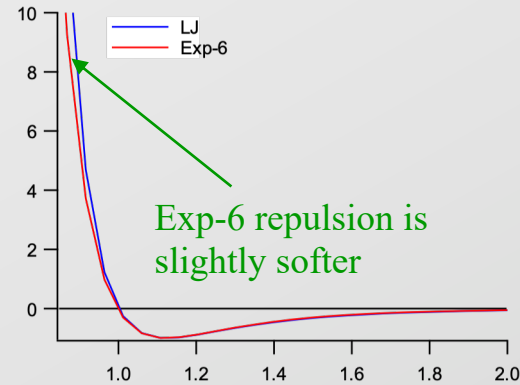
- Combine with attraction term
  - Lennard-Jones $U = \dfrac{A}{r^{12}} - \dfrac{C}{r^{-6}} = 4\varepsilon\left[\left(\dfrac{\sigma}{r}\right)^{12} - \left(\dfrac{\sigma}{r}\right)^{6}\right]$

  Exp-6 repulsion is slightly softer

  - Exp-6 $U = Ae^{-Br} - \dfrac{C}{r^{-6}}$

  Beware of anomalous Exp-6 short-range attraction

  a.k.a. "Buckingham" or "Hill" potential
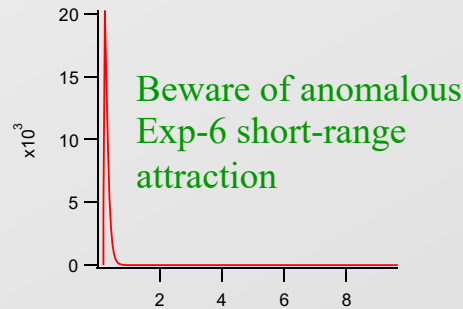
Combining rules are used to estimate parameters for unlike atoms

- Approach is to use same model potential, but with "averaged" parameters
  - No ambiguity for Coulomb interactions $u(r) = \dfrac{q_i q_j}{r}$
  - For effective potential (e.g., LJ), it is not clear what to do

- Lorentz-Berthelot is a widely used choice

$$\sigma_{12} = \tfrac{1}{2}(\sigma_1 + \sigma_2)$$
$$\varepsilon_{12} = \sqrt{\varepsilon_1 \varepsilon_2}$$

  - Others have been proposed

- Treatment is a very weak link in quantitative applications

This is just a few of the most popular ones

Force field	E_{str}	E_{bend}	E_{oop}	E_{vdw}	E_{el}	E_{cross}	Molecules
AMBER[82]	P2	P2	imp.	12–6	Charge, PD	None	Biomolecules
AMOEBA[83]	P2	P2		14–7	Quad, PD	None	Biomolecules
CFF91/93/95[84]	P4	P4	P2	9–6	Charge	ss, bb, st, sb, bt, btb	General
CHARMM[85]	P2	P2	P2(imp.)	12–6	Charge DO	None	Biomolecules
COMPASS[86]	P4	P4	P2	9–6	Charge	ss, sb, st, bb, bt, bbt	Organic
COSMIC[87]	P2	P2		Morse	Charge	None	General
CVFF[88]	P2 or Morse	P2	P2	12–6	Charge	ss, bb, sb, btb	General
DREIDING[89]	P2 or Morse	P2(cos)	P2(cos)	12–6 or Exp–6	Charge	None	General
EAS[90]	P2	P3	None	Exp–6	None	None	Alkanes
ECEPP[91]	Fixed	Fixed	Fixed	12–6 and 12–10	Charge	None	Proteins
EFF[92]	P4	P3	None	Exp–6	None	ss, bb, sb, st, btb	Alkanes
ENCAD[93]	P2	P2	imp.	12–6	Charge	None	Biomolecules
ESFF[94]	Morse	P2(cos)	P2	9–6	Charge	None	All elements
GAFF[95]	P2	P2	imp	12–6	Charge	None	Organic
GROMOS[96]	P2	P2	P2(imp.)	12–6	Charge, DO	None	Biomolecules
MM2[6]	P3	P2+P6	P2	Exp–6	Dipole	sb	General
MM3[7]	P4	P6	P2	Exp–6	Dipole or charge	sb, bb, st	General (all elements)
MM4[97]	P6	P6	imp.	Exp–6	Charge	ss, bb, sb, tt, st, tb, btb	General
MMFF[98]	P4	P3	P2	14–7	Charge	sb	General
MOMEC[99]	P2	P2	P2	Exp–6	Charge, FQ	None	Metal coordination
NEMO[100]	Fixed	Fixed	None	Exp–6	Quad, PD	None	Special
OPLS[101]	P2	P2	imp.	12–6	Charge	None	Biomolecules
PFF[102]	P2	P2	imp.	12–6	Charge, FQ, PD	None	Proteins
PROSA[58]	P2	P2	imp.	12–6	Charge, FQ, PD	None	Proteins
QMFF[103]	P4	P4	P2	9–6	Charge	ss, sb, st, bb, bt, btb	General
SDFF[104]	P4	P4		9–6	Quad, PD	ss, st, tt	Hydrocarbons
SHAPES[105]	P2	$\cos(n\theta)$	P2(imp.)	12–6	Charge	None	Metal coordination
TraPPE[106]	Fixed	P2	Fixed	12–6	Charge	None	Organic
TRIPOS[107]	P2	P2	P2	12–6	Charge	None	General
UFF[80]	P2 or Morse	$\cos(n\theta)$	imp.	12–6	Charge	None	All elements
YETI[108]	P2	P2	imp.	12–6 and 12–10	Charge	None	Proteins

F. Jensen

Notation. Pn: polynomial of order n; Pn(cos): polynomial of order n in cosine to the angle; Pn(imp.): polynomial of order n in the improper angle; $\cos(n\theta)$: Fourier term(s) in cosine to the angle; Exp–6: exponential $+ R^{-6}$; $n - m$: $R^{-n} + R^{-m}$ Lennard-Jones-type potential; Quad: electric moments up to quadrupoles; FQ: fluctuating charge; DO: Drude oscillator, PD: point dipole; Fixed: not a variable; imp.: improper torsional angle; ss: stretch–stretch; bb: bend–bend: sb: stretch–bend; st: stretch–torsional; bt: bend–torsional; tt: torsional–torsional; btb: bend–torsional–bend.

22

Suggested Reading/Viewing

- Frank Jensen, *Introduction to Computational Chemistry*, 3rd ed., Wiley (2017). Chapter 2.
  Available online via UB library:

  - https://search.lib.buffalo.edu/permalink/01SUNY_BUF/9qhqtp/alma9939265811804803

- C.G. Gray and K.E. Gubbins, *Theory of Molecular Fluids*, Vol. 1: Fundamentals (1984).

  - Detailed, comprehensive discussion of molecular electrostatics
  - Not required reading. Recommended for anyone needed to look at the topic in more detail.