

CHEM-E4115

Computational Chemistry I (5op)

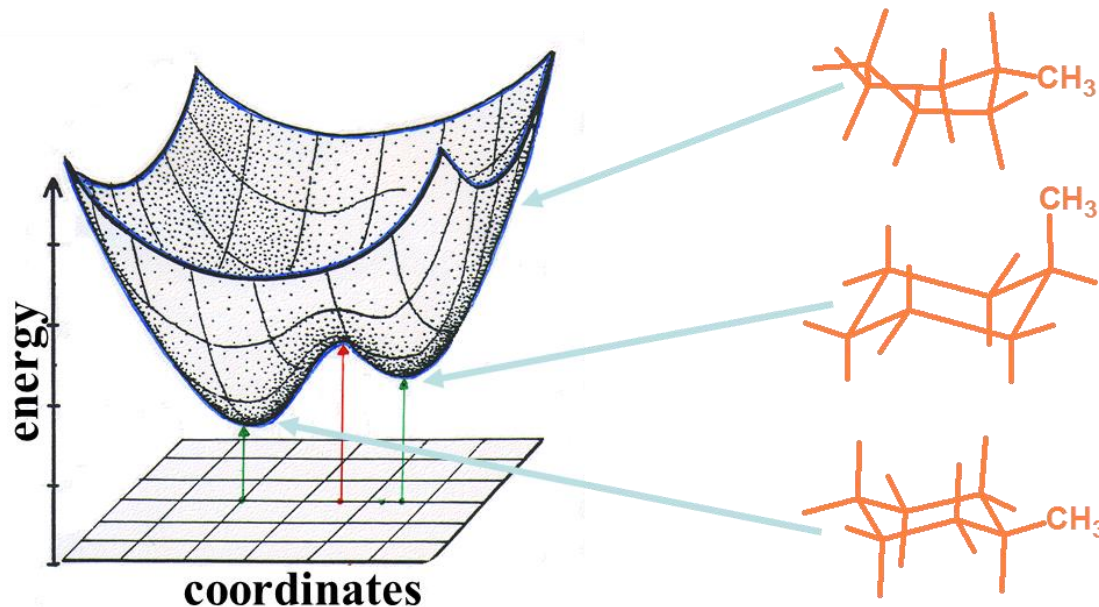
2nd part: molecular modelling

Book Chapter 4.1-4.12

Empirical Force Field Models:
Molecular Mechanics

Introduction to force-fields

- Revision
 - Potential energy surface: defined by force-field for each molecule or molecule system
 - Each point represents a molecular conformation



Revision: From quantum mechanics to molecular mechanics

- Many molecular systems in chemistry unfortunately too large to be considered by quantum mechanics
- Force-field methods (molecular mechanics) ignore electronic motion and calculate **the energy of the system as a function of nuclei positions** (molecular subunit positions in coarse-grained force-fields)
 - Enables treating large number of atoms (up to $\sim 10^6$ - 10^7)
 - Loses most electron based characteristics (conductivity, i.e., band-gaps, most often also reaction kinetics*, all chemical reactions* and charge re-distribution*)

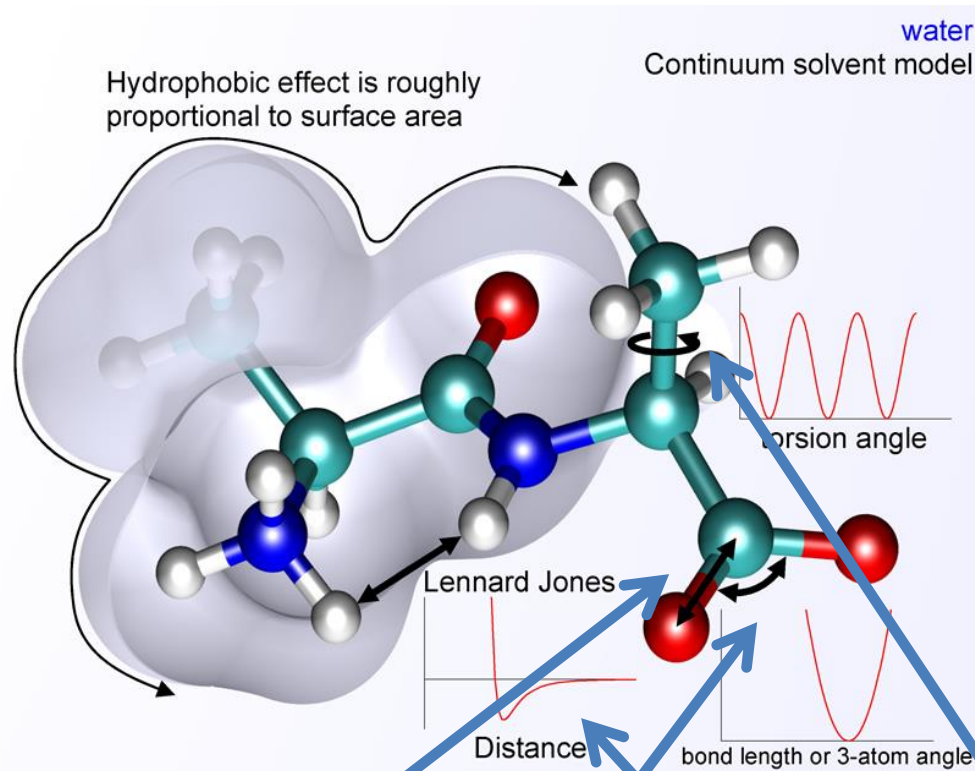
* Typically. That is, some specific force-fields are designed to reproduce also reaction barriers and limited reactions (typically bond-order type advanced force fields) and some enable charge re-distribution (polarization) to some extent

Why do force-field methods work, or do they?

- Assumptions to obtain a functional force-field
 - Born-Oppenheimer approximation (electron motion can be treated separately from nuclei motion due to different time scales)
 - Energy can be written as a function of nuclear coordinates
 - Nuclei follow classical mechanics
 - Force-field terms can be written as separate, simple expressions with separated contributions due different molecular conformation and coordinate changes
 - Typically: Bond stretching, angle between two bonds, twisting (dihedrals), van der Waals, and electrostatic interaction terms
 - Force-field needs to be transferable! (tested on a small number of cases -> must be usable to a much wider set of molecules and problems)

Revision: Typical representation of a force-field (Potential energy surface)

Dialanine peptide in implicit (continuum) solvent



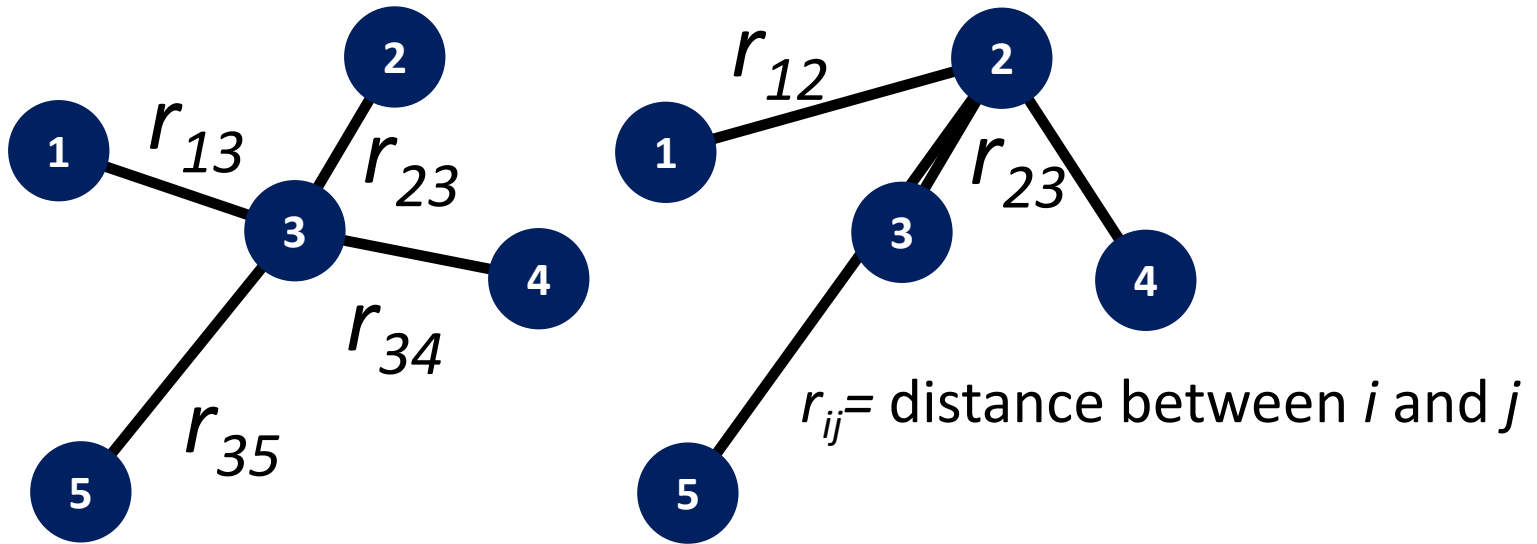
$$E_{\text{bonded}} = E_{\text{bond}} + E_{\text{angle}} + E_{\text{dihedral}}$$
$$E_{\text{nonbonded}} = E_{\text{electrostatic}} + E_{\text{van der Waals}}$$

Force-fields: A diverse family

- Two-body force-fields (pair potentials)
 - Simple, extremely fast
 - Liquids, gases, solids
 - Lennard-Jones, Morse, ...
- **Many-body chemically non-reactive force-fields**
 - **Many different atom types and molecules covered**
 - **Typically: a wide variety of organic molecules such as proteins, hydrocarbons, lipids, polymers, ...**
 - **Non-reactive!**
- Many-body (reactive) force-fields
 - A wide variety of typically inorganic materials and compounds including also metals (structural & mechanical properties). Organic molecules tend to be too complex.
 - Some are **reactive!**

Pair potentials (two-body force-fields)

- Total potential energy calculated as sum over pairs of interacting objects

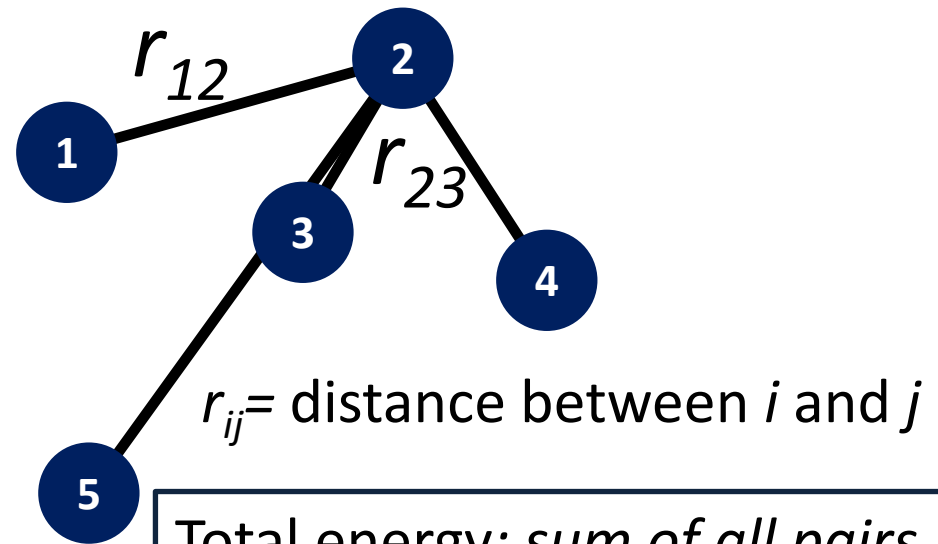
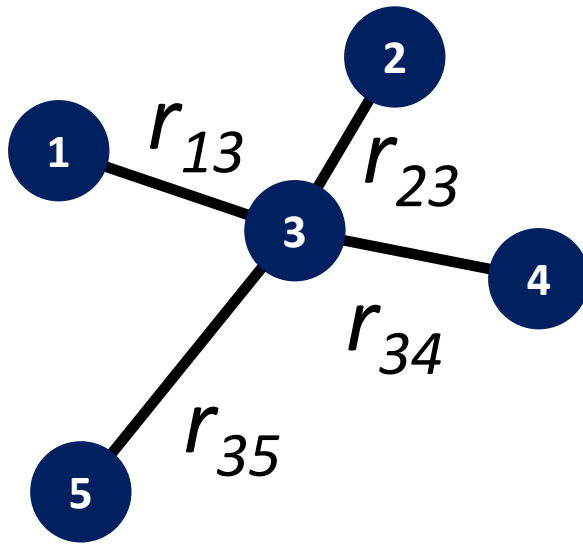


Energy of atom i

$$V_i = \sum_j^N V_{ij}(r_{ij})$$

Pair potentials (two-body force-fields)

- Total potential energy calculated as sum over pairs of interacting objects



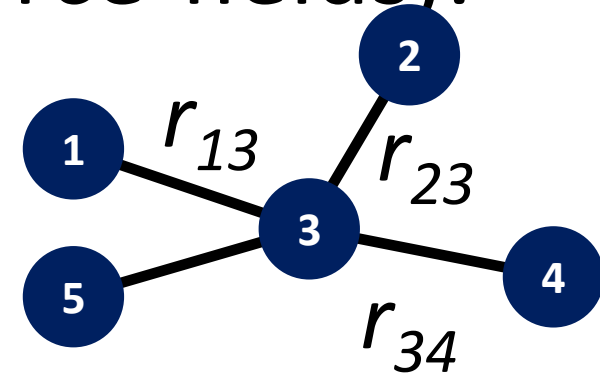
Total energy: *sum of all pairs*

Energy of atom i

$$V_i = \sum_j^N V_{ij}(r_{ij}) \quad V_{tot} = \frac{1}{2} \sum_{i \neq j} \sum_j^N V_{ij}(r_{ij})$$

Avoid double counting

Pair potentials (two-body force-fields): examples



$$V(r_{ij}) = D e^{-2\alpha(r_{ij}-r_0)} - 2D e^{-\alpha(r_{ij}-r_0)}$$

$$V(r_{ij}) = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right]$$

$$V(r_{ij}) = A e^{\left(-\frac{r_{ij}}{\sigma} \right)} - C \left(\frac{\sigma}{r_{ij}} \right)^6$$

$$V(r_{ij}) = a_0 + \frac{1}{2} k (r_{ij} - r_0)^2$$

Morse potential

Lennard-Jones 12-6
potential

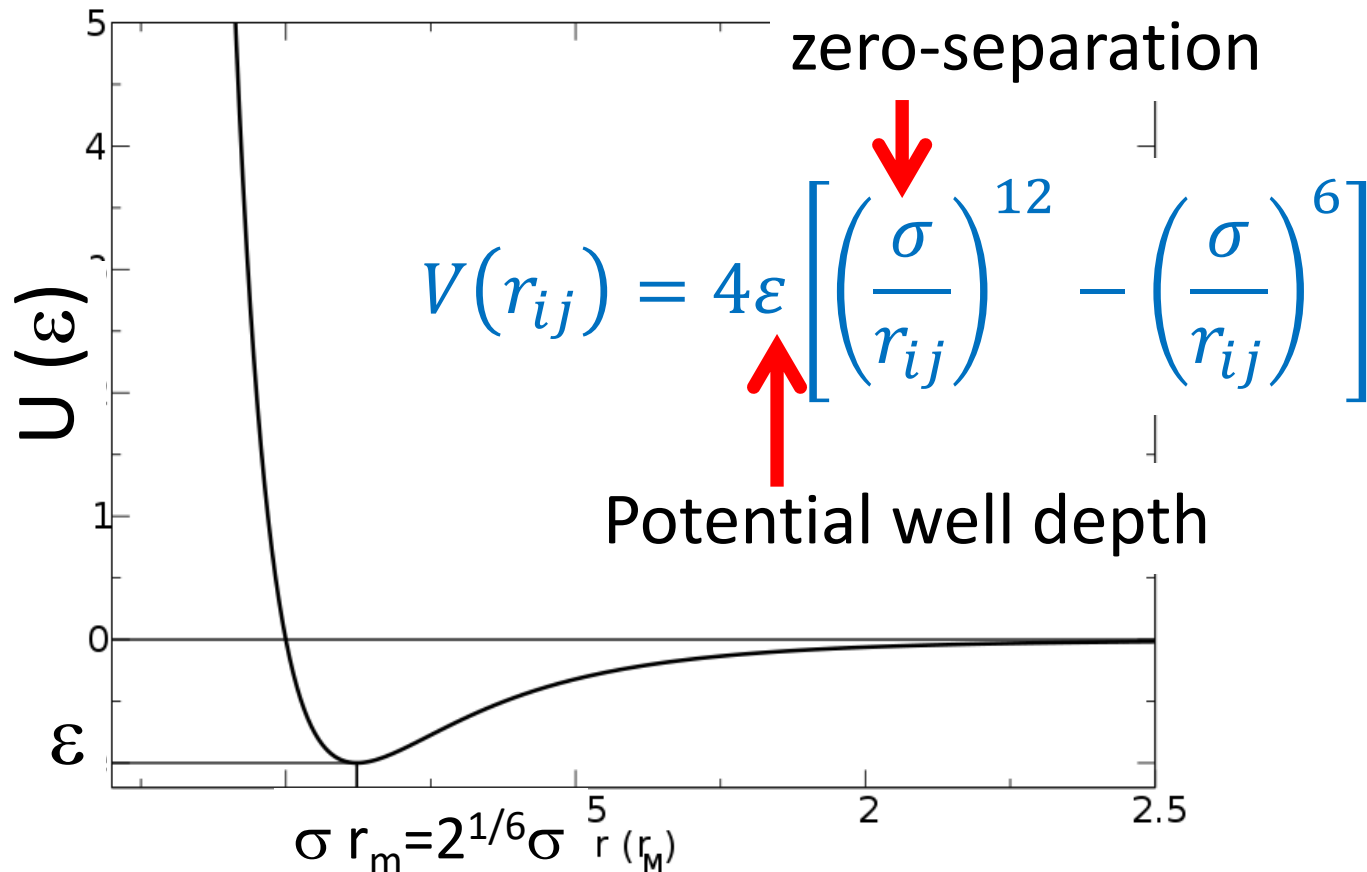
Buckingham potential

Harmonic approximation
(spring potential)

Outside molecular modeling:
Newton's law of gravity,
Coulomb's law, ...

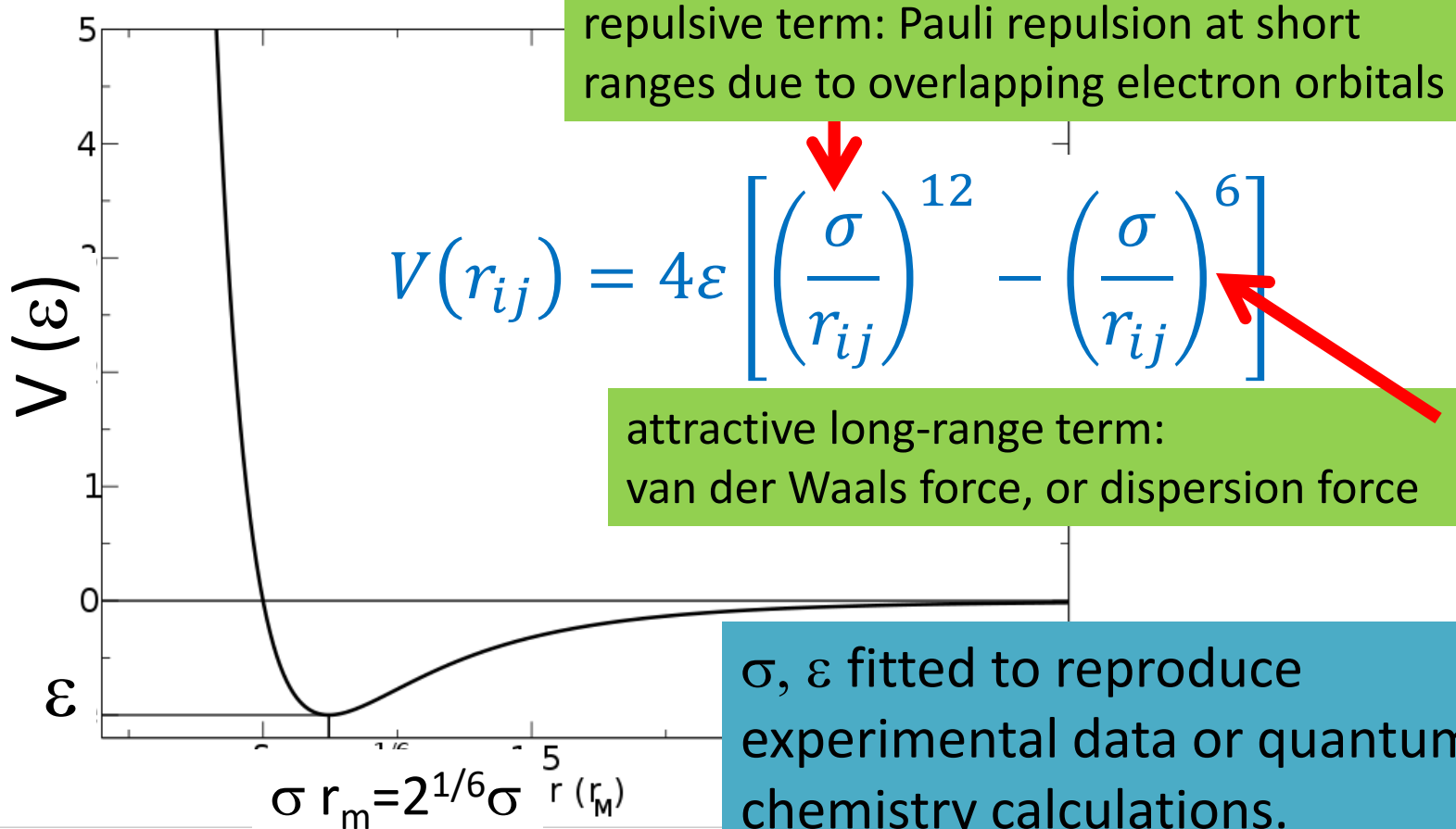
Pair potentials: Lennard-Jones 12-6

~interaction between a pair of neutral atoms or molecules

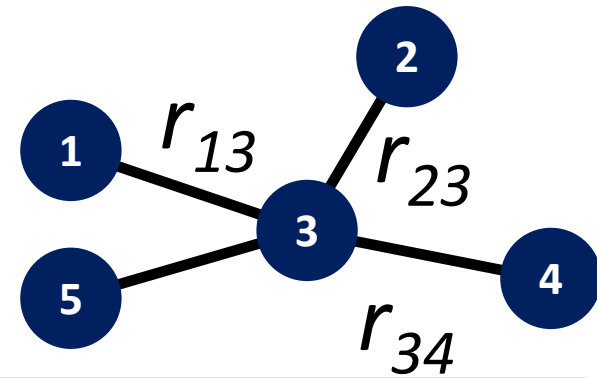


Pair potentials: Lennard-Jones 12-6

~interaction between a pair of neutral atoms or molecules



Pair-potentials: summary



Total energy: *sum of all pairs*

Energy of atom i

$$V_i = \sum_j^N V_{ij}(r_{ij}) \quad V_{tot} = \frac{1}{2} \sum_{i \neq j} \sum_j^N V_{ij}(r_{ij})$$

Avoid double counting

- Interaction based on just pair-wise distance
- Good for: noble gases, non-directed bonding
- Simple, fast!
- Failures:
 - bond strength explicitly independent of environment
 - Vacancy formation energy in lattice fundamentally overestimated
 - Only close-packed lattice structures
 - Elastic moduli $C_{12}=C_{44}$ (not true!)

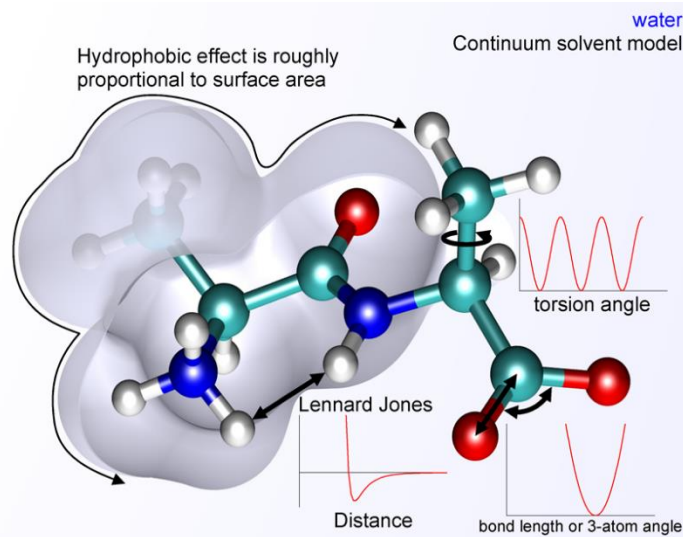
Force-fields: A diverse family

- Two-body force-fields (pair potentials)
 - Simple, extremely fast
 - Liquids, gases, solids
 - Lennard-Jones, Morse, ...
- **Many-body chemically non-reactive force-fields**
 - **Many different atom types and molecules covered**
 - **Typically: a wide variety of organic molecules such as proteins, hydrocarbons, lipids, polymers, ...**
 - **Non-reactive!**
- Many-body (reactive) force-fields
 - A wide variety of typically inorganic materials and compounds including also metals (structural & mechanical properties). Organic molecules tend to be too complex.
 - Some are **reactive!**

In the following: Force-field = Many-body chemically non-reactive force-field

Typical approach for many-body chemically non-reactive force-fields:

Division of interactions into analytical expression that has separate terms each corresponding to physical interactions of different origin/magnitude -> force-field (Potential energy surface)



Dialanine peptide in implicit (continuum) solvent

$$E_{\text{bonded}} = E_{\text{bond}} + E_{\text{angle}} + E_{\text{dihedral}}$$
$$E_{\text{nonbonded}} = E_{\text{electrostatic}} + E_{\text{van der Waals}}$$

Many-body chemically non-reactive force-fields: Typical functional form (Leach's notation)

$$\begin{aligned} V &= V_{bonded} + V_{nonbonded} \\ V_{bonded} &= V_{bonds} + V_{angles} + V_{dihedrals} \\ V_{nonbonded} &= V_{van\ der\ Waals} + V_{electrostatic} \end{aligned}$$

$$\begin{aligned} V(\vec{r}^N) &= \frac{1}{2} \sum_{bonds} k_i (l_i - l_{i,0})^2 + \frac{1}{2} \sum_{angles} k'_i (\theta_i - \theta_{i,0})^2 \\ &\quad + \sum_{torsions} \frac{V_N}{2} k''_i (1 + \cos(n\omega - \gamma)) \\ &\quad + \sum_{i=1}^N \sum_{j=i+1}^N \left(4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \right) \end{aligned}$$

For example, AMBER force-field has this form

Many-body chemically non-reactive force-fields: Typical functional form (Leach's notation)

$$\begin{aligned}
 V(\vec{r}^N) = & \frac{1}{2} \sum_{bonds} k_i (l_i - l_{i,0})^2 + \frac{1}{2} \sum_{angles} k'_i (\theta_i - \theta_{i,0})^2 \\
 & + \sum_{torsions} \frac{V_N}{2} k''_i (1 + \cos(n\omega - \gamma)) \\
 & + \sum_{i=1}^N \sum_{j=i+1}^N \left(4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \right)
 \end{aligned}$$

Potential energy
 Bond i length
 Bond i reference length
 Angle i
 Angle i reference
 Bond rotation energy
 n=multiplicity
 γ shift
 Summation over all particle pairs
 Lennard-Jones 12-6 potential van der Waals (dispersion interaction)
 Coulomb energy charge-charge interaction

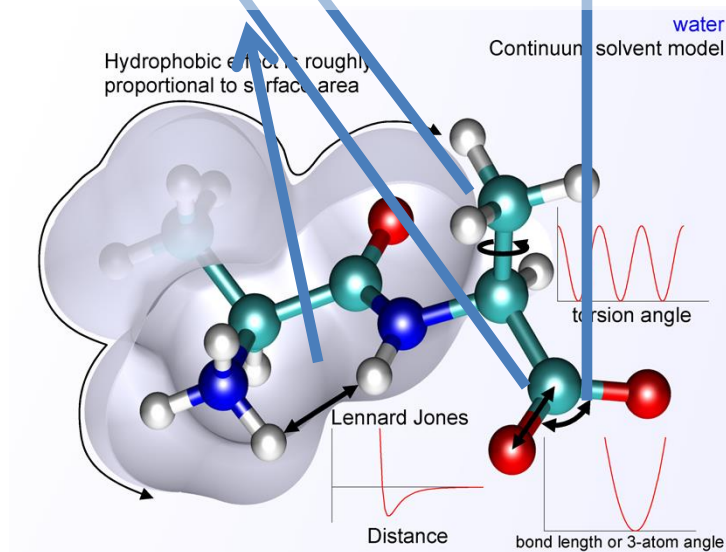
For example, AMBER force-field has this form

Dialanine peptide in implicit (continuum) solvent

$$V(\vec{r}^N) = \frac{1}{2} \sum_{bonds} k_i (l_i - l_{i,0})^2 + \frac{1}{2} \sum_{angles} k'_i (\theta_i - \theta_{i,0})^2$$

$$+ \sum_{torsions} \frac{V_N}{2} k''_i (1 + \cos(n\omega - \gamma))$$

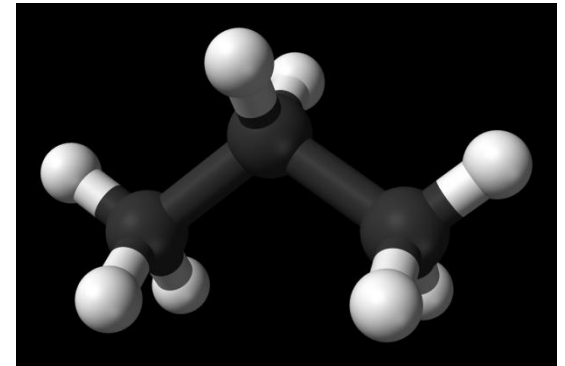
$$+ \sum_{i=1}^N \sum_{j=i+1}^N \left(4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \right)$$



Force-field parameters

$$\begin{aligned}
 V(\vec{r}^N) = & \frac{1}{2} \sum_{bonds} k_i (l_i - l_{i,0})^2 + \frac{1}{2} \sum_{angles} k'_i (\theta_i - \theta_{i,0})^2 \\
 & + \sum_{torsions} \frac{V_N}{2} k''_i (1 + \cos(n\omega + \gamma)) \\
 & + \sum_{i=1}^N \sum_{j=i+1}^N \left(4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \right)
 \end{aligned}$$

- Inherently huge number of parameters
- Grouping of similar / same -> reduces complexity, more generally usable force fields, but may cause problems going outside original parametrization regime
- Sources: Reproducing experimental data and ab initio (quantum chemical calculations)



Propane C₃H₈

Example of variation in functional form: OPLS-force-field

Note: Force-fields are empirical. There is no right or wrong functional form. A form may become popular if it works well and is computationally efficient. This energy term division is common.

$$E(r^N) = E_{\text{bonds}} + E_{\text{angles}} + E_{\text{dihedrals}} + E_{\text{nonbonded}}$$

$$E_{\text{bonds}} = \sum_{\text{bonds}} K_r (r - r_0)^2$$

$$E_{\text{angles}} = \sum_{\text{angles}} k_\theta (\theta - \theta_0)^2$$

$$E_{\text{dihedrals}} = \frac{V_1}{2} [1 + \cos(\phi - \phi_0)] + \frac{V_2}{2} [1 - \cos 2(\phi - \phi_0)] + \frac{V_3}{2} [1 + \cos 3(\phi - \phi_0)] + \frac{V_4}{2} [1 - \cos 4(\phi - \phi_0)]$$

$$E_{\text{nonbonded}} = \sum_{i>j} f_{ij} \left(\frac{A_{ij}}{r_{ij}^{12}} - \frac{C_{ij}}{r_{ij}^6} + \frac{q_i q_j e^2}{4\pi\epsilon_0 r_{ij}} \right)$$

$$\text{with the combining rules } A_{ij} = \sqrt{A_{ii}A_{jj}} \text{ and } C_{ij} = \sqrt{C_{ii}C_{jj}}.$$

Intramolecular nonbonded interactions $E_{\text{nonbonded}}$ are counted only for atoms three or more bonds apart; 1,4 interactions are scaled down by the "fudge factor" $f_{ij} = 0.5$, otherwise $f_{ij} = 1.0$.

Force-fields and parameters

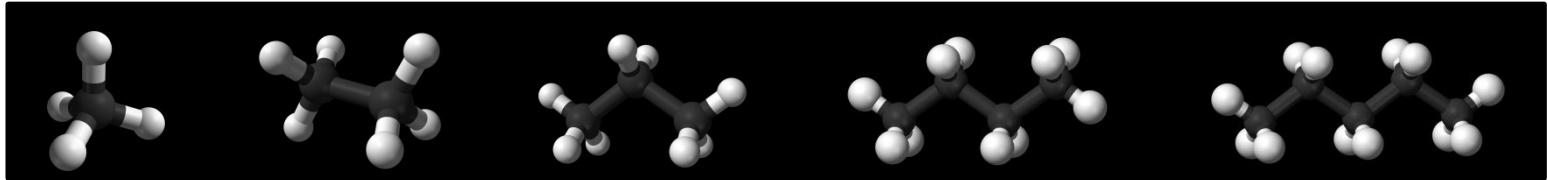
- Force-field requires: Both functional form and parameter values
- Two force fields may have
 - Same functional form but different parameter values
 - Different functional form but same accuracy on same problem
- Force-field should be considered as an entity, not as divided into individual components
 - Parameters from one force-field are not transferable to another even though functional forms may be same!
 - Bond length and angle form an exception (some cases)

Force-field parameters

- Typically designed to reproduce structural properties, can also be designed to reproduce spectra (vibrations)
 - A force-field may predict other quantities outside the parametrization regime but if it does not, it is not a failure!
- Important to know what each force-field has been parameterized to reproduce
- Examples: Liquid properties (density, heat of vaporization) (OPLS), condensed phase properties of alkenes (GROMOS) partition properties between two different solvents (MARTINI), model peptide structure formation accuracy, ...
- Examples for pair potentials & inorganic potentials (typically): Lattice structures, phase behavior, mechanical properties, bond dissociation, ...

Force-fields and parameters

- Transferability important
 - Same set can be used to model related molecules



- Computational efficiency important
 - Compromise between accuracy and computational efficiency
- Calculation methods such as energy minimization or molecular dynamics require first and second derivatives, preferably in simple analytic form

Common features in force-fields

- Atom type
 - Contains information about hybridization and local environment
 - For example: sp , sp^2 , sp^3 carbon are different atom types (in a non-reactive force-field)
 - Force-fields for specific class of molecules (for example, protein force-fields) have more atom types than general force-fields
- Partial charge (in non-polarizable force-fields)
 - Electron localization described by assigning each nucleus a fraction charge

Example from course book: Fig. 4.3 AMBER atom types for histidine, tryptophan, and phenylalanine

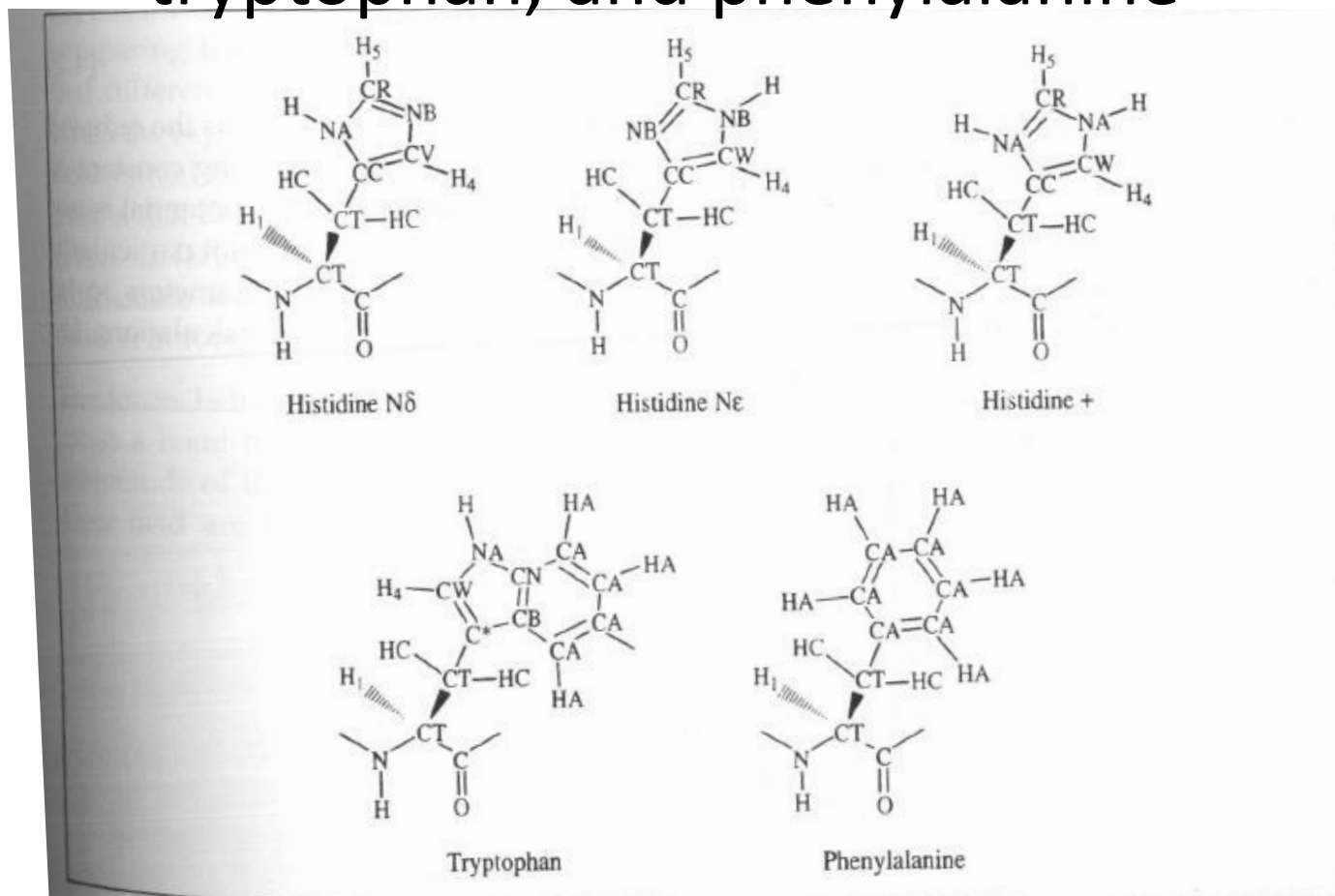


Fig. 4.3: AMBER atom types for the amino acids histidine, tryptophan and phenylalanine. There are three possible protonation states of histidine.

Many-body chemically non-reactive force-fields: terms

$$\begin{aligned} V &= V_{\text{bonded}} + V_{\text{nonbonded}} \\ V_{\text{bonded}} &= V_{\text{bonds}} + V_{\text{angles}} + V_{\text{dihedrals}} \\ V_{\text{nonbonded}} &= V_{\text{van der Waals}} + V_{\text{electrostatic}} \end{aligned}$$

$$\begin{aligned} V(\vec{r}^N) &= \frac{1}{2} \sum_{\text{bonds}} k_i (l_i - l_{i,0})^2 + \frac{1}{2} \sum_{\text{angles}} k'_i (\theta_i - \theta_{i,0})^2 \\ &\quad + \sum_{\text{torsions}} \frac{V_N}{2} k''_i (1 + \cos(n\omega - \gamma)) \\ &\quad + \sum_{i=1}^N \sum_{j=i+1}^N \left(4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \right) \end{aligned}$$

Next: 1) Bonds, 2) Angles, 3) Torsions (dihedrals), 4) van der Waals (dispersion) forces, and 5) Electrostatics

Bonds vs. Angles vs. Torsions (dihedrals) vs van der Waals (dispersion) forces vs Electrostatics in force-fields

- Most variation in molecular structure in molecular modelling due to interplay between torsional and non-bonded contributions
 - Bonds and angles require higher energies for significant deviations
- Electrostatics is a long-range interaction. Molecular modelling typically sensitive to long-range electrostatics (computationally heavy)

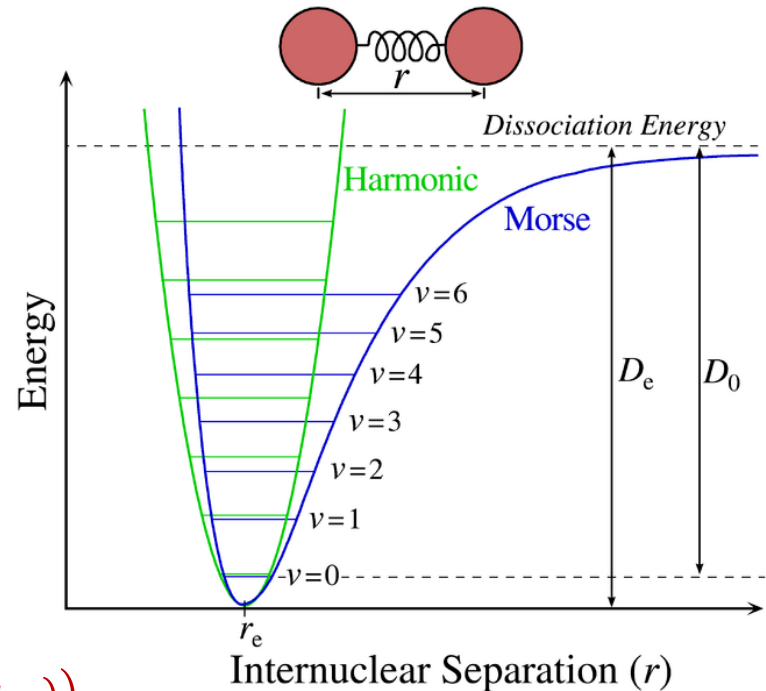
Bond stretching in force-field

$$V(l_i) = \frac{1}{2}k(l_i - l_{i,0})^2$$

Most common: Hookean spring
harmonic approximation
behavior close to reference
bond length $l_{i,0}$ only
Requires 2 parameters:
 k (spring) force constant, $l_{i,0}$

$$\begin{aligned} V(l_i) &= D_e(1 - e^{-\alpha(l-l_{i,0})})^2 \\ &= D_e e^{-2\alpha(l-l_{i,0})} - 2D_e e^{-\alpha(l-l_{i,0})} + C \end{aligned}$$

Less common but more realistic: Morse potential
Describes wider range of behavior (also bond dissociation), vibration anharmonicity
Requires 3 parameters



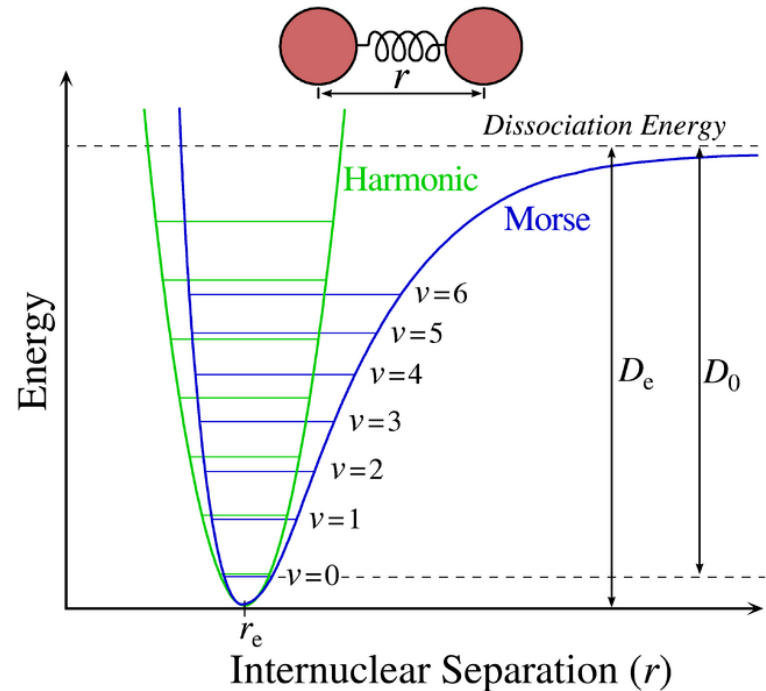
Bond stretching in force-field

$$V(l_i) = \frac{1}{2}k(l_i - l_{i,0})^2$$

Most common: Hookean spring
harmonic approximation
behavior close to reference
bond length $l_{i,0}$ only

Why harmonic approximation:

Bonds are "stiff", i.e., force constants relatively large and typically small deviations from reference! Exception: high temperature, dissociation and association. Special case: irradiation simulations



Bond stretching in force-field

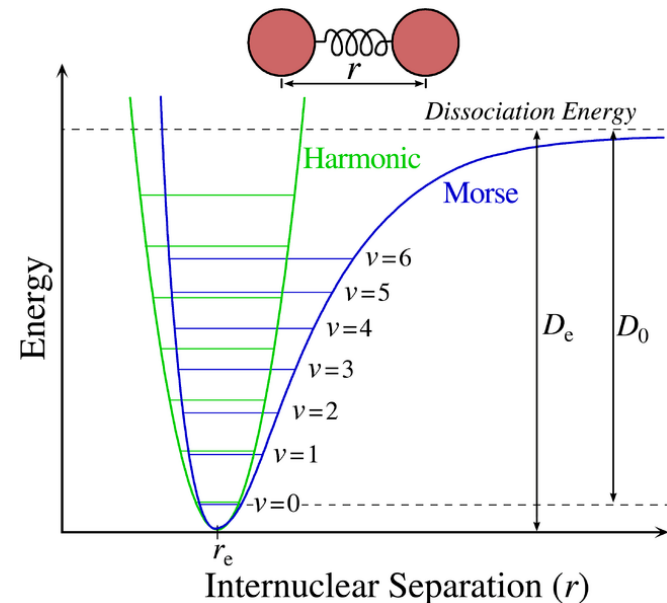
$$V(l_i) = \frac{1}{2}k(l_i - l_{i,0})^2$$

Most common: Hookean spring
harmonic approximation

$$V(l_i) = \frac{1}{2}k(l_i - l_{i,0})^2 [1 - k'(l_i - l_{i,0}) - k''(l_i - l_{i,0})^2 - k'''(l_i - l_{i,0})^3 \dots]$$

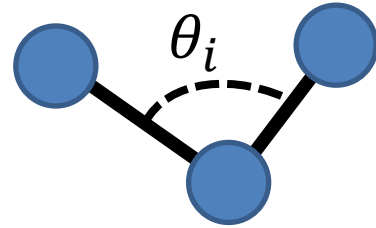
Taylor expansion of any potential energy functional (with analytic derivatives) around reference bond length $l_{i,0}$.

Higher order expansion terms also sometimes used. Note: higher order terms may pass through maxima \rightarrow catastrophic lengthening of bonds.



Angle bending in force-field

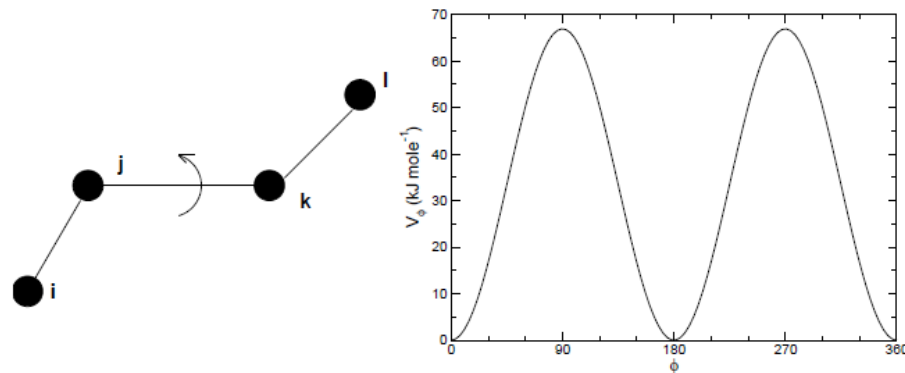
$$V(\theta) = \frac{1}{2} \sum_{\text{angles}} k'_i (\theta_i - \theta_{i,0})^2$$



- Most common: Hooke's law (harmonic potential)
- As with bonds, force constant and reference angle
- Angle bending force constants significantly smaller than bond stretching!
- Like with bonds, higher order terms (of Taylor's expansion) can be used to improve accuracy but at computational cost (quadratic term is sometimes used)

Torsions (dihedrals) in force-fields

Proper and improper dihedrals



Proper dihedral:
Bond rotation in-plane
Improper dihedral:
Out-of-plane bending

Figure 4.10: Principle of proper dihedral angle (left, in *trans* form) and the dihedral angle potential (right).

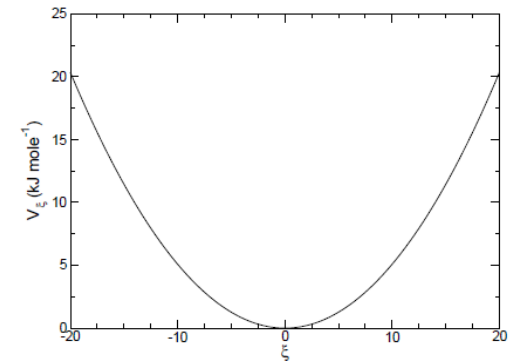
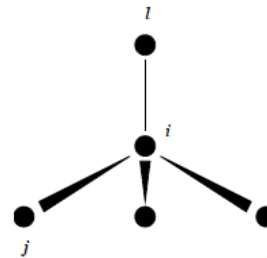
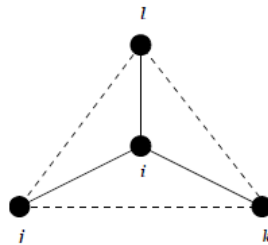
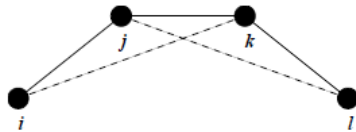


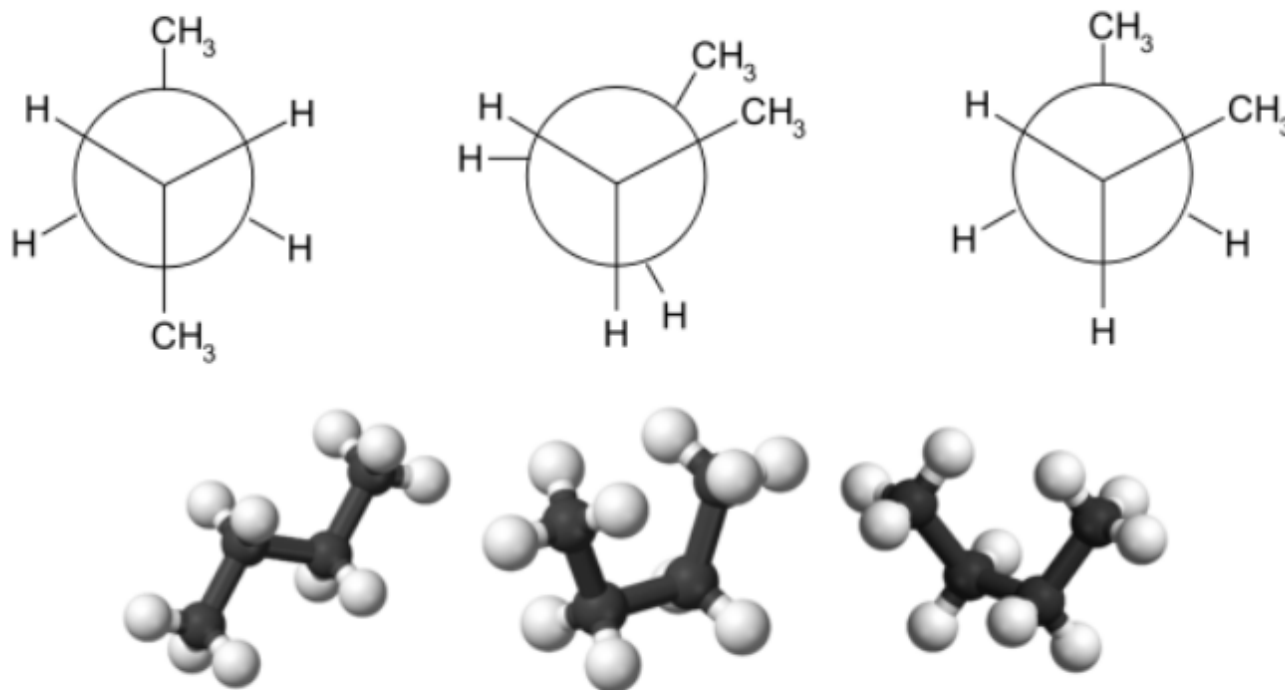
Figure 4.8: Principle of improper dihedral angles. Out of plane bending for rings (left), substituents of rings (middle), out of tetrahedral (right). The improper **dihedral** angle ξ is defined as the angle between planes (i,j,k) and (j,k,l) in all cases.

<http://www.gromacs.org/@api/deki/files/152/=manual-4.5.4.pdf>

Gromacs Manual 4.5.4

Proper dihedrals: Let's rotate a butane

In **butane**, the two staggered conformations are no longer equivalent and represent two distinct conformers: the **anti-conformation** (left-most, below) and the **gauche conformation** (right-most, below).

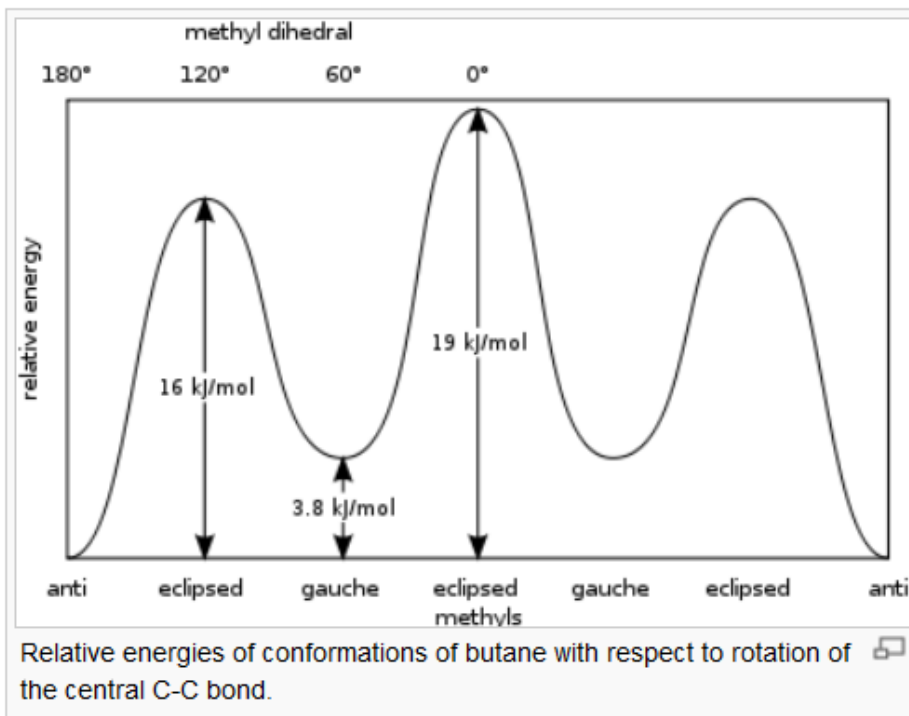


Both conformations are free of torsional strain, but, in the gauche conformation, the two **methyl** groups are in closer proximity than the sum of their van der Waals radii. The interaction between the two methyl groups is repulsive (**van der Waals strain**), and an energy barrier results.

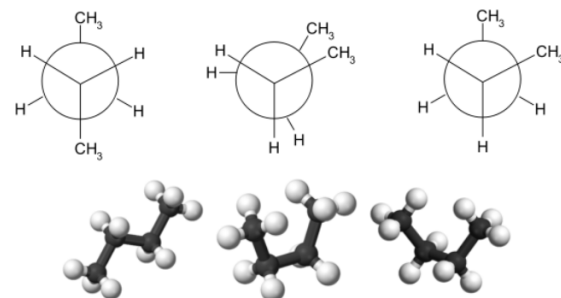
Proper dihedrals : Let's rotate a butane

- Gauche, conformer - 3.8 kJ/mol
- Eclipsed H and CH₃ - 16 kJ/mol
- Eclipsed CH₃ and CH₃ - 19 kJ/mol.

The eclipsed **methyl groups** exert a greater steric strain because of their greater **electron density** compared to lone **hydrogen** atoms.



In **butane**, the two staggered conformations are no longer equivalent and represent two distinct conformers: the **anti-conformation** (left-most, below) and the **gauche conformation** (right-most, below).



Both conformations are free of torsional strain, but, in the gauche conformation, the two **methyl** groups are in closer proximity than the sum of their van der Waals radii. The interaction between the two methyl groups is repulsive (**van der Waals strain**), and an energy barrier results.

(Proper) dihedrals in force-fields

- Barriers for rotation necessary for reproducing basic chemical structure
- Torsion potentials can be defined either for (all) 4 atom sets or as general torsions around central bond
- 1-fold dihedral: bond dipoles (difference in electronegativity); 2-fold dihedral: double bond character; 3-fold and higher: steric interactions
 - parameterization becomes complex and molecule-specific with high-order dihedrals

Improper dihedrals

- Example: cyclobutanone C_4H_6O (course book Fig 4.9)
 - Experimentally known the oxygen remains in the plane of the carbon atoms; To achieve this a out-of-plane bending term added

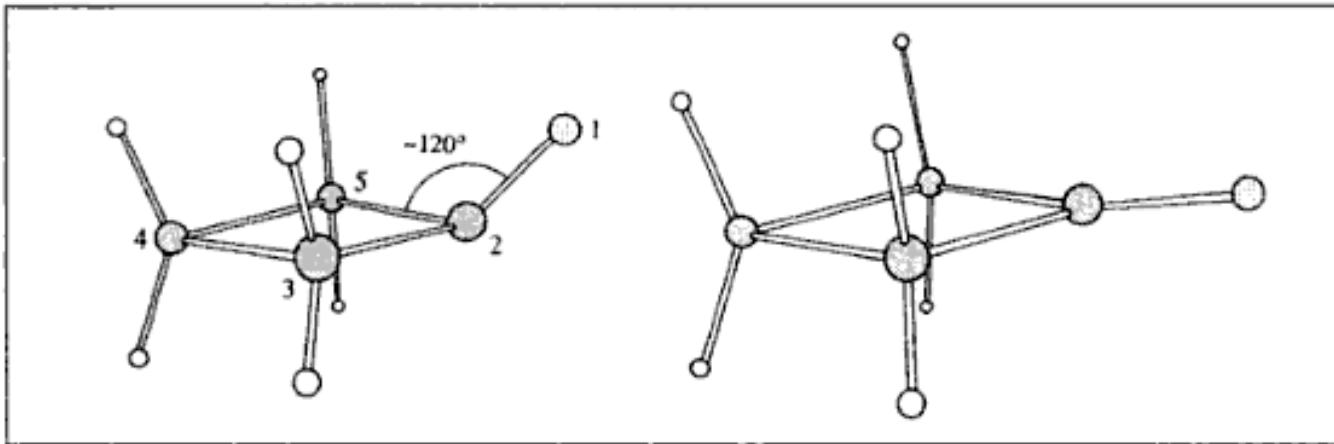


Fig. 4.9: Without an out-of-plane term, the oxygen atom in cyclobutanone is predicted to lie out of the plane of the ring (left) rather than in the plane.

A torsional potential of the following form is then used to maintain the **improper** torsion angle at 0° or 180° :

$$v(\omega) = k(1 - \cos 2\omega) \quad (4.11)$$

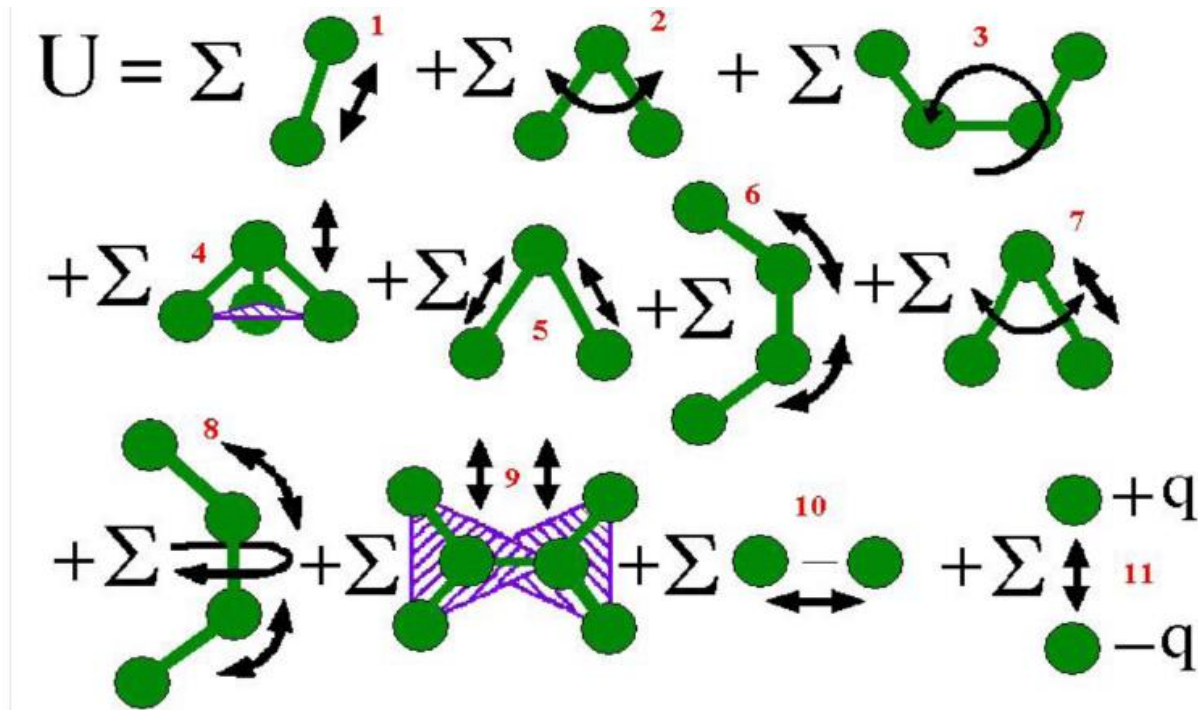
Improper dihedrals

- Necessary for (for example)
 - aromatic rings (planar)
 - stereochemistry in united-atom force-fields (force-fields which combine non-polar hydrogens with adjacent heavy atom)
- Quite often omitted in force-fields because
 - Necessary only for some molecular configurations (when necessary, cannot be omitted)
 - Including out-of-plane terms often has bad effect on force-field behaviour
 - Vibration frequencies sensitive

Examples of less common bonded interaction terms

- Cross-terms
 - Cross-interaction of 2 bonds stretching
 - Cross-interaction of bond stretching and angle
- Relating 2nd neighbor distance with angle (=1-3 distance energy term instead of angle energy term)
- Including bond stretching into dihedrals
- Including angle bending into dihedrals

Many-body chemically non-reactive force-fields: functional form



1. Bond stretching term;
2. Angle term;
3. Torsion term;
4. Out of plane term;

5. Bond -Bond term;
6. Angle - Angle term;
7. Bond - Angle term;
8. Angle - Angle - Torsion term;

9. Out of plane - Out of plane term;
10. Non bonded term;
11. Electrostatic term; etc..

Revision: Force-fields: A diverse family

- Two-body force-fields (pair potentials)
 - Simple, extremely fast
 - Liquids, gases, solids
 - Lennard-Jones, Morse, ...
- **Many-body chemically non-reactive force-fields**
 - **Many different atom types and molecules covered**
 - **Typically: a wide variety of organic molecules such as proteins, hydrocarbons, lipids, polymers, ...**
 - **Non-reactive!**
- Many-body (reactive) force-fields
 - A wide variety of typically inorganic materials and compounds including also metals (structural & mechanical properties). Organic molecules tend to be too complex.
 - Some are **reactive!**



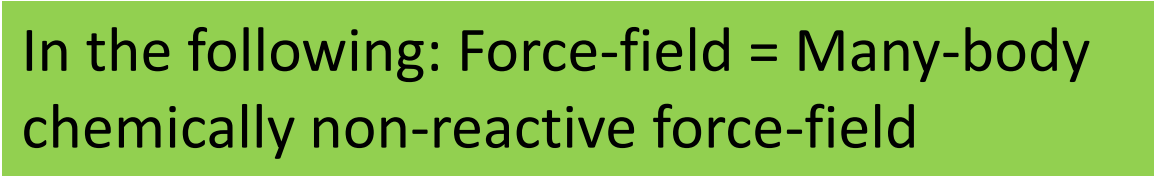
Intro



Main



Briefly



In the following: Force-field = Many-body chemically non-reactive force-field

Revision: Many-body chemically non-reactive force-fields: terms

$$\begin{aligned} V &= V_{\text{bonded}} + V_{\text{nonbonded}} \\ V_{\text{bonded}} &= V_{\text{bonds}} + V_{\text{angles}} + V_{\text{dihedrals}} \\ V_{\text{nonbonded}} &= V_{\text{van der Waals}} + V_{\text{electrostatic}} \end{aligned}$$

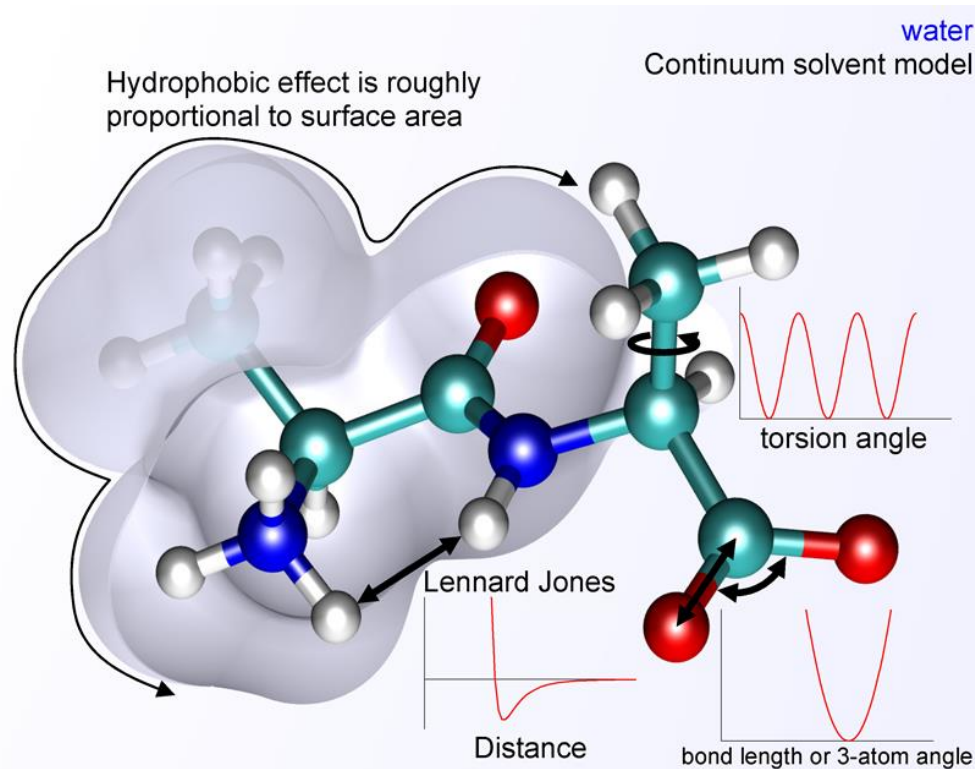
$$\begin{aligned} V(\vec{r}^N) &= \frac{1}{2} \sum_{\text{bonds}} k_i (l_i - l_{i,0})^2 + \frac{1}{2} \sum_{\text{angles}} k'_i (\theta_i - \theta_{i,0})^2 \\ &\quad + \sum_{\text{torsions}} \frac{V_N}{2} k''_i (1 + \cos(n\omega - \gamma)) \\ &\quad + \sum_{i=1}^N \sum_{j=i+1}^N \left(4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \right) \end{aligned}$$

Last time: 1) Bonds, 2) Angles, 3) Torsions (dihedrals),

Next: 4) van der Waals (dispersion) forces, and 5) Electrostatics

Revision: Typical representation of a force-field (Potential energy surface)

Dialanine peptide in implicit (continuum) solvent



$$E_{\text{bonded}} = E_{\text{bond}} + E_{\text{angle}} + E_{\text{dihedral}}$$
$$E_{\text{nonbonded}} = E_{\text{electrostatic}} + E_{\text{van der Waals}}$$

Many-body chemically non-reactive force-fields:

Now moving on to non-bonded terms

$$V = V_{bonded} + V_{nonbonded}$$
$$V_{bonded} = V_{bonds} + V_{angles} + V_{dihedrals}$$
$$V_{nonbonded} = V_{van\ der\ Waals} + V_{electrostatic}$$

$$V(\vec{r}^N) = \frac{1}{2} \sum_{bonds} k_i (l_i - l_{i,0})^2 + \frac{1}{2} \sum_{angles} k'_i (\theta_i - \theta_{i,0})^2$$
$$+ \sum_{torsions} \frac{V_N}{2} k''_i (1 + \cos(n\omega - \gamma))$$
$$+ \sum_{i=1}^N \sum_{j=i+1}^N \left(4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \right)$$

For example, AMBER force-field has this form

Many-body chemically non-reactive force-fields:

Now moving on to non-bonded terms

Potential energy

Bond i length

Bond i reference length

Angle i

Angle i reference

$$V(\vec{r}^N) = \frac{1}{2} \sum_{bonds} k_i (l_i - l_{i,0})^2 + \frac{1}{2} \sum_{angles} k'_i (\theta_i - \theta_{i,0})^2$$

+ $\sum_{torsions} \frac{V_N}{2} k''_i (1 + \cos(n\omega - \gamma))$ Bond rotation energy
n=multiplicity
 γ shift

+ $\sum_{i=1}^N \sum_{j=i+1}^N \left(4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \right)$

Summation over all particle pairs

Lennard-Jones 12-6 potential
van der Waals (dispersion interaction)

Coulomb energy
charge-charge interaction

For example, AMBER force-field has this form

Non-bonded interactions

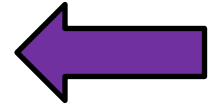
- Long range
- Not dictated by "bonds"
- Both within molecules and between different molecules
- Long-range nature introduces a need for either cut-off distance in computation or long-range calculation scheme

Non-bonded interactions

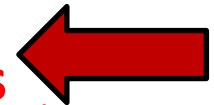
On this course:
(nomenclature varies
in different books)

- Typically 4 components
 - **Repulsive component resulting from the Pauli exclusion principle** (prevents the collapse of molecules)
 - **Attractive or repulsive electrostatic interactions between permanent charges, dipoles, multipoles**
 - **Polarization** (induced electrostatic interactions) (Debye forces)
 - **Dispersion** arising from the interactions of instantaneous multipoles (London forces)
- Most common in molecular modelling to divide these into **van der Waals** and **electrostatic interactions**

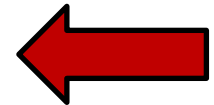
van der Waals



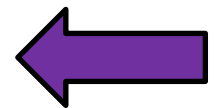
electrostatic



electrostatic



van der Waals

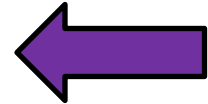


Non-bonded interactions

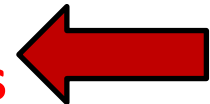
On this course:
(nomenclature varies
in different books)

- Typically 4 components
 - Repulsive component resulting from the Pauli exclusion principle (prevents the collapse of molecules)
 - Attractive or repulsive **electrostatic interactions between permanent charges, dipoles, multipoles**
 - **Polarization** (induced electrostatic interactions) (Debye forces)
 - **Dispersion** arising from the interactions of instantaneous multipoles (London forces)
- Most common in molecular modelling to divide these into **van der Waals** and **electrostatic interactions**

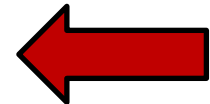
van der Waals



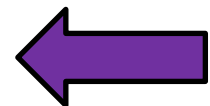
electrostatic



electrostatic

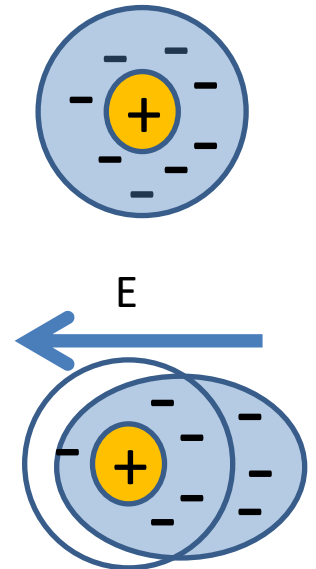
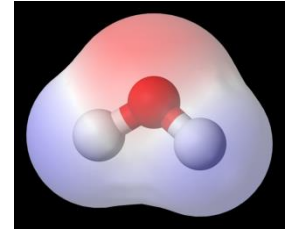


van der Waals



Electrostatic interactions: basics

- Electronegative elements attract electrons more than less electronegative elements
 - Unequal charge distribution in molecule
 - Electric field changes this distribution (polarization)
 - Can be external field or caused by molecular environment
 - Most commonly, polarization not taken into account in force-fields but instead fixed charge distribution used
 - Polarizable force-fields an important method development direction in molecular modelling



Electrostatics by fractional point charges

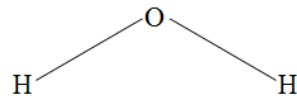
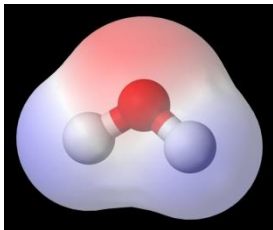
- One common approach in molecular modelling to assign fractional point charges throughout the molecule
 - Point charges designed to reproduce electrostatic properties of the molecule
 - Do not need to be at same locations as nuclei
 - If located at nuclei positions: partial atomic charges

$$V = \sum_{i=1}^N \sum_{j=i+1}^N \left(\frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \right)$$

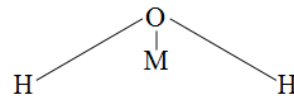
- Downsides of using fractional point charges
 - No dynamical charge redistribution due to changes in electric field (due to changes in molecular environment)

Electrostatics by fractional point charges

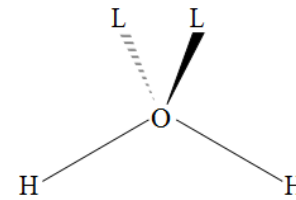
- Electrostatics can be represented by multipole expansion of the electrostatic interaction energy
- Sufficient number of fractional point charges reproduce all electric moments of the multipole expansion
 - This may require charges at other positions besides nuclei locations
 - Example: Water molecule



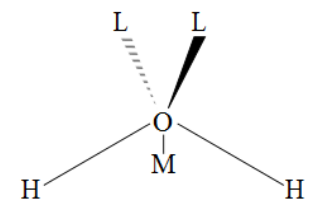
3-site



4-site



5-site



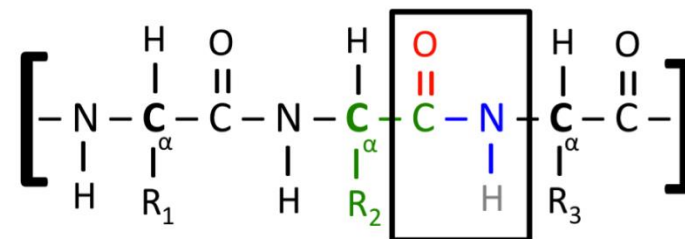
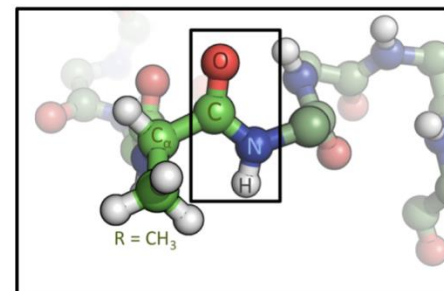
6-site

Fractional point charges: where do the numbers come from?

- For simple molecules, can be calculated exactly based on experimental multipole moments
- Sometimes chosen to reproduce thermodynamic properties (large number of simulations required)
- Ab initio simulations: several ways to determine partial charges
- Charge distribution validated by ability to reproduce experimental multipole moments, electrostatic potential, or thermodynamic quantities

Fractional point charges of large molecules

- Look at a small fraction of the larger system
 - Proteins: dipeptide, tripeptide
 - Polymers: oligomers
- Charge distribution will depend on conformation
 - Possible to average over a number of conformations, can be problematic for large molecules

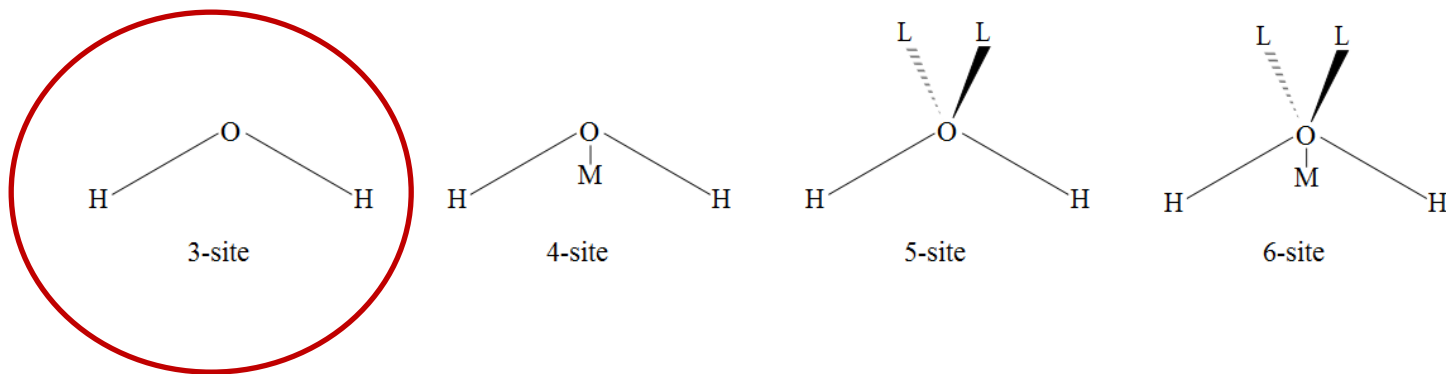


Fractional point charges

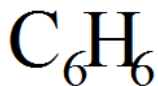
- Charges determined from ab initio calculations depend on
 - Basis set (larger does not necessary improve charges, or force-field performance)
 - Molecular conformation
- In parameterizing new molecules, must be consistent with existing parameterization

Fractional point charges at atom positions (partial atomic charge)

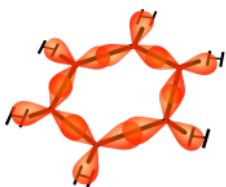
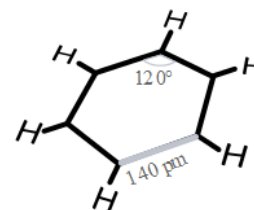
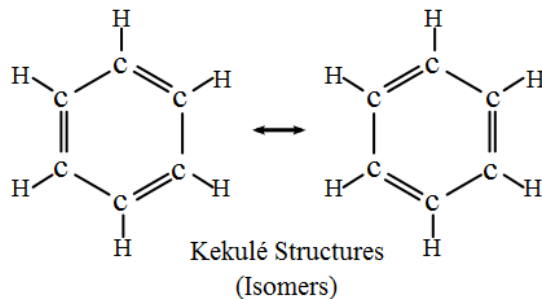
- Electrostatic forces act directly on nuclei
 - Makes things more simple computationally
- Assume charge distribution spherically symmetric
- Incapability to reproduce some higher multipole moments



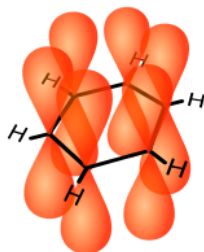
Benzene



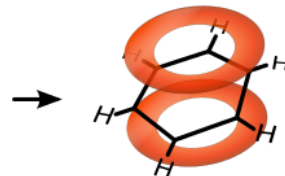
Benzene
Molecular formula



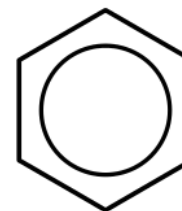
Sigma Bonds
 p^2 Hybridized orbitals



6 p_z orbitals



delocalized pi
system

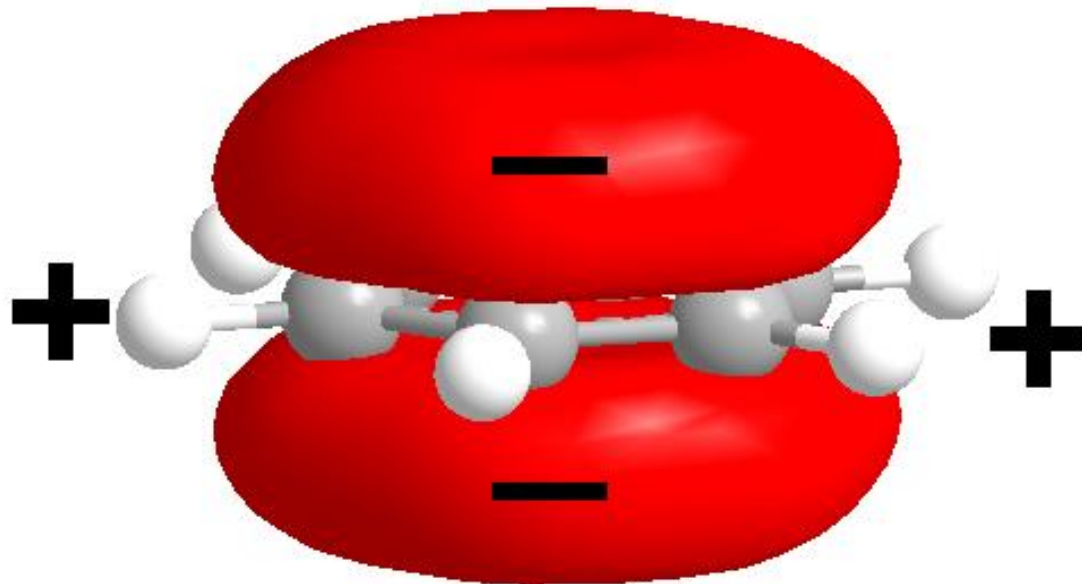


Benzene ring
Simplified depiction

- Question: How should the partial charges be distributed? Why?

http://upload.wikimedia.org/wikipedia/commons/9/9a/Benzene_Representations.svg

Benzene



- Question: How should the partial charges be distributed? Why?

http://upload.wikimedia.org/wikipedia/commons/9/9a/Benzene_Representations.svg

Example of aromatic-aromatic interactions

- P-stacking difficult to model (nucleic acids, benzene, ring-like molecules)

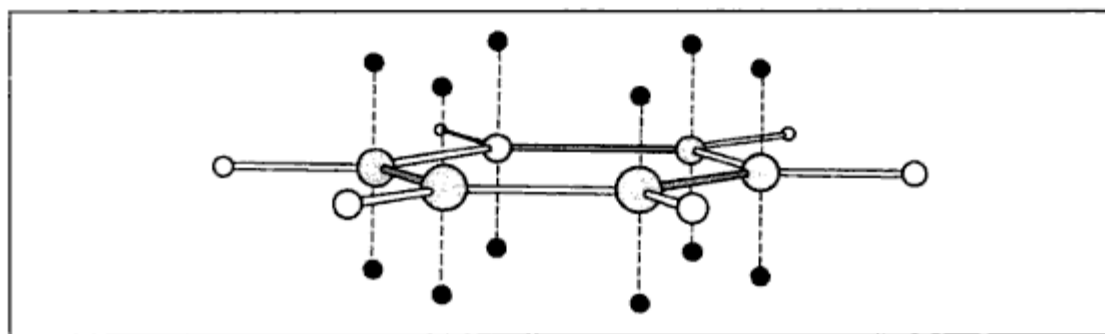


Fig. 4.25: Anisotropic model of benzene developed by Hunter and Saunders [Hunter and Saunders 1990].

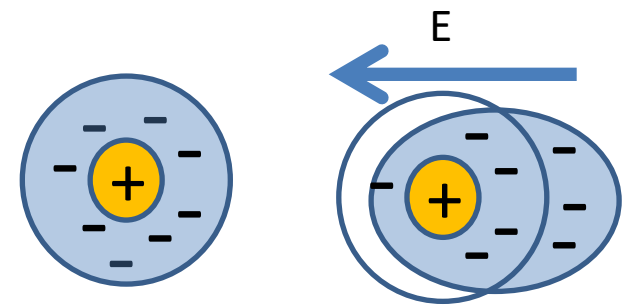
- Hunter-Saunders: Carbons have +1 charge on plane, -1/2 above and below plane of ring
- Classical force-fields can be tuned to a wide variety of behavior . Most typical force-fields do not have this benzene property.

Polarization

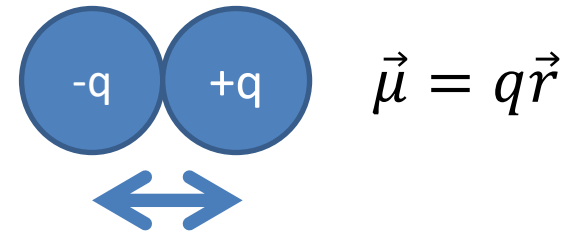
Induced dipole moment

$$\vec{\mu}_{ind} = \alpha \vec{E}$$

electric field
polarizability



Dipole moment

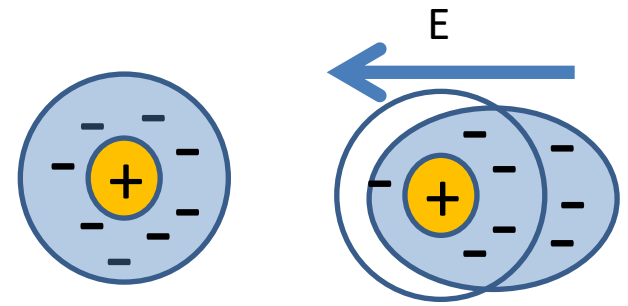


$$v(\alpha, E) = - \int_0^E d\vec{E} \vec{\mu}_{ind} = \int_0^E d\vec{E} \alpha \vec{E} = -\frac{1}{2} \alpha E^2$$

Energy of interaction for each dipole calculated by work done when charging field from zero to E

At high electric fields also higher order terms may be important (typically quadrupole moment).

Polarization




- Polarization of one molecule will affect electric field observed by another molecule; other molecules influence the effect: A collective (cooperative) effect
 - Modeled by coupled equations
 - Typically iterative solution methods
 - Dipoles get an initial value
 - Value updated
 - Iterated until dipoles do not change significantly
 - Computationally costly

Electrostatic interactions in medium

Vacuum

$$V = \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}}$$

Permittivity of vacuum



In medium

$$V = \frac{1}{4\pi\epsilon_0 \epsilon_r} \frac{q_i q_j}{r_{ij}}$$

Relative permittivity of medium
Permittivity of vacuum

- Medium, for example, solvent, can be modelled by explicit molecules
- In addition, dielectric screening of electrostatic interactions can be taken into account without explicit solvent molecules (implicit solvent)

Electrostatic interactions in medium

Vacuum

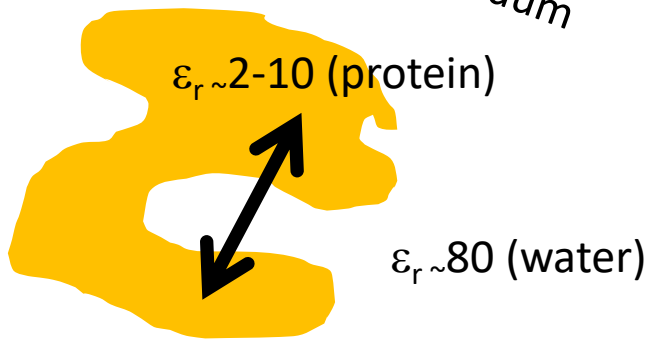
$$V = \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}}$$

Permittivity of vacuum

In medium

$$V = \frac{1}{4\pi\epsilon_0 \epsilon_r} \frac{q_i q_j}{r_{ij}}$$

Relative permittivity of medium
Permittivity of vacuum



- Choosing appropriate value for bulk dielectric may be difficult, solvent is not present everywhere especially with large molecules

Vacuum $\epsilon_r = 1$
Ar gas $\epsilon_r \sim 1.0005$ (~ 1)
Ar liquid $\epsilon_r \sim 1.5$ (van der Waals)
NaCl crystal $\epsilon_r \sim 1.0005$ Ar gas (~ 1)
Water $\epsilon_r \sim 80$
PVC $\epsilon_r \sim 7$
Lipid bilayer $\epsilon_r \sim 2-4$
Protein $\epsilon_r \sim 2-10$

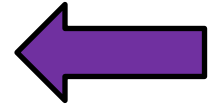
Non-bonded interactions

On this course:
(nomenclature varies
in different books)

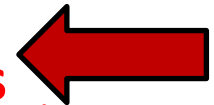
- Typically 4 components

- **Repulsive component resulting from the Pauli exclusion principle** (prevents the collapse of molecules)
- **Attractive or repulsive electrostatic interactions between permanent charges, dipoles, multipoles**
- **Polarization** (induced electrostatic interactions) (Debye forces)
- **Dispersion** arising from the interactions of instantaneous multipoles (London forces)

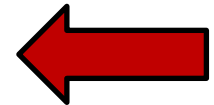
van der Waals



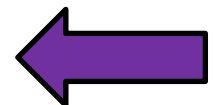
electrostatic



electrostatic



van der Waals



- Most common in molecular modelling to divide these into **van der Waals** and **electrostatic interactions**

Now

Now

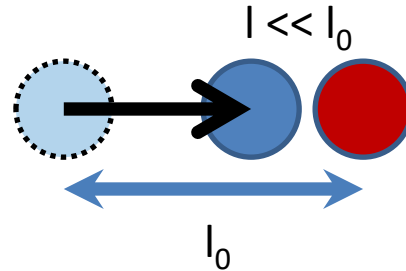
What is left?

- A repulsive component resulting from the Pauli exclusion principle
- Dispersion: attractive interaction between any pair of molecules due to interactions of instantaneous multipoles
 - Relatively weak (compared to other molecular interactions)
 - Highly relevant in molecular self-assembly, supramolecular chemistry, structural biology (proteins etc.), surface science (surface interactions), ...

What is left?

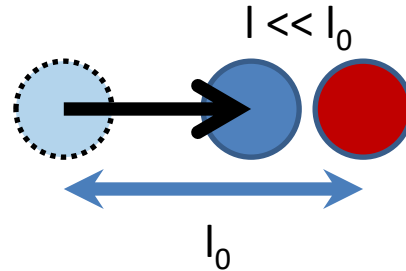
- 1 • A repulsive component resulting from the Pauli exclusion principle
- 2 • Dispersion: attractive interaction between any pair of molecules due to interactions of instantaneous multipoles
 - Relatively weak (compared to other molecular interactions)
 - Highly relevant in molecular self-assembly, supramolecular chemistry, structural biology (proteins etc.), surface science (surface interactions), ...

Repulsive Contribution



- Pauli principle: no two fermions (here electrons) in a system can have exactly the same quantum numbers
- Forbids electrons to occupy the same region of space (internuclear region at short separations) -
> reduced electron density between nuclei -> repulsion between incompletely shielded nuclei
- Also called: exchange forces, overlap forces

Repulsive Contribution



- Pauli principle: no two fermions (here electrons) in a system can have exactly the same quantum numbers
- Functional form

$$\propto \frac{1}{r}, \text{ at very short distances}$$

$$\propto e^{-2r/a_0}, \text{ at larger separations, } a_0 \text{ Bohr radius}$$

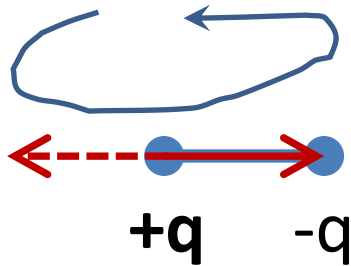
What is left?

- 1 • A repulsive component resulting from the Pauli exclusion principle
- 2 • Dispersion: attractive interaction between any pair of molecules due to interactions of instantaneous multipoles
 - Relatively weak (compared to other molecular interactions)
 - Highly relevant in molecular self-assembly, supramolecular chemistry, structural biology (proteins etc.), surface science (surface interactions), ...

Attractive contribution (dispersion)

- Long range (opposed to very short range repulsive)
- Due to dispersive forces induced by instantaneous dipoles arising from fluctuations in the electron clouds
 - (instantaneous) dipole can induce a dipole in neighboring atoms -> attractive effect
- Also called: London forces

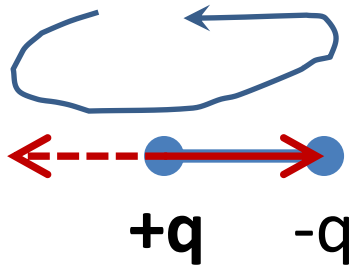
Drude model for dispersive interaction (a simple model): Isolated molecule



Molecule with two charges, $+q$ and $-q$

$-q$: Harmonic motion around $+q$, angular frequency ω

Drude model for dispersive interaction (a simple model): Isolated molecule



Molecule with two charges, +q and -q
-q: Harmonic motion around +q, angular frequency ω

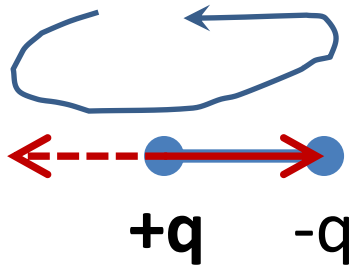
Potential energy (z separation, $\omega^2=k/m$, k force constant)
Schrödinger equation

$$V = \frac{1}{2}kz^2$$

$$\left(-\frac{\hbar}{2m} \frac{\partial}{\partial z^2} + V\right) \psi = E \psi$$

$$-\frac{\hbar}{2m} \frac{\partial \psi}{\partial z^2} + \frac{1}{2}kz^2 \psi = E \psi$$

Drude model for dispersive interaction (a simple model): Isolated molecule



Simple harmonic oscillator

Energies: $E_v = (v + \frac{1}{2}) \times \hbar\omega$

$$E_0 = \frac{1}{2} \hbar\omega$$

Molecule with two charges, +q and -q

-q: Harmonic motion around +q, angular frequency ω

Potential energy (z separation, $\omega^2 = k/m$, k force constant)

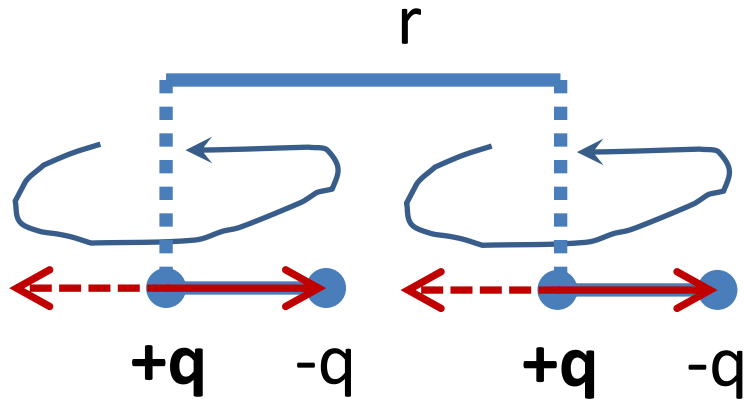
Schrödinger equation

$$V = \frac{1}{2} k z^2$$

$$\left(-\frac{\hbar}{2m} \frac{\partial}{\partial z^2} + V \right) \psi = E \psi$$

$$-\frac{\hbar}{2m} \frac{\partial \psi}{\partial z^2} + \frac{1}{2} k z^2 \psi = E \psi$$

Drude model for dispersive interaction (a simple model): Interacting molecules



Simple harmonic oscillator
When separated, energy
 2 x isolated Drude
 molecule energy $E_0 = \frac{1}{2} \hbar \omega$

Molecules with two charges, +q and -q
 -q: Harmonic motion around +q, angular frequency ω

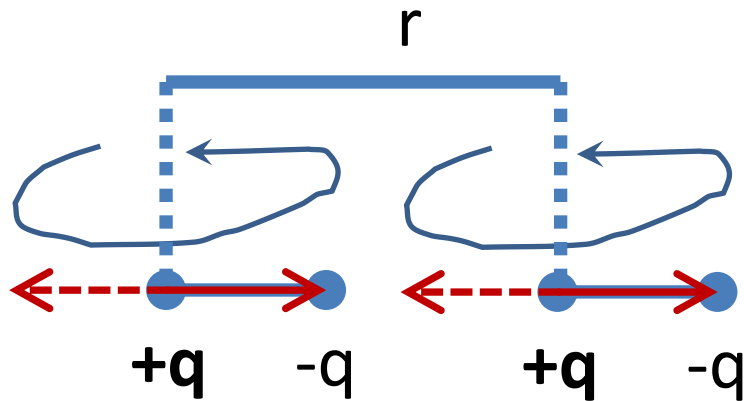
When interacting, energy

$$1D: v(r) = -\frac{\alpha^4 \hbar \omega}{2(4\pi\epsilon_0)^2 r^6}$$

$$3D: v(r) = -\frac{3\alpha^4 \hbar \omega}{2(4\pi\epsilon_0)^2 r^6}$$

$$-\frac{\hbar}{2m} \frac{\partial^2 \psi}{\partial z^2} + \frac{1}{2} k z^2 \psi = E \psi$$

Drude model for dispersive interaction (a simple model): Summary



Molecules with two charges, +q and -q
-q: Harmonic motion around +q, angular frequency ω

Interaction
proportional to

$$\propto \frac{1}{r^6}$$

When interacting, energy

$$1D: v(r) = -\frac{\alpha^4 \hbar \omega}{2(4\pi\epsilon_0)^2 r^6}$$

$$3D: v(r) = -\frac{3\alpha^4 \hbar \omega}{2(4\pi\epsilon_0)^2 r^6}$$

Interaction always attractive
(also with higher order multipoles)

Summary of Pauli exclusion repulsion and dispersion attraction (van der Waals interactions)

- A repulsive short range component resulting from the Pauli exclusion principle
 - $\propto \frac{1}{r}$, at very short distances
 - $\propto e^{-2r/a_0}$, at larger separations, a_0 Bohr radius
- Dispersion: attractive interaction between any pair of molecules due to interactions of instantaneous multipoles
 - proportional to $1/r^6$
 - Long-range

Modeling van der Waals interactions

- Most common model: Lennard-Jones

$$v(r) = 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right]$$

- No solid theoretical arguments for repulsive part, attractive is the dispersion term (Drude model)
- 12th power reasonable for noble gases, too steep for most other systems, also 9th or 10th power used sometimes
- More general: n-m Lennard-Jones (12-6 a special case)

$$v(r) = k\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^n - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^m \right]$$

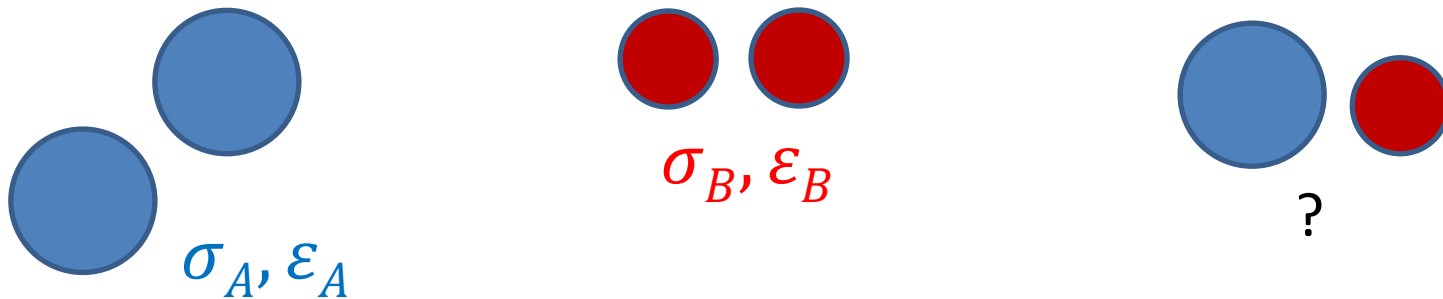
Modeling van der Waals interactions

- Theoretically more realistic alternative to Lennard-Jones: Buckingham potential

$$v(r_{ij}) = \varepsilon \left[\frac{6}{\alpha - 6} e^{\left(-\alpha \left(\frac{r_{ij}}{r_m} - 1\right)\right)} - \frac{6}{\alpha - 6} \left(\frac{r_m}{r_{ij}}\right)^6 \right]$$

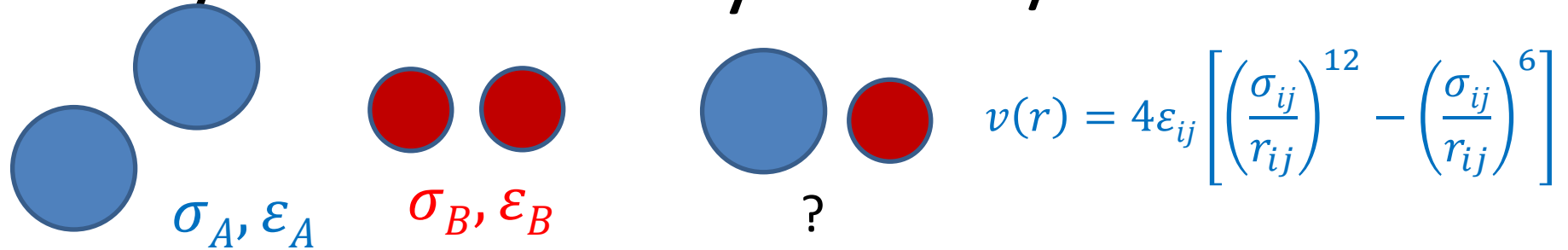
- α approx 14 or 15 corresponds to Lennard-Jones 12-6 close to minimum
- Collapses at very short distances!!!
 - must check
- Morse potential is also sometimes used for van der Waals interactions

Modeling van der Waals interactions: Systems of many atoms / molecules



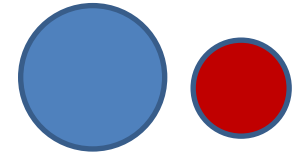
$$v(r) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right]$$

Modelling van der Waals interactions: Systems of many atoms / molecules



- van der Waals interactions usually parametrized for one atom / molecule type for one orientation / conformation
- Parameters for cross-interaction between different atoms typically calculated using mixing rules from parameters of same type of atoms interacting

Mixing rules of van der Waals parameters



- Arithmetic mean or geometric mean
- Common: Lorentz-Berthelot

$$\sigma_{AB} = \frac{1}{2} (\sigma_{AA} + \sigma_{BB})$$

$$\varepsilon_{AB} = \sqrt{\varepsilon_{AA} \varepsilon_{BB}}$$

- Arithmetic mean (minimum position) + geometric mean (potential well depth)
- Works well for similar atoms
- Well depth may be overestimated

Many body terms in non-bonded interactions

$$V = \sum_{i=1}^N \sum_{j=i+1}^N \left(4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \right) + \sum_{i=1}^N \sum_{j=i+1}^N \sum_{k=j+1}^N V_3$$

Until now, two-body interactions Here, three-body interactions

- Lennard-Jones terms can be affected 10% by 3-body interactions
- 2-body: $\sim N^2$ interactions (N number of particles); 3-body: $\sim N^3$ interactions
- Axilrod-Teller terms

van der Waals summary

- Obtaining van der Waals parameter values
 - Sources: Experimental lattice packing, density, sublimation energy, enthalpy of vaporization, vapor pressure
 - Computationally long-range

Force-fields: A diverse family

- Two-body force-fields (pair potentials)
 - Simple, extremely fast
 - Liquids, gases, solids
 - Lennard-Jones, Morse, ...
- **Many-body chemically non-reactive force-fields**
 - **Many different atom types and molecules covered**
 - **Typically: a wide variety of organic molecules such as proteins, hydrocarbons, lipids, polymers, ...**
 - **Non-reactive!**
- Many-body (reactive) force-fields
 - A wide variety of typically inorganic materials and compounds including also metals (structural & mechanical properties). Organic molecules tend to be too complex.
 - Some are **reactive!**



Intro



Main



Briefly



Modelling inorganic molecules

- Inorganic molecules have a wider range of geometries and highly delocalized bonds
 - Model needs to capture also these properties
 - More complex / different than organic molecular models (often)
 - Coordination numbers vary
- More specialized force-fields than for organic compounds, quite often capture also bond reorganization (changes in bond order)

Empirical potentials for semiconductors and metals

- Bond-order potentials
 - Examples: Finnis-Sinclair; Tersoff; Brenner; Stillinger-Weber; Sutton; Pettifor (several models)
 - Physical basis: relating quantum mechanical electronic density of states and its moments to classical bond order (bond strength)
 - Binding energy strongly correlated with square root of the second moment of the electronic density of states
 - In practice, local density of states is used
 - Second moment approximation for binding energy $E_i^{\text{el}} \propto \sqrt{Z_i}$, Z_i number of neighbors

Bond-order potentials

- Can describe several different bonding states of an atom with the same parameters
- May be able to describe chemical reactions (correctly)
- strength of a chemical bond depends on the bonding environment

Bond-order potentials

- Two alternative ways to write potential energy expression (equivalent)
 - $V_{ij} = V_{repulsive}(r_{ij}) + b_{ijk} V_{attractive}(r_{ij})$
 - $V_{ij} = V_{pair}(r_{ij}) + A\sqrt{\rho_i}$, ρ_i local electron density
- $\rho_i = \sum_{j=1, j \neq i}^N \varphi_{ij}(r_{ij})$
- Relies on number of neighbors which is not always straightforward to define (disordered materials, bond reorganization, ...)
- Continuous transition between different numbers of neighbors

Example: Brenner bond-order potential for hydrocarbons

$$E_b = \sum_i \sum_{j(>i)} [V_R(r_{ij}) - \bar{B}_{ij} V_A(r_{ij})], \quad \bar{B}_{ij} = (B_{ij} + B_{ji})/2 + F_{ij}(N_i^{(t)}, N_j^{(t)}, N_{ij}^{\text{conj}}),$$

where the repulsive and attractive pair terms are given by

$$V_R(r_{ij}) = f_{ij}(r_{ij}) D_{ij}^{(e)} / (S_{ij} - 1) e^{-\sqrt{2/S_{ij}} \beta_{ij} (r - R_{ij}^{(e)})} \quad (7)$$

and

$$V_A(r_{ij}) = f_{ij}(r_{ij}) D_{ij}^{(e)} S_{ij} / (S_{ij} - 1) e^{-\sqrt{2/S_{ij}} \beta_{ij} (r - R_{ij}^{(e)})}, \quad (8)$$

respectively. The function $f_{ij}(r)$, which restricts the pair potential to nearest neighbors, is given by

$$f_{ij}(r) = \begin{cases} 1, & r < R_{ij}^{(1)} \\ \left[1 + \cos \left[\frac{\pi(r - R_{ij}^{(1)})}{(R_{ij}^{(2)} - R_{ij}^{(1)})} \right] \right] / 2, & R_{ij}^{(1)} < r < R_{ij}^{(2)} \\ 0, & r > R_{ij}^{(2)}. \end{cases}$$

$$B_{ij} = \left[1 + \sum_{k(\neq i, j)} G_i(\theta_{ijk}) f_{ik}(r_{ik}) e^{\alpha_{ijk} [(r_{ij} - R_{ij}^{(e)}) - (r_{ik} - R_{ik}^{(e)})]} + H_{ij}(N_i^{(H)}, N_i^{(C)}) \right]^{-\delta_i}$$

$$G_C(\theta) = a_0 \{ 1 + c_0^2/d_0^2 - c_0^2/[d_0^2 + (1 + \cos\theta)^2] \} \quad (18)$$

$$N_{ij}^{\text{conj}} = 1 + \sum_{\text{carbons } k(\neq i, j)} f_{ik}(r_{ik}) F(x_{ik}) + \sum_{\text{carbons } l(\neq i, j)} f_{jl}(r_{jl}) F(x_{jl}) \quad (15)$$

where

$$F(x_{ik}) = \begin{cases} 1, & x_{ik} \leq 2 \\ \{ 1 + \cos[\pi(x_{ik} - 2)] \} / 2, & 2 < x_{ik} < 3 \\ 0, & x_{ik} \geq 3 \end{cases} \quad (16)$$

and

$$x_{ik} = N_k^{\text{tot}} - f_{ik}(r_{ik}). \quad (17)$$

Example: Brenner bond-order potential

TABLE VI. Predicted energetics and intramolecular carbon-carbon bond lengths for various single molecules chemisorbed on terrace sites on a hydrogen-terminated diamond {111} surface.

Molecule	Potential I		Potential II	
	Potential energy (eV)	Bond length (Å)	Potential energy (eV)	Bond length (Å)
Hydrogen atom	-4.1 ^a		-4.2 ^a	
Methyl radical	-3.7 ^a		-4.0 ^a	
Acetyl radical	-3.9 ^a	1.20	-4.1 ^a	1.29
Hydrogen molecule	-3.6 ^b		-3.6 ^b	
Acetylene	-5.0 ^b	1.33	-4.9 ^b	1.39
Ethylene	-4.3 ^b	1.59	-4.3 ^b	1.57

^aRelative to a hydrogen-terminated surface with one radical site and the gas-phase molecule.

^bRelative to a hydrogen-terminated surface with two adjacent radical sites and the gas-phase molecule.

TABLE VII. Predicted energetics and intramolecular carbon-carbon bond lengths for a monolayer of various molecules chemisorbed on the diamond {111} surface. The energies are relative to a relaxed clean surface and the gas-phase molecules.

Molecule	Potential I		Potential II	
	Potential energy	Bond length (Å)	Potential energy	Bond length (Å)
Hydrogen atom	-4.2 eV/atom ^a		-4.3 eV/atom ^a	
Methyl radical	-3.2 eV/molecule ^a		-3.0 eV/molecule ^a	
Acetyl radical	-4.2 eV/molecule ^a	1.20	-4.3 eV/molecule ^a	1.29
Hydrogen molecule	-3.7 eV/molecule ^b		-3.9 eV/molecule ^b	
Acetylene	-5.2 eV/molecule ^b	1.33	-5.2 eV/molecule ^b	1.39
Ethylene	-4.0 eV/molecule ^b	1.58	-3.9 eV/molecule ^b	1.57

^aOne surface atom per chemisorbed molecule.

^bTwo surface atoms per chemisorbed molecule.

Stillinger-Weber bond-order potential

$$U = \sum_i \sum_{j>i} \phi_2(r_{ij}) + \sum_i \sum_{j \neq i} \sum_{k>j} \phi_3(r_{ij}, r_{ik}, \theta_{ijk})$$

$$\phi_2(r_{ij}) = A_{ij} \epsilon_{ij} \left[B_{ij} \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{p_{ij}} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{q_{ij}} \right] \exp \left(\frac{\sigma_{ij}}{r_{ij} - a_{ij} \sigma_{ij}} \right)$$

$$\phi_3(r_{ij}, r_{ik}, \theta_{ijk}) = \lambda_{ijk} \epsilon_{ijk} [\cos \theta_{ijk} - \cos \theta_{0ijk}]^2 \exp \left(\frac{\gamma_{ij} \sigma_{ij}}{r_{ij} - a_{ij} \sigma_{ij}} \right) \exp \left(\frac{\gamma_{ik} \sigma_{ik}}{r_{ik} - a_{ik} \sigma_{ik}} \right)$$

Effective Medium Theory (EMT)

- approximation in which models based on density-functional theory are used to describe the properties of solids, usually metals
- Environment around each atom replaced by "jellium",
 - corresponds to homogeneous electron gas (a constant positive background density (metal ions))
 - Atoms embedded into this jellium (Daw and Baskes: Embedded atom method EAM)

Summary: Empirical bond-order and effective medium potentials

- Can be quite accurate (and fast) within their parametrization regime
- Increased computational speed: Modern tight binding simulations compete
- Can be reactive, can allow for bond-reorganization and can describe non-localized bonds
- Structural properties, not electronic properties!

Movies for visualizing molecular modelling

- Materials simulations (metals, surfaces, shear flows, liquids, some molecular materials...)
 - <http://lammps.sandia.gov/movies.html>
- Biomolecules
 - <http://www.ks.uiuc.edu/Gallery/Movies/>