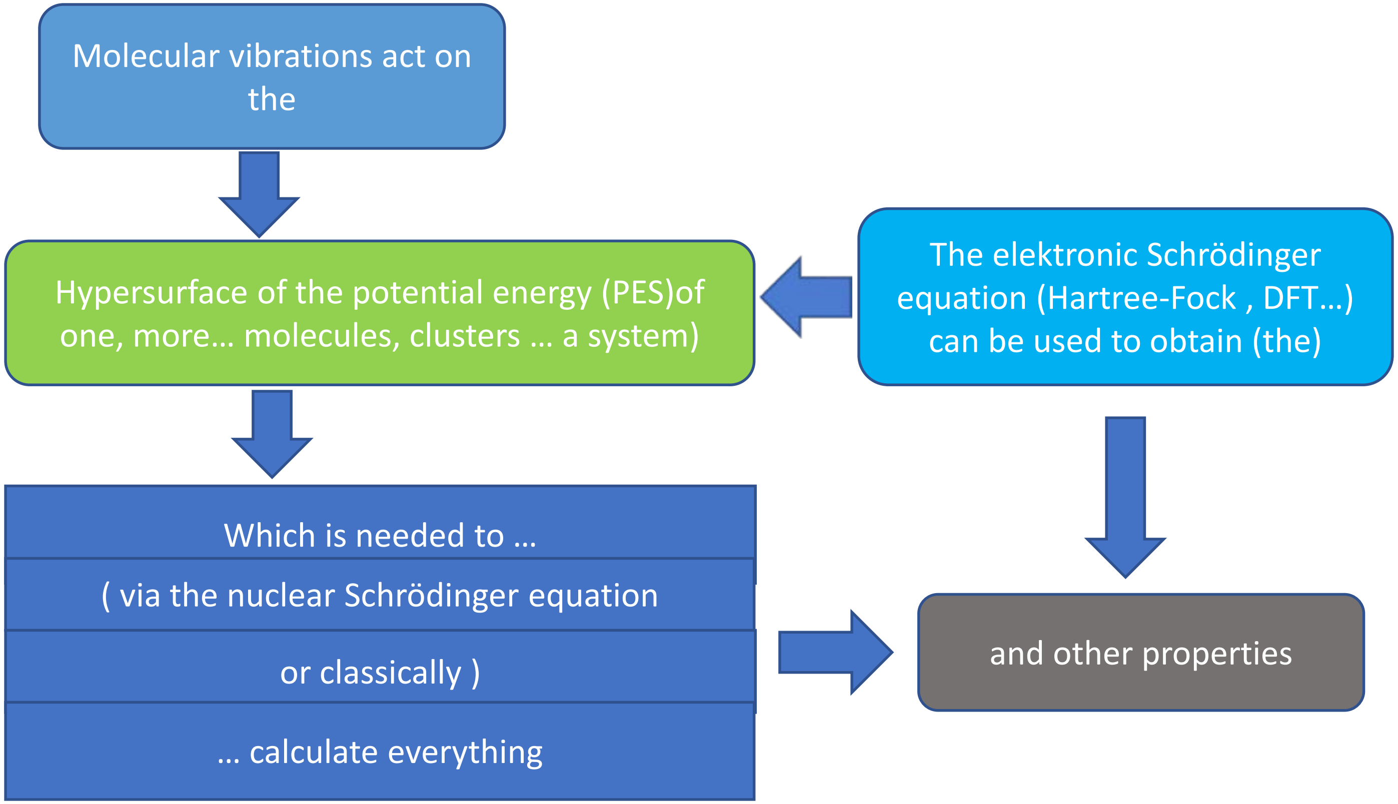
Topic:
Modeling the molecular interactions

The PES of a molecule (cluster …)

- Without PES no chemistry and no molecules:
  - every ‘Molecule’ would be different (its energy would not only depend on its geometry but also on its history.
- The Born-Oppenheimer – approximation states that a PES exists.
- But: one PES for each electronic state.
- The PES allows a eine topographical interpretation of reactions and conversions of molecules.
- Next slide

To remember: Relations



Molecular vibrations act on the

Hypersurface of the potential energy (PES)of one, more… molecules, clusters … a system)

The elektronic Schrödinger equation (Hartree-Fock , DFT…) can be used to obtain (the)

Which is needed to …

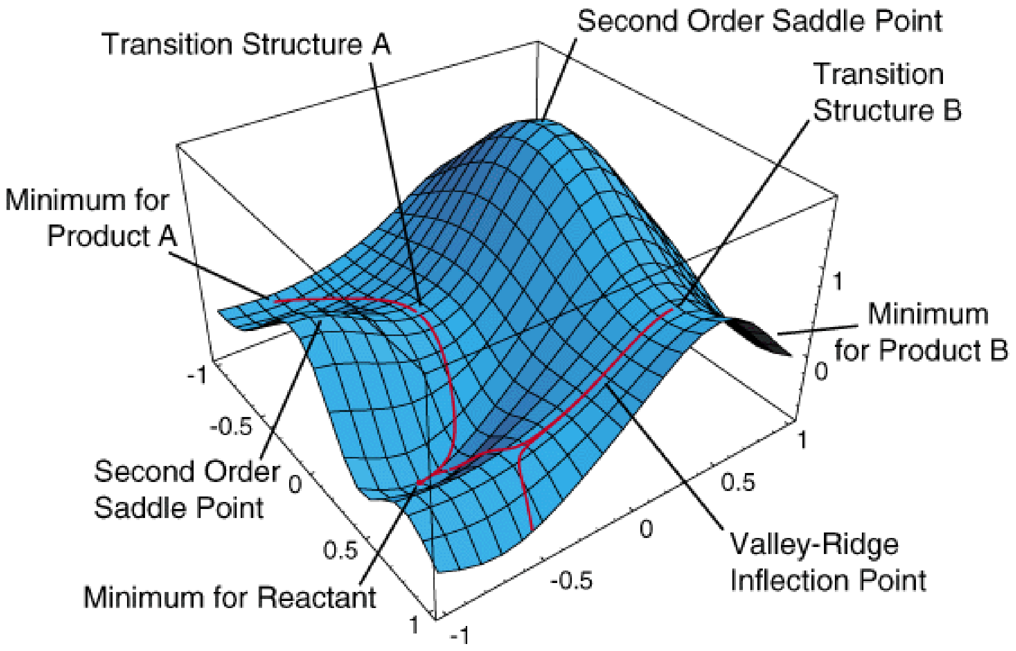
(via the nuclear Schrödinger equation

or classically)

… calculate everything

and other properties

The PES of a molecule (cluster …)



Modeling the molecular interactions - general

- **The potential energy in an N-particle system V = f(r) must be expressed in some tractable way since it needs to be *known* and it needs to be *calculable*.**
- **It can either be calculated quantum mechanically or be derived from a mathematical expression (‘energy formula’) that includes some physics.**

Modeling the molecular interactions - general

Which energy formulas are useful ?

- **For r_{ij}=0, E_{ij} should be ∞**
  - **… not fulfilled by exp(-a r_{ij})**
- **For r_{ij}=∞, E_{ij} should be 0**
  - **… not fulfilled by a polynomial in r_{ij}**
- **Normally, E_{ij} should have none or one minimum**
  - **No minmum → repulsion**
  - **One minimum → attraction**
- **Sometimes but rarely, E_{ij} has one maximum (and therefore how many minima ?)**

Modeling the molecular interactions - general

(discuss Electron-electron interaction
Long- and short range, Energy vs. force …

The potential energy in the pair approximation:

In the pair approximation one assumes that the total energy is a sum of pairwise interactions. For example, if Eij is set to be a sum of ak/rk terms:

- **The total energy is then:**
  (*ji* … pairs of molecules
  lm* … interaction centers in pair *ij
  ***k* … term in sum over 1/r powers)**

$$\mathbf{V}_{tot}=\sum_{ij}\sum_{lm}\sum_{k}\frac{a_k}{r_{lm}^{k}}$$

The potential Energy V

Functional forms:

Sutmann chapter 2

- The pair approximation needs distances as input:
  Angular → Radial

$$\mathbf{V}=\sum_{ij}\mathbf{f}_{kl}(C_{ij}) \qquad \mathbf{V}=\sum_{\mathbf{ij}}\sum_{kl}\mathbf{f}(\mathbf{r}_{kl})$$

$$\mathbf{f}(\mathbf{r}_{ij})=\sum_{k=1}^{n}\frac{a_k}{r_{ij}^{k}}$$

Modeling the molecular interactions

Deficiencies of the pair approximation:

The pair approximation is a truncation of the energy expression:

E=f(i)+f(ij)+f(ijk)+f(ijkl)…

the pair term is always the most important …

… but unfortunately the series converges slowly

- Polarisability normally what causes the largest deviation from the pair approximation
- Charge transfer
- Directional effects (bonds)

Polarisability concepts, examples for going beyond the pair approximation, …

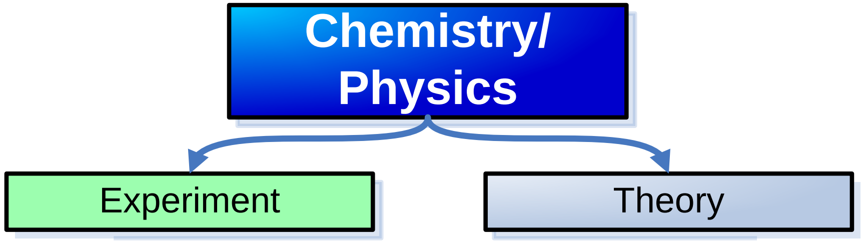
Discussion: polarisation

Potential Energy Functions II: step-by-step

Potential functions

(**1**) What it is about ...

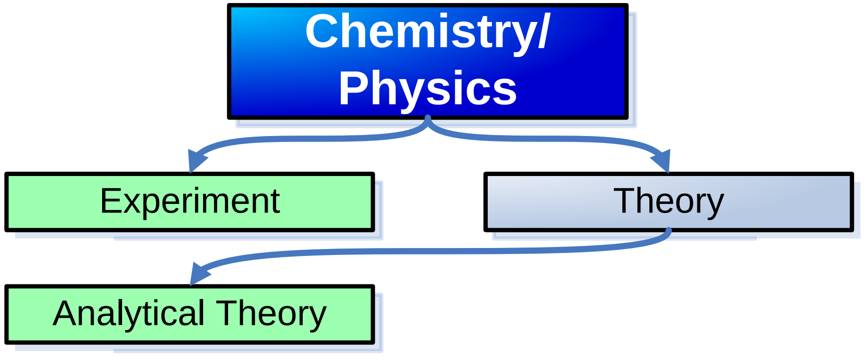
Chemistry/ Physics



Chemistry/ Physics

Experiment

Theory

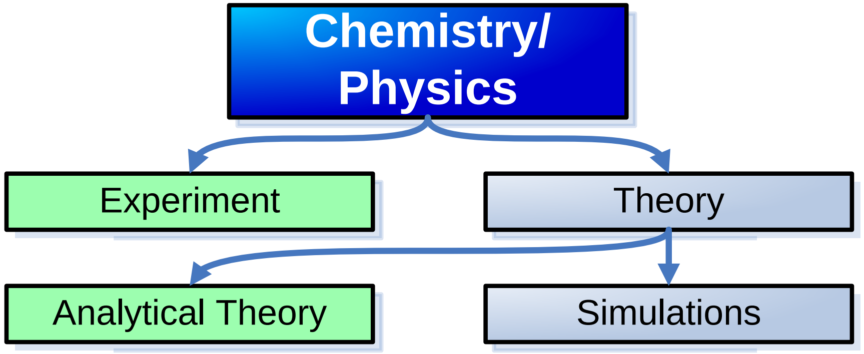


Chemistry/ Physics

Experiment

Theory

Analytical Theory



Chemistry/ Physics

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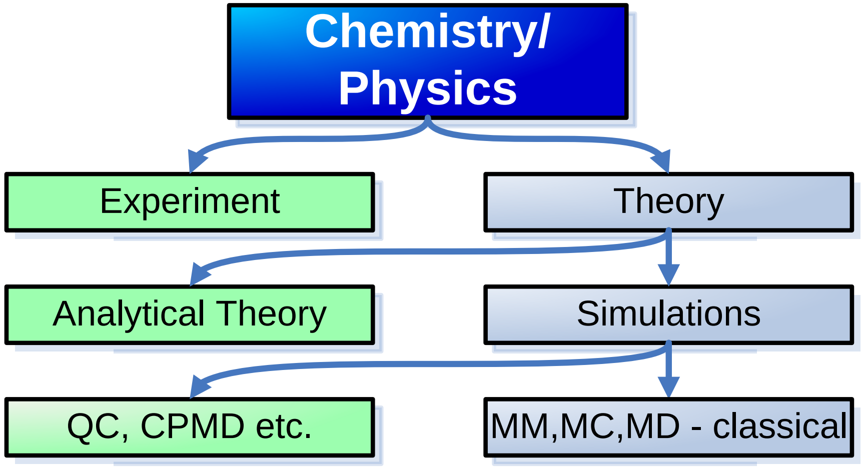
Simulations



Chemistry/ Physics

Experiment

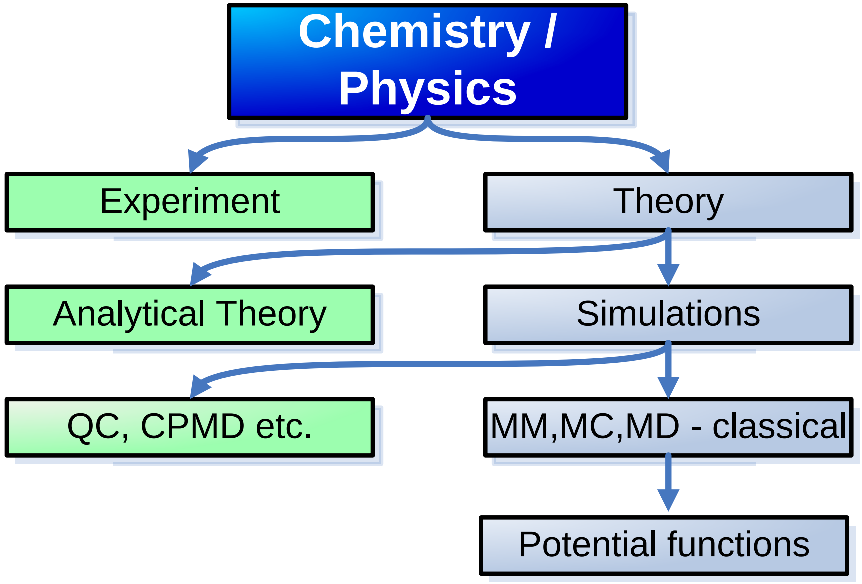
Theory

Analytical Theory

Simulations

QC, CPMD etc.

MM,MC,MD - classical



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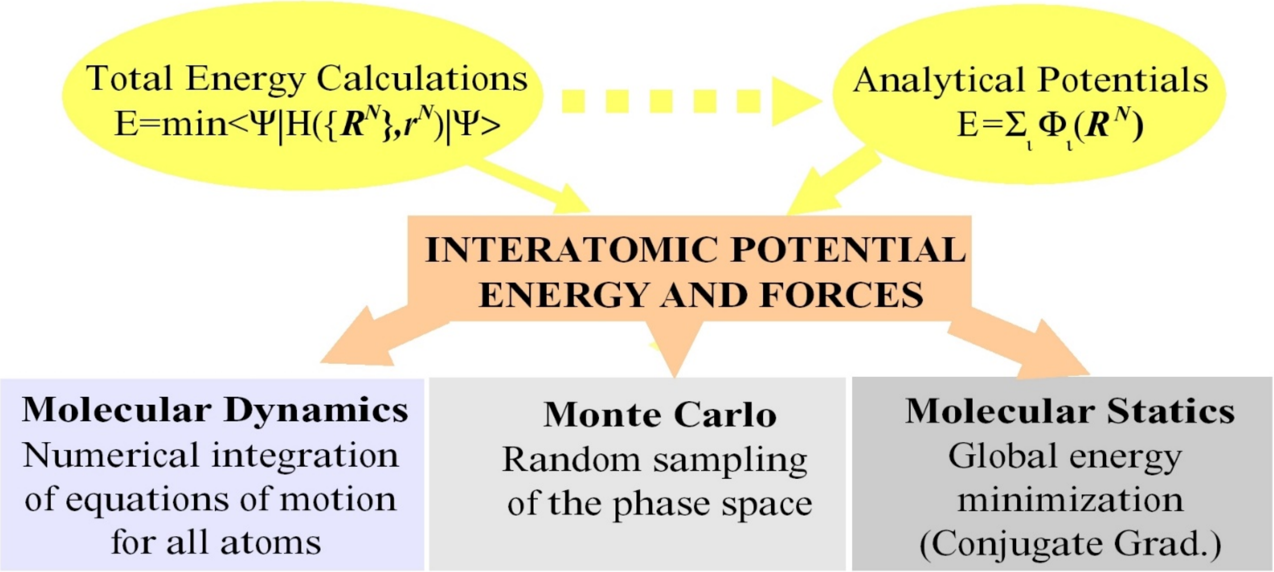
Potential functions

Atomistic Computer Simulation Methods



Total Energy Calculations
$E=\min\langle\Psi|H(\{\boldsymbol{R}^N\},\boldsymbol{r}^N)|\Psi\rangle$

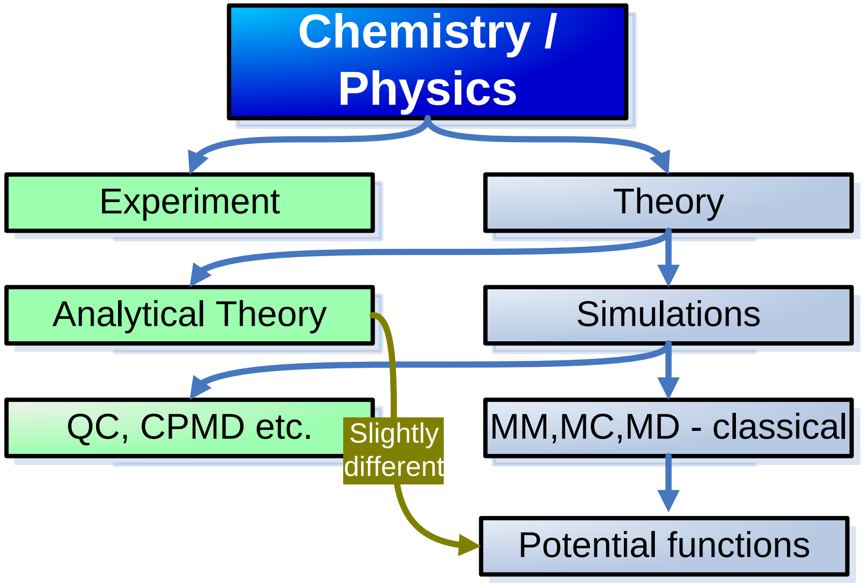
Analytical Potentials
$E=\sum_i \Phi_i(\boldsymbol{R}^N)$

INTERATOMIC POTENTIAL ENERGY AND FORCES

Molecular Dynamics
Numerical integration of equations of motion for all atoms

Monte Carlo
Random sampling of the phase space

Molecular Statics
Global energy minimization (Conjugate Grad.)



Chemistry / Physics

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QC, CPMD etc.

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Slightly different

Potential functions

Potential functions

An analytical potential function is an expression for the total energy of a system as function of the atomic coordinates.

Potential functions

Why does one need them ?
(in the context of molecular simulations)

Properties via Simulations ?

- A system consists of n particles. (Atoms, molecules, ions ...).
  Their behavior results from their electronic structure which governs the interaction between them (their attraction and repulsion).
- A potential energy function E which is a scalar function of the coordinates of the particles is containing all this in is containing all information about these interactions.
- How can one calculate macroscopic properties from E ?

(Macroscopic properties could be, for example:

  - the pressure p=f(V),
  - average geometries at a given temperature or
  - (vibrational, electronic) spectra ?

- This is normally not possible in a simple way.
- One needs MD simulations because of the lack of analytical formulas.
  There are no formulas like ‘p=nRT / V’ for properties of real systems.

- Therefore, there are two problems
- The first one is the **potential energy function** $E_{pot}=f(X)$.
- *Experience (of the last 30 years) has shown that quantum chemistry is a powerful tool to tackle the problem of the potential energy function.*
- The second problem is the **calculation of properties** if $E_{pot}=f(X)$ is known. Computer simulations (especially MD) can do this numerically.

- (**2**)
  The general scheme of fitting quantum chemically derived data to analytical expressions:
  How to get a potential function

Potential functions

i.E. Lennard-Jones

$$E = E_{LJ} + E_{qq}$$

$$E_{LJ}(r) = \left\{ 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right] \right\}$$

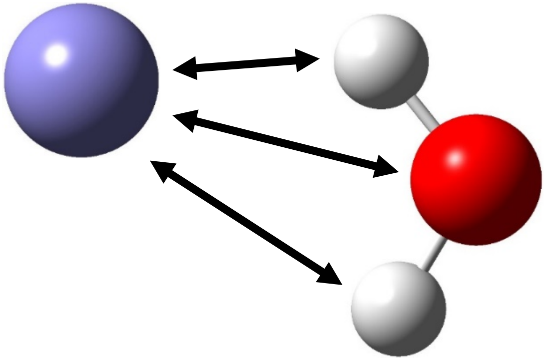
$$E_{qq}(r) = \frac{q_i q_j}{r_{ij}}$$

r is the distance between 2 atoms

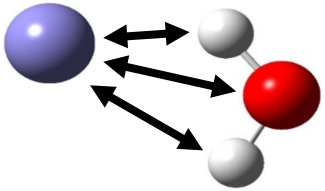
Potential functions

$$E(r_{ij}) = \left\{ 4\varepsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^{6} \right] \right\} + \frac{q_i q_j}{r_{ij}}$$

For a water molecule interacting with i.E. an atomic ion I^{+} there would be 3 such terms:



We can write the formula slightly different so that it becomes a polynomial in 1/r:

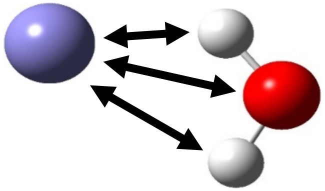


$$E(r_{ij}) = \frac{A}{r_{ij}^{12}} + \frac{B}{r_{ij}^{6}} + \frac{q_i q_j}{r_{ij}}$$

We need different parameters A,B for the interaction between I$^+$-O and I$^+$-H but the two I+-H interactions have the same parameters A,B.
The total interaction energy is:

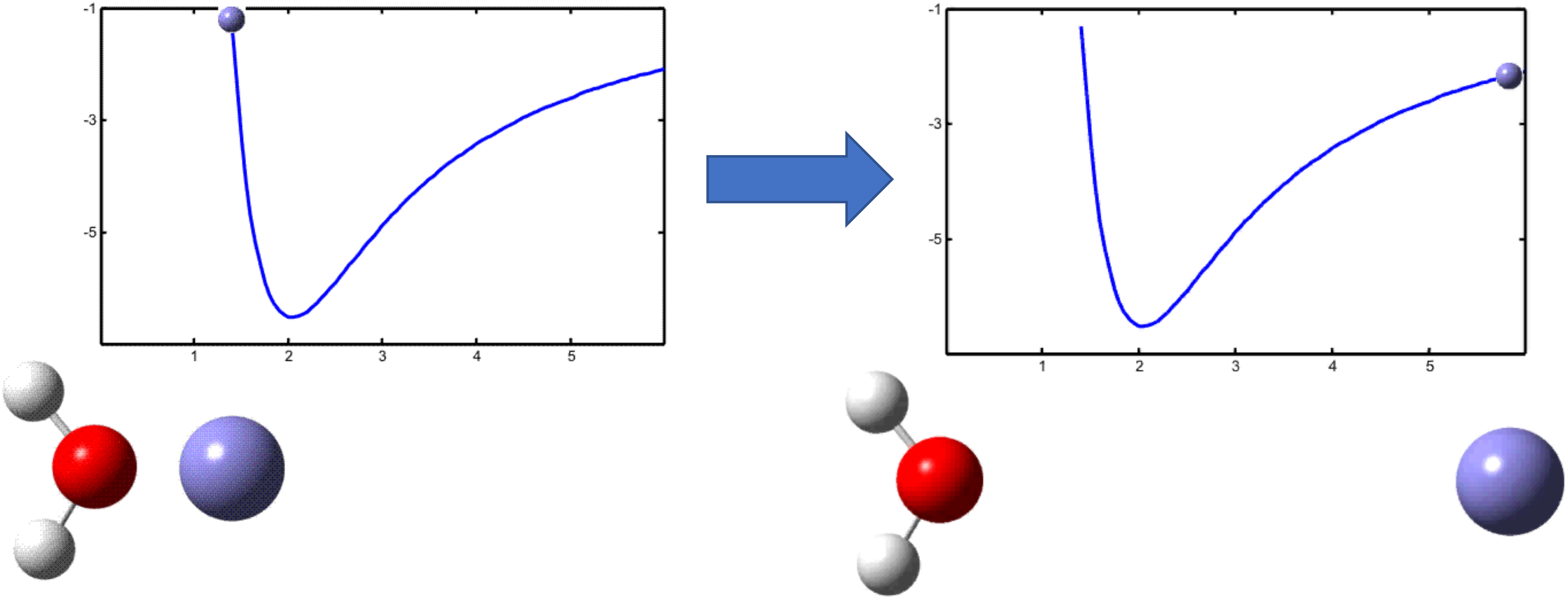
$$E_{I^+-W} = \frac{A_{I^+-O}}{r_{I^+-O}^{12}} + \frac{B_{I^+-O}}{r_{I^+-O}^{6}} + \frac{q_{I^+} q_O}{r_{I^+-O}} + \\ + \frac{A_{I^+-H}}{r_{I^+-H^1}^{12}} + \frac{B_{I^+-H}}{r_{I^+-H^1}^{6}} + \frac{q_{I^+} q_H}{r_{I^+-H^1}} + \\ + \frac{A_{I^+-H}}{r_{I^+-H^2}^{12}} + \frac{B_{I^+-H}}{r_{I^+-H^2}^{6}} + \frac{q_{I^+} q_H}{r_{I^+-H^2}}$$

We have now the 7 parameters



$$A_{I^+-O}, B_{I^+-O}, A_{I^+-H}, B_{I^+-H}, q_{I^+}, q_O, q_H$$

- In general, a set of atoms in a certain environment q_H (like H in H_2O which, for example, is different from H of CH_4) is called a ‘class’.
  In this example, atoms and classes are the same.
- The q – parameters are *class-specific* parameters for which good values often can be calculated via so-called ‘population analysis’, (atomic partial charge analysis), a standard quantum chemical method.
- The A and B – parameters are *class-pair specific* parameters that can be calculated via fitting to quantum chemical energies.


-1
-3
-5
1
2
3
4
5
-1
-3
-5
1
2
3
4
5

To consider:

- Many orientations and distances
- Scanning a 3-dimensional (in the example) or 6-dimensional (in the general case) space.
- Computationally demanding
- The energy is linear in the A, B – parameters in
  a polynomial expression. Expressions like ‘exp(-C r)’ are also commonly used, where this is not the case.

(3) The (non)additivity of interactions

- A formula like $E_{I^+ - H_2O} = \sum_{O,H,H} \frac{A}{r^{12}} + \frac{B}{r^6} + \frac{q_i q_j}{r}$

  describes the interaction between the ion and water. If we have many water molecules, can we simply say:

$$E_{total} = \sum_{(H_2O_i)} \sum_{O_i, H_i, H_i} \frac{A}{r^{12}} + \frac{B}{r^6} + \frac{q_i q_j}{r} + E_{H_2O} \quad ?$$

- If we do so, we use the so-called pair approximation.

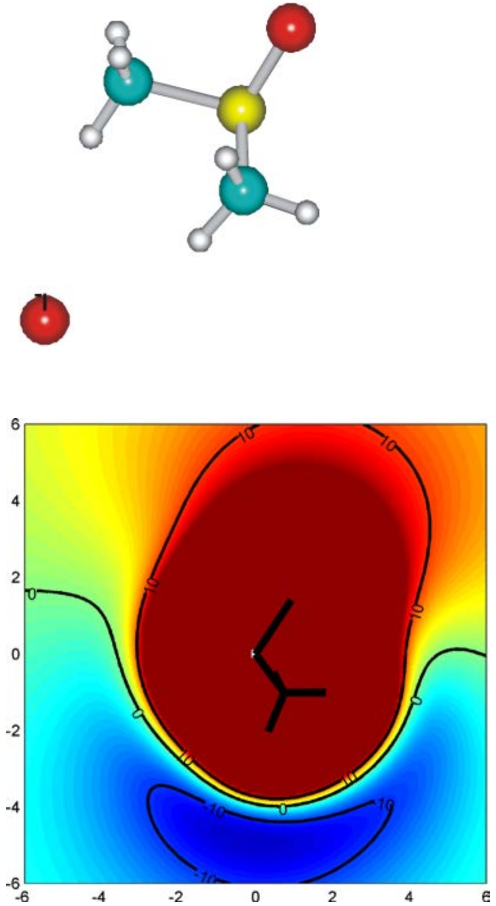
(4)

An example (where the pair approximation is used):

Interaction between Be^{2+} / I^- and DMSO:

After the construction of the potential energy function, it must be checked.

- Example for I$^-$:

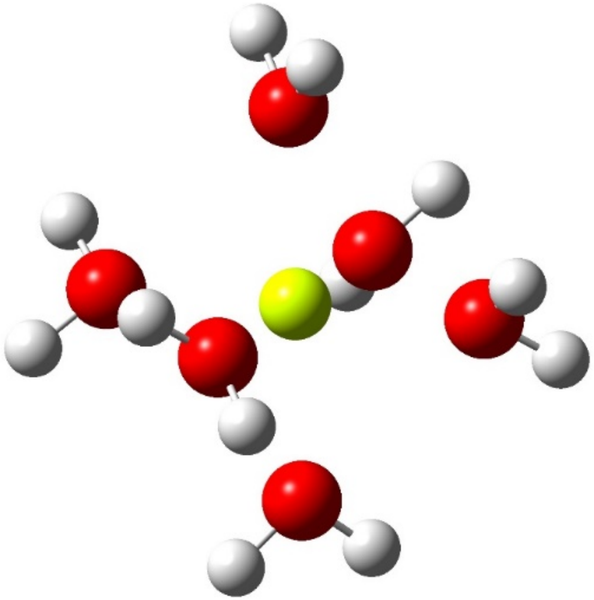


-14 kcal/mol →

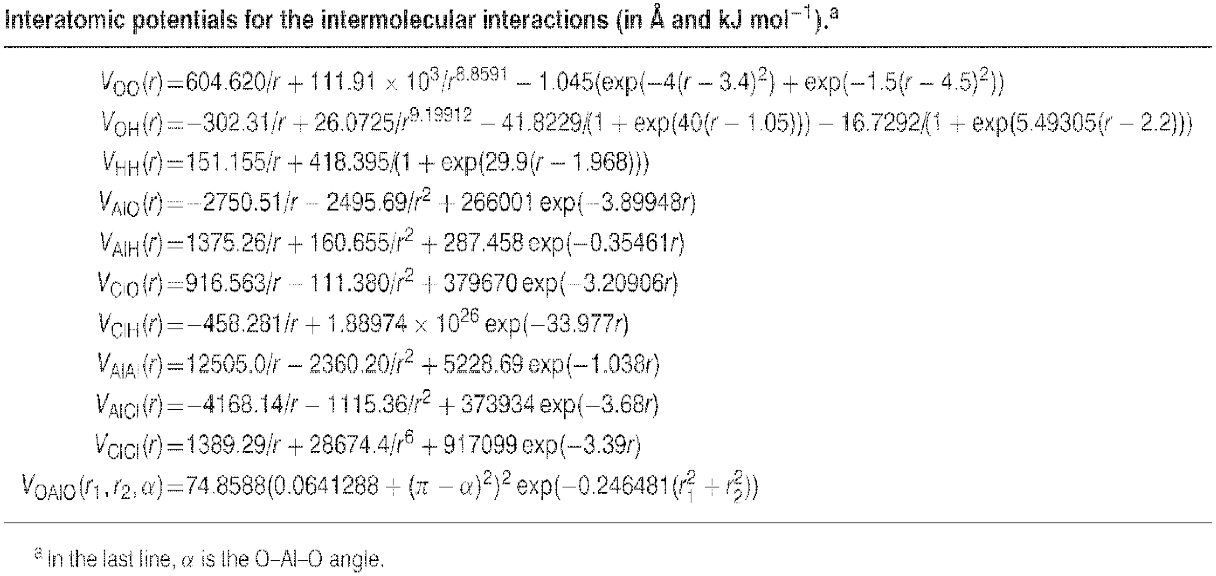
∞

(5)
Another example (beyond the pair approximation)

The pair approximation is often not good enough, especially for ion-ligand interactions:



$AlCl_3$ in water with the following potential energy function:



Interatomic potentials for the intermolecular interactions (in Å and kJ mol^{-1}).[a]

$$V_{OO}(r) = 604.620/r + 111.91 \times 10^3/r^{8.8591} - 1.045(\exp(-4(r-3.4)^2) + \exp(-1.5(r-4.5)^2))$$
$$V_{OH}(r) = -302.31/r + 26.0725/r^{9.19912} - 41.8229/(1 + \exp(40(r-1.05))) - 16.7292/(1 + \exp(5.49305(r-2.2)))$$
$$V_{HH}(r) = 151.155/r + 418.395/(1 + \exp(29.9(r-1.968)))$$
$$V_{AlO}(r) = -2750.51/r - 2495.69/r^2 + 266001\exp(-3.89948r)$$
$$V_{AlH}(r) = 1375.26/r + 160.655/r^2 + 287.458\exp(-0.35461r)$$
$$V_{ClO}(r) = 916.563/r - 111.380/r^2 + 379670\exp(-3.20906r)$$
$$V_{ClH}(r) = -458.281/r + 1.88974 \times 10^{26}\exp(-33.977r)$$
$$V_{AlAl}(r) = 12505.0/r - 2360.20/r^2 + 5228.69\exp(-1.038r)$$
$$V_{AlCl}(r) = -4168.14/r - 1115.36/r^2 + 373934\exp(-3.68r)$$
$$V_{ClCl}(r) = 1389.29/r + 28674.4/r^6 + 917099\exp(-3.39r)$$
$$V_{OAlO}(r_1, r_2, \alpha) = 74.8588(0.0641288 + (\pi - \alpha)^2)^2\exp(-0.246481(r_1^2 + r_2^2))$$

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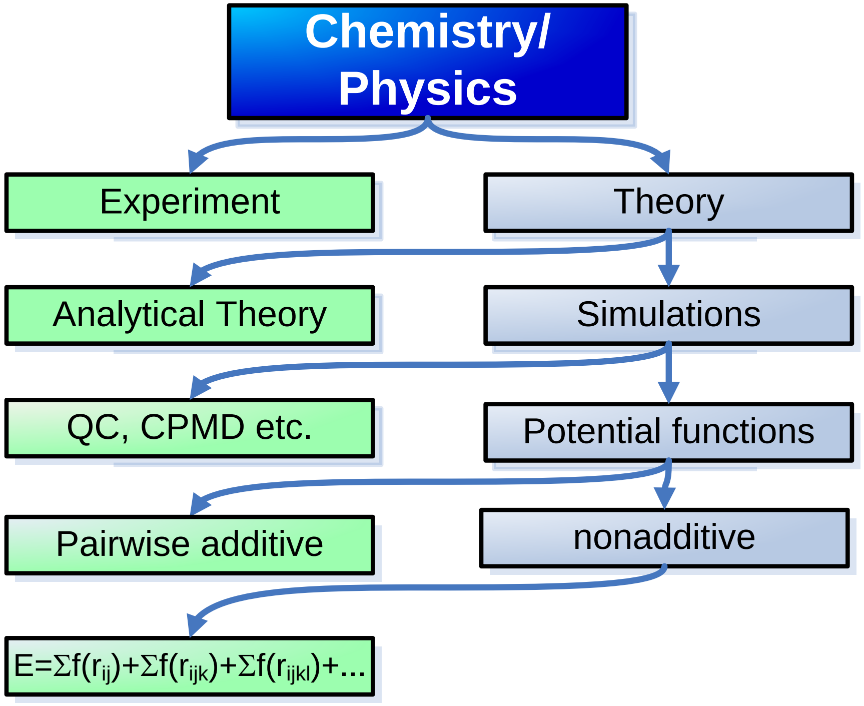
[a] In the last line, α is the O–Al–O angle.



Chemistry/ Physics

Experiment

Theory

Analytical Theory

Simulations

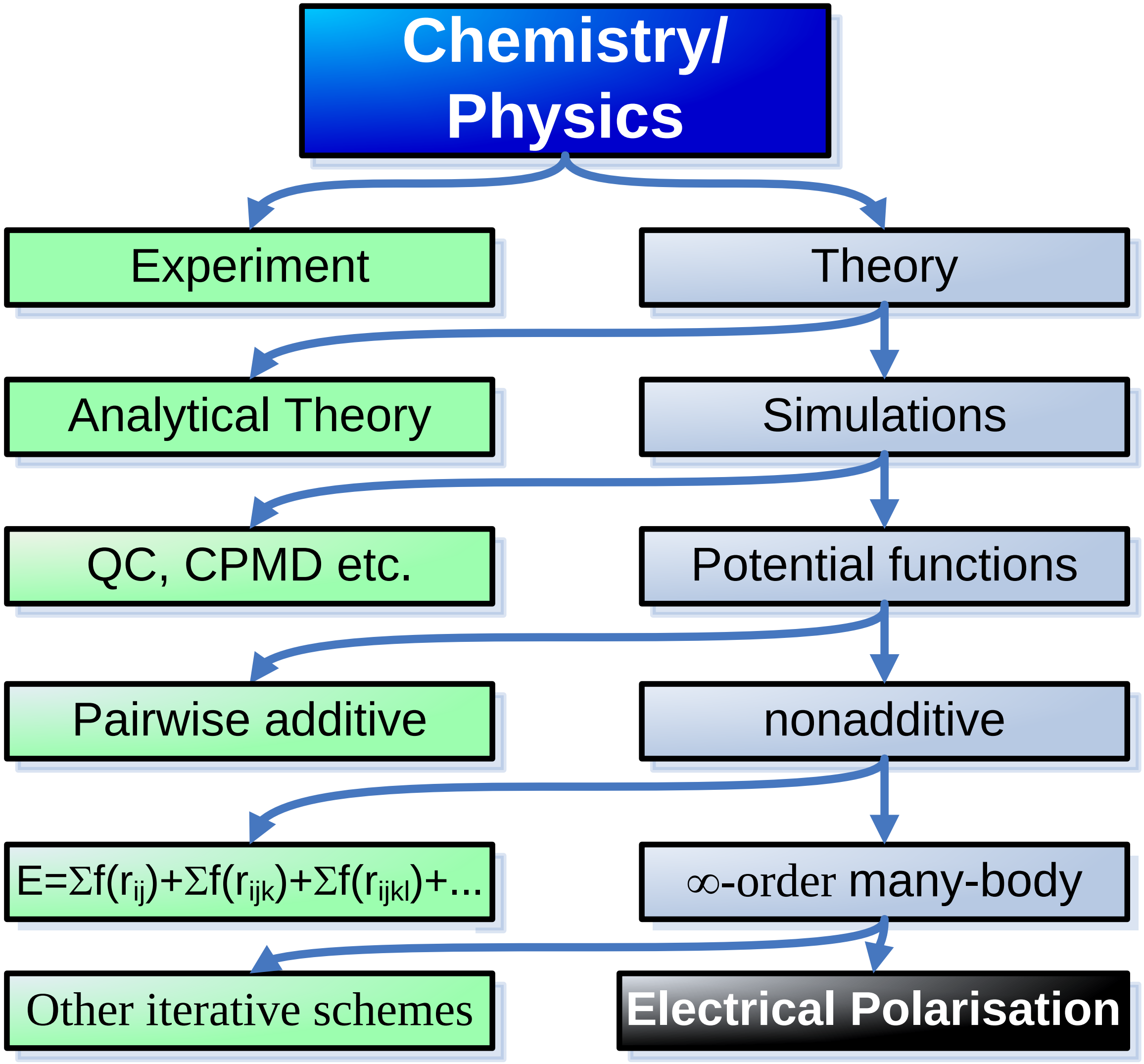
QC, CPMD etc.

Potential functions

Pairwise additive

nonadditive

$E=\Sigma f(r_{ij})+\Sigma f(r_{ijk})+\Sigma f(r_{ijkl})+\ldots$



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$E=\Sigma f(r_{ij})+\Sigma f(r_{ijk})+\Sigma f(r_{ijkl})+\ldots$

∞-order many-body

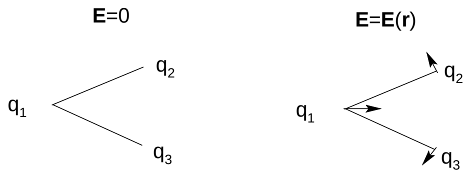
Other iterative schemes

Electrical Polarisation

Ways to deal with nonadditive interactions:

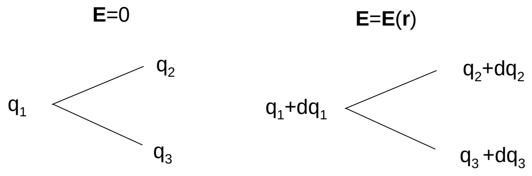
The point-dipole model (PDM):

Atomic polarizabilities α_i are assigned to some molecular site and the electric field induces the formation of a point dipole μ_i



The fluctuating charge model (FQ):

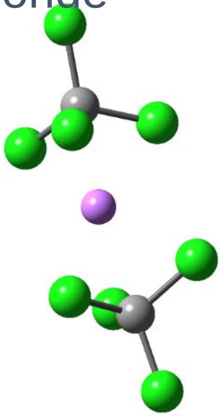
Charges are allowed to fluctuate according to the electronic properties of the molecule as atomic electronegativity and atomic hardness.

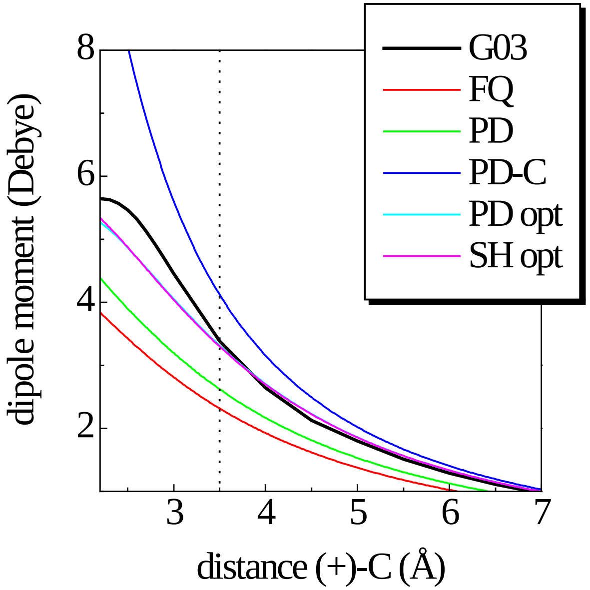


$dq_1 + dq_2 + dq_3 = 0$

Comparison of the behaviour of these ‘polarisation models’:

Example:
Li^+ ion near
Carbon
Tetrachloride

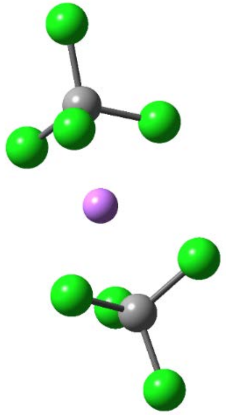




Conclusion:

Induced dipole moments (=polarization) can be large.
The effect on the electrostatic energy can be large

(keep in mind, however, that Li^+ ion near carbon tetrachloride is an extreme example.)



Modeling the molecular interactions: The reality for everyday systems

Normally one divides between:

- Inter- and
- intramolecular interactions

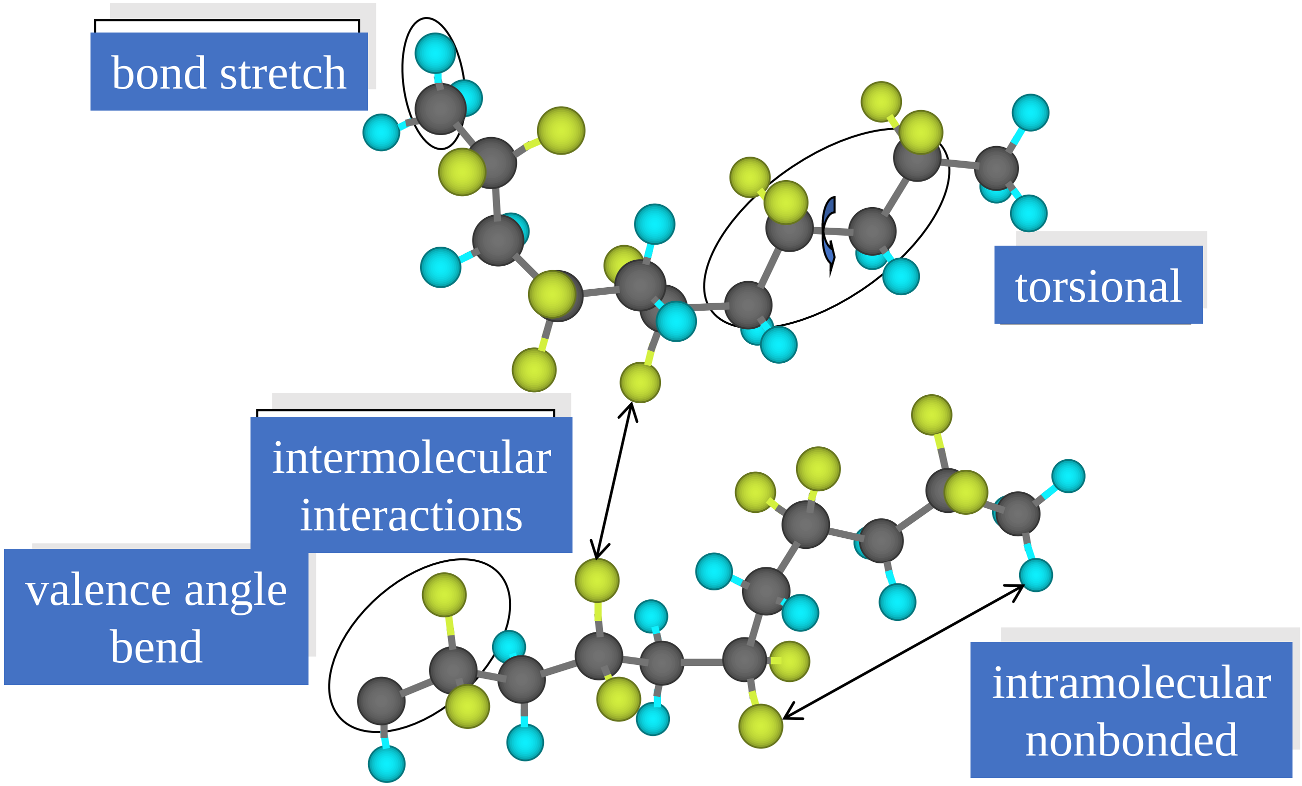
Modeling the molecular interactions

Inter- and intramolecular interactions

Why distinguish between them ?

- In the ideal case, no difference
- In reality:
    - Equal treatment leads is difficult/expensive
    - Examples
        - UFF
        - Central force model of water
        - Reactive potentials
- Why is it advantageous to differenciate ?
    - Bond breaking is difficult to describe
    - Angular (3body) and 4-body terms are natural and needed in a network of bonded atoms (A-B-C-D)
    - but difficult and less necessary between non-bonded atoms (H2O-M++-OH2)

1) Typical intermolecular energy functions (=force field)



Every atom will be affected by the potential energy functions of every atom in the system. Either from

- Bonded Neighbors
- Non-Bonded Atoms
  (=other atoms in the same molecule or atoms from different molecules)

$$V(R) = E_{bonded} + E_{non-bonded}$$

2) Non-Bonded Atoms

In the simplest case, there are three types of potential energy which we need to consider for the interaction between non-bonded atoms:

- Repulsion of electron shells
- van der Waals Potential

$$E_{non-bonded} = E_{repulsion} + E_{van-der-Waals} + E_{electrostatic}$$

The Lennard-Jones form is a compromise between accuracy and fast computability.

Repulsive (~r^{-12}) and van der Waals (~r^{-6}) potential terms:

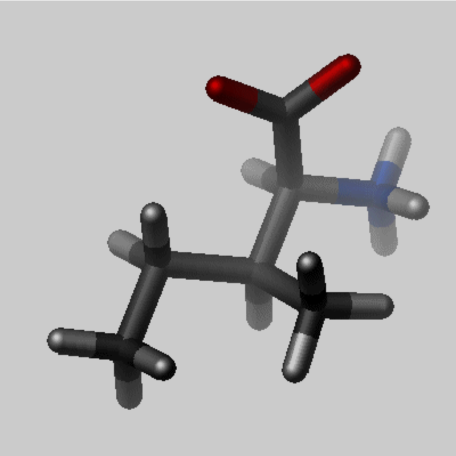
$$E_{Lennard-Jones} = \sum_{\substack{nonbonded\\pairs}} \left(\frac{A_{ik}}{r_{ik}^{12}} - \frac{C_{ik}}{r_{ik}^{6}} \right)$$

Scaling, parameters, alternative versions, accuracy, deficits, improvements, physical foundations

Electrostatic Potential

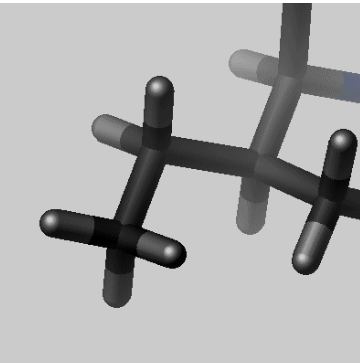
$$E_{electrostatic} = \sum_{\substack{nonbonded \\ pairs}} \frac{q_i q_k}{D r_{ik}}$$

Bonded Atoms

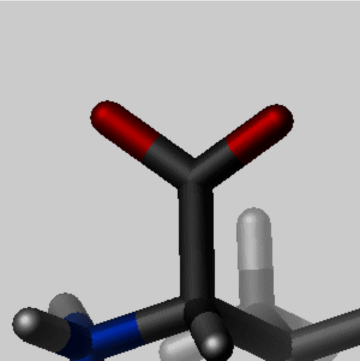


$$E_{bonded} = E_{bond-stretch} + E_{angle-bend} + E_{rotate-along-bond}$$

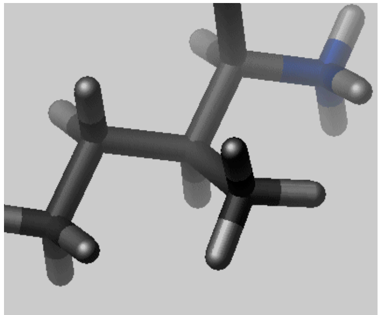
$$E_{bond-stretch} = \sum_{1,2\ pairs} K_b (b - b_0)^2$$



$$E_{bond-bend} = \sum_{angles} K_\theta (\theta - \theta_0)^2$$



$$E_{rotate-bond} = \sum_{1,4\ pairs} K_\phi (1 - \cos(n\phi))$$



Side issue:
the electrostatic energy in a crystal:
Ewald

$$
\begin{aligned}
U = {} & \underbrace{\frac{1}{4\pi\epsilon_0}\sum_{\mathbf{n}}{}^{\dagger}\sum_{i=1}^{N}\sum_{j=i+1}^{N} q_i q_j \frac{\operatorname{erfc}(\alpha|\mathbf{r}_{ij}+\mathbf{n}|)}{|\mathbf{r}_{ij}+\mathbf{n}|}}_{\text{Real-space term}} \\
& + \underbrace{\frac{1}{\epsilon_0 V}\sum_{\mathbf{k}>0}\frac{1}{k^2}e^{-\frac{k^2}{4\alpha^2}}\left\{\left|\sum_{i=1}^{N} q_i\cos(\mathbf{k}\cdot\mathbf{r}_i)\right|^2+\left|\sum_{i=1}^{N} q_i\sin(\mathbf{k}\cdot\mathbf{r}_i)\right|^2\right\}}_{\text{Reciprocal-space term}} \\
& - \underbrace{\frac{\alpha}{4\pi^{\frac{3}{2}}\epsilon_0}\sum_{i=1}^{N} q_i^2}_{\text{Point self-energy}} - \underbrace{\frac{1}{4\pi\epsilon_0}\sum_{n=1}^{M}\sum_{\kappa=1}^{N_m}\sum_{\lambda=\kappa+1}^{N_m} q_{n\kappa}q_{n\lambda}\frac{\operatorname{erf}(\alpha|\mathbf{r}_{\kappa\lambda}|)}{|\mathbf{r}_{\kappa\lambda}|}}_{\text{Intra-molecular self energy}} \\
& - \underbrace{\frac{1}{8\epsilon_0 V\alpha^2}\left|\sum_{i=1}^{N} q_i\right|^2}_{\text{Charged system term}} + \underbrace{\left[\frac{1}{6\epsilon_0 V}\left|\sum_{i=1}^{N} q_i\mathbf{r}_i\right|^2\right]}_{\text{Surface dipole term}}
\end{aligned}
$$

κ, λ	indices of sites within a single molecule
N	total number of charged sites
M	total number of molecules
N_m	number of sites on molecule m
$\mathbf{p}_i$	co-ord of site i relative to molecular centre-of-mass,
$\mathbf{r}_i - \mathbf{R}_i$	
q_i	charge on absolute site i
$q_{m\kappa}$	charge on site κ of molecule m
$\mathbf{r}_i$	Cartesian co-ordinate of site i
$\mathbf{r}_{ij}$	
$\mathbf{r}_j - \mathbf{r}_i$	
α	real/reciprocal space partition parameter
π_{lm}	instantaneous stress tensor
δ_{lm}	Kronecker delta symbol
l, m	xyz tensor indices
V	volume of MD cell

Ewald force

$$= \underbrace{\frac{q_i}{4\pi\epsilon_0}\sum_{\mathbf{n}}^{\dagger}\sum_{\substack{j=1\\j\neq i}}^{N} q_j \left\{\frac{\operatorname{erfc}(\alpha|\mathbf{r}_{ij}+\mathbf{n}|)}{|\mathbf{r}_{ij}+\mathbf{n}|} + \frac{2\alpha}{\sqrt{\pi}} e^{-\alpha^2|\mathbf{r}_{ij}+\mathbf{n}|^2}\right\}\frac{\mathbf{r}_{ij}+\mathbf{n}}{|\mathbf{r}_{ij}+\mathbf{n}|^2}}_{\text{Real-space term}}$$

$$+ \underbrace{\frac{2}{\epsilon_0 V}\sum_{\mathbf{k}>0} q_i \frac{\mathbf{k}}{k^2} e^{-\frac{k^2}{4\alpha^2}} \left\{\sin(\mathbf{k}\cdot\mathbf{r}_i)\sum_{j=1}^{N} q_j\cos(\mathbf{k}\cdot\mathbf{r}_j) - \cos(\mathbf{k}\cdot\mathbf{r}_i)\sum_{j=1}^{N} q_j \sin(\mathbf{k}\cdot\mathbf{r}_j)\right\}}_{\text{Reciprocal-space term}}$$

$$+ \underbrace{\left[\frac{q_i}{6\epsilon_0 V}\left(\sum_{j=1}^{N} q_j\mathbf{r}_j\right)\right]}_{\text{Surface dipole term}}$$

en.wikipedia.org/wiki/Ewald_summation

Sketching the Ewald potential

(discuss TV shape, infinity considerations, convergence,

Sketching the Ewald potential

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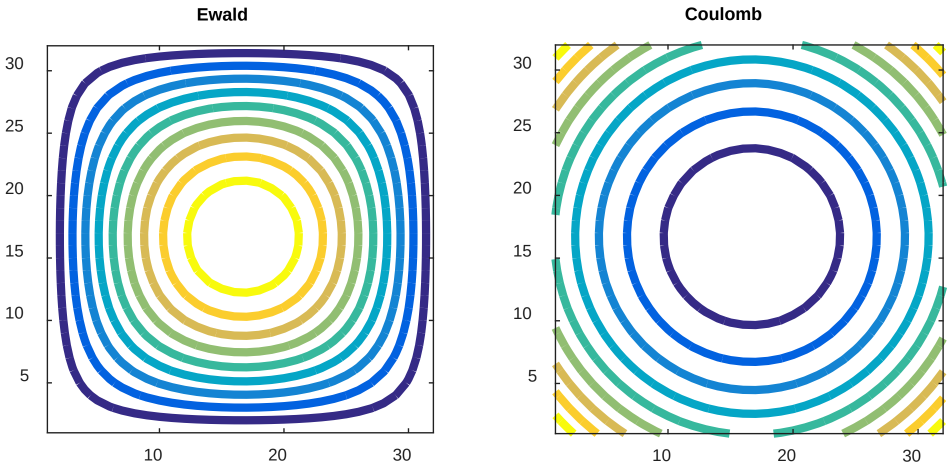
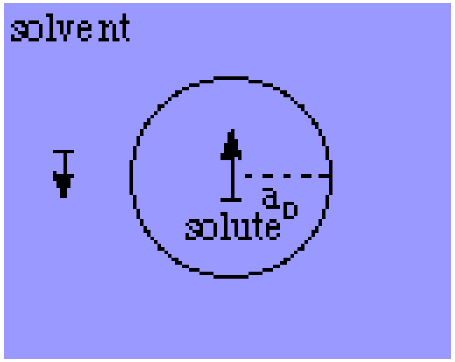
```
[x y]=meshgrid(0:0.1:pi);
z1=sin(x).^2.*cos(y).^2;
subplot 121
[a,b]=contour(z1);
set(b,'linewidth',3); axis square
title('Ewald');
z2=(x-pi/2).^2+(y-pi/2).^2;
subplot 122
[c,d]=contour(z2);
set(d,'linewidth',3); axis square
title('Coulomb');
```



Reaction field:

simpler, not periodic, equally good as Ewald
Also useful in quantum chemistry



$$\vec{R} = \frac{2(\varepsilon - 1) \cdot \vec{\mu}}{(2\varepsilon + 1) \cdot a_0^3}$$

$\vec{R}$ = reaction field

a_0 = cavity radius

$\vec{\mu}$ = molecular dipole moment

Bond breaking

In many instances, potentials where bonds can break are needed.

For example (the so-called Tersoff-Abel potential):

$$\boxed{E = \sum\nolimits_{i>j} f_{ij}(r_{ij}) \left[\phi_R^{ij}(r_{ij}) - \frac{b_{ij} + b_{ji}}{2} \phi_A^{ij}(r_{ij}) \right] .}$$

$$b_{ij} = (1 + \sum_{k(\neq i,j)} f_{ik}(r_{ik}) g_{ik}(\theta_{ijk}) \exp[2\mu_{ik}(r_{ij} - r_{ik})])^{-1/2}$$