

C8855 Advanced Molecular Modelling Methods

Lesson 1 Reactive Force Fields

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Petr Kulhánek

kulhanek@chemi.muni.cz

National Centre for Biomolecular Research, Faculty of Science
Masaryk University, Kamenice 5, CZ-62500 Brno

Classical Force Field Methods

Molecular Mechanics

Schrodinger equation - quantum mechanical description

$$\hat{H}\psi_k^{\mathbf{R}}(\mathbf{r}_e) = E_k(\mathbf{R})\psi_k^{\mathbf{R}}(\mathbf{r}_e)$$

approximation

electron motions is omitted

(electron motions is implicitly included in empirical parameters)

$$E_k(\mathbf{R}) = \underbrace{E_{bonds} + E_{angles} + E_{torsions}}_{\text{bonded contributions}} + \underbrace{E_{ele} + E_{vdw} + \dots}_{\text{non-bonded contributions}}$$

bonded contributions

non-bonded contributions

Classical physics - mechanical description

Nomenclature

Molecular mechanics uses classical mechanics to model molecular systems. The **Born–Oppenheimer approximation is assumed valid**, and the potential energy of all systems is calculated as a function of the atomic coordinates using force fields.

In the context of chemistry and molecular modelling, a **force field** is a **computational method** that is used to estimate the forces between atoms within molecules and between molecules.

More precisely, the force field refers to the **functional form** and **parameter sets** used to calculate the **potential energy of a system** of atoms or coarse-grained particles.

$$E_k(\mathbf{R}) = E_{bonds} + E_{angles} + E_{torsions} + E_{ele} + E_{vdw} + \dots$$

+ parameters

[https://en.wikipedia.org/wiki/Force_field_\(chemistry\)](https://en.wikipedia.org/wiki/Force_field_(chemistry))

https://en.wikipedia.org/wiki/Coarse-grained_modeling

https://en.wikipedia.org/wiki/Molecular_mechanics

Bonded Contributions

Main contributions

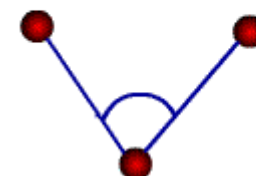
Bond stretching

$$E_{bonds} = \sum_{b=1}^{bonds} \frac{1}{2} K_b (d_b - d_{b0})^2$$



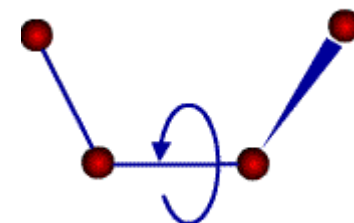
Angle bending

$$E_{angles} = \sum_{a=1}^{angles} \frac{1}{2} K_a (\theta_a - \theta_{a0})^2$$



Bond rotation

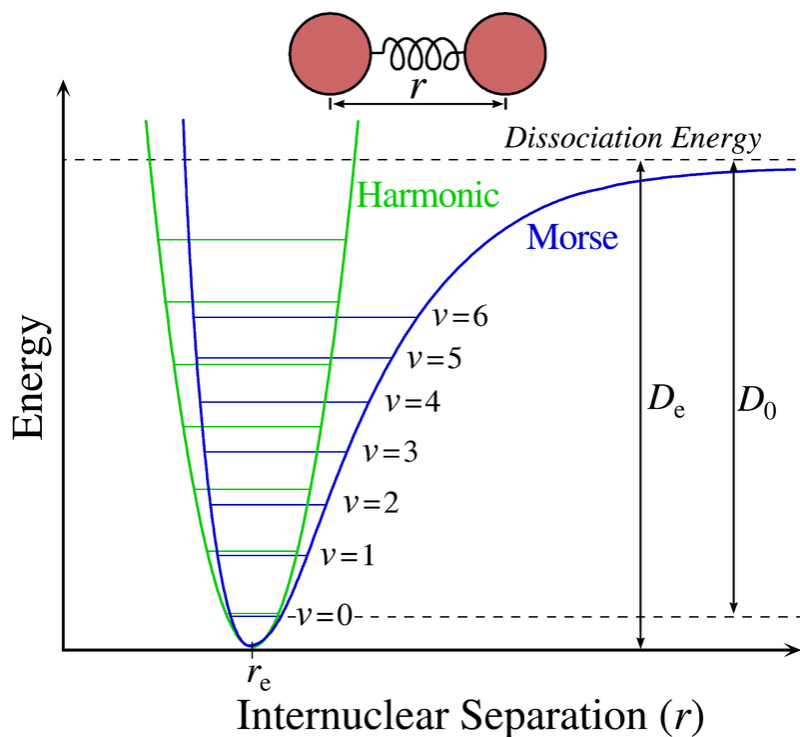
$$E_{torsions} = \sum_{t=1}^{torsions} \sum_n \frac{V_{t,n}}{2} (1 + \cos[n\varphi_t - \delta_{t,n}])$$



 empirical parameters

Bond stretching, cont.

- The harmonic potential does not have dissociation limit. Thus, **force fields employing the harmonic approximation cannot describe reactivity.**
- The reactivity is difficult to describe even with Morse potential properly, a noticeable exceptions are **ReaxFF (reactive force field)** and **EVB (empirical valence bond).**



Harmonic potential

$$V(r) = \frac{1}{2} K (r - r_0)^2$$

Morse potential

$$V(r) = D_e \left(1 - e^{-a(r-r_0)} \right)^2$$

Disadvantage of Morse potential

- more parameters are needed
- more computationally demanding

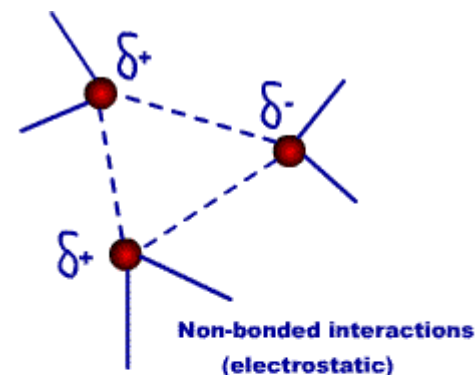
Non-bonded Contributions

Main contributions

Electrostatic interactions

$$E_{ele} = \sum_{i=1}^N \sum_{j=i+1}^N \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}}$$

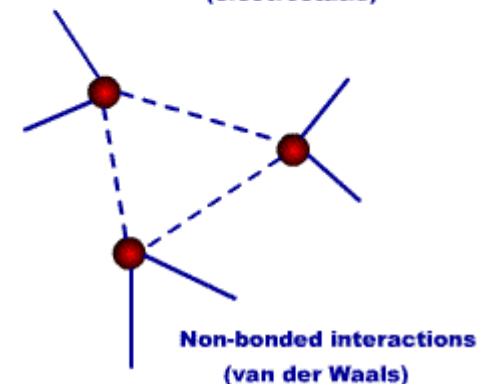
Coulomb Law



van der Waals interactions

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

Lennard-Jones 12-6 potential



N – number of atoms

 empirical parameters

Reactive Force Field Methods

Reactive Molecular Dynamics

Overview

Farah, K.; Müller-Plathe, F.; Böhm, M. C. Classical Reactive Molecular Dynamics Implementations: State of the Art. *ChemPhysChem* **2012**, *13* (5), 1127–1151.
<https://doi.org/10.1002/cphc.201100681>.

- **ReaxFF (Reactive Force Field)**
- **COMB (Charge Optimized Many Body) Potential**
- **EVB (Empirical Valence Bond)**

ReaxFF

ReaxFF (for “reactive force field”) is a bond order-based force field developed by Adri van Duin, William A. Goddard, III, and co-workers at the California Institute of Technology.

- ReaxFF uses a general relationship between bond distance and bond order on one hand and between bond order and bond energy on the other hand that leads to proper dissociation of bonds to separated atoms.
- Other valence terms present in the force field (angle and torsion) are defined in terms of the same bond orders so that all these terms go to zero smoothly as bonds break.
- In addition, ReaxFF has Coulomb and Morse (van der Waals) potentials to describe nonbond interactions between all atoms (no exclusions). These nonbond interactions are shielded at short range so that the Coulomb and van der Waals interactions become constant as $R_{ij} \rightarrow 0$.
- Generally, the results are of an accuracy similar or better than PM3, while ReaxFF is about 100 times faster.

van Duin, A. C. T.; Dasgupta, S.; Lorant, F.; Goddard, W. A. ReaxFF: A Reactive Force Field for Hydrocarbons. *J. Phys. Chem. A* **2001**, *105* (41), 9396–9409. <https://doi.org/10.1021/jp004368u>.

COMB

The **COMB (Charge Optimized Many Body) potential** developed by Sinnott, Phillpot, and coworkers can describe the different types of bonding in an integrated manner. The first generation was developed to reproduce the phase orders in SiO₂ and Cu, respectively.

Yu, J.; Sinnott, S. B.; Phillpot, S. R. Charge Optimized Many-Body Potential for the Si/SiO₂ System. *Phys. Rev. B* **2007**, 75 (8), 085311. <https://doi.org/10.1103/PhysRevB.75.085311>.

Questions

- Is it possible to use ReaxFF for studying biomolecules?
- How are partial atomic charges calculated in ReaxFF?
- How many parameters per atom are necessary in ReaxFF?
- What is the primary use of COMB potential?