

Forcefields

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1 UFF

The theory presented here is adapted from Rappe et. al, JACS, 1992.

1.1 Bond distances

Equilibrium pairwise distances are given by

$$r_0 = r_i + r_j + r_{BO} + r_{EN} \quad (1)$$

where r_k is the covalent radius of atom k , r_{BO} a correction based on the bond order between the two atoms and r_{EN} a correction for the electronegativity.

$$r_{BO} = -\lambda(r_i + r_j) \ln(n) \quad (2)$$

where $\lambda = 0.1332$ and n the bond order. For example, $n = 1.5$ for aromatic bonds.

$$r_{EN} = r_i r_j \frac{(\sqrt{\chi_i} - \sqrt{\chi_j})^2}{\chi_i r_i \chi_j r_j} \quad (3)$$

where χ_k is the GMP electronegativity of atom k . The energy is then a simple harmonic

$$E_b = \frac{k_{ij}}{2}(r - r_0)^2 \quad (4)$$

The derivative is

$$\frac{\partial E}{\partial X_{i,n}} = k_{ij} \left(1 - \frac{r_0}{r}\right) (X_{i,n} - X_{j,n}) \quad (5)$$

where $X_{i,n}$ is the n^{th} component of the Cartesian coordinate of atom i e.g. x, y, or z.

1.2 Bond Force Constants

Bond stretch force constants are defined as

$$k_{ij} = 664.12 \frac{Z_i^* Z_j^*}{r_{ij}^3} \quad (6)$$

where Z_k^* is the effective atomic charges in units of e and the energy in kcal mol⁻¹.

1.3 Angle Bends

In general, UFF defines the energy of an angle bend as

$$E_\theta = k_{ijk} \sum_{n=0}^m C_n \cos(n\theta) \quad (7)$$

where for linear ($n = 1$), trigonal-planar ($n = 3$), square-planar ($n = 4$) and octahedral ($n = 4$)

$$E_\theta^{\text{Type A}} = \frac{k_{ijk}}{n^2} (1 - \cos(n\theta)) \quad (8)$$

the derivative is evaluated using sympy¹

For other coordination environments with an equilibrium bond angle (θ_0)

$$E_\theta^{\text{Type B}} = k_{ijk} (C_0 + C_1 \cos(\theta) + C_2 \cos(2\theta)) \quad (9)$$

$$C_2 = \frac{1}{4 \sin^2(\theta_0)} \quad ; \quad C_1 = -4C_2 \cos(\theta_0) \quad ; \quad C_0 = C_2 (2 \cos^2(\theta_0) + 1) \quad (10)$$

1.4 Angle Force Constants

Angle force constants are defined as

$$k_{ijk} = \beta \frac{Z_i^* Z_k^*}{r_{ik}^5} r_{ij} r_{jk} [r_{ij} r_{jk} (1 - \cos^2(\theta_0)) - r_{ik}^2 \cos(\theta_0)] \quad (11)$$

$$\beta = \frac{664.12}{r_{ij} r_{jk}} \quad (12)$$

¹<https://docs.sympy.org/>

1.5 Torsional Dihedrals

For a sequence of bonded atoms $i - j - k - l$ the torsional energy is given by

$$E_\phi = \frac{V_\phi}{2} [1 - \cos(n_\phi \phi_0) \cos(n_\phi \phi)] \quad (13)$$

where ϕ is the torsional angle, V_ϕ a force constant and n_ϕ the multiplicity. The general cases are

1. sp³-sp³: $n_\phi = 3$; $\phi_0 = 180^\circ$ unless j, k are group 16 atoms where $n_\phi = 2$; $\phi_0 = 90^\circ$.
2. sp²-sp³: $n_\phi = 6$; $\phi_0 = 0^\circ$
3. sp²-sp²: $n_\phi = 2$; $\phi_0 = 180^\circ$
4. sp²-sp²-sp³-X: $V_0 = 2.0$; $n_\phi = 3$; $\phi_0 = 180^\circ$

and

$$V_{\text{sp}^3} = \sqrt{V_j V_k} \quad (14)$$

where V_m are tabulated values, while bonds containing for sp² centres

$$V_{\text{sp}^2} = 5\sqrt{U_j U_k} (1 + 4.18 \ln(n_{BO,jk})) \quad (15)$$

where U_m are values based on the period of the atom (indexed by m) and $n_{BO,jk}$ is the value of the bond order between atoms j and k .

Torsional potentials are only considered where the central bonds are main group and the atoms non sp hybridised.

If either of the bond angles approaches 180° then the potential is set to zero.

1.6 Inversion

Trigonal(-pyramidal) geometries are enforced using a cosine expansion in the angle (γ) made the axis $c-k$ with the normal to the plane made by the atoms c, i, j where c is the central atom and i, j, k are bonded neighbours.

$$E_\gamma = k_{cijk} (C_0 + C_1 \sin(\gamma) + C_2 \cos(2\gamma)) \quad (16)$$

where k_{cijk} is a force constant and C_n are constants defined by fitting the function to a minimum at γ_0 and a maximum at the inversion point (for group 15 central atoms).

As there are three potential axes ($c-m$) an average is taken over all three.

1.7 Non-bonded: van der waals

Dispersion + repulsive terms to the energy are given by a standard Lennard-Jones 12-6 potential

$$E_{\text{vdw}} = D_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - 2 \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (17)$$

where r_{ij} are the distance between atoms i and j and the distance terms σ_{ij} are generated using geometric mixing $\sigma_{ij} = \sqrt{r_i r_j}$ and likewise for the well depth $D_{ij} = \sqrt{D_i D_j}$ where r_k, D_k are tabulated parameters.

2 RB

The theory here is based on T. Young et. al, ACIE, 2021.

2.1 Bonds

Bonds between atoms are described by harmonic terms

$$E_b = \frac{k}{2} (r - r_0)^2 \quad (18)$$

where k is constant for all bonds and r_0 is simply the sum of covalent radii of atoms i and j .

2.2 Repulsion

To simulate angle, torsional and repulsive non-bonded terms of a standard force-fields a repulsion between all atom pairs is added.² Attractive dispersive terms are neglected.

$$E_r = \frac{c}{r_{ij}^n} \quad (19)$$

where c is a fixed constant, r_{ij} is the distance between atoms i and j and n is a flexible positive integer e.g. 2.

²This implementation adds bonded pair exclusions.