

# 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  $\chi_k$  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  $n^{\text{th}}$  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<sup>-1</sup>.

## 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 sympy<sup>1</sup>

For other coordination environments with an equilibrium bond angle ( $\theta_0$ )

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

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

## 1.4 Angle Force Constants

Angle force constants are defined as

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

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

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<sup>1</sup><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  $\phi$  is the torsional angle,  $V_\phi$  a force constant and  $n_\phi$  the multiplicity. The general cases are

1. sp<sup>3</sup>-sp<sup>3</sup>:  $n_\phi = 3; \phi_0 = 180^\circ$  unless  $j, k$  are group 16 atoms where  $n_\phi = 2; \phi_0 = 90^\circ$ .
2. sp<sup>2</sup>-sp<sup>3</sup>:  $n_\phi = 6; \phi_0 = 0^\circ$
3. sp<sup>2</sup>-sp<sup>2</sup>:  $n_\phi = 2; \phi_0 = 180^\circ$
4. sp<sup>2</sup>-sp<sup>2</sup>-sp<sup>3</sup>-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 sp<sup>2</sup> 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  $180^\circ$  then the potential is set to zero.

## 1.6 Inversion

Trigonal(-pyramidal) geometries are enforced using a cosine expansion in the angle ( $\gamma$ ) 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  $\gamma_0$ .