

# 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 stretch

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

### 1.2 Bond Force Constants

Bond stretch force constants are defined as

$$k_{ij} = 664.12 \frac{Z_i^* Z_j^*}{r_{ij}^3} \quad (5)$$

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

$$E_\theta = k_{ijk} \sum_{n=0}^m C_n \cos(n\theta) \quad (6)$$

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

$$E_\theta^{\text{Type A}} = \frac{k_{ijk}}{n^2} (1 - \cos(n\theta)) \quad (7)$$

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

$$E_\theta^{\text{Type B}} = k_{ijk} (C_0 + C_1 \cos(\theta) + C_2 \cos(2\theta)) \quad (8)$$

$$C_2 = \frac{1}{4 \sin^2(\theta_0)} \quad ; \quad C_1 = -4C_2 \cos(\theta_0) \quad ; \quad C_0 = C_2 (2 \cos^2(\theta_0) + 1) \quad (9)$$

### 1.4 Angle Force Constants

Angle force constants are defined as

$$k_{ijk} = \beta \frac{Z_i^* Z_k^*}{r_{ik}^5} r_{ij} r_{jk} [r_{ij} r_{jk} (1 - \cos^2(\theta_0)) - r_{ik}^2 \cos(\theta_0)] \quad (10)$$

$$\beta = \frac{664.12}{r_{ij} r_{jk}} \quad (11)$$