Forcefields

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1 UFF

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

1.1 Bond distances

Equlibrium pairwise distances are given by

$$r_0 = r_i + r_j + r_{\mathrm{BO}} + r_{\mathrm{EN}} \tag{1}$$

where r_k is the covalant 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.

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

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

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

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

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

The derivative is

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

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

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

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

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

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

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

and for other coordination envrionments with an equilibrum bond angle (θ_0)

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

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

1.4 Angle Force Constants

Angle force constants are defined as

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

$$\beta = \frac{664.12}{r_{ij} r_{jk}} \tag{12}$$