Forcefields

...

May 5, 2022

1 UFF

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

1.1 Bond distances

Equlibrium pairwise distances are given by

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

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.

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

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

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

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

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

where $X_{i,n}$ is the nth 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 ($n = 4$)

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

the derivative is evaluated using sympy[1]
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

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

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

---

[1] https://docs.sympy.org/

1.5 Torisional Dihedrals

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

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

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

1. sp^3-sp^3: $n_\phi = 3; \phi_0 = 180°$ unless j, k are group 16 atoms where $n_\phi = 2; \phi_0 = 90°$.

2. sp^2-sp^3: $n_\phi = 6; \phi_0 = 0°$

3. sp^2-sp^2: $n_\phi = 2; \phi_0 = 180°$

4. sp^2-sp^2-sp^3-X: $V_0 = 2.0; n_\phi = 3; \phi_0 = 180°$

and

$$V_{\mathrm{sp}^3} = \sqrt{V_j V_k} \tag{14}$$

where V_m are tabulated values, while bonds containing for sp^2 centres

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

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) geomateries 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.

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

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

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

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.