

ReaxFF Potential Functions

Supporting information for the manuscript “*A ReaxFF Reactive Force Field for Molecular Dynamics Simulations of Hydrocarbon Oxidation*” by Kimberly Chenoweth, Adri C.T. van Duin and William A. Goddard, III

This document contains all the general ReaxFF-potential functions. In the current ReaxFF code all the energy contributions in this document are calculated regardless of system composition. All parameters that do not bear a direct physical meaning are named after the partial energy contribution that they appear in. For example, p_{val1} and p_{val2} are parameters in the valence angle potential function. Parameters with a more direct physical meaning, like the torsional rotational barriers (V_1 , V_2 , V_3) bear their more recognizable names.

1. Overall system energy

Equation (1) describes the ReaxFF overall system energy.

$$E_{system} = E_{bond} + E_{lp} + E_{over} + E_{under} + E_{val} + E_{pen} + E_{coa} + E_{C2} + E_{triple} + E_{tors} + E_{conj} + E_{H-bond} + E_{vdWaals} + E_{Coulomb} \quad (1)$$

Below follows a description of the partial energies introduced in equation (1).

2. Bond Order and Bond Energy

A fundamental assumption of ReaxFF is that the bond order BO'_{ij} between a pair of atoms can be obtained directly from the interatomic distance r_{ij} as given in Equation (2). In calculating the bond orders, ReaxFF distinguishes between contributions from sigma bonds, pi-bonds and double pi bonds.

$$BO'_{ij} = BO_{ij}^{\sigma} + BO_{ij}^{\pi} + BO_{ij}^{\pi\pi} = \exp\left[p_{bo1} \cdot \left(\frac{r_{ij}}{r_o^{\sigma}}\right)^{P_{bo2}}\right] + \exp\left[p_{bo3} \cdot \left(\frac{r_{ij}}{r_o^{\pi}}\right)^{P_{bo4}}\right] + \exp\left[p_{bo5} \cdot \left(\frac{r_{ij}}{r_o^{\pi\pi}}\right)^{P_{bo6}}\right] \quad (2)$$

Based on the uncorrected bond orders BO' , derived from Equation 1, an uncorrected

overcoordination Δ' can be defined for the atoms as the difference between the total bond order around the atom and the number of its bonding electrons Val .

$$\Delta'_i = -Val_i + \sum_{j=1}^{neighbours(i)} BO'_{ij} \quad (3a)$$

ReaxFF then uses these uncorrected overcoordination definitions to correct the bond orders BO'_{ij} using the scheme described in Equations (4a-f). To soften the correction for atoms bearing lone electron pairs a second overcoordination definition Δ'^{boc} (equation 3b) is used in equations 4e and 4f. This allows atoms like nitrogen and oxygen, which bear lone electron pairs after filling their valence, to break up these electron pairs and involve them in bonding without obtaining a full bond order correction.

$$\Delta'_i{}^{boc} = -Val_i{}^{boc} + \sum_{j=1}^{neighbours(i)} BO'_{ij} \quad (3b)$$

$$\begin{aligned} BO'_{ij}{}^\sigma &= BO'_{ij}{}^\sigma \cdot f_1(\Delta'_i, \Delta'_j) \cdot f_4(\Delta'_i, BO'_{ij}) \cdot f_5(\Delta'_j, BO'_{ij}) \\ BO'_{ij}{}^\pi &= BO'_{ij}{}^\pi \cdot f_1(\Delta'_i, \Delta'_j) \cdot f_1(\Delta'_i, \Delta'_j) \cdot f_4(\Delta'_i, BO'_{ij}) \cdot f_5(\Delta'_j, BO'_{ij}) \\ BO'_{ij}{}^{\pi\pi} &= BO'_{ij}{}^{\pi\pi} \cdot f_1(\Delta'_i, \Delta'_j) \cdot f_1(\Delta'_i, \Delta'_j) \cdot f_4(\Delta'_i, BO'_{ij}) \cdot f_5(\Delta'_j, BO'_{ij}) \\ BO'_{ij} &= BO'_{ij}{}^\sigma + BO'_{ij}{}^\pi + BO'_{ij}{}^{\pi\pi} \end{aligned} \quad (4a)$$

$$f_1(\Delta'_i, \Delta'_j) = \frac{1}{2} \cdot \left(\frac{Val_i + f_2(\Delta'_i, \Delta'_j)}{Val_i + f_2(\Delta'_i, \Delta'_j) + f_3(\Delta'_i, \Delta'_j)} + \frac{Val_j + f_2(\Delta'_i, \Delta'_j)}{Val_j + f_2(\Delta'_i, \Delta'_j) + f_3(\Delta'_i, \Delta'_j)} \right) \quad (4b)$$

$$f_2(\Delta'_i, \Delta'_j) = \exp(-p_{boc1} \cdot \Delta'_i) + \exp(-p_{boc1} \cdot \Delta'_j) \quad (4c)$$

$$f_3(\Delta'_i, \Delta'_j) = -\frac{1}{p_{boc2}} \cdot \ln \left\{ \frac{1}{2} \cdot \left[\exp(-p_{boc2} \cdot \Delta'_i) + \exp(-p_{boc2} \cdot \Delta'_j) \right] \right\} \quad (4d)$$

$$f_4(\Delta'_i, BO'_{ij}) = \frac{1}{1 + \exp(-p_{boc3} \cdot (p_{boc4} \cdot BO'_{ij} \cdot BO'_{ij} - \Delta'_i{}^{boc}) + p_{boc5})} \quad (4e)$$

$$f_5(\Delta'_j, BO'_{ij}) = \frac{1}{1 + \exp(-p_{boc3} \cdot (p_{boc4} \cdot BO'_{ij} \cdot BO'_{ij} - \Delta'_j{}^{boc}) + p_{boc5})} \quad (4f)$$

A corrected overcoordination Δ_i can be derived from the corrected bond orders using equation (5).

$$\Delta_i = -Val_i + \sum_{j=1}^{neighbours(i)} BO_{ij} \quad (5)$$

Equation (6) is used to calculate the bond energies from the corrected bond orders BO_{ij} .

$$E_{bond} = -D_e^\sigma \cdot BO_{ij}^\sigma \cdot \exp\left[p_{be1} \left(1 - (BO_{ij}^\sigma)^{p_{be2}}\right)\right] - D_e^\pi \cdot BO_{ij}^\pi - D_e^{\pi\pi} \cdot BO_{ij}^{\pi\pi} \quad (6)$$

3. Lone pair energy

Equation (8) is used to determine the number of lone pairs around an atom. Δ_i^e is determined in Equation (7) and describes the difference between the total number of outer shell electrons (6 for oxygen, 4 for silicon, 1 for hydrogen) and the sum of bond orders around an atomic center.

$$\Delta_i^e = -Val_i^e + \sum_{j=1}^{neighbours(i)} BO_{ij} \quad (7)$$

$$n_{lp,i} = \text{int}\left(\frac{\Delta_i^e}{2}\right) + \exp\left[-p_{lp1} \cdot \left(2 + \Delta_i^e - 2 \cdot \text{int}\left\{\frac{\Delta_i^e}{2}\right\}\right)^2\right] \quad (8)$$

For oxygen with normal coordination (total bond order=2, $\Delta_i^e=4$), equation (8) leads to 2 lone pairs. As the total bond order associated with a particular O starts to exceed 2, equation (8) causes a lone pair to gradually break up, causing a deviation Δ_i^{lp} , defined in equation (9), from the optimal number of lone pairs $n_{lp,opt}$ (e.g. 2 for oxygen, 0 for silicon and hydrogen).

$$\Delta_i^{lp} = n_{lp,opt} - n_{lp,i} \quad (9)$$

This is accompanied by an energy penalty, as calculated by equation (10).

$$E_{lp} = \frac{p_{lp2} \cdot \Delta_i^{lp}}{1 + \exp(-75 \cdot \Delta_i^{lp})} \quad (10)$$

4. Overcoordination

For an overcoordinated atom ($\Delta_i > 0$), equations (11a-b) impose an energy penalty on the system. The degree of overcoordination Δ is decreased if the atom contains a broken-up lone electron pair. This is done by calculating a corrected overcoordination (equation 11b), taking the deviation from the optimal number of lone pairs, as calculated in equation (9), into account.

$$E_{over} = \frac{\sum_{j=1}^{nbond} p_{ovun1} \cdot D_e^\sigma \cdot BO_{ij}}{\Delta_i^{lpcorr} + Val_i} \cdot \Delta_i^{lpcorr} \cdot \left[\frac{1}{1 + \exp(p_{ovun2} \cdot \Delta_i^{lpcorr})} \right] \quad (11a)$$

$$\Delta_i^{lpcorr} = \Delta_i - \frac{\Delta_i^{lp}}{1 + p_{ovun3} \cdot \exp\left(p_{ovun4} \cdot \left\{ \sum_{j=1}^{neighbours(i)} (\Delta_j - \Delta_j^{lp}) \cdot (BO_{ij}^\pi + BO_{ij}^{\pi\pi}) \right\}\right)} \quad (11b)$$

5. Undercoordination

For an undercoordinated atom ($\Delta_i < 0$), we want to take into account the energy contribution for the resonance of the π -electron between attached under-coordinated atomic centers. This is done by equations 12 where E_{under} is only important if the bonds between under-coordinated atom i and its under-coordinated neighbors j partly have π -bond character.

$$E_{under} = -p_{ovun5} \cdot \frac{1 - \exp(p_{ovun6} \cdot \Delta_i^{lpcor})}{1 + \exp(-p_{ovun2} \cdot \Delta_i^{lpcor})} \cdot \frac{1}{1 + p_{ovun7} \cdot \exp\left[p_{ovun8} \cdot \left\{ \sum_{j=1}^{\text{neighbours}(i)} (\Delta_j - \Delta_j^{lp}) (BO_{ij}^\pi + BO_{ij}^{\pi\pi}) \right\}\right]} \quad (12)$$

6. Valence Angle Terms

6.1 Angle energy. Just as for bond terms, it is important that the energy contribution from valence angle terms goes to zero as the bond orders in the valence angle goes to zero. Equations (13a-g) are used to calculate the valence angle energy contribution. The equilibrium angle Θ_o for Θ_{ijk} depends on the sum of π -bond orders (SBO) around the central atom j as described in Equation (13d). Thus, the equilibrium angle changes from around 109.47 for sp^3 hybridization (π -bond=0) to 120 for sp^2 (π -bond=1) to 180 for sp (π -bond=2) based on the geometry of the central atom j and its neighbors. In addition to including the effects of π -bonds on the central atom j , Equation (13d) also takes into account the effects of over- and under-coordination in central atom j , as determined by equation (13e), on the equilibrium valency angle, including the influence of a lone electron pair. Val^{angle} is the valency of the atom used in the valency and torsion angle evaluation. Val^{angle} is the same as Val^{boc} used in equation (3c) for non-metals. The functional form of Equation (13f) is designed to avoid singularities when $SBO=0$ and $SBO=2$. The angles in Equations (13a)-(13g) are in radians.

$$E_{val} = f_7(BO_{ij}) \cdot f_7(BO_{jk}) \cdot f_8(\Delta_j) \cdot \left[p_{val1} - p_{val1} \exp\left[- p_{val2} (\Theta_o(BO) - \Theta_{ijk})\right] \right] \quad (13a)$$

$$f_7(BO_{ij}) = 1 - \exp(-p_{val3} \cdot BO_{ij}^{p_{val4}}) \quad (13b)$$

$$f_8(\Delta_j) = p_{val5} - (p_{val5} - 1) \cdot \frac{2 + \exp(p_{val6} \cdot \Delta_j^{angle})}{1 + \exp(p_{val6} \cdot \Delta_j^{angle}) + \exp(-p_{val7} \cdot \Delta_j^{angle})} \quad (13c)$$

$$SBO = \sum_{n=1}^{neighbors(j)} (BO_{jn}^\pi + BO_{jn}^{\pi\pi}) + \left[1 - \prod_{n=1}^{neighbours(j)} \exp(-BO_{jn}^8) \right] \cdot (-\Delta_j^{angle} - p_{val8} \cdot n_{lp,j}) \quad (13d)$$

$$\Delta_j^{angle} = -Val_j^{angle} + \sum_{n=1}^{neighbours(j)} BO_{jn} \quad (13e)$$

$$SBO2 = 0 \text{ if } SBO \leq 0$$

$$SBO2 = SBO^{p_{val9}} \text{ if } 0 < SBO < 1 \quad (13f)$$

$$SBO2 = 2 - (2 - SBO)^{p_{val9}} \text{ if } 1 < SBO < 2$$

$$SBO2 = 2 \text{ if } SBO > 2$$

$$\Theta_0(BO) = \pi - \Theta_{0,0} \cdot \{1 - \exp[-p_{val10} \cdot (2 - SBO2)]\} \quad (13g)$$

6.2 Penalty energy. To reproduce the stability of systems with two double bonds sharing an atom in a valency angle, like allene, an additional energy penalty, as described in Equations (14a) and (14b), is imposed for such systems. Equation (9b) deals with the effects of over/undercoordination in central atom j on the penalty energy.

$$E_{pen} = p_{pen1} \cdot f_9(\Delta_j) \cdot \exp[-p_{pen2} \cdot (BO_{ij} - 2)^2] \cdot \exp[-p_{pen2} \cdot (BO_{jk} - 2)^2] \quad (14a)$$

$$f_9(\Delta_j) = \frac{2 + \exp(-p_{pen3} \cdot \Delta_j)}{1 + \exp(-p_{pen3} \cdot \Delta_j) + \exp(p_{pen4} \cdot \Delta_j)} \quad (14b)$$

6.3 Three-body conjugation term. The hydrocarbon ReaxFF potential contained only a four-body conjugation term (see section 7.2), which was sufficient to describe most conjugated hydrocarbon systems. However, this term failed to describe the stability obtained from conjugation by the $-\text{NO}_2$ -group. To describe the stability of such groups a three-body conjugation term is included (equation 15).

$$E_{coa} = p_{coa1} \cdot \frac{1}{1 + \exp(p_{coa2} \cdot \Delta_j^{val})} \cdot \exp\left[-p_{coa3} \cdot \left(-BO_{ij} + \sum_{n=1}^{neighbours(i)} BO_{in}\right)^2\right] \cdot \exp\left[-p_{coa3} \cdot \left(-BO_{jk} + \sum_{n=1}^{neighbours(i)} BO_{kn}\right)^2\right] \cdot \exp\left[-p_{coa4} \cdot (BO_{ij} - 1.5)\right] \cdot \exp\left[-p_{coa4} \cdot (BO_{jk} - 1.5)\right] \quad (15)$$

7. Torsion angle terms

7.1 Torsion rotation barriers. Just as with angle terms we need to ensure that dependence of the energy of torsion angle ω_{ijkl} accounts properly for $BO \rightarrow 0$ and for BO greater than 1. This is done by Equations (16a)-(16c).

$$E_{tors} = f_{10}(BO_{ij}, BO_{jk}, BO_{kl}) \cdot \sin \Theta_{ijk} \cdot \sin \Theta_{jkl} \cdot \left[\frac{1}{2} V_1 \cdot (1 + \cos \omega_{ijkl}) + \frac{1}{2} V_2 \cdot \exp\left\{p_{tor1} \cdot (BO_{jk}^\pi - 1 + f_{11}(\Delta_j, \Delta_k))\right\} (1 - \cos 2\omega_{ijkl}) + \frac{1}{2} V_3 \cdot (1 + \cos 3\omega_{ijkl}) \right] \quad (16a)$$

$$f_{10}(BO_{ij}, BO_{jk}, BO_{kl}) = [1 - \exp(-p_{tor2} \cdot BO_{ij})] \cdot [1 - \exp(-p_{tor2} \cdot BO_{jk})] \cdot [1 - \exp(-p_{tor2} \cdot BO_{kl})] \quad (16b)$$

$$f_{11}(\Delta_j, \Delta_k) = \frac{2 + \exp[-p_{tor3} \cdot (\Delta_j^{angle} + \Delta_k^{angle})]}{1 + \exp[-p_{tor3} \cdot (\Delta_j^{angle} + \Delta_k^{angle})] + \exp[p_{tor4} \cdot (\Delta_j^{angle} + \Delta_k^{angle})]} \quad (16c)$$

7.2 Four body conjugation term. Equations (17a-b) describe the contribution of conjugation effects to the molecular energy. A maximum contribution of conjugation energy is obtained when successive bonds have bond order values of 1.5 as in benzene and other aromatics.

$$E_{conj} = f_{12}(BO_{ij}, BO_{jk}, BO_{kl}) \cdot p_{cot1} \cdot [1 + (\cos^2 \omega_{ijkl} - 1) \cdot \sin \Theta_{ijk} \cdot \sin \Theta_{jkl}] \quad (17a)$$

$$f_{12}(BO_{ij}, BO_{jk}, BO_{kl}) = \exp\left[-p_{cot2} \cdot \left(BO_{ij} - 1\frac{1}{2}\right)^2\right] \cdot \exp\left[-p_{cot2} \cdot \left(BO_{jk} - 1\frac{1}{2}\right)^2\right] \cdot \exp\left[-p_{cot2} \cdot \left(BO_{kl} - 1\frac{1}{2}\right)^2\right] \quad (17b)$$

8. Hydrogen bond interactions

Equation (18) described the bond-order dependent hydrogen bond term for a X-H—Z system as incorporated in ReaxFF.

$$E_{Hbond} = p_{hb1} \cdot [1 - \exp(p_{hb2} \cdot BO_{XH})] \cdot \exp\left[p_{hb3} \cdot \left(\frac{r_{hb}^o}{r_{HZ}} + \frac{r_{HZ}}{r_{hb}^o} - 2\right)\right] \cdot \sin^8\left(\frac{\Theta_{XHZ}}{2}\right) \quad (18)$$

9. Correction for C₂

ReaxFF erroneously predicts that two carbons in the C₂-molecule form a very strong (triple) bond, while in fact the triple bond would get de-stabilized by terminal radical electrons, and for that reason the carbon-carbon bond is not any stronger than a double bond. To capture the stability of C₂ we introduced a new partial energy contribution (E_{C2}). Equation (19) shows the potential function used to de-stabilize the C₂ molecule:

$$E_{C_2} = k_{c_2} \cdot (BO_{ij} - \Delta_i - 0.04 \cdot \Delta_i^4 - 3) \quad \text{if } BO_{ij} - \Delta_i - 0.04 \cdot \Delta_i^4 > 3$$

$$E_{C_2} = 0 \quad \text{if } BO_{ij} - \Delta_i - 0.04 \cdot \Delta_i^4 \leq 3 \quad (19)$$

where Δ_i is the level of under/overcoordination on atom i as obtained from subtracting the valency of the atom (4 for carbon) from the sum of the bond orders around that atom and k_{c_2} the force field parameter associated with this partial energy contribution.

11. Triple bond energy correction.

To describe the triple bond in carbon monoxide a triple bond stabilization energy is used, making CO both stable and inert. This energy term only affects C-O bonded pairs. Equation (20) shows the energy function used to describe the triple bond stabilization energy.

$$E_{trip} = p_{trip1} \exp[-p_{trip2} (BO_{ij} - 2.5)] \frac{\exp[-p_{trip4} \cdot (\sum_{k=1}^{neighbours(i)} BO_{ik} - BO_{ij})] + \exp[-p_{trip4} \cdot (\sum_{k=1}^{neighbours(j)} BO_{jk} - BO_{ij})]}{1 + 25 \cdot \exp[p_{trip3} (\Delta_i + \Delta_j)]}$$

12. Nonbonded interactions

In addition to valence interactions which depend on overlap, there are repulsive interactions at short interatomic distances due to Pauli principle orthogonalization and attraction energies at long distances due to dispersion. These interactions, comprised of van der Waals and Coulomb forces, are included for *all* atom pairs, thus avoiding awkward alterations in the energy description during bond dissociation.

12.1 Taper correction. To avoid energy discontinuities when charged species move in and out of the non-bonded cutoff radius ReaxFF employs a Taper correction, as developed by de Vos

Burchart (1995). Each nonbonded energy and derivative is multiplied by a Taper-term, which is taken from a distance-dependent 7th order polynomial (equation 21)).

$$Tap = Tap_7 \cdot r_{ij}^7 + Tap_6 \cdot r_{ij}^6 + Tap_5 \cdot r_{ij}^5 + Tap_4 \cdot r_{ij}^4 + Tap_3 \cdot r_{ij}^3 + Tap_2 \cdot r_{ij}^2 + Tap_1 \cdot r_{ij} + Tap_0 \quad (21)$$

The terms in this polynomial are chosen to ensure that all 1st, 2nd and 3rd derivatives of the non-bonded interactions to the distance are continuous and go to zero at the cutoff boundary. To that end, the terms Tap₀ to Tap₇ in equation (21) are calculated by the scheme in equation (22), where R_{cut} is the non-bonded cutoff radius.

$$\begin{aligned} Tap_7 &= 20/R_{cut}^7 \\ Tap_6 &= -70/R_{cut}^6 \\ Tap_5 &= 84/R_{cut}^5 \\ Tap_4 &= -35/R_{cut}^4 \\ Tap_3 &= 0 \\ Tap_2 &= 0 \\ Tap_1 &= 0 \\ Tap_0 &= 1 \end{aligned} \quad (22)$$

12.2 van der Waals interactions. To account for the van der Waals interactions we use a distance-corrected Morse-potential (Equations. 23a-b). By including a shielded interaction (Equation 23b) excessively high repulsions between bonded atoms (1-2 interactions) and atoms sharing a valence angle (1-3 interactions) are avoided.

$$E_{vdWaals} = Tap \cdot D_{ij} \cdot \left\{ \exp \left[\alpha_{ij} \cdot \left(1 - \frac{f_{13}(r_{ij})}{r_{vdW}} \right) \right] - 2 \cdot \exp \left[\frac{1}{2} \cdot \alpha_{ij} \cdot \left(1 - \frac{f_{13}(r_{ij})}{r_{vdW}} \right) \right] \right\} \quad (23a)$$

$$f_{13}(r_{ij}) = \left[r_{ij}^{P_{vdW1}} + \left(\frac{1}{\gamma_w} \right)^{P_{vdW1}} \right]^{\frac{1}{P_{vdW1}}} \quad (23b)$$

12.3 Coulomb Interactions

As with the van der Waals-interactions, Coulomb interactions are taken into account between *all* atom pairs. To adjust for orbital overlap between atoms at close distances a shielded Coulomb-potential is used (Equation 24).

$$E_{coulomb} = Tap \cdot C \cdot \frac{q_i \cdot q_j}{\left[r_{ij}^3 + (1/\gamma_{ij})^3 \right]^{1/3}} \quad (24)$$

Atomic charges are calculated using the Electron Equilibration Method (EEM)-approach. The EEM charge derivation method is similar to the QEq-scheme; the only differences, apart from parameter definitions, are that EEM does not use an iterative scheme for hydrogen charges (as in QEq) and that QEq uses a more rigorous Slater orbital approach to account for charge overlap.