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ABSTRACT

In recent work, we have presented a new ReaxFF formulation with a superior conservation of energy in reactive molecular dynamics simulations. The key ingredient in the approach involved the tapering of bond order and bond distance discontinuities using Hermite polynomials. This Communication extends the previous formulation by alleviating additional sources of numerical instability in the original formalism. These "numerical pathologies" are rooted in the counting of lone-pair electrons, the sum of bond orders between atoms that form a valence angle, and the definition of a torsional potential. Based on a theoretical analysis, new functions that mitigate these limitations are designed and validated. The extent of their transferability with previous parameterizations is discussed. The new enhancements provide further gains in numerical stability to facilitate exploration of reactive energy landscapes.

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Recently, we have devised the *Tapered ReaxFF*[1] formulation, which effectively eliminates energy and force discontinuities in the original ReaxFF formalism.[2] The key ingredient of the approach is the use of Hermite polynomials as smooth tapering functions to interpolate between bonding and non-bonding atomic environments. Besides orders of magnitude increases in energy conservation and numerical stability, the new formulation remains compatible with the original and allows previous force field parameters to be used without adjustment.

Nevertheless, several significant problems that originate from the ReaxFF formalism require further attention. To describe reactive intermediates and transition states, without restricting the number or type of reactions,[3] ReaxFF uses a set of rather complex mathematical functions, which are parameterized against reference quantum chemical databases.[2,4,5] When properly parameterized, ReaxFF allows the study of reactive complex systems.[6–8] The range of attractive bonding interactions is strongly influenced by the coordination of the respective atoms. For fully coordinated atoms, these interactions decay quickly with bond distance, while under-coordinated, radical atoms have more delocalized valence electrons, resulting in a much longer attractive range.[9] Thus, unlike the case of non-reactive force fields, theoretical abstractions, such as lone-pair electrons, over- and under-coordination, are among the required characteristic ingredients. Lone pairs of electrons are used to reproduce the correct geometries and stabilities of molecules, such as H_2O, NH_3, and SO_2.

The number of lone pairs in an atom, $n_{\mathrm{lp},i}$, depends on the difference, Δ_i^e, between the number of valence shell electrons, Val_i^e, and the sum of bond orders (SBO) between the atom and its neighbors according to

$$\Delta_i^e = -\mathrm{Val}_i^e + \sum_{j=1}^{N_i} \mathrm{BO}_{ij}, \tag{1a}$$

$$n_{\mathrm{lp},i} = -\mathrm{int}\left(\frac{\Delta_i^e}{2}\right) + \exp\left[-p_{\mathrm{lp1}} \times \left(2 + \frac{\Delta_i^e}{2} - 2 \times \mathrm{int}\left(\frac{\Delta_i^e}{2}\right)\right)^2\right], \tag{1b}$$

where int(x) is a function that converts a floating point argument to the nearest integer (from below) given that $|x| \geq 1$; otherwise, it evaluates to zero, and p_{lp1} is a general parameter. As the total bond order for an atom starts to exceed its valence, Eq. (1a) causes a lone pair to

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gradually break up, causing a deviation, Δ_i^{lp}, from a predefined optimal number of lone pairs, $n_{\mathrm{lp,opt}}$, with an associated energy change, $E_{\mathrm{lp},i}$, according to

$$\Delta_i^{\mathrm{lp}} = n_{\mathrm{lp,opt}} - n_{\mathrm{lp},i}, \tag{2a}$$

$$E_{\mathrm{lp},i} = \frac{p_{\mathrm{lp2}} \times \Delta_i^{\mathrm{lp}}}{1 + \exp\left(-75 \times \Delta_i^{\mathrm{lp}}\right)}. \tag{2b}$$

At this stage, it is helpful to examine the functional form of Eq. (1b) more closely. The first term on the RHS effectively discretizes the number of lone pairs with a step size of $2e$ compared to the continuous form of Eq. (1a). The second term is responsible for "stitching" the sudden discontinuity that appears when lone pairs are broken. However, as shown in Fig. 1(a), the exponential part has no effect for the reverse pathway, namely, when an atom with many bonded neighbors "restores" its lone pairs as a result of a diminishing number of bonding interactions. Thus, the number of lone pairs becomes a discontinuous function for the positive side of the Δ_i^e axis. As a result, the associated energy in Fig. 1(b) becomes non-differentiable, and the corresponding force is undefined. In fact, close inspection reveals that for every whole number, $x_0 \neq 0$, the derivative of int(x) at x_0 is undefined. As a result of these numerical pathologies in Eq. (1b), additional potential energy terms that have a functional dependence on $n_{\mathrm{lp,i}}$, other than the lone-pair energy, become undefined. These are the under- and over-coordination and valence angle energies.[4]

To circumvent the associated difficulties of integer functions, we should acknowledge that the difference $x - \lfloor x \rfloor$ is an increasing periodic function. As such, well-established methods of Fourier analysis can be exploited to approximate it *smoothly*.[10] A function that allows us to smoothly approximate the correct *steplike* behavior expected for discrete electron pairs and has a single fitting parameter, λ, is defined as follows:

$$f_L(\Delta_i^e) = \Delta_i^e - \frac{1}{2} - \frac{1}{\pi}\tan^{-1}\left[\frac{\lambda \sin\left(2\pi\Delta_i^e\right)}{\lambda\cos\left(2\pi\Delta_i^e\right) - 1}\right], \tag{3a}$$

$$f_R(\Delta_i^e) = \Delta_i^e + \frac{1}{2} - \frac{1}{\pi}\tan^{-1}\left[\frac{\lambda \sin\left(-2\pi\Delta_i^e\right)}{\lambda\cos\left(2\pi\Delta_i^e\right) - 1}\right], \tag{3b}$$

$$n_{\mathrm{lp},i} = \begin{cases} f_L(\Delta_i^e) & \text{if } \Delta_i^e < l_1 \\ f_L(\Delta_i^e) \times \mathrm{Tap}^{7\mathrm{th}}(\Delta_i^e) & \text{if } l_1 \le \Delta_i^e < l_2 \\ 0 & \text{if } l_2 \le \Delta_i^e < r_1 \\ f_R(\Delta_i^e) \times \mathrm{Tap}^{7\mathrm{th}}(\Delta_i^e) & \text{if } r_1 \le \Delta_i^e \le r_2 \\ f_R & \text{if } \Delta_i^e > r_2, \end{cases} \tag{3c}$$

where $\mathrm{Tap}^{7\mathrm{th}}(\Delta_i^e)$ is a seventh degree tapering Hermite polynomial, as defined elsewhere,[1] without loss of generality $l_1 < l_2$ and $r_1 < r_2$. The functions in Eqs. (3a) and (3b) are symmetric with respect to the origin, decrease for every $0 < \lambda < 1$, and converge uniformly to $x - \lfloor x \rfloor$ on any closed interval not containing an integer. The tapering function guarantees that both $f_L(\Delta_i^e)$ and $f_R(\Delta_i^e)$ approach zero near $\Delta_i^e = \pm 2.0$, where the lone-pair energy should vanish. Thus, we see in Fig. 1 that the new functions are both continuous and smooth and can closely reproduce the expected behavior. At this point, two remarks are worth mentioning. First, apart from

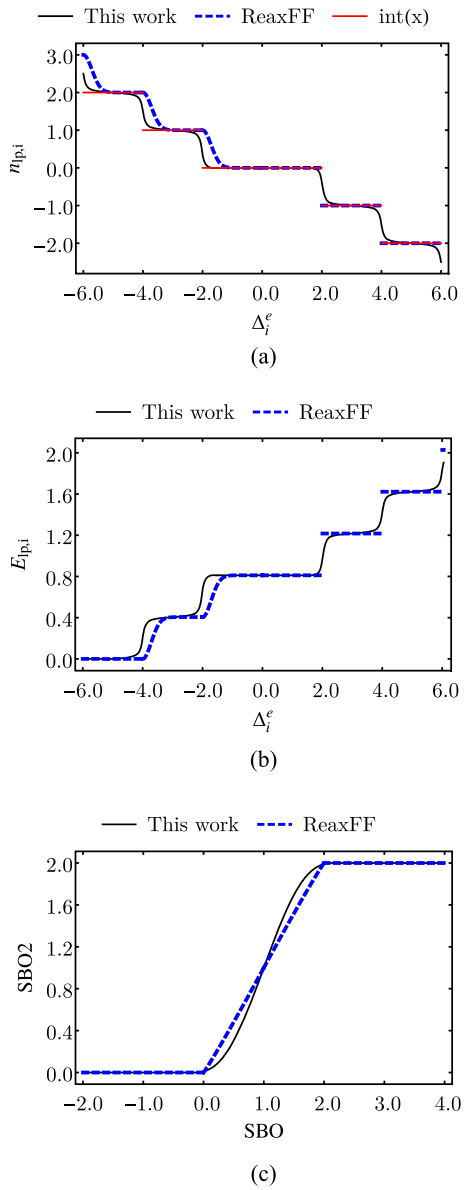


FIG. 1. (a) The number of lone pairs and (b) the associated potential energy as a function of the difference between the number of valence electrons and sum of bond orders as defined by ReaxFF [Eq. (1)] with fitting parameter values taken from a published force field[11] for the atomic parameters of oxygen and as developed in this work [Eq. (3)] with λ = 0.8, l_1 = −2.3, l_2 = −1.5, r_1 = 1.5, and r_2 = 2.3. (c) Dependence of the SBO2 clipping function on the sum of bond orders (SBO) as defined in ReaxFF [Eq. (4)] and as developed in this work [Eq. (5)] with x_l = −0.2 and x_r = 2.2.

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the lone-pair energy term, the under- and over-coordination energy terms also become smooth functions of Δ_i^e due to their dependence on $n_{\mathrm{lp},i}$.[4] Second, the preceding pathologies are system specific and may not manifest in every system or under all conditions. Clearly, systems in which a large proportion of atoms are characterized by $\Delta_i^e > 0$ are particularly susceptible. While the new definition of the number of lone electron pairs successfully eliminates the discontinuities associated with discrete electron pairs, other existing issues also require attention.

Accordingly, we turn our focus to the valence and torsion angle potentials. Equations (4a)–(4e) are used to calculate the potential energy associated with a valence angle, Θ_{ijk},

$$E_{\mathrm{val}} \propto 1 - \exp\left[-p_{\mathrm{val2}} \times \left(\Theta_0(\mathrm{BO}) - \Theta_{ijk}\right)^2\right], \tag{4a}$$

$$\mathrm{SBO} = \sum_{n=1}^{N_j}\left(\mathrm{BO}_{jn}^{\pi} + \mathrm{BO}_{jn}^{\pi\pi}\right) + \left[1 - \prod_{n=1}^{N_j}\exp\left(-\mathrm{BO}_{jn}^{8}\right)\right] \times \left(-\Delta_j^{\mathrm{angle}} - p_{\mathrm{val8}} \times n_{\mathrm{lp},j}\right), \tag{4b}$$

$$\Delta_j^{\mathrm{angle}} = -\mathrm{Val}_j^{\mathrm{angle}} + \sum_{n=1}^{N_j}\mathrm{BO}_{jn}, \tag{4c}$$

$$\mathrm{SBO2} = \begin{cases} 0 & \text{if SBO} \le 0 \\ \mathrm{SBO}^{\mathrm{pval}_9} & \text{if } 0 < \mathrm{SBO} < 1 \\ 2 - (2 - \mathrm{SBO})^{\mathrm{pval}_9} & \text{if } 1 \le \mathrm{SBO} < 2 \\ 2 & \text{if SBO} \ge 2, \end{cases} \tag{4d}$$

$$\Theta_0(\mathrm{BO}) = \pi - \Theta_{0,0} \times \left[1 - \exp\left[-p_{\mathrm{val10}} \times (2 - SBO2)\right]\right], \tag{4e}$$

where we have omitted the multiplicative bond order dependent terms from Eq. (4a) for brevity. These terms are mainly used to ensure that the valence angle energy goes smoothly to zero when any of the two associated bonds dissociates and are irrelevant for the current analysis. p_{val2} is a fitting parameter, Θ_0 is an equilibrium valence angle that depends on the bond order, and Θ_{ijk} is the valence angle. The equilibrium angle Θ_0 for Θ_{ijk} depends on the sum of π bond orders (SBO) around the central atom j, as described in Eq. (4c). In addition to including the effects of π bonds on the central atom j, Eq. (4b) also takes into account the effects of over- and under-coordination for j, as determined by Eq. (4c), on the equilibrium valence angle, including the influence of a lone pair. Both SBO and SBO2 are intermediate calculations for Θ_0. SBO is the sum of neighboring bonds to central atom j, whereas SBO2 is a clipped version of SBO, which ensures that the sum of bond orders is less than two (each angle has only two bonds). Thanks to the fitting parameter, p_{val9}, the exponential form can be tuned with a high sensitivity.

A careful inspection of Eq. (4d) reveals that although the clipping occurs in a continuous fashion and avoids singularities when SBO = 0 or SBO = 2, the derivative at these points is ill-defined due to cusp discontinuities at the corners [Fig. 1(c)]. Fortunately, it is straightforward to design a similar function without these problems. In this case, we choose to use a fifth degree tapering Hermite polynomial [Eqs. (5a)–(5c)] due to its steepness compared to higher degree polynomials and because it offers continuous second and third derivatives for increased numerical stability.[1] As seen from Fig. 1(c), the new function closely follows the intended behavior with a smooth attenuation on both sides,

$$\mathrm{SBO2} = \begin{cases} 0 & \text{if SBO} \le 0 \\ 2 \times \mathrm{Tap}^{5th}(\mathrm{SBO}) & \text{if } 0 < \mathrm{SBO} < 2 \\ 2 & \text{if SBO} \ge 2, \end{cases} \tag{5a}$$

$$Tap^{5th}(x) = \frac{s_5 \times x^5 + s_4 \times x^4 + s_3 \times x^3 + s_2 \times x^2 + s_1 \times x^1 + s_0}{(x_r - x_l)^5}, \tag{5b}$$

$$\begin{aligned} s_0 &= 10x_r^2x_l^3 - 5x_rx_l^4 + x_l^5, & s_1 &= -30x_r^2x_l^2, \\ s_2 &= 30\left(x_r^2x_l + x_rx_l^2\right), & s_3 &= -10\left(x_r^2 + 4x_rx_l + x_l^2\right), \\ s_4 &= 15(x_r + x_l), & s_5 &= -6. \end{aligned} \tag{5c}$$

At this stage, we shift our attention to a numerical pathology that prevails in the torsional potential in the ReaxFF force field. For any consecutive set of four atoms within bonding distance, a torsion angle, ω_{ijkl}, may be defined. Using the law of cosines for torsion angles,[12] it may be expressed in the form shown in Eq. (6a). When three atoms in a bending sequence move into a linear configuration, any torsion angle involving those atoms becomes undefined and its Cartesian derivatives become singular. This situation is most likely to occur during and after bond-breaking processes, leading to pathological errors.[13] The torsion potential energy has the well-known three-term Fourier expansion representation[14] [Eq. (6b)].

Similar to the valence angle energy, the potential energy associated with a torsion angle should decay to zero whenever one of its constituent bonds breaks apart. Since our primary concern is the angular dependence and for the sake of brevity, we have omitted the bond-order related terms in Eq. (6b). The relevant terms involve the bending potential (i.e., sine product of the two valence angles) and the bending-uncoupled torsion potential. The terms V_1, V_2 and V_3 are energy barriers, and $g(\mathrm{BO}_{jk}^{\pi}, \Delta_j, \Delta_k)$ is specifically designed to avoid excessive torsion contributions in systems containing two attached over-coordinated sp^3 atoms,[15]

$$\cos\omega_{ijkl} = \frac{r_{ij}^2 + d_{jl}^2 - 2r_{ij}d_{jl}\cos\Theta_{ijk}\cos\Theta_{jkl} - d_{il}^2}{2r_{ij}d_{jl}\sin\Theta_{ijk}\sin\Theta_{jkl}}, \tag{6a}$$

$$\begin{aligned} E_{\mathrm{tors}} \propto \sin\Theta_{ijk} \times \sin\Theta_{jkl} \times \big[&V_1 \times \left(1 + \cos\omega_{ijkl}\right) \\ &+ V_2 \times g(\mathrm{BO}_{jk}^{\pi}, \Delta_j, \Delta_k) \times \left(1 - \cos 2\omega_{ijkl}\right) \\ &+ V_3 \times \left(1 + \cos 3\omega_{ijkl}\right)\big]. \end{aligned} \tag{6b}$$

Two points are particularly noteworthy: (a) for the evaluation of the derivatives of the torsion potential, the actual form that is being used for each of the multiple-angle cosine terms is the equivalent polynomial in $\cos\omega_{ijkl}$ to avoid the known $1/\sin\omega_{ijkl}$ singularity,[16,17] and (b) it is evident from Eq. (6a) that $\cos\omega_{ijkl}$ tends to infinity whenever any of the bending angles approaches 0° or

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180°. Unlike the previous case, the source of the latter singularity has a clear geometrical basis, which cannot be overcome by a change of representation. Accordingly, the coupling between bending and torsion degrees of freedom is necessary to ensure that the torsion energy contribution disappears whenever colinearity occurs. To ensure numerical stability, the product of sines has to be raised to the third power to exactly cancel the term that appears during evaluation of the Cartesian derivative $\partial\cos_{\omega_{ijkl}}/\partial q_i$. As well as providing superior numerical stability, the third-power form has a clear physical origin.[18,19] Figure 2(b) compares between the third-power form as suggested in this work, the original ReaxFF form, and the bending-uncoupled, pathological case of the torsion potential. The new form decays faster than the original sine product, but otherwise remains very similar to the original torsion potential.

From the viewpoint of mathematical and numerical rigor, it is clear that a successful and robust application of the ReaxFF reactive force field requires the use of differentiable energies and forces, as developed in this work. However, from a practical point of view, one question remains: *Can we use parameterizations based on the old ill-behaved functions with the new formalism?*

Judging from Fig. 3, which compares the performance of tapered ReaxFF[1] with and without the newly designed functions, the answer seems to be very encouraging. Overall, a surprisingly good match is observed compared to quantum mechanical (QM) energies for an extensive set of chemical reactions. However, some deviations in the bottom left part of Fig. 3 are noticeable. A careful inspection of the training set reveals that these differences can be attributed to a small subset of reactions that were given an insignificant weight during training. Hence, they are expected to be very susceptible to small changes in the functional forms or in the numerical values of parameters. This sensitivity can be further diagnosed by the observation that neither reference formulation reproduces these systems well enough compared to the QM values. In any case, these less satisfactory systems can be refined with additional force field training.[5]

As mentioned before, the accurate computation of forces is very important for tasks such as geometry optimization, locating transition states, constructing reaction pathways, and performing vibrational analysis. However, the consequences of numerical imprecisions may not be so obvious in MD simulations, even though the effects are present. Considering that ReaxFF is heavily used for MD simulations, we wish to highlight the main implications of our work in this context.

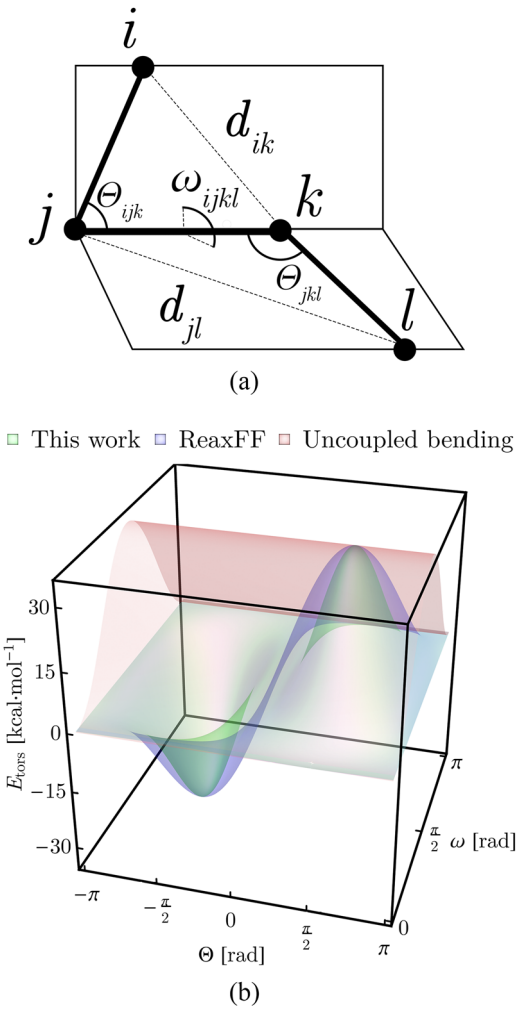


FIG. 2. (a) Schematic definition of a torsion angle used in ReaxFF. The bold lines represent chemical bonds, while dashed lines are auxiliary lines. (b) Torsion angle energy as a function of the bending angle, θ, and torsion angle, ω, as defined in this work (green) and in ReaxFF with and without a coupled-bending term (blue and red, respectively). The values for the rotational barriers were taken from a published force field[11] and are related to the all-carbon torsion angle.

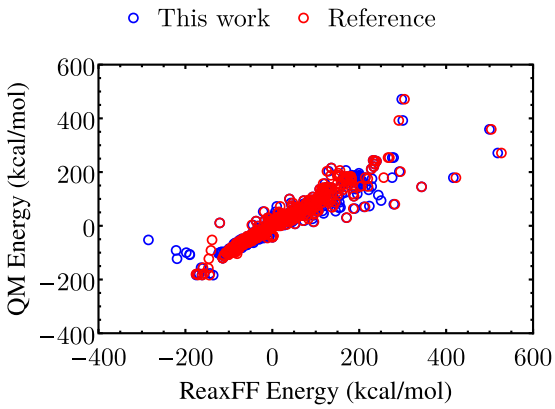


FIG. 3. Comparison between the reference Tapered ReaxFF formulation[1] (red circles) and the same formulation with improved functional forms for lone pairs, valence, and torsion interactions as developed in this work (blue circles). The data belong to the energy section from an extensive training set of hydrocarbons and combustion products with over 1500 equilibrated species containing reactants, transition states, and intermediates.[4]

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TABLE I. Lowest RMSG (kcal mol^{-1} Å^{-1}), total energy conservation (%), and total energy drift rate (kcal mol^{-1} ps^{-1}) for a test system using the reference tapered ReaxFF formulation with the old and new functional forms.

Tapered ReaxFF	*trans*-1,2-dicyanoethylene	
Functional form	old	new
Lowest RMSG	1.49×10^{-1}	7.30×10^{-7}
Energy conservation	1.16	0.00
Energy drift rate	2.48	0.00

We note that the condition $\Delta_i^e > 0$ [Eq. (1a)] is somewhat unphysical, but nevertheless possible during a ReaxFF simulation as a "rare event." Since the bond order is a function of bond distance, under extreme conditions (e.g., hypervelocity impacts[20]), atoms can make very short-lived, close encounters with an artificially amplified bond order (especially with insufficient bond order corrections). In such instances, $\sum_{j=1}^{N_i} \mathrm{BO}_{ij}$ becomes larger than Val_i^e. These conditions pertain to highly unlikely situations during standard simulations and are usually not a concern for the MD practitioner. However, in the case of valence and torsion angle pathologies, the situation is markedly different: it is common for linear triples of atoms to be part of a torsion angle, especially when chemical reactions are involved. In this case, even relatively "tolerant" methods could break.

Thus, to test this supposition, we have performed a series of MD simulations with and without the new functional forms. The system consisted of ten *trans*-1,2-dicyanoethylene molecules, each with two linear (CC≡N) moieties. The simulation protocol used an available parameterisation[21] and was identical to the one employed in our previous study.[1] Table I reports the lowest root-mean-squared gradient (RMSG) obtained during an initial geometry optimization and the conservation of total energy and drift rate during a 50 ps simulation at constant number of atoms, volume, and energy (NVE).

With the old functional forms, the system fails to converge to a local minimum (for which we require an RMSG below 10^{-6} kcal mol^{-1} Å^{-1}; see Table I). In addition, we noticed that during the thermalization stage (at 300 K), four molecules underwent a dimerization reaction to form two $C_8H_4N_4$ covalent dimers. Similar behavior also occurred in our previous study, where an insufficient structural optimization had caused the system to cross a dissociation barrier.[1] Regarding the NVE stage, the violation of total energy conservation and the rate of energy drift are quite substantial for the old functional forms, while the new forms exhibit no significant deviations and no artificial side-reactions.

In summary, we have presented an improved theoretical framework for ReaxFF, which avoids significant numerical pathologies, is fully differentiable, and is numerically stable for any type of system. The new framework should be particularly useful for applications that rely heavily on accurate energies and gradients, such as the computational energy landscape methodology.[22–25]

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES

[1] D. Furman and D. J. Wales, "Transforming the accuracy and numerical stability of ReaxFF reactive force fields," J. Phys. Chem. Lett. **10**, 7215–7223 (2019).
[2] T. P. Senftle, S. Hong, M. M. Islam, S. B. Kylasa, Y. Zheng, Y. K. Shin, C. Junkermeier, R. Engel-Herbert, M. J. Janik, H. M. Aktulga *et al.*, "The ReaxFF reactive force-field: Development, applications and future directions," npj Comput. Mater. **2**, 15011 (2016).
[3] B. Hartke and S. Grimme, "Reactive force fields made simple," Phys. Chem. Chem. Phys. **17**, 16715–16718 (2015).
[4] K. Chenoweth, A. C. T. van Duin, and W. A. Goddard, "ReaxFF reactive force field for molecular dynamics simulations of hydrocarbon oxidation," J. Phys. Chem. A **112**, 1040–1053 (2008).
[5] D. Furman, B. Carmeli, Y. Zeiri, and R. Kosloff, "Enhanced particle swarm optimization algorithm: Efficient training of ReaxFF reactive force fields," J. Chem. Theory Comput. **14**, 3100–3112 (2018).
[6] D. Furman, R. Kosloff, F. Dubnikova, S. V. Zybin, W. A. Goddard, N. Rom, B. Hirshberg, and Y. Zeiri, "Decomposition of condensed phase energetic materials: Interplay between uni- and bimolecular mechanisms," J. Am. Chem. Soc. **136**, 4192–4200 (2014).
[7] N.-H. Kalson, D. Furman, and Y. Zeiri, "Cavitation-induced synthesis of biogenic molecules on primordial earth," ACS Cent. Sci. **3**, 1041–1049 (2017).
[8] Y. Elbaz, D. Furman, and M. Caspary Toroker, "Modeling diffusion in functional materials: From density functional theory to artificial intelligence," Adv. Funct. Mater. **30**, 1900778 (2019).
[9] A. van Duin, "Reactive force fields: Concepts of ReaxFF," in *Computational Methods in Catalysis and Materials Science* (John Wiley & Sons, Ltd., 2009), Chap. 9, pp. 167–181.
[10] G. Arfken, m. Hans-Jürgen Weber, H. Weber, and F. Harris, *Mathematical Methods for Physicists* (Elsevier, 2005).
[11] Y. K. Shin, H. Kwak, A. V. Vasenkov, D. Sengupta, and A. C. van Duin, "Development of a ReaxFF reactive force field for Fe/Cr/O/S and application to oxidation of butane over a pyrite-covered Cr_2O_3 catalyst," ACS Catal. **5**, 7226–7236 (2015).
[12] L. Liberti, C. Lavor, and N. Maculan, "A branch-and-prune algorithm for the molecular distance geometry problem," Int. Trans. Oper. Res. **15**, 1–17 (2008).
[13] R. E. Tuzun, D. W. Noid, and B. G. Sumpter, "Molecular dynamics treatment of torsional interactions accompanied by dissociation," Macromol. Theory Simul. **4**, 909–920 (1995).
[14] A. R. Leach and A. R. Leach, *Molecular Modelling: Principles and Applications* (Pearson education, 2001).
[15] A. C. T. van Duin, S. Dasgupta, F. Lorant, and W. A. Goddard, "ReaxFF: A reactive force field for hydrocarbons," J. Phys. Chem. A **105**, 9396–9409 (2001).
[16] A. Blondel and M. Karplus, "New formulation for derivatives of torsion angles and improper torsion angles in molecular mechanics: Elimination of singularities," J. Comput. Chem. **17**, 1132–1141 (1996).
[17] K. J. Miller, R. J. Hinde, and J. Anderson, "First and second derivative matrix elements for the stretching, bending, and torsional energy," J. Comput. Chem. **10**, 63–76 (1989).
[18] R. A. Scott and H. A. Scheraga, "Conformational analysis of macromolecules. II. The rotational isomeric states of the normal hydrocarbons," J. Chem. Phys. **44**, 3054–3069 (1966).
[19] L. Pauling, *The Nature of the Chemical Bond and the Structure of Molecules and Crystals: An Introduction to Modern Structural Chemistry* (Cornell University Press, 1960).

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[20]A. Jaramillo-Botero, Q. An, P. L. Theofanis, and W. A. Goddard, "Large-scale molecular simulations of hypervelocity impact of materials," in *Proceedings of the 12th Hypervelocity Impact Symposium* [Procedia Eng. **58**, 167–176 (2013)].
[21]L. Zhang, A. C. T. v. Duin, S. V. Zybin, and W. A. Goddard III, "Thermal decomposition of hydrazines from reactive dynamics using the ReaxFF reactive force field," J. Phys. Chem. B **113**, 10770–10778 (2009).
[22]D. J. Wales, "Exploring energy landscapes," Annu. Rev. Phys. Chem. **69**, 401–425 (2018).
[23]D. Wales *et al.*, *Energy Landscapes: Applications to Clusters, Biomolecules and Glasses* (Cambridge University Press, 2003).
[24]D. J. Wales, "A microscopic basis for the global appearance of energy landscapes," Science **293**, 2067–2070 (2001).
[25]S. T. Chill, J. Stevenson, V. Ruehle, C. Shang, P. Xiao, J. D. Farrell, D. J. Wales, and G. Henkelman, "Benchmarks for characterization of minima, transition states, and pathways in atomic, molecular, and condensed matter systems," J. Chem. Theory Comput. **10**, 5476–5482 (2014).

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