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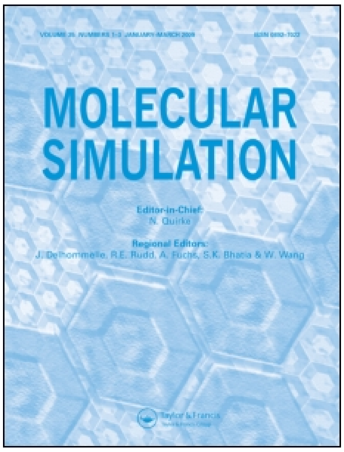

Molecular Simulation

Publication details, including instructions for authors and subscription information:
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Gradient fit functions for two-body potential energy surfaces based upon a harmonic series

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First published on: 30 November 2009

To cite this Article Wander, Matthew C. F. and Clark, Aurora E.(2010) 'Gradient fit functions for two-body potential energy surfaces based upon a harmonic series', Molecular Simulation, 36: 5, 335 — 340, First published on: 30 November 2009 (iFirst)

To link to this Article: DOI: 10.1080/08927020903433739

URL: http://dx.doi.org/10.1080/08927020903433739

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Molecular Simulation
Vol. 36, No. 5, April 2010, 335–340

Gradient fit functions for two-body potential energy surfaces based upon a harmonic series

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(*Received 17 September 2009; final version received 22 October 2009*)

While force-field development has been discussed extensively in the literature, the question of what analytical expressions make the best function choices, particularly in the context of matching quantum mechanic potential energy surfaces (PES), is less explored. Traditional forms based upon harmonic oscillators and Lennard-Jones types have dominated the field owing to the focus on fitting properties. However, with the advent of gradient-fitting approaches, it is now possible with the correct force-field expressions to achieve consistent high-accuracy results with molecular dynamics calculations. Using the general principle that power series can fit surfaces of any shape well, we have utilised harmonic series functions to fit a two-body PES represented by a Morse function. The harmonic functions are fast because they have only integer exponents, and they fit accurately with a limited number of terms.

Keywords: potential energy surface; force field; Morse potential; two-body

1. Introduction

In a molecular dynamics (MD) simulation, the force field (or potential) acts as a representation of the true quantum mechanical potential energy surface (PES) that governs the motions of the nuclei and determines all characteristics of the system. A force-field expression is developed by partitioning the energy according to component decomposition [1,2], wherein a proxy solution for the molecular Hamiltonian is written as

$$\hat{H}\Psi_{\text{elec}} + \hat{T}\Psi_{\text{nuc}} + \hat{V}\Psi_{\text{nuc}} = E_{\text{elec}}\Psi_{\text{elec}} + E_{\text{kinetic}}\Psi_{\text{nuc}} + E_{\text{potential}}\Psi_{\text{nuc}}, \qquad (1)$$

and the force-field expression is set up in parallel form

$$E_{\text{total}} = E_{\text{electrostatic}} + E_{\text{bonds}} + E_{\text{angle}} + E_{\text{dihedral}} + E_{\text{improper}} + E_{\text{vdw}}, \qquad (2)$$

where vdw means van der Waals forces, or all intermolecular forces, which are not accounted for by electrostatics. It is also common that the terms in the force field are derived from body decomposition, wherein the different contributions to energy in Equation (2) are written as *n*-body terms. These functions are then further decomposed into other types of chemical energy: electrostatic, exchange, etc. as in [3]. Component decomposition can use body decomposition to split a force field into *n*-body terms that are chemically intuitive descriptions of the chemical energy of a molecule. Here, the one-body term gets adsorbed into the zero of energy, while the two-body terms include bonds, electrostatics and van der Waals/intermolecular terms. The three-body terms are angles, and the four-body terms are dihedrals and out-of-plane (improper) bends, etc.

Historically, much effort has been devoted to creating new analytical expressions to represent the two-body PES from spectroscopic data (e.g. the Ogilvie–Tipping anharmonic oscillator [4,5], the generalised and modified Morse oscillators [6–15] and the modified Lennard-Jones oscillator [16,17]). However, in practical MD applications, only a limited set of force fields is typically used (*vide infra*). The choice of the expression is often based upon which region of the two-body PES is considered important in the MD simulation: the harmonic (quadratic) region and/or the tail region (which exhibits an $\sim 10^{-6}$ rate of decay). Bonding and intermolecular forces are divided into separate functions based on the perceived importance of the quadratic region to bonding and the tail region to intermolecular forces. Among the traditional forms, the Morse potential [18] can be used to represent both bonding and intermolecular potentials,

$$E_{\text{Morse}} = D_{\text{e}}(1 - \text{e}^{-\alpha(r-r_0)})^2, \quad \text{where } \alpha = \sqrt{\frac{k}{2D_{\text{e}}}}. \qquad (3)$$

The Morse function has three independent parameters, which represent well depth, bond distance and well basin curvature. The classic Lennard-Jones 12-6 (LJ 12-6) potential [19]

$$E_{\text{LJ}} = 4\varepsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right) \qquad (4)$$

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ISSN 0892-7022 print/ISSN 1029-0435 online

DOI: 10.1080/08927020903433739
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is also often used to describe intermolecular interactions, where σ is the shortest distance at which that energy is zero (the hard-sphere radius) and ε corresponds to the dissociation energy. Other two-body intermolecular functions share a constant feature of the r^{-6} term, but can vary in the representation of the inside slope of the PES, and numerous variations of the r^{-n} formulation exist with $n = 8$, 9, 10, 12 and exponential forms (see, for example, [20,21] and numerous other examples). Importantly, within all of the 12-6 variants, the second derivative of the bottom of the well depends on the well depth (ε). In general, the Morse potential (and its variants) is considered to yield the most accurate fits to the two-body PES for homonuclear diatomics calculated by the highest level *ab initio* methods (see, for example, [22,23]); however, because it is slower to evaluate than other traditional functions, such as the LJ 12-6 potential, it is rarely used.

The commonly used semi-empirical approach to fitting a force field takes empirical data from a class of standard molecules, and uses a mixture of least-squares minimisation and combination rules to create a set of parameters optimised to the data-set [24–26]. When using these semi-empirical potentials, the physical properties obtained from simulation will have varying accuracy and those properties used in the fit will often have minimal error relative to experiment [27,28]. Yet, in principle, the PES can be reproduced using first-principles *ab initio* methods, enabling direct fits of the potential's parameters to a calculated PES by numerically matching the gradients (or energy) [29,30]. This idea has been pursued for a number of years and has grown in popularity given advances in computational capabilities and algorithmic development in highly parallelised *ab initio* methods. Given a potential with a sufficiently large number of parameters, a precise fit to the gradient of a highly accurate *ab initio* PES will yield physical observables from the MD simulation that are equally 'accurate'. What constitutes a 'highly accurate *ab initio* PES' varies from system to system, but will often necessitate the use of highly correlated methods such as coupled cluster with single, double and triple excitations [31].

In this work, we examine which mathematical expressions exhibit the highest accuracy in fitting all of the chemically important regions of the two-body PES within the gradient-fitting paradigm. Accuracy is first discussed, followed by an examination of the important pieces of chemical information in the PES. Finally, the limitations of traditional forms are assessed and alternatives are suggested which are capable of fitting the PES within a specified accuracy range (defined by the numerical integral over the difference between the curves divided by the numerical integral over the Morse function). The proposed functions are based on the hypothesis that the most accurate forms are composed of power series. This allows the accuracy of the higher body terms to be increased proportionally, using a Morse potential as the proxy for the *ab initio* PES.

2. Methodology

Obtaining an 'accurate *ab initio* PES' is beyond the scope of this work and, as such, we rely on the known accuracy of the Morse potential as a proxy for an ideal two-body PES (e.g. homonuclear diatomics; see, for example, [22,23]). Use of the Morse potential avoids issues associated with the accuracy of *ab initio* data, particularly at the intermediate/tail region which can be problematic if one is using a single determinant method such as Hartree–Fock and even some highly correlated methods [32]. A least-squared fit to the gradient of the Morse PES from 0.5 to 12.0 Å was used with Microsoft Excel's solver add-in (see the Supplementary Data). The Morse potential was gridded to allow for a numerical fit. In the quadratic region of the curve, points were spaced every 0.01 Å, in the quasi-harmonic region, points were spaced every 0.05 Å and, in the tail region, points were spaced every 0.1 Å. The grid spacing was chosen so as to emphasise the importance of these regions; however, a uniform grid over all three regions did not make a difference, within a few per cent, in the overall quality of the fits (see the Supplementary Data). An iterative procedure was used so as to create the best initial guess possible for the fit.

Three conditional qualities of force-field functions are discussed when fitting the Morse potential: accuracy, speed and the presence of chemically meaningful parameters. In matching to the PES, both 10 and 1% accuracy are considered; however, the quality of the fit will depend somewhat on the initial guess and the span of the data included. This allows a certain flexibility of approach, as the ideal two-body function is one that easily scales between these two accuracy regimes. For computational speed, only those function types that require combinations of addition, multiplication and division are considered, as they are substantially faster to evaluate than logarithms, exponentials and fractional powers. Short classical MD simulations with DL_POLY were performed to time the speed of certain functions relative to the Morse potential [33]. The simulation consisted of 125 Xe atoms in a cube with each dimension being 17.36 Å, run for an NVE simulation of 100,000 ps time steps. The Morse force-field parameters for this simulation were taken from experimental data [34].

3. Results and discussion

This work is limited to the fitting of a two-body PES, without comment on the nature of the chemical attraction between the two bodies. As shown in Figure 1, there are

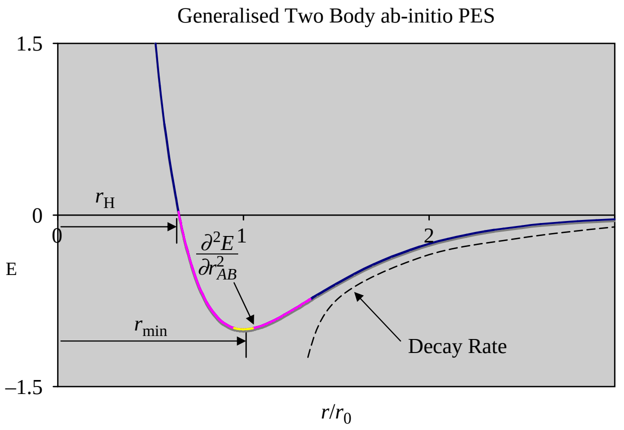

Figure 1. Schematic of the intermolecular two-body PES (E in arbitrary units): yellow, quadratic region; purple, quasi-harmonic region; blue, intermediate/tail region.

five pieces of chemical information in a two-body PES:

(1) r_{min},
(2) minimum curvature $(\partial^2 E/\partial r^2)_{r=r_{\mathrm{min}}}$,
(3) dissociation energy (D_e),
(4) decay rate $(\partial E/\partial r)_{r \gg r_{\mathrm{min}}}$ and
(5) hard-sphere radius, r_H.

These are present regardless of whether the system contains a covalent bond or is a van der Waals complex. Thus, there is a deliberate blurring of the boundary between bonded and intermolecular potentials. The first four pieces of information in the two-body PES have clear definitions, whereas (5) defines the inner portion of the curve and is the smallest radius of where the energy is equal to D_e, assuming $E(r_{\mathrm{min}}) = 0$. Figure 1 further highlights the quadratic, quasi-harmonic/quartic and intermediate/tail regions of a Morse PES, which can be defined using quadratic and quartic fits to the minimum. Here, the quadratic region is defined by a regime where the quadratic function deviates from the Morse potential by $< 10\%$; the quartic region is similarly defined. Finally, the intermediate/tail region is delineated by the remaining space that neither the quadratic nor quartic curve fits by less than 10%. While a system has a probability of existing in each of these regions, it is the second region (quasi-harmonic/quartic) that is the most important to fit properly, because many categories of chemical processes will occur there [35]. A force field that combines only quadratic and vdw-type functions cannot fit the quartic region.

3.1 Fitting traditional function forms in the gradient-fitting paradigm

The ability of four traditional function forms to fit the Morse PES gradients was first examined. These include the LJ 12-6 potential (Equation (4)); the Buckingham potential, which replaces the r^{-12} term with an exponential form [2],

$$E_{\mathrm{Buckingham}} = A(\mathrm{e}^{-Br} - Cr^{-6}), \tag{5}$$

and is very popular in solid materials where the steeper internal slope in the PES is relevant; the m–n potential wherein the exponentials can be values other than 12 and 6,

$$E_{m-n} = \frac{D_0}{n-m}\left(m\left(\frac{r_0}{r}\right)^n - n\left(\frac{r_0}{r}\right)^m\right) \tag{6}$$

and the general 12-6 function

$$E_{6\text{-}12\mathrm{gen}} = \frac{A}{r^{12}} - \frac{B}{r^6}, \tag{7}$$

where A and B are arbitrary constants. As shown in Figure 2, nearly all of the intermolecular forms (Equations (4)–(7)) fit the Morse curve poorly. In the case of the 12-6 functions, the poor fit is due to the fact that the parameters σ and ε are not independent of one another; the curvature at the bottom of the well is mathematically related to D_e. Thus, the 12-6 functions can fit either the curvature of the PES or the dissociation energy, but large deviations relative to the remainder of the PES must be expected. In the case of the m–n fit (Equation (6)), the best results are observed with $m = 0.1$ and $n = 7.9$, but this function no longer meets the requirements of the class due to the non-integer exponents, which will also lead to slow evaluation of the function. The quality of the m–n fit suggests that it is worth considering using lower powers of r to fit the quadratic and quartic regions of the curve.

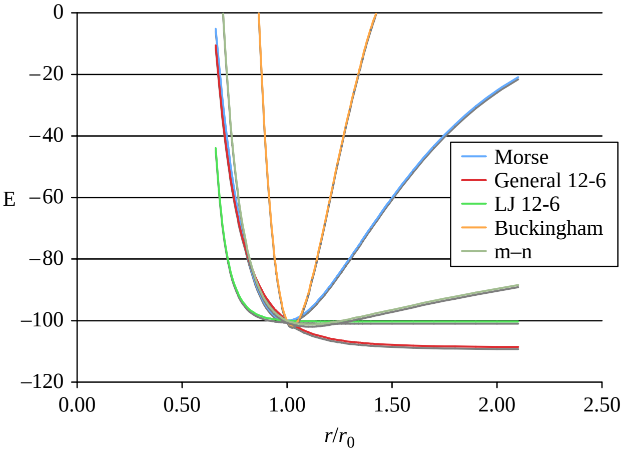

Figure 2. Gradient fits of traditional force-field types to a Morse potential (plotted in terms of energy in arbitrary units).

3.2 Gradient fitting a polynomial series to the Morse PES

The possibility of chemical bonds within the system has led to the consideration of additional function types for fitting the Morse which include the quadratic function

$$E_{\text{quadratic}} = \frac{1}{2}k(r - r_0)^2 \tag{8}$$

and the quartic function

$$E_{\text{quartic}} = \sum_{n=2}^{4} \frac{1}{n} k_n (r - r_0)^n. \tag{9}$$

Since these two functions are components of a Taylor series, they can be used as a baseline for testing the hypothesis that the most accurate force-field forms for fitting two-body PESs are composed of power series. Figure 3 illustrates the energy results of gradient-matching polynomials of the form

$$E_{\text{poly}} = \sum_{n=2}^{N} \frac{1}{n} k_n (r - r_0)^n \tag{10}$$

to the Morse potential gradients. The first and third members of this series are the traditional quadratic and quartic functions for bonding interactions. In the case of the fourth through sixth-order polynomials, it is clear that they perform better qualitatively than the quadratic function in fitting the intermediate or quasi-harmonic portions of the curve (Figure 3). While increasing the number of terms in an orthogonal series improves the fit, none of these functions fit the total length of the curve better than ~10%, nor do they dissociate properly (see the Supplementary Data). The quartic function has an error of 52% (Figure 3, $N = 4$), which decreases to 9.1% for the sextic function (Figure 3, $N = 6$). Thus, while increasing the overall power of the function leads to substantial improvements to the fit, simultaneously accurate representations of the quartic and tail regions necessitate the use of better mathematical expressions to mimic the PES.

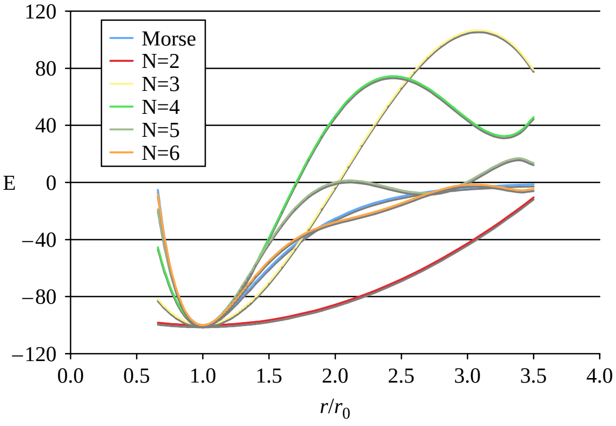

Figure 3. Gradient fits of the polynomial function (Equation (10)) to a Morse PES (plotted in terms of energy in arbitrary units).

3.3 Gradient fitting a harmonic series to the Morse PES

The harmonic series

$$E_{\text{harmonic}} = \sum_{n=1}^{N} \frac{k_n}{r^n} \tag{11}$$

is an interesting alternative to the polynomials in Equation (10) as it smoothly approaches zero as r approaches infinity, and it goes to infinity as r approaches zero (note that oscillations may be observed very close to zero, below the hard-sphere radius of any atom). As shown in Figure 4, fitting Equation (11) to the Morse potential within 3.2% accuracy requires only three terms. The four-term harmonic series fits with only 2.8% error and it integrates and differentiates more closely to the Morse potential than the three-term series. At six terms, better than 1% accuracy is achieved, and at 12 terms, 0.5% accuracy is achieved, which suggests a diminishing return to the accuracy of this series. Achieving greater than 1% accuracy depends not only on the quality of the fit, but also on obtaining *ab initio* data with comparable accuracy over all three regions, a non-trivial task for many systems of interest.

While it may be considered a disadvantage that the harmonic series has no chemically intuitive meaning, removing the constraint of such tradition enables a larger variety of functional forms to be examined for performing high-quality fits to the PES. There are a number of advantages of the harmonic series, including the fact that they limit to zero for large distances. Further, by fitting the full PES to a Morse first, all five chemically important pieces of information are fit: three exactly (D_e, ν and r_0)

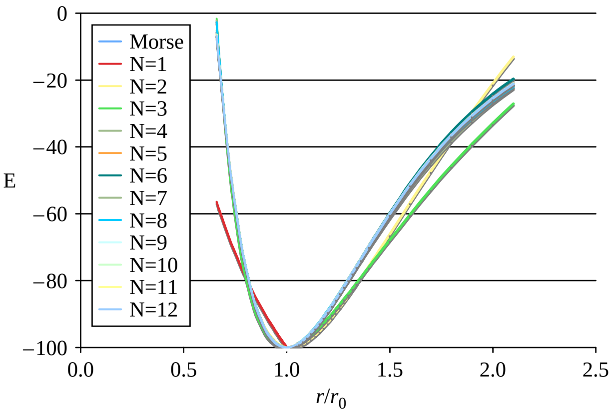

Figure 4. Gradient fits of the harmonic series (Equation (11)) to the Morse potential (plotted in terms of energy in arbitrary units).

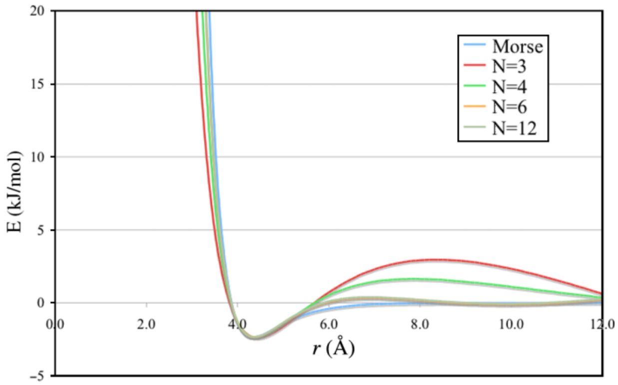

Figure 5. Gradient fits of the harmonic series (Equation (11)) to the Morse potential of Xe_2, plotted in terms of E in kJ/mol [34].

and two approximately (hard-sphere radii and tail decay rate). Perhaps, more importantly, by fitting the anharmonic region well, there is a much greater range of temperature over which the force field will produce accurate results. Thus, the harmonic series fit is equally applicable to simulations at 1000 K as at 300 K. An added feature is that when an r^{-1} term is included in all of the harmonic series force-field representations, a coulombic term is incorporated directly into the two-body PES force field. As a result, small changes in the coulombic attraction/repulsions, resulting from changes in the two-body interaction distance, can be accounted for implicitly.

To examine the computational speed of the harmonic series, the 3-, 4-, 6- and 12-term functions were first fit to the experimentally obtained Morse PES for Xe_2 [34], and MD simulations of Xe in a cubic box were performed (force-field parameters are given in the Supplementary Data). The quality of the fits for each series based on Equation (13) is shown in Figure 5. In comparison to the simulation using the Morse potential, the 3-term harmonic series was 33% faster, the 4-term was 24% faster, the 6-term was 12% faster and the 12-term was 85% slower. This indicates that it is possible to obtain both 10 and 1% accuracy with the harmonic series functions while saving time relative to the Morse function.

3.4 *Higher body functions*

While the harmonic curves do not fit torsions, angles or higher body terms, these functions have mathematical analogues in the power series of polynomials of either θ or $\cos(n\varphi)$ [36],

$$E_{\text{angle}} = \sum_{n=2}^{N} \frac{1}{n} k_n (\theta - \theta_0)^n \tag{12}$$

and

$$E_{\text{dihedral}} = \sum_{n=1}^{N} k_n \cos\left(n(\phi - \phi_0)\right). \tag{13}$$

These power series should work well for approximating higher body terms, as they do in the two-body case.

3.5 *Transferability*

A feature of any force field that must be considered is the transferability. Transferability results from similarities in analogous chemical interactions, e.g. if we know the PES for the interactions of Ar with Ar and Kr with Kr, then the interaction of Ar with Kr approximates an ‘average’ of the first two. In the 12-6 force fields, the dependence of the vibrational frequency on the dissociation energy means that only two terms, $r_{\min}$ and D_e, have to be transferable between related chemical systems. However, because the harmonic series fit is to a Morse potential, three terms are required: $r_{\min}$ (arithmetic average), D_e (geometric average) and the force constant of the curve at the minimum (k in Equation (3)). The mixing, or averaging rule, of the force constant k is not known, but limited data on van der Waals clusters suggest that the frequencies, not the force constants, mix arithmetically (see the Supplementary Data) [37–39]. In this case, the k’s will mix as

$$\frac{\nu_a + \nu_b}{2} = \frac{1}{2\pi}\sqrt{\frac{\alpha_{ab}}{\mu}}, \tag{14}$$

where ν_a and ν_b are the two vibrational frequencies of the chemically related molecules ‘a’ and ‘b’, respectively, μ is the reduced mass and k_{ab} is the force constant between ‘a’ and ‘b’. Surprisingly, the force constants themselves do not mix either arithmetically or geometrically, which may be due to a complex interaction of μ and $r_{\min}$.

4. Conclusions

The gradient-fitting paradigm has been explored, as it represents a mechanism to create force fields that, when used in an MD simulation, will yield non-biased physical properties of similar accuracy across the entire PES (as opposed to semi-empirical potentials). Using the general principle that power series can fit surfaces of any shape well, we have utilised harmonic series functions to fit a two-body PES represented by a Morse function. The harmonic functions are fast because they have only integer exponents, and they fit accurately with a limited number of terms. The four-term harmonic series fits with only 2.8% error and it integrates and differentiates more closely to the Morse potential than the three-term series. At six terms, better than 1% accuracy is achieved and at 12 terms 0.5%

accuracy is achieved, which suggests a diminishing return to the accuracy of this series. The error of the harmonic series converges at approximately 0.5%. Matching to a Morse-type function, which contains the relevant chemical information, compensates for the lack of chemical meaning to the constants.

Acknowledgements

This work was sponsored by the US Department of Energy, Office of Nuclear Energy Science and Technology, Junior Faculty Award Program award #DE-FG07-051D14692/IDNE006. This research was performed using the Molecular Science Computing Facility (MSCF) in the William R. Wiley Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the US Department of Energy's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory, operated for the Department of Energy by Battelle.

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