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Citation: The Journal of Chemical Physics **140**, 214117 (2014); doi: 10.1063/1.4881255
View online: http://dx.doi.org/10.1063/1.4881255
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/140/21?ver=pdfcov
Published by the AIP Publishing

Improved parameterization of interatomic potentials for rare gas dimers with density-based energy decomposition analysis

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(Received 6 March 2014; accepted 21 May 2014; published online 6 June 2014)

We examine interatomic interactions for rare gas dimers using the density-based energy decomposition analysis (DEDA) in conjunction with computational results from CCSD(T) at the complete basis set (CBS) limit. The unique DEDA capability of separating frozen density interactions from density relaxation contributions is employed to yield clean interaction components, and the results are found to be consistent with the typical physical picture that density relaxations play a very minimal role in rare gas interactions. Equipped with each interaction component as reference, we develop a new three-term molecular mechanical force field to describe rare gas dimers: a smeared charge multipole model for electrostatics with charge penetration effects, a B3LYP-D3 dispersion term for asymptotically correct long-range attractions that is screened at short-range, and a Born-Mayer exponential function for the repulsion. The resulted force field not only reproduces rare gas interaction energies calculated at the CCSD(T)/CBS level, but also yields each interaction component (electrostatic or van der Waals) which agrees very well with its corresponding reference value. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4881255]

I. INTRODUCTION

One of the main challenges in the force field development is to model van der Waals (vdW) interactions. Currently vdW parameters are often the last to be determined among non-bonded interactions terms, as complements needed to fit either experimentally measured thermodynamic properties or total intermolecular binding energies from electronic structure calculations.[1–11] A more appealing approach would be to directly determine vdW interaction energies from high-level quantum mechanical calculations and then use them to examine force field function forms and determine corresponding vdW parameters.[12–38] To make further progresses along this direction, here we present a novel supermolecule computational procedure to determine reference vdW interaction energies, and demonstrate its applicability by examining interatomic interactions and developing a new force field for rare gas dimers. Specifically, the total binding energy is obtained with CCSD(T) calculations at the complete basis set (CBS) limit, and the vdW interaction component is separated out from electrostatics and density-relaxation contributions by employing B3LYP[39–41] Kohn-Sham calculations and our recently developed density-based energy decomposition analysis (DEDA) approach.[42]

One of the most important and unique features of DEDA is that it variationally calculates the total frozen density energy through constrained search; thus it enables a clean separation of the frozen density interaction energy (i.e., electrostatic and van der Waals interactions) from the density relaxation (i.e., polarization and charge transfer) contribution.[42–44] On the other hand, in all wave-function-based energy decomposition analysis (EDA) approaches,[45–56] the Heitler-London antisymmetrization of wave functions has been used to determine the Pauli repulsion energy, and it actually deforms the frozen density.[53] This key difference enables the definition of each interaction component in DEDA to be more consistent with the typical physical picture of intermolecular interactions. Taking advantage of this novel feature, we have systematically investigated the directional dependence of hydrogen bonding and our results clearly indicate that the frozen density interaction energy term is the key factor in determining the hydrogen bonding (HB) orientation, while the density relaxation energy term shows very little HB directional dependence.[57] This finding is very different from the current dominant view regarding the origin of hydrogen bonding directionality, and cannot be obtained with wave-function-based EDA approaches. On the other hand, these results indicate the importance of improving non-polarizable force fields by focusing on the frozen density interaction terms, and thus clearly demonstrate the novelty and power of the DEDA approach.

Over the years a number of interatomic potentials have been developed to describe rare gas dimers, which are prototypical systems to examine and model van der Waals interactions.[58–62] For most of these interatomic potentials, they do not take into account charge-penetration effects. Instead, it has been generally assumed that the total interaction energy between rare gas dimers is all due to van der Waals interactions. With total interactions between rare gas atoms as van der Waals reference energies, a seminal work to examine vdW function forms found that the Exp-6 form, which has the physically correct long-range behavior, failed to reproduce the

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high quality reference data; instead, a Buf-14-7 potential was found to yield much better performance.[59] However, it is well known that there are significant charge-penetration effects at the short range, and recently a series of works have shown that a smeared charge multipole model not only is more physically grounded but also yields much better performance in modeling electrostatic interactions.[20,24,63–73] Thus an open question is that if the charge-penetration effects were explicitly modeled, can a function form with correct long-range behavior be a good representation of vdW interactions?

In this work, by employing each interaction component from DEDA as the reference, we have indeed found that a B3LYP-D3 dispersion term, which is screened at short-range and has a correct long-rang behavior, plus a Born-Mayer exponential function[74] for repulsion is an excellent function form to model vdW interactions between rare gas atoms. In combination with a smeared charge multipole model for electrostatics interactions, the resulted force field is found to yield excellent results in reproducing rare gas interaction energies calculated at the CCSD(T)/CBS level.

II. THEORY AND METHODS

A. CCSD(T)-DEDA supermolecule computational protocol to determine reference vdW interaction energies

From first principles, accurate account of vdW interactions requires very high level quantum mechanical calculations. Currently, the "gold standard"[75,76] to describe intermolecular interactions is the coupled cluster method with singles and doubles model corrected for triple excitations[77] at the complete basis set limit, namely, CCSD(T)/CBS.[78–81] It has been demonstrated to recover more than 95% of the interaction energy even for very weak interactions including the dispersion-dominant rare-gas dimers binding,[82] and has been widely employed to generate benchmark data sets to parameterize and examine density functional approximations as well as force field models.[78,83–85] Thus, the CCSD(T)/CBS method has been employed to calculate the reference total intermolecular binding energies. Specifically, given two fragments A and B, the reference total binding energy for the complex AB is calculated by

$$\Delta E_{bind}^{ref} = E_{AB}^{CCSD(T)} - E_{A}^{CCSD(T)} - E_{B}^{CCSD(T)}, \tag{1}$$

where $E_I^{CCSD(T)}$ refers to the total energy for the molecule I calculated with the CCSD(T)/CBS approach.

To separate out the vdW interaction component from other contributions, here we employ B3LYP Kohn-Sham calculations and our recently developed DEDA approach to calculate electrostatics and density-relaxation contributions. The density-relaxation contribution to intermolecular interaction can be calculated by

$$\Delta E_{relax}^{ref} = E[\rho_{AB}] - E\left[\rho_A^0 + \rho_B^0\right], \tag{2}$$

where $E[\rho_{AB}]$ is the total energy of the binding complex AB; ρ_A^0 and ρ_B^0 are densities of noninteracting molecules A and B, respectively. They are determined with Kohn-Sham B3LYP calculations in which the energy and the density for each noninteracting fragment are calculated with all basis functions in the complex, as done in the standard counterpoise method.[86,87] $E[\rho_A^0 + \rho_B^0]$ is the frozen density energy, which is variationally determined with a constrained search formalism, i.e., $E[\rho_A^0 + \rho_B^0] = \min_{\rho \to \rho_A^0 + \rho_B^0} E[\rho]$. This novel feature of the DEDA method allows a clean separation of the density relaxation contribution, ΔE_{relax}^{ref}, which includes both polarization and charge transfer effects, from the total binding energy. Then the electrostatic contribution to the intermolecular interaction can be calculated by

$$\Delta E_{es}^{ref} = E_{coulomb}\left[\rho_A^0 + \rho_B^0\right] - E_{coulomb}\left[\rho_A^0\right] - E_{coulomb}\left[\rho_B^0\right], \tag{3}$$

where $E_{coulomb}$ refers to the classical Coulomb electrostatic interaction for a given system. By separating out both density-relaxation and electrostatic contributions, the remaining binding energy, consisting of both dispersion and Pauli repulsion terms, can be considered as the van der Waals interaction term:

$$\Delta E_{vdw}^{ref} = \Delta E_{bind}^{ref} - \Delta E_{es}^{ref} - \Delta E_{relax}^{ref}. \tag{4}$$

B. vdW interaction model and its combination rule

In this work, we have found that reference van der Waals interaction energies for rare gas dimers, as determined by Eq. (4) with the CCSD(T)-DEDA supermolecule computational protocol, can be very well modeled by the sum of a B3LYP-D3 dispersion term and a Born-Mayer exponential function for describing repulsive interaction.

The B3LYP-D3 dispersion term is an add-on correction term[88,89] to overcome the well-known challenge in describing dispersions by standard Kohn-Sham B3LYP calculations, which has been parameterized to achieve the CCSD(T) accuracy.[88] Its two-body interaction term can be cast into the following formula,

$$\Delta E_{disp}^{B3LYP-D3} = \sum_{ij} \sum_{n=6,8} s_n \frac{C_n^{ij}}{r_{ij}^n} f_{d,n}(r_{ij}), \tag{5}$$

where C_n^{ij} are atom-pairwise specific dispersion coefficients for atoms i and j, which have been computed from first principles. $f_{d,n}(r_{ij})$ is a damping function proposed by Chai and Head-Gordon[90] with the form of $f_{d,n}(r_{AB}) = \frac{1}{1+6[r_{AB}/(s_{r,n}R_0^{AB})]^{-\alpha_n}}$, where $s_{r,n}$ is the order-dependent scaling factor of the cutoff radii R_0^{ij}. Thus, this dispersion term is screened at short-range and has physically correct long-rang behavior. We utilized the available DFT-D3 program[88,89] to calculate the dispersion energies without changing any parameters.

A physically appealing model to describe the repulsion interaction is the Born-Mayer exponential function:

$$\Delta E_{rep}^{BM} = \sum_{ij} C_{ij} e^{-D_{ij} r_{ij}}, \tag{6}$$

where C_{ij} and D_{ij} are atom-pairwise specific parameters. In this work, the natural logarithm of the calculated difference

between ΔE_{vdw}^{ref} (as in Eq. (4)) and $\Delta E_{disp}^{B3LYP-D3}$ (as in Eq. (5)), i.e., $\ln(\Delta E_{vdw}^{ref} - \Delta E_{disp}^{B3LYP-D3})$, has been shown to have almost perfect linearity against the interatomic distance at short range until the sum of Bondi radii.[91] Thus, C_{ij} and D_{ij} in Eq. (6) can be directly determined by fitting to these semi-logarithmic plots. Here we determined both C_{ii} and D_{ii} values by doing such linear regressions at the range of 0.6–0.75 Bondi distance of two homogeneous rare gas dimers.

For hetero-dimers, their parameters have been found to be very well reproduced by the following physically motivated combination rule:[92]

$$D_{ij} = 2D_{ii}D_{jj}/(D_{ii} + D_{jj}), \tag{7}$$

$$(C_{ij}D_{ij})^{\frac{2}{D_{ij}}} = (C_{ii}D_{ii})^{\frac{1}{D_{ii}}}(C_{jj}D_{jj})^{\frac{1}{D_{jj}}}. \tag{8}$$

C. Smeared charge multipole model for electrostatics

In the smeared charge multipole model, each atom i is represented by a nuclear charge Z_i, an exponential charge density $\rho(r) = \frac{qa^3}{8\pi}e^{-ar}$, a point dipole, and a point quadrupole. The nuclear charge Z_i is taken from the number of valence electrons, for example, Z = 2 for the He atom and Z = 8 for Ne and Ar. All electrostatic interactions for the smeared charge multipole model are calculated analytically as described in Ref. 57. With monopoles, dipoles, and quadrupoles directly calculated with the GDMA program[93–95] and quantum mechanical calculations, q_i is obtained by the corresponding monopole subtracting Z_i, and the width parameter of charge distribution a_i is determined by minimizing the electrostatic potential difference between QM calculations and the smeared charge multipole model. The potential fitting is carried out with 10 spherical shells on each element, starting at 0.5 Bondi radius of the element with a 0.1 Bondi radius increment for each larger shell. To improve the stability of the fitting, a modified Hu-Lu-Yang (HLY) weighting function,[67,96,97] which decays at both the short and the long range, was employed,

$$W(\mathbf{r}) = \exp\{-\sigma[\ln \rho(\mathbf{r}) - \ln \rho_{ref}]^2\}, \tag{9}$$

where $\rho(\mathbf{r})$ is the *ab initio* electron density, $\sigma = 0.42$ and $\ln(\rho_{ref}) = -7.0$ are the same as in the previous study.[97] The object function of electrostatic fitting is

$$f = \sum_r W(\mathbf{r})[V_{FF}(\mathbf{r}) - V_{QM}(\mathbf{r})]^2, \tag{10}$$

where $V_{FF}(\mathbf{r})$ and $V_{QM}(\mathbf{r})$ are the electrostatic potentials calculated by the force field and by *ab initio* quantum mechanical calculation, respectively.

III. COMPUTATIONAL DETAILS

All CCSD(T)/CBS calculations were carried out using Gaussian 09[98] with extrapolations similar to other studies.[79] The CCSD(T)/CBS total energy was calculated as the sum of the MP2 energy at the complete basis set (E_{MP2}^{CBS}) and the higher order corrections at the complete basis set ($\delta_{MP2\to CCSD(T)}^{CBS}$): $E_{CCSD(T)}^{CBS} = E_{MP2}^{CBS} + \delta_{MP2\to CCSD(T)}^{CBS}$.[80,81] E_{MP2}^{CBS} was obtained by two-point Helgaker extrapolations[80,81] using the smaller aug-cc-pVTZ (N = 3) and the larger aug-cc-pVQZ (N = 4) augmented Dunning basis set.[99] $\delta_{MP2\to CCSD(T)}$ is the energy difference between CCSD(T) and MP2 with a specific basis set, whose basis set convergence is much faster.[100] Thus, it is common to use $\delta_{MP2\to CCSD(T)}^{aug-cc-pVTZ}$, which is the CCSD(T) correction at the aug-cc-pVTZ basis set, as the CCSD(T) correction at the complete basis set, $\delta_{MP2\to CCSD(T)}^{CBS}$.[79] For the distance scans, the dimer distances were set to start from 0.6 Bondi distances[91] to 2.5 Bondi distances with a 0.025 Bondi distances increment. The first six points have been employed for determining C_{ii} and D_{ii} in Eq. (6) by linear fitting to the plot of $\log(\Delta E_{vdw}^{ref} - \Delta E_{disp}^{B3LYP-D3})$ versus the interatomic distance for homo-dimers. All DEDA calculations were carried out with a modified NWChem 5.1[101] at the level of B3LYP/aug-cc-pVTZ. The corresponding MO-EDA calculations were done with Q-Chem 4.0,[102] in which the corresponding frozen density sate is represented by the Heitler-London antisymmetrization of two fragments' wave functions.

IV. RESULTS AND DISCUSSION

In this section, we first present interatomic interaction results for rare gas dimers calculated by CCSD(T)/CBS and DEDA. Then we demonstrate that the calculated reference van der Waals interaction energies for rare gas dimers can be very well modeled by the sum of a B3LYP-D3 dispersion term and a Born-Mayer exponential function for describing repulsive interactions. Finally, we show that in combination with a screened charge model, the resulting non-polarizable force field can well reproduce rare gas interaction energies calculated at the CCSD(T)/CBS level.

A. Interaction energy decomposition analysis of rare gas dimers

With the CCSD(T)-DEDA supermolecule computational protocol, we carried out calculations for all six rare gas dimers. The results are presented in Table I and Figure 1. Both well depths and minimum distances from the CCSD(T)/CBS calculations are in excellent agreement with corresponding experimental results (Refs. 62 and 103–106). For each rare gas dimer, its total binding energy almost entirely comes from the sum of electrostatic and van der Waals interaction energies. This finding is very consistent with the general physical picture of rare gas interaction, in which the electronic relaxation term, including both charge transfer and polarization contributions, is expected to play a very minor role. On the other hand, the corresponding wave function-based energy decomposition analysis (MO-EDA), in which the frozen density sate is represented by the Heitler-London antisymmetrization of two fragments' wave functions, yields a quite different physical picture of rare gas interaction. As shown in Fig. 2, MO-EDA would yield the result that the contribution of the electronic relaxation term to the rare gas dimer formation is not negligible, which is due to the fact that

TABLE I. Energy components and total binding energy for each rare gas dimers at the minimum-energy distance r_{min} (Å) calculated with the CCSD(T)-DEDA supermolecule computational protocol. ΔE_{bind}, ΔE_{relax}, ΔE_{frz}, and ΔE_{pol} are in kCal/mol, and they are calculated by Eqs. (1)–(4), respectively.

	r_{min}	ΔE_{bind}	ΔE_{relax}	ΔE_{ele}	ΔE_{vdw}	Reference r_{min}	Reference ΔE_{bind}
He-He	2.978	−0.020	0.000	−0.005	−0.015	2.97	− 0.022
Ne-Ne	3.114	−0.089	0.000	−0.037	−0.051	3.09	− 0.084
Ar-Ar	3.798	−0.280	− 0.001	−0.142	−0.136	3.76	− 0.285
He-Ne	3.014	−0.045	0.000	−0.016	−0.028	3.02,[a] 3.03[b]	− 0.043,[a] −0.042[b]
He-Ar	3.513	−0.059	0.000	−0.018	−0.041	3.48,[a] 3.48[b]	− 0.059,[a] −0.059[b]
Ne-Ar	3.500	−0.138	0.000	−0.069	−0.069	3.42,[a] 3.49,[c] 3.52[d]	− 0.137,[a] −0.134,[c] −0.132[d]

[a]Reference 103. Also summarized in Ref. 62.
[b]Reference 104. Also summarized in Ref. 62.
[c]Reference 105. Also summarized in Ref. 62.
[d]Reference 106. Also summarized in Ref. 62.

the Heitler-London antisymmetrization of wave functions actually deforms the frozen density.[53] It has been previously suggested such density deformation would give rise to additional energy terms, including the exchange-polarization term,[107,108] which has not been separated out in most EDA methods. Thus, Figure 2 further demonstrates the novelty and advantage of DEDA that allows a clean separation of the frozen density interaction term from the density relaxation contribution.

From the results in Table I and Figure 1, we can see that the electrostatic interaction term has a similar magnitude as the vdW interaction term at the minimum-energy distance, except for He-He. This result shows that charge penetration effects contribute significantly to the binding of each rare gas dimmer. The conventional assumption that the total interaction energy between rare gas dimers all comes from vdW interactions is limited; thus charge penetration effect should be explicitly considered and modeled in a more physically grounded description of electrostatics interaction.

B. Examination of van der Waals models

With the calculated reference van der Waals interaction energies for rare gas dimers from the CCSD(T)-DEDA supermolecule computational protocol, we address the question of whether it can be modeled with a physically grounded function form. As shown in Fig. 3, the natural logarithm of the calculated difference between ΔE_{vdw}^{ref}

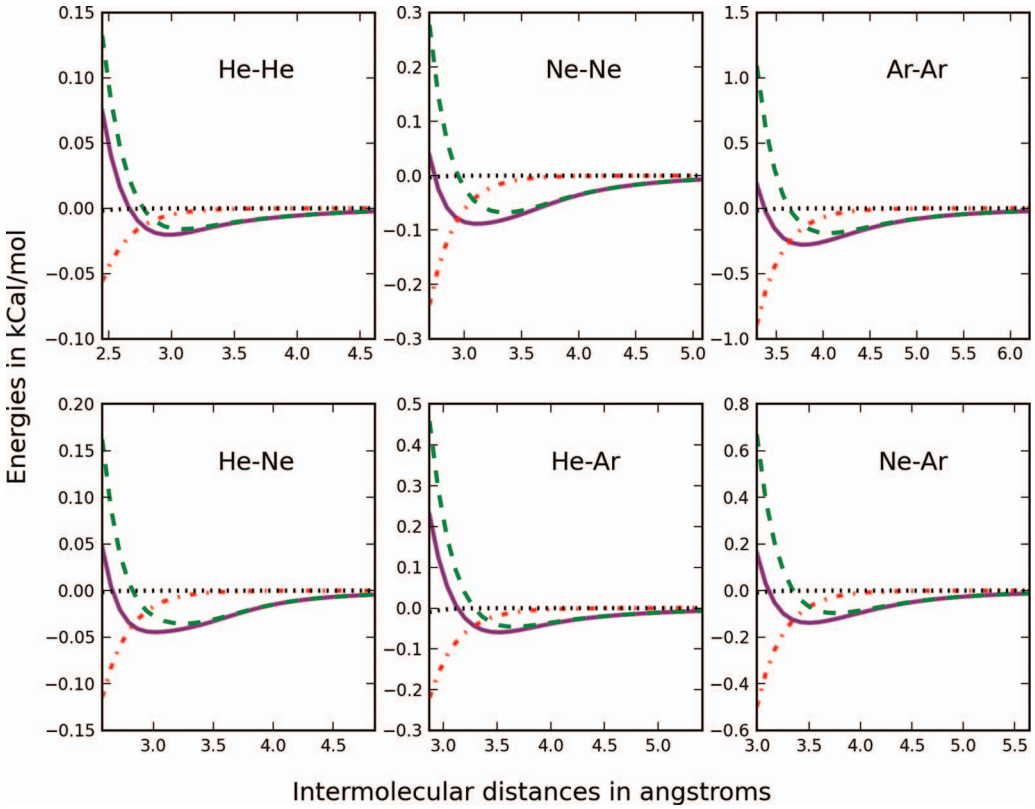

FIG. 1. Energy components and total binding energy for each rare gas dimers along the bond distance calculated with the CCSD(T)-DEDA supermolecule computational protocol. ΔE_{bind}, ΔE_{relax}, ΔE_{frz}, and ΔE_{vdw} are calculated by Eqs. (1)–(4), respectively. The lines in the figures are (a) purple solid lines: ΔE_{bind}; (b) red dashed-dotted lines: ΔE_{vdw}; (c) green dashed lines: ΔE_{ele}; and (d) black dotted lines: ΔE_{relax}.

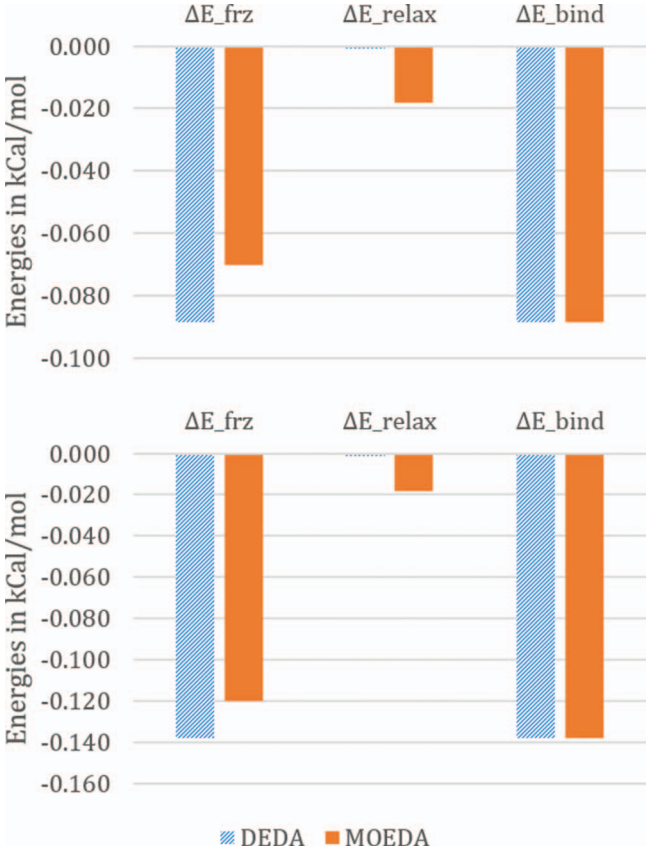

FIG. 2. Comparison between MO-EDA and DEDA for Ne-Ne and Ne-Ar rare gas dimers at the energy minimum. $\Delta E_{frz} = \Delta E_{ele} + \Delta E_{vdw}$. Upper: Ne-Ne. Lower: Ne-Ar.

(as in Eq. (4)) and $\Delta E_{disp}^{B3LYP-D3}$ (as in Eq. (5)), i.e., $\log(\Delta E_{vdw}^{ref} - \Delta E_{disp}^{B3LYP-D3})$ has an almost perfect linearity against the interatomic distance until the sum of Bondi van der Waals radius. We therefore propose that van der Waals interaction energies for rare gas dimers can be accurately modeled by the sum of two physically correct terms: a B3LYP-D3 dispersion term for long-rang attractions, and a Born-Mayer exponential function $C\exp(-D \cdot r)$ for short-range repulsions. The parameters in B3LYP-D3 are used as they are, while the parameters C and D can be directly determined by linear fitting to these semi-logarithmic plots as in Figure 3.

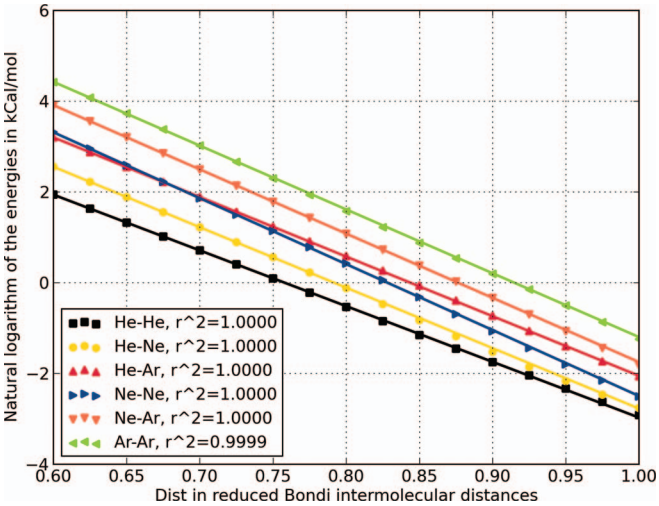

FIG. 3. Plot of $\ln(\Delta E_{vdw}^{ref} - \Delta E_{disp}^{B3LYP-D3})$ against reduced interatomic distance r/r^* for rare gas dimers, where r* is the sum of Bondi radii (He: 1.40, Ne: 1.54, Ar: 1.88).[1–11,91]

TABLE II. MURE (mean unsigned relative error) in percentage of each combining rule combination on the repulsions of the three heterogeneous rare gas dimers. Rows: the combining rules on the parameter C; columns: the combining rules on the parameter D. All values in percentage.

C/D	a	b	c	d	e
a	103.62	104.65	109.07	106.40	131.80
b	11.96	9.43	6.77	8.11	13.65
c	48.02	45.88	43.63	44.77	42.87
d	35.57	33.18	30.67	31.94	32.01
e	66.80	65.22	63.55	64.39	56.18
f	6.71	5.49	4.30	4.89	5.11

For the force field development, it is essential to use optimal combination rules to obtain parameters for heterodimers so that the total number of parameters can be greatly reduced. For parameters C and D in the Born-Mayer exponential function, we have examined the following combination rules:[92]

(a) $a_{12} = (a_1 + a_2)/2$.

(b) $a_{12} = \sqrt{a_1 a_2}$.

(c) $a_{12} = 2a_1a_2/(a_1 + a_2)$.

(d) $a_{12} = \dfrac{4a_1a_2}{(\sqrt{a_1} + \sqrt{a_2})^2}$.

(e) $\dfrac{1}{a_{12}} = \left(\dfrac{1}{a_1^3} + \dfrac{1}{a_2^3}\right) \Big/ \left(\dfrac{1}{a_1^2} + \dfrac{1}{a_2^2}\right)$.

(f) $(C_{12}D_{12})^{\frac{2}{D_{12}}} = (C_{11}D_{11})^{\frac{1}{D_{11}}}(C_{22}D_{22})^{\frac{1}{D_{22}}}$.

Performance of these combining rules is compared by the mean unsigned relative errors (MURE) on heterogeneous rare gas dimers as tabulated in Table II. We can see that the choice of the combining rule on the parameter C is crucial. Among all the combining rules, the Smith rule[92] (rule f) for parameter C with the harmonic average rule (rule c) for the parameter D yield the lowest MURE.

C. Performance of the smeared-charge molecular mechanical force field

Based on the above results, our new molecular mechanical force field for rare gas atoms has three components: a smeared charge multipole model for charge penetrating

TABLE III. Electrostatic and repulsion interaction force field parameters for rare gas atoms. For rare gas atoms, their point dipoles and point quadrupoles are zero. Dispersion parameters of the B3LYP-D3 model can be found in Refs. 88 and 89, as implemented in the available DFT-D3 program.

	Electrostatic			Born-Mayer repulsion		DFT-D3 dispersion		
	Z_i	q_i	$\frac{1}{a_i}$ (Å^{-1})	C (kCal/mol)	D (Å^{-1})	C_6	C_8	C_{10}
He	2	−2	0.1777	11 013	4.3849	1.6	11.5	103.4
Ne	8	−8	0.1738	168 317	4.7173	6.3	92.6	1669.8
Ar	8	−8	0.2467	386 013	3.7394	64.6	2304	100 594

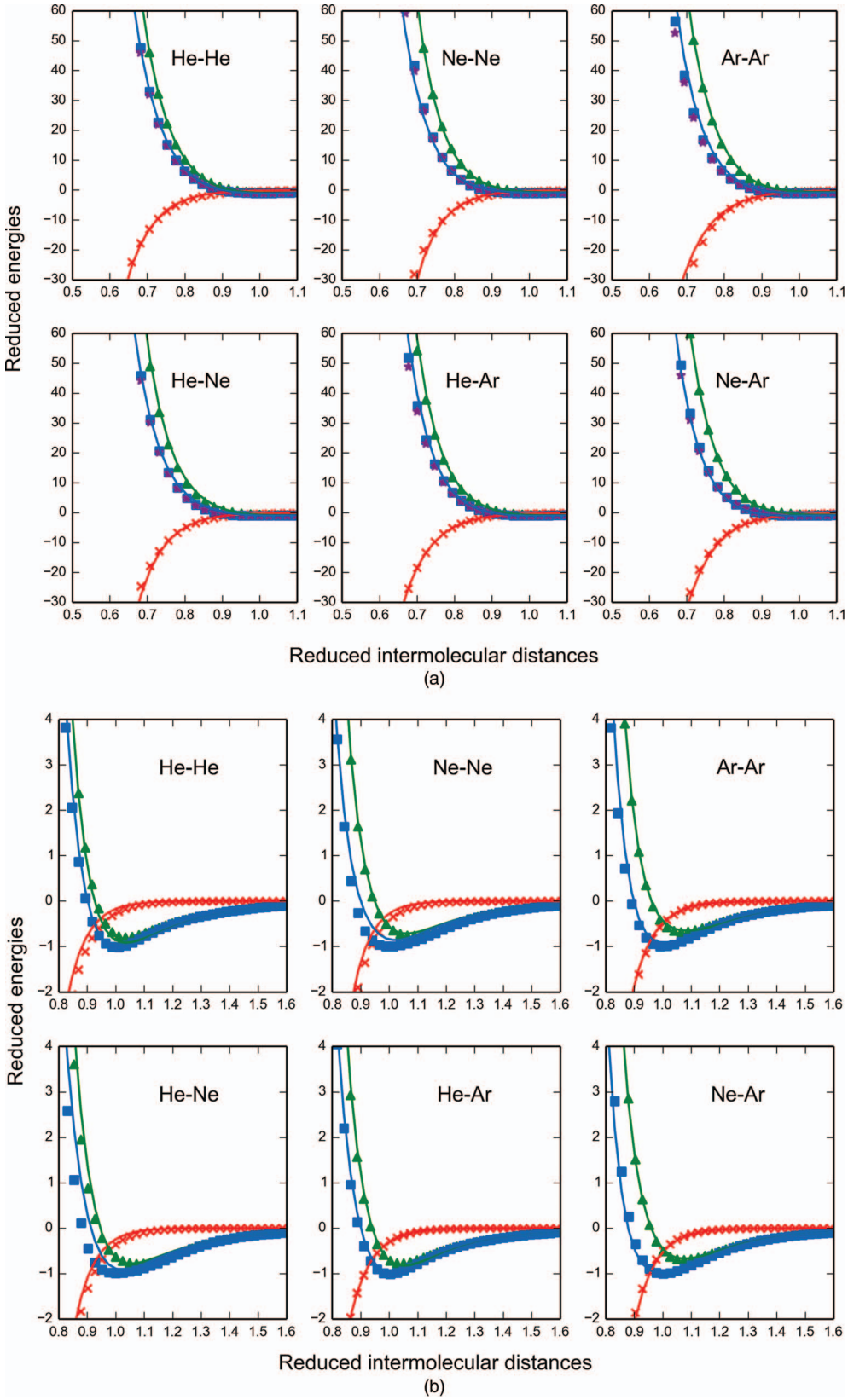

FIG. 4. Comparison between MM force field results and corresponding reference energies from the CCSD(T)-DEDA supermolecule computational protocol for all six rare gas dimers, both at the short range (a) and around the minimum (b). The colors in the figures denote, red: electrostatic energies; green: van der Waals energies; blue: frozen energies; and purple: binding energies from CCSD(T)/CBS. The lines show results from the force field. Cross/triangle/square/star markers show the reference QM energies. The y axes in the figures denote the energies in ε, where ε is the depth of the dimerization well given by CCSD(T)/CBS. The ε values are taken as the ΔE_{bind} values with the opposite sign from Table I. The x axes in the figures denote the dimer separations in Bondi distances. (a) Performance at the short range, with reduced units. (b) Performance around the minimum, with reduced units.

electrostatics, a B3LYP-D3 dispersion term for long-range attractions, and a Born-Mayer exponential function for short-range repulsive interactions. The force field parameters for three rare gas elements, He, Ne, and Ar are summarized in Table III, where the dispersion parameters (C_6, C_8, and C_{10}) were directly taken from the DFT-D3 program.[88,89]

We examine the performance of this force field for all six rare gas dimers by comparing the total binding energy as well as its electrostatic and vdW components to the corresponding reference values from the CCSD(T)-DEDA supermolecule computational protocol. Full sets of the reference energies can be found in the supplementary material.[109] Here we plot the comparisons separately at the short range (Fig. 4(a)) and around the minimum (Fig. 4(b)). We can see that not only the total binding energies calculated by the force field can well reproduce rare gas interaction energies calculated at the CCSD(T)/CBS level, but also each interaction component (electrostatic or vdW) agrees very well with its corresponding reference energy for all six dimers. This result is significant because: (1) our electrostatic parameters are fitted from atomic calculations, not to reproduce the reference interaction energies; (2) we have made no adjustment of the B3LYP-D3 parameters for long-range vdW interactions; and (3) the short range repulsion parameters are fitted from the homo-dimer reference energies only, but reproduce heterodimer interaction energies. It demonstrates the validity of our proposed force field function forms, parameterization protocol and the combination rule.

V. SUMMARY

In this work, we have presented a CCSD(T)-DEDA supermolecule computational procedure to determine reference vdW interaction energies, and examined interatomic interactions for rare gas dimers. Our main results are: (1) The electronic relaxation term, including both charge transfer and polarization contributions, plays a very minor role in rare gas binding. This finding is very consistent with the general physical picture of rare gas interaction, but would not be obtained with wave-function obtained EDA approaches. (2) Electrostatic interaction term contributes significantly to the binding of each rare gas dimer due to strong charge penetration effects. These effects can be described well by a smeared charge model. (3) The reference vdW interaction energy can be excellently modeled by the sum of a B3LYP-D3 dispersion term, which is screened at short-range and has a correct long-rang behavior, and a Born-Mayer exponential function for repulsion with the Smith-harmonic combination rule. It is worth mentioning that the Born-Mayer form with an R-6 dispersion was shown to be inferior to the buffered 14-7 form in reproducing the total binding energy curves for rare gas dimers in previous studies.[59] Thus this work emphasizes the importance of energy decomposition in the force field development, and sets a solid foundation for systematic force field development based on first principle quantum mechanics calculations with density-based energy decomposition analysis.

ACKNOWLEDGMENTS

This work carried out in part at NYU was supported by NIH (R01-GM079223) and NIH (R21-GM097530). Research carried out in part at the Center for Functional Nanomaterials was supported by the U.S. Department of Energy, Office of Basic Energy Sciences under Contract No. DE-AC02-98CH10886. We thank NYU-ITS and CFN for providing computational resources.

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