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Density functional method including weak interactions: Dispersion coefficients based on the local response approximation

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A new method to calculate the atom-atom dispersion coefficients in a molecule is proposed for the use in density functional theory with dispersion (DFT-D) correction. The method is based on the local response approximation due to Dobson and Dinte [Phys. Rev. Lett. **76**, 1780 (1996)], with modified dielectric model recently proposed by Vydrov and van Voorhis [J. Chem. Phys. **130**, 104105 (2009)]. The local response model is used to calculate the distributed multipole polarizabilities of atoms in a molecule, from which the dispersion coefficients are obtained by an explicit frequency integral of the Casimir–Polder type. Thus obtained atomic polarizabilities are also used in the damping function for the short-range singularity. Unlike empirical DFT-D methods, the local response dispersion (LRD) method is able to calculate the dispersion energy from the ground-state electron density only. It is applicable to any geometry, free from physical constants such as van der Waals radii or atomic polarizabilities, and computationally very efficient. The LRD method combined with the long-range corrected DFT functional (LC-BOP) is applied to calculations of S22 weakly bound complex set [Phys. Chem. Chem. Phys. **8**, 1985 (2006)]. Binding energies obtained by the LC-BOP+LRD agree remarkably well with *ab initio* references. © 2009 American Institute of Physics. [doi:10.1063/1.3269802]

I. INTRODUCTION

The importance of weak interactions, such as hydrogen-bonding and van der Waals interactions, cannot be overemphasized in view of roles they play in diverse area of chemical physics, biochemistry, and material science.^{1,2} Such interactions have different physical origins: the electrostatic, exchange-repulsion, charge-transfer, induction, and dispersion interactions, although all of them can ultimately be attributed to the Coulomb interaction between electrons and nuclei constituting a system.¹ Among them, the dispersion interaction is distinguished from others by ubiquitous and growing importance in larger systems.

Theoretical treatment of the dispersion interaction has faced difficulty because it is entirely an electron correlation effect. In *ab initio* wave function theories, correlated methods are necessary to include the dispersion energy. The second-order Møller–Plesset perturbation (MP2) method performs well for interactions between saturated molecules, although is problematic for aromatic interactions.^{3–5} The coupled-cluster with single, double, and perturbative triple excitations [CCSD(T)] is established as a powerful tool to predict accurate interaction energies of weakly bound systems. The major drawbacks of these methods are the slow convergence with respect to the number of basis functions and unfavorable scaling of the computational cost against the system size. A method that can capture the essential part of the dispersion interaction with computational cost signifi-

cantly lower than these accurate but demanding methods is required.

Density functional theory⁶ (DFT) has gained attention as an ideally cost-effective method for calculations of large systems. In particular, the Kohn–Sham (KS) method⁷ has a distinct advantage that it can include the electron correlation essentially with the mean-field equation. The exchange-correlation (XC) functional is the key to such formal simplicity. The generalized gradient approximation (GGA),^{8–11} meta-GGA,^{12–19} and the Hartree–Fock (HF)/DFT hybrid functionals^{20–22} have been proposed as useful tools for broad chemical applications. However, these XC functionals have problems in describing weak van der Waals interactions.^{23,24} The problem stems from the nearsightedness of both exchange and correlation functionals.

The problem of exchange functionals was first noted by Lacks and Gordon.²⁵ They applied local density approximation (LDA) and several GGA exchange functionals to calculations of helium and neon dimers, and revealed that the behavior of the exchange energy density at the low-density-high-gradient region had the crucial impact on calculated interaction energies. Wesolowski *et al.*²⁶ and Zhang *et al.*²⁷ derived the similar conclusion from calculations of other systems. These observations motivated several studies which aimed to adjust parameters for curing exchange functionals for such region.^{28–30} Kamiya *et al.*³¹ suggested that the long-range correction (LC) scheme,³² which is the range separated HF/DFT hybrid method, can solve this problem by showing that the LC-applied functionals give closely resembling repulsive potential curves for rare-gas interactions irrespective

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of an employed exchange functional. Several authors also used LC (Refs. 33–41) or so-called range-separation^{42,43} techniques with different treatments of the short-range exchange and the dispersion interactions.

Various approaches have also been suggested to treat the dispersion interaction within the DFT formalism. Here, we review some of these approaches restricting our focus on such methods that are essentially within the KS formalism and computationally not much more demanding than the KS method with conventional XC functionals. For comprehensive review of below-mentioned and other approaches, we guide readers to the recent paper by Gräfenstein and Cremer,³⁹ in which the authors categorized various DFT based approaches and analyzed the strengths and limitations of each method.

According to the philosophy of KS theory, the desired route may be improving accuracy of an XC functional to describe weak interactions. In this respect, recent progress in the (hybrid) meta-GGA functionals,^{44–46} especially those due to Zhao and Truhlar,^{44,45} have to be mentioned. Another recent progress has been made on the construction of dispersion-corrected atom-centered potentials by the group of Rothlisberger^{47–50} and dispersion correcting potentials due to DiLabio and co-workers.^{51,52} A practical advantage of these methods is that they can benefit from the sophisticated computational code for the KS calculation without large modifications; gradients and Hessians as well as various properties are readily available. The limitation of these methods is the inability to describe the long-range part of the dispersion interaction. (Here, the term “dispersion” is loosely used.) The physics of dispersion interaction, the synchronized fluctuation of electron distributions, cannot be described by the (semi-) local XC functionals or the atom-centered potentials.⁵³

Probably the most widely used approach is explicitly adding damped atom-atom corrections of the form $C_6 R^{-6} f_{\text{damp}}(R)$ to the DFT total energy (DFT-D),^{38,54–58} with dispersion coefficients determined empirically. The DFT-D approaches have been quite successful in describing weak interactions among organic systems or carbonic materials.^{38,56–58} However, the highly empirical nature of the method is unsatisfactory from a theoretical point of view; it might eventually suffer from the limited applicability and transferability. A promising alternative to these empirical approaches was proposed by Becke and Johnson,^{59,60} in which the exchange-hole dipole moment (XDM) is used to model the dispersion coefficients. Subsequent studies by Geerlings and co-workers,^{61,62} Kannemann and Becke,⁶³ and Kong *et al.*⁶⁴ showed that the XDM model can be a practically useful tool.

Yet another theoretically more sound approaches are based on the nonlocal dispersion functionals derived from the first principles.^{36,37,65–68} The older Andersson–Langreth–Lundqvist (ALL) functional,⁶⁶ which was also derived by Dobson and Dinte⁶⁷ independently, is for the asymptotic interaction between nonoverlapping fragments, while the newer *seamless* van der Waals density functional (vdW-DF) (Ref. 68) is applicable to any geometries. Kamiya *et al.*³¹ and Sato *et al.*^{33–35} successfully described various weak interac-

tions by applying a damping function to the ALL functional combined with the long-range corrected XC functional. A similar approach with more efficient and rigorous implementation was recently reported by Gräfenstein and Cremer.³⁹ Silvestrelli,^{69,70} and co-workers⁷¹ cleverly simplified the ALL-based dispersion correction using the Wannier functions. On the other hand, the seamless vdW-DF (Ref. 68) has been applied to both extended⁷² and finite^{73,74} systems mainly with revPBE (Ref. 75) XC functional and plane-wave basis. An implementation with Gaussian orbitals was first made by Vydrov *et al.*⁷⁶ Vydrov and van Voorhis³⁶ introduced a modified construction of the seamless functional (vdW-DF-09), achieving accuracy improvement with the LC- ω PBE functional.⁷⁷ Recently, Vydrov and van Voorhis also derived a new analytical form of the seamless functional (VV09) (Ref. 37) based on the physically motivated dielectric model and simpler wavevector screening. A problem shared by nonlocal functional (NLF) approaches is the high computational cost for the explicit evaluation of the double spatial integral. See Refs. 78 and 79 for efficient implementations of vdW-DF (Ref. 68) with pseudoatomic orbitals. A more serious limitation relating to the ALL-type asymptotic functionals^{31,33–35,39} is the lack of general applicability: It requires *a priori* fragmentation of a system to non- (or only weakly) overlapping subsystems.

In the present article, we propose an approach similar to the DFT-D methods, but with dispersion coefficients calculated nonempirically and directly in KS calculations. They are subsequently used for correcting DFT energy with an (exchange-corrected/dispersion-lacking) XC functional via the following form:

$$E_{\text{disp}}[\rho] = - \sum_{a>b} \sum_{n \geq 6} C_n^{ab}[\rho] R_{ab}^n f_{\text{damp}}^{(n)}(R_{ab}), \quad (1)$$

where a and b label atoms. To this end, the atom-atom dispersion coefficients in a molecule are derived based on the same theoretical model employed to derive the ALL-type NLF.^{66,67} One can expect that this approach complements the deficiencies of both empirical DFT-D and NLF approaches mentioned above, allowing efficient and accurate calculations with minimal empiricism. In subsequent sections, we will show that this is in fact the case. Our theory and implementation are detailed in Sec. II, its numerical applications are described in Sec. III, and the concluding remarks with prospects to the future work are given in Sec. IV.

II. THEORY AND IMPLEMENTATION

Let us begin with the second-order dispersion energy expression between isolated (distinguishable) molecules A and B ,

$$E_{\text{disp}}^{AB} = - \sum_m^A \sum_n^B \frac{|\langle m^A n^B | \hat{V}_{AB} | 0^A 0^B \rangle|^2}{\omega_m^A + \omega_n^B}, \quad (2)$$

where \hat{V}_{AB} is the electrostatic interaction operator between molecules A and B , $|0^A\rangle$ and $|m^A\rangle$ are the ground and the m th excited states of the molecule A , and ω_m^A is the corresponding excitation energy, with similarly defined quantities for B . The

atomic units are used throughout in this section. Applying the following integral transformation:

$$\frac{1}{a+b} = \frac{2}{\pi} \int_0^\infty \frac{a}{a^2+u^2} \frac{b}{b^2+u^2} du, \quad (3)$$

Eq. (2) is equivalently expressed as^{80–82}

$$E_{\text{disp}}^{AB} = -\frac{1}{2\pi} \int d\mathbf{r}_1 d\mathbf{r}_1' d\mathbf{r}_2 d\mathbf{r}_2' \times \int_0^\infty du \frac{\chi^A(\mathbf{r}_1, \mathbf{r}_1', iu) \chi^B(\mathbf{r}_2, \mathbf{r}_2', iu)}{|\mathbf{r}_1 - \mathbf{r}_2| \cdot |\mathbf{r}_1' - \mathbf{r}_2'|} \quad (4)$$

in terms of the dynamic density response functions χ^A and χ^B defined by

$$\chi^A(\mathbf{r}, \mathbf{r}', \omega) = 2 \sum_m^A \frac{\omega_m^A}{(\omega_m^A)^2 - \omega^2} \times \langle 0^A | \hat{\rho}^A(\mathbf{r}) | m^A \rangle \langle m^A | \hat{\rho}^A(\mathbf{r}') | 0^A \rangle, \quad (5)$$

with B analogs, where $\hat{\rho}^A(\mathbf{r}) = \sum_i \delta^3(\mathbf{r}_i - \mathbf{r})$ is the density operator. The response function is a complicated quantity, of which calculations require solution of the time-dependent response equation. In order to avoid such a demanding computation, a simple approximation to the response function is required.

A. Review of local response model and its application to nonlocal functional

In 1996, Dobson and Dinte⁶⁷ proposed a local approximation to the response function. In this approximation, the real-space density response is locally expressed in terms of the total electron density ρ as

$$\chi(\mathbf{r}, \mathbf{r}', \omega) = \nabla \cdot \nabla' \left[\frac{\rho(\mathbf{r})}{\omega_0^2(\mathbf{r}) - \omega^2} \delta^3(\mathbf{r} - \mathbf{r}') \right], \quad (6)$$

where ω_0 is the long wavelength limit of the dispersion relation of the dielectric medium. Equation (6) was obtained by forcing the charge conservation and the reciprocity constraints on the response for the homogeneous electron density, which gives the long wavelength limit of the plasmon-pole approximated response in the Fourier space, $\chi(\mathbf{q} \rightarrow 0, \omega) = -q^2 \rho / (\omega_0^2 - \omega^2)$. By utilizing Eq. (6) in the response functions in Eq. (4) and reversely applying the Casimir–Polder transformation of Eq. (3), Dobson and Dinte⁶⁷ derived the following NLF for the asymptotic dispersion energy:

$$E_{\text{disp}}^{AB} = -\frac{3}{32\pi^2} \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\omega_0^A(\mathbf{r}_1) \omega_0^B(\mathbf{r}_2)}{\omega_0^A(\mathbf{r}_1) + \omega_0^B(\mathbf{r}_2)} \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|^6}. \quad (7)$$

The resulting functional was identical to the ALL functional mentioned in Sec. I.⁶⁶ Derivation by ALL (Ref. 66) was based on the approximation to the screened long-range inter-electron interactions, which is equivalent to the approximation to the response function by Dobson and Dinte.⁶⁷

In ALL and the original work of Dobson and Dinte,^{66,67} ω_0 was taken to be the local-plasma frequency, $\omega_p = \sqrt{4\pi\rho}$.

This formulation requires the real-space cutoff introduced by Rapcewicz and Ashcroft⁶⁵ in the integration of the response function,

$$\frac{|\nabla\rho|}{6\rho} \geq \frac{\omega_p}{k_F}, \quad (8)$$

where $k_F = (3\pi^2\rho)^{1/3}$ is the local Fermi wave vector. The cutoff has been incorporated in the direct^{31,33–35} or the smoothed^{39,69,70} manner in practical calculations. However, from our experience,^{33–35} results obtained with this cutoff are sensitive to the implementation at least with the direct approach.^{31,33–35} This is because condition (8) has equality at the spatial points where the response is not small.

In the vdW-DF approach,⁶⁸ the above difficulty has been avoided by the use of a modified dispersion relation and the introduction of the gradient correction. The latter has been the key to the seamless theory.⁸³ In the present study, we focus on the simplified dispersion relation recently proposed by Vydrov and van Voorhis,³⁶ of which the long wavelength limit reads

$$\omega_0(\mathbf{r}) = \frac{q_0^2(\mathbf{r})}{3}, \quad q_0(\mathbf{r}) = k_F(1 + \lambda s^2), \quad (9)$$

where $s = |\nabla\rho| / (2k_F\rho)$ is the reduced density gradient and λ is an empirical parameter introduced for adjusting decay of the response at the density tail.

B. Derivation of atom-atom expression of dispersion energy

A key to the atom-atom expression of the dispersion energy is a multicenter multipole expansion of the intermolecular Coulomb operator.^{84–87} A molecular volume has to be divided or *distributed* into constituent atoms somehow. For this purpose, we adopt the atomic partition function used in XC numerical quadrature.⁸⁸ Thus, Coulomb interaction between electrons at \mathbf{r}_1 in molecule A and \mathbf{r}_2 in molecule B reads

$$\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = \sum_a^A \sum_b^B \frac{w_a(\mathbf{r}_1) w_b(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} = \sum_a^A \sum_b^B \frac{w_a(\mathbf{r}_1) w_b(\mathbf{r}_2)}{|\mathbf{R}_{ab} - \mathbf{r}_{a1} + \mathbf{r}_{b2}|}, \quad (10)$$

where we insert the normalization conditions $\sum_a^A w_a(\mathbf{r}_1) = 1$ (also for b/B) of Becke-type function,⁸⁸ and rewrite vectors using $\mathbf{R}_{ab} = \mathbf{R}_b - \mathbf{R}_a$, $\mathbf{r}_{a1} = \mathbf{r}_1 - \mathbf{R}_a$, and $\mathbf{r}_{b2} = \mathbf{r}_2 - \mathbf{R}_b$, with \mathbf{R}_a and \mathbf{R}_b being position vectors of atoms a and b . Here and in the following, labels $\{a, a'\}$ and $\{b, b'\}$ are used for atoms belonging to molecules A and B , respectively. All vectors, multipole moments, and polarizabilities are in the space-fixed global coordinate system.

Being scaled by the weight functions inside summations of Eq. (10), the Coulomb operator is reasonably expanded on its centers a and b . Such an expansion in terms of spherical harmonics is a well-established matter. We follow Stone's book¹ within the required generality for our purpose. We have

$$\frac{1}{|\mathbf{R}_{ab} - \mathbf{r}_{a1} + \mathbf{r}_{b2}|} = \sum_{l_1=0}^{\infty} \sum_{l_2=0}^{\infty} R_{ab}^{-l_1-l_2-1} \sum_{m_1 m_2} S_{m_1 m_2}^{ab(l_1 l_2)} \times R_{m_1}^{(l_1)}(\mathbf{r}_{a1}) R_{m_2}^{(l_2)}(\mathbf{r}_{b2}), \quad (11)$$

where R_{ab} is the internuclear distance, $R_{m_1}^{(l_1)}$ is the regular solid harmonics, and the angular factor $S_{m_1 m_2}^{ab(l_1 l_2)}$ is defined by

$$S_{m_1 m_2}^{ab(l_1 l_2)} = (-1)^{l_1} \left[\frac{(2l_1 + 2l_2 + 1)!}{(2l_1)! (2l_2)!} \right]^{1/2} \delta_{L, l_1 + l_2} \times \begin{pmatrix} l_1 & l_2 & L \\ m_1 & m_2 & M \end{pmatrix} C_M^{(L)}(\hat{\mathbf{R}}_{ab}), \quad (12)$$

where the 2×3 matrix is Wigner's 3-j symbol and $C_M^{(L)}$ is the spherical harmonics with Racah's normalization factor evaluated at the polar angles of the unit vector $\hat{\mathbf{R}}_{ab} = \mathbf{R}_{ab}/R_{ab}$.

Using Eqs. (10)–(12) for intermolecular Coulomb operators in Eq. (4), the dispersion energy between molecules A and B is expanded in terms of multipole moments centered on atoms $\{a\}$ in A and $\{b\}$ in B,

$$E_{\text{disp}}^{AB} = -\frac{1}{2\pi} \sum_{aa'}^A \sum_{bb'}^B \sum_{l_1 l_1'} \sum_{l_2 l_2'} R_{ab}^{-l_1-l_2-1} R_{a'b'}^{-l_1'-l_2'-1} \times \sum_{m_1 m_1'} \sum_{m_2 m_2'} S_{m_1 m_2}^{ab(l_1 l_2)} S_{m_1' m_2'}^{a'b'(l_1' l_2')} \times \int_0^\infty \alpha_{m_1 m_1'}^{aa'(l_1 l_1')}(iu) \alpha_{m_2 m_2'}^{bb'(l_2 l_2')}(iu) du. \quad (13)$$

Here, $\alpha_{mm'}^{aa'(l'l')}$ is given by

$$\alpha_{mm'}^{aa'(l'l')}(iu) = \int d\mathbf{r} \int d\mathbf{r}' w_a(\mathbf{r}) w_{a'}(\mathbf{r}') \chi^A(\mathbf{r}, \mathbf{r}', iu) \times R_m^{(l)}(\mathbf{r} - \mathbf{R}_a) R_{m'}^{(l')}(\mathbf{r}' - \mathbf{R}_{a'}), \quad (14)$$

which is interpreted as distributed polarizability. Equation (13) has the *nonlocal* dependence^{82,84} on the atom-atom distances involving R_{ab} and $R_{a'b'}$. This is because the second-order energy involves two intermolecular operators. In order to obtain the convenient additive atom-atom expression of Eq. (1), the polarizabilities have to be localized. Here, this is achieved by relying on the local response model discussed in Sec. II A. Substituting Eq. (6) into Eq. (14), we have

$$\alpha_{mm'}^{aa'(l'l')}(iu) = \int d\mathbf{r} \int d\mathbf{r}' w_a(\mathbf{r}) w_{a'}(\mathbf{r}') \times \nabla \cdot \nabla' \left[\frac{\rho(\mathbf{r})}{\omega_0^2(\mathbf{r}) + u^2} \delta^3(\mathbf{r} - \mathbf{r}') \right] \times R_m^{(l)}(\mathbf{r} - \mathbf{R}_a) R_{m'}^{(l')}(\mathbf{r}' - \mathbf{R}_{a'}) = \int d\mathbf{r} w_a(\mathbf{r}) w_{a'}(\mathbf{r}) \frac{\rho(\mathbf{r})}{\omega_0^2(\mathbf{r}) + u^2} \times \nabla R_m^{(l)}(\mathbf{r} - \mathbf{R}_a) \cdot \nabla R_{m'}^{(l')}(\mathbf{r} - \mathbf{R}_{a'}). \quad (15)$$

In deriving the second equation, we integrate by parts on each space variable and then use the delta function, essentially following the derivation of Eq. (7) by Dobson and Dinte.⁶⁷ The exponential decay of the polarization density $\rho/(\omega_0^2 + u^2)$ at the density tail³⁶ is also utilized. Note that the weight function derivative terms are ignored, discarding some contributions from the overlapping region of the weight functions on different centers. If we further assume $w_a(\mathbf{r}) w_{a'}(\mathbf{r}) \approx \delta_{aa'} w_a^2(\mathbf{r})$, different weight functions do not overlap significantly and/or contributions from such region are small, the off-diagonal blocks of polarizabilities can be omitted as $\alpha^{aa'} = \delta_{aa'} \alpha^a$ with

$$\alpha_{mm'}^{a(l'l')}(iu) = \int d\mathbf{r} w_a^2(\mathbf{r}) \frac{\rho(\mathbf{r})}{\omega_0^2(\mathbf{r}) + u^2} \times \nabla R_m^{(l)}(\mathbf{r} - \mathbf{R}_a) \cdot \nabla R_{m'}^{(l')}(\mathbf{r} - \mathbf{R}_a). \quad (16)$$

Equation (13) is then simplified to the desired atom-atom dispersion expression,

$$E_{\text{disp}}^{AB} = \sum_a^A \sum_b^B \sum_{n \geq 6} C_n^{ab} R_{ab}^{-n}, \quad (17)$$

where the n th order interaction consists of contributions from various multipole-multipole interactions,

$$C_n^{ab} = \sum_{l_1 l_1' l_2 l_2'} C^{ab}(l_1 l_1', l_2 l_2'), \quad (18)$$

with $l_1 + l_1' + l_2 + l_2' + 2 = n$. Finally, $C^{ab}(l_1 l_1', l_2 l_2')$ is given in terms of imaginary frequency integrals of the product of atomic polarizabilities,

$$C^{ab}(l_1 l_1', l_2 l_2') = \frac{1}{2\pi} \sum_{m_1 m_1' m_2 m_2'} S_{m_1 m_2}^{ab(l_1 l_2)} S_{m_1' m_2'}^{ab(l_1' l_2')} \times \int_0^\infty \alpha_{m_1 m_1'}^{a(l_1 l_1')}(iu) \alpha_{m_2 m_2'}^{b(l_2 l_2')}(iu) du. \quad (19)$$

At this moment, we note the crucial difference between Eqs. (1) and (17) (apart from the damping function). The latter is for the dispersion energy between isolated two molecules. It does not apply to *intramolecular* interactions from the beginning of derivation: Eq. (2). Nevertheless, we dare to extend it to intramolecular interactions by eliminating the restriction for atomic labels in Eq. (17) and using the total (rather than monomer) weight functions and the electron density in Eq. (16). This is inspired by the success of empirical DFT-D approaches,^{38,55–58} where such an intramolecular expression is intrinsically assumed. It seems possible to justify this extension for a well-separated pair of atoms for which the antisymmetry of the wave function gets irrelevant. For a pair of nearby atoms, such as those directly connected by a chemical bond, the treatment is clearly inappropriate. We have to rely on the damping function discussed in Sec. II C.

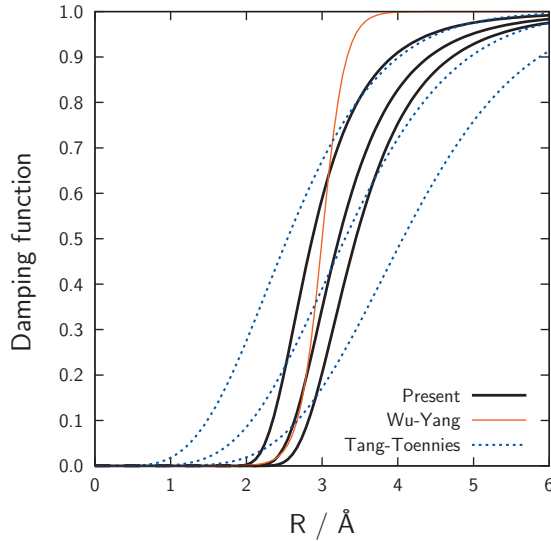


FIG. 1. Comparison of damping functions. Deep solid: functions used in the present work, Eq. (22), with $n=6, 8$, and 10 from the leftmost. Fine solid: Wu-Yang function, Eq. (20). Dotted: Tang-Toennies functions, Eq. (21), with $n=6, 8$, and 10 from the leftmost.

C. Damping function

The most widely used damping function in DFT-D approaches is the Fermi-type function first proposed by Wu and Yang,⁵⁴

$$f_{\text{damp}}(R_{ab}) = \frac{1}{1 + \exp[-d(R_{ab}/\bar{R} - 1)]}, \quad (20)$$

where parameters d and \bar{R} determine the shape and position of the switching region, respectively. The function converges to zero quickly at the short distance. In spite of success in many DFT-D studies,^{55–58} we found in our preliminary test that this function was not suited for damping higher-order interactions beyond C_6/R^6 . This is because the function is too steep with a reasonable d value ($d=20-25$; necessary for a good behavior of C_6 terms). This is shown in Fig. 1, in which the Fermi-type function as well as other two types of functions introduced shortly (optimized for neon dimer interaction) are compared. On the other hand, the older HF-D approaches^{89–92} often incorporated higher-order terms for intermolecular interactions and various damping functions have been proposed. Among them is the one proposed by Tang and Toennies,⁹³

$$f_{\text{damp}}^{(n)}(R_{ab}) = 1 - \left[\sum_{k=0}^n \frac{1}{k!} \left(\frac{R_{ab}}{\bar{R}} \right)^k \right] \exp\left(-\frac{R_{ab}}{\bar{R}}\right). \quad (21)$$

In our test calculations, the Tang and Toennies (TT) function was found to work well for rare-gas interactions. However, in contrast to the Fermi-type function, the TT function decays too slowly at the short distance (see Fig. 1), hence is inappropriate for damping intramolecular interactions. In order to supplement the above two types of damping functions, we make an arbitrary choice of the following exponential form:

$$f_{\text{damp}}^{(n)}(R_{ab}) = \exp\left[-m\left(\frac{R_{ab}}{\bar{R}}\right)^{-6}\right], \quad n = 2m + 4, \quad (22)$$

which is, with $n=6$, identical to the function proposed by Kamiya *et al.*³¹ As shown in Fig. 1, the new damping function varies slowly at long distance and vanishes quickly inside the critical point. We notice that the function proposed by Chai and Head-Gordon³⁸ shows a similar behavior as the present damping function.

For the effective radii, \bar{R} , predetermined free atomic radii are often used. However, the damping function should take into account the effects of molecular environment. Tkatchenko and Schffler⁹⁴ realized this by noting the relation between polarizability and volume⁹⁵ and employing the Hirshfeld partitioning of the electron density for the latter. A similar idea was also proposed by Johnson and Becke.⁹⁶ For the same purpose, we use the information from the local response of Sec. II B,

$$\bar{R} = \kappa[(\alpha_a^{\text{eff}})^{1/3} + (\alpha_b^{\text{eff}})^{1/3}] + R_0, \quad (23)$$

where $\alpha_a^{\text{eff}} = 1/3 \text{Tr}[\alpha^{a(11)}(0)]$ is from Eq. (16) evaluated at zero frequency, which should correspond to the average dipole polarizability of an atom in a molecule. κ and R_0 are global constants which should be determined empirically. These parameters are discussed in Sec. III.

We call the method described thus far the local response dispersion (LRD) method. It is defined by the use of Eq. (1) and followings:

- (1) local response approximation of Eq. (6) with the dielectric model of Eq. (9);
- (2) dispersion coefficients determined by Eqs. (16), (18), and (19) using Becke-type atomic partition function;
- (3) damping by Eqs. (22) and (23).

D. Implementation

Now we briefly describe our implementation of the LRD method. In the present study, we restrict atomic polarizabilities of Eq. (16) to those having two identical multipole rank, $\alpha_{mm'}^{a(l_l)}$. Thus Eqs. (18) and (19) are brought together as

$$C_n^{ab} = \sum_{l_1 l_2} \sum_{m_1 m_2} \sum_{m'_1 m'_2} S_{m_1 m_2}^{ab(l_1 l_2)} I_{m_1 m_2, m'_1 m'_2}^{ab(l_1 l_2)} S_{m'_1 m'_2}^{ab(l_1 l_2)}, \quad (24)$$

where $l_1 + l_2 + 1 = n/2$ and the Casimir-Polder-type integral $I_{m_1 m_2, m'_1 m'_2}^{ab(l_1 l_2)}$ is given by

$$I_{m_1 m_2, m'_1 m'_2}^{ab(l_1 l_2)} = \frac{1}{2\pi} \int_0^\infty \alpha_{m_1 m_1}^{a(l_1 l_1)}(iu) \alpha_{m_2 m_2}^{b(l_2 l_2)}(iu) du. \quad (25)$$

The restriction is reasonable since the terms in Eq. (16) make by far the dominant contribution. Due to this simplification, the number of polarizability elements for each atom is significantly reduced.

To facilitate the evaluation of Eq. (25) we change the variable to $t = u / \sqrt{1 + u^2}$ and note that the integrand is an even function, then

$$I_{m_1 m_2, m'_1 m'_2}^{ab(l_1 l_2)} = \frac{1}{4\pi} \int_{-1}^1 \frac{dt}{\sqrt{1-t^2}} \bar{\alpha}_{m_1 m'_1}^{a(l_1)}(t) \bar{\alpha}_{m_2 m'_2}^{b(l_2)}(t), \quad (26)$$

and

$$\begin{aligned} \bar{\alpha}_{mm'}^{a(l)}(t) &\equiv (1-t^2)^{-1/2} \alpha_{mm'}^{a(l)}(iu) \\ &= \int d\mathbf{r} w_a^2(\mathbf{r}) \frac{(1-t^2)^{1/2} \rho(\mathbf{r})}{(1-t^2) \omega_0^2(\mathbf{r}) + t^2} \\ &\quad \times \nabla R_m^{(l)}(\mathbf{r} - \mathbf{R}_a) \cdot \nabla R_{m'}^{(l)}(\mathbf{r} - \mathbf{R}_a), \end{aligned} \quad (27)$$

which is calculated by means of a usual single-center integration technique used in the evaluation of XC functional. Explicitly applying the Gauss–Chebyshev rule to Eq. (26) gives

$$I_{m_1 m_2, m'_1 m'_2}^{ab(l_1 l_2)} = \frac{1}{4N} \sum_{k=1}^N \bar{\alpha}_{m_1 m'_1}^{a(l_1)}(t_k) \bar{\alpha}_{m_2 m'_2}^{b(l_2)}(t_k), \quad (28)$$

with N quadrature points, $t_k = \cos[(2k-1)/4N\pi]$.

In the present study, the LRD method is implemented in a post-KS manner. The computational cost for the method is expected to be similar to that for a single XC energy calculation since the atomic polarizabilities of Eq. (27) at N required frequencies are calculated simultaneously by (partition function-aided) single-center integrations as in (grid-based) XC energy calculations. The evaluation of the integrand of Eq. (27), given the density and density gradient, is an $O(n^0)$ procedure at each spatial grid point, where n measures the system size, and inexpensive relative to the formally $O(n^2)$ density evaluation. Importantly, the density formation can be shared with XC energy and potential matrix evaluation in realizing a self-consistent field (SCF) implementation of the LRD method. Costs for Eqs. (1), (24), and (28) are negligibly small. In consequence, the LRD method is capable of calculating the dispersion energy with small additional cost to a usual KS calculation.

E. Comparison with similar approaches

At the end of this section, we compare the LRD method with other similar approaches for the dispersion problem of DFT. First, the LRD method shares much philosophy with the XDM model of Becke and Johnson,^{59,60,96–98} which also obtains the system-dependent dispersion coefficients from the electron density⁶⁰ or from the occupied orbitals.⁵⁹ Theoretical investigations of the XDM model by Ángyán⁸⁷ and Heßelmann⁹⁹ clarified the closely relating physics underlying the local response⁶⁷ and XDM (Ref. 59) models.

Next, we have to be back to the original work by ALL,⁶⁶ in which the authors already used the local response model to compute the average C_6 coefficients between numbers of molecules. Recently Vydrov and van Voorhis³⁶ also reported C_6 values based on exactly the same model employed in the present work, Eq. (9). In this sense, the LRD method is only an extension of the previous work to (i) general multipole interactions (ii) between atoms in a molecule. However, these extensions are crucial for the method to be practically useful, as shown in Sec. III.

It is worth mentioning that the imaginary frequency integrals in Eq. (19) are easily avoidable by a reverse use of the Casimir–Polder integral transformation, Eq. (3), just as in deriving ALL functional.^{66,67} The average dipole-dipole interaction, for example, is then given by

$$\begin{aligned} C_6^{ab} &= \frac{3}{2} \int \int d\mathbf{r}_1 d\mathbf{r}_2 w_a^2(\mathbf{r}_1) w_b^2(\mathbf{r}_2) \\ &\quad \times \frac{\rho(\mathbf{r}_1) \rho(\mathbf{r}_2)}{\omega_0(\mathbf{r}_1) \omega_0(\mathbf{r}_2) [\omega_0(\mathbf{r}_1) + \omega_0(\mathbf{r}_2)]}, \end{aligned} \quad (29)$$

which is essentially what Vydrov and van Voorhis³⁶ noted for intermolecular interactions. The proposition of the current work is the calculation of multipole polarizabilities for each atom followed by the explicit Casimir–Polder integration, which is more efficient than the double spatial integrals such as Eq. (29) while not sacrificing the accuracy. Silvestrelli and co-workers^{69,70} took a different route. Their use of the maximally localized Wannier function formalism¹⁰⁰ allows analytical representation of the localized polarization density, reducing the computational cost for the analogs of Eq. (29) without reintroducing the frequency integral.

III. RESULTS AND DISCUSSIONS

In this section, the LRD method described thus far is numerically applied to calculations of several weakly bound systems. Although the LRD method can be combined with any XC functionals, the LC-BOP (Ref. 32) functional [short-range Becke-88 (Ref. 9) plus long-range HF exchanges with one-parameter progressive (OP) correlation¹⁰¹ functional] is employed throughout this study (LC-BOP+LRD). The range-separation parameter of $\mu=0.47$ a.u. in the LC scheme is taken from Ref. 102. The NLF of Eq. (7) is also examined (LC-BOP+NLF) for comparison. The NLF is numerically calculated as described in Ref. 35 using the grid-wise damping function with cutoff parameters optimized as $C_1=0.4294$ and $C_2=3.226$ a.u. following the procedure detailed therein.³⁵

All calculations are performed with the modified version of GAUSSIAN 03 program package,¹⁰³ in which the LC scheme, the OP correlation functional, the LRD method, and NLF of Eq. (7) are locally implemented. The KS-SCF calculations are converged with the “tight” option.¹⁰³ The reduced 99×590 grids^{104,105} are used unless otherwise noted for spatial integrals in XC, LRD, and NLF computations with Becke’s atomic partition function.⁸⁸ All the reported interaction energies are corrected for the basis set superposition error by counterpoise method.¹⁰⁶ Further details of computations are presented separately.

A. Rare-gas diatoms: Parameter fitting

Before proceeding to calculations of real interests, several parameters left unfixed are determined in this subsection based on calculations of rare-gas diatoms: He–He, He–Ne, He–Ar, Ne–Ne, Ne–Ar, and Ar–Ar. The rare-gas diatoms are ideal systems for setting up the LRD method since the only source of attractions is the dispersion interaction. The aug-cc-pVQZ basis set is used in this subsection.

TABLE I. C_6 dispersion coefficients (a.u.) of rare-gas diatoms calculated using Eq. (29) (using the LC-BOP/aug-cc-pVQZ SCF density). Experimental results (from Ref. 107) are also shown for comparison.

	He-He	He-Ne	He-Ar	Ne-Ne	Ne-Ar	Ar-Ar
This work	1.543	3.047	9.539	6.119	18.60	59.77
Experiment ^a	1.458	3.029	9.538	6.383	19.50	64.30

^aDOSD values from Ref. 107.

Following Vydrov and van Voorhis,³⁶ the parameter λ was fixed to give accurate C_6 coefficients for the six rare-gas diatoms. To avoid errors due to finite N and weight functions in Eq. (27), the average C_6 coefficients were calculated using Eq. (29) with a large (100 Å) internuclear distance. The smallest mean absolute percent error of 3.7% relative to the experimental values was obtained with $\lambda=0.232$ a.u. This is near $\lambda=0.22$ a.u. obtained using the LC- ω PBE functional and a larger benchmark set.³⁶ The C_6 coefficients calculated with this value of λ are listed in Table I.

Next, the C_6 , C_8 , and C_{10} coefficients between rare-gas diatoms (100 Å parted) were calculated using Eqs. (24) and (28), with various values of N . The results for neon dimer are shown in Table II. As seen in the table, calculated dispersion coefficients converge rapidly to the values obtained with Eq. (29) and its analogs for C_8 and C_{10} , which correspond to the exact integration of Eq. (26). In the following calculations, $N=12$ is used unless otherwise noted.

Table II reveals disappointing failure in reproducing *ab initio* C_8 and C_{10} . This was also found for other rare-gas diatoms. In contrast, Becke and Johnson^{97,98} obtained reasonable values for the higher-order coefficients. We note that the problem is not due to the multipole expansion, rather it is reflecting the intrinsic accuracy of the local response approximation of Eqs. (6) and (9). This point is clearly shown in Fig. 2, in which the potential energy curves of neon dimer obtained by the LC-BOP, the LC-BOP+LRD without damping, and the LC-BOP+NLF are compared to the CCSD(T) potential.¹⁰⁹ As shown in the inset of Fig. 2, at the long distance, the LC-BOP+LRD potential curves converge to the LC-BOP+NLF curve in increasing the interaction order. This reflects the fact that the LRD corresponds to the multipole expansion of the NLF of Eq. (7) for interactions be-

TABLE II. Dispersion coefficients (a.u.) of neon dimer calculated using Eqs. (24), (27), and (28) (using the LC-BOP/aug-cc-pVQZ SCF density), varying N in Eq. (28).

N	C_6	C_8	C_{10}
6	6.1312	163.20	3264.3
8	6.1228	163.13	3263.7
10	6.1204	163.11	3263.6
12	6.1196	163.10	3263.6
14	6.1193	163.10	3263.6
16	6.1191	163.10	3263.6
18	6.1191	163.10	3263.6
∞^a	6.1189	163.10	3263.5
Reference ^b	6.5527	90.344	1535.6

^aFrom Eq. (29) and its analogs to C_8 and C_{10} .^bMany-body perturbation theory values from Ref. 108. DOSD value reads $C_6=6.383$ in Ref. 107.

tween free atoms. The overestimation of higher-order coefficients in Table II is consistent with the overstabilized LC-BOP+NLF potential compared to the CCSD(T) curve. However, the overall agreement of LC-BOP+NLF and CCSD(T) potential curves is reasonably good. This fact, with previous success of similar LC-BOP+ALL approach,^{31,33–35} leaves us optimistic about the above disagreement.

For practical applications of the LRD method, the multipole expansion has to be truncated at a certain order. As seen in Fig. 2, inclusion of higher-order interactions results in better agreement with the NLF at the long range but encounters severe divergence at the short range. Considering these aspects, in the present article, we truncate the expansion after C_{10} terms and use the damping function of the exponential form discussed in Sec. II. In order to fix the parameters in Eq. (23), we first optimized \bar{R} values in Eq. (22) for each rare-gas interaction to reproduce the experimental equilibrium distances.^{110,111} Then the optimal values were least square fitted to the linear form of Eq. (23) with the polarizabilities of constituent atoms calculated at the equilibrium distance. The fitting was nicely done with an R^2 value greater than 0.989, giving $\kappa=0.64192$ a.u. and $R_0=3.2925$ a.u.

Potential energy curves of neon dimer obtained by the LC-BOP+LRD including the damping function are shown in Fig. 3. The LC-BOP+LRD curve with up to C_{10} contributions well reproduces the CCSD(T) curve. Other rare-gas diatoms were also described accurately. In Table III, the

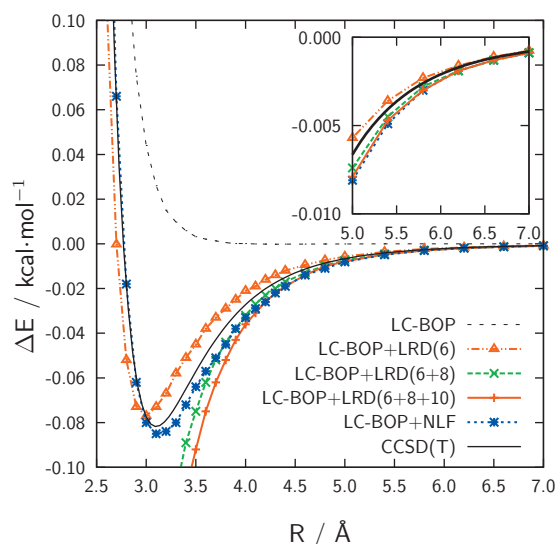


FIG. 2. Potential energy curves of Ne dimer calculated by the LC-BOP, the LC-BOP+LRD without damping, and the LC-BOP+NLF. The CCSD(T) curve from Ref. 109 is also shown for comparison. The upper-right inset is a closer view of the curves at the long distance region.

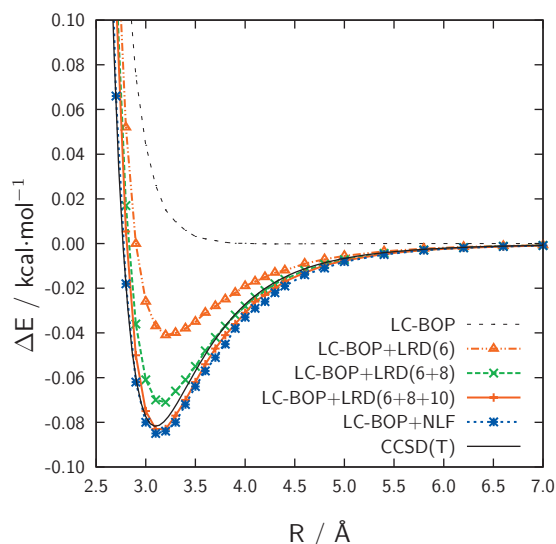


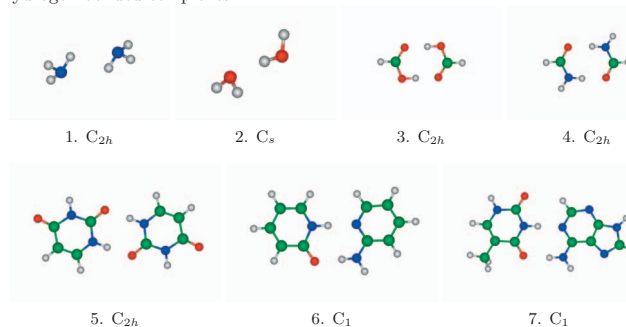
FIG. 3. Potential energy curves of Ne dimer calculated by the LC-BOP, the LC-BOP+LRD with damping, and the LC-BOP+NLF. The CCSD(T) curve from Ref. 109 is also shown for comparison.

binding energies and equilibrium bond distances of the rare-gas diatoms calculated by the LC-BOP+LRD are listed with the CCSD(T) results.¹⁰⁹ The mean absolute deviations (MADs) from the CCSD(T) results for binding energies and bond distances are 0.013 kcal/mol and 0.04 Å, respectively.

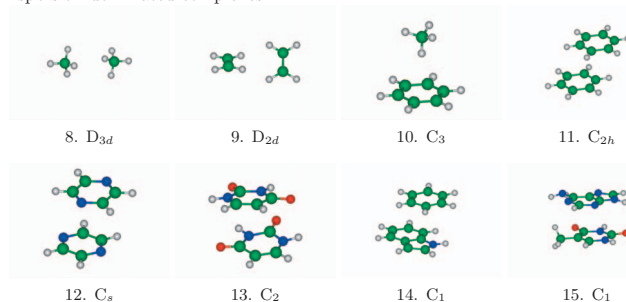
B. S22 database: Initial application

In this subsection, the LC-BOP+LRD method is applied to interaction energy (ΔE) calculations of S22 database complexes introduced by Jurečka *et al.*¹¹² The database has been constructed to be a reliable accuracy checker of a newly developed method. It includes 22 weakly bound complexes conveniently grouped into hydrogen-bonded, dispersion-dominated, and mixed complexes. Figure 4 shows the geometries of the complexes with their point group symmetries. The estimated complete basis set limit CCSD(T) ΔE 's reported in Ref. 112 are accurate enough (with errors within few tenths of kcal/mol) for judging the overall performance of a tested method. The 6-311++G(3df,3pd) basis set is used in this subsection. Single-point energy calculations are performed at the reference geometries. The LC-BOP+LRD ΔE calculations are performed within a supermolecular approach: The total energies including dispersion contributions from Eq. (1) calculated for a dimer and monomers are sub-

Hydrogen-bonded complexes



Dispersion-dominated complexes



Mixed complexes

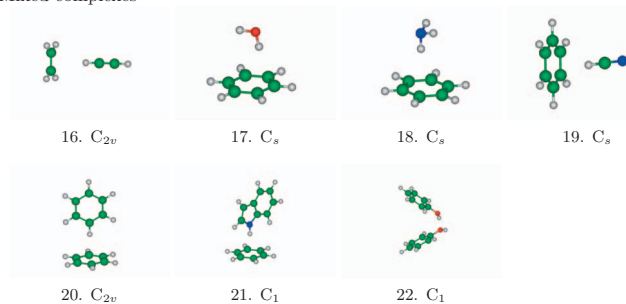


FIG. 4. Structures of complexes in S22 database taken from the supporting information of Ref. 112, with the point group symmetries.

tracted. This is different from the LC-BOP+NLF calculations, in which the NLF is explicitly applied between pre-indicated monomers and added to the supermolecular LC-BOP ΔE .^{33–35}

In Table IV, ΔE 's of S22 molecules calculated by the LC-BOP, the LC-BOP+LRD with up to C_6 , C_8 , and C_{10} contributions, and the LC-BOP+NLF are listed with the reference CCSD(T) results. The LC-BOP functional totally underestimates ΔE 's, showing the general importance of the dispersion interaction. Inclusion of the C_6 terms roughly halves the MAD and mean absolute percentage deviation

TABLE III. Binding energies (kcal/mol) and equilibrium bond lengths (Å) of rare-gas diatoms calculated by the LC-BOP+LRD/aug-cc-pVQZ. The CCSD(T) results (from Ref. 109) are also shown for comparison.

	He–He	He–Ne	He–Ar	Ne–Ne	Ne–Ar	Ar–Ar
Binding energy						
LC-BOP+LRD	0.025	0.047	0.074	0.086	0.147	0.306
CCSD(T) ^a	0.021	0.042	0.059	0.082	0.129	0.277
Equilibrium bond length						
LC-BOP+LRD	3.03	3.07	3.50	3.14	3.52	3.85
CCSD(T) ^a	2.98	3.03	3.49	3.10	3.50	3.78

^aReference 109.

TABLE IV. Interaction energies (kcal/mol) of S22 complexes calculated by the LC-BOP, the LC-BOP+LRD, and the LC-BOP+NLF methods [with 6-311++G(3df,3pd) basis set]. Estimated CCSD(T)/complete basis set values (from Ref. 112) are also listed for comparison.

		LC-BOP+LRD				LC-BOP+NLF	CCSD(T) ^d
		LC-BOP	6 ^a	6+8 ^b	6+8+10 ^c		
Hydrogen-bonded complexes							
1	(NH ₃) ₂	-2.50	-2.82	-2.95	-3.01	-3.17	-3.17
2	(H ₂ O) ₂	-4.88	-5.09	-5.19	-5.23	-5.33	-5.02
3	(HCOOH) ₂	-18.94	-19.77	-20.11	-20.24	-20.58	-18.61
4	(HCONH ₂) ₂	-14.89	-15.75	-16.10	-16.23	-16.65	-15.96
5	Uracil dimer	-18.70	-19.94	-20.42	-20.59	-20.96	-20.65
6	2-pyridoxine-2-aminopyridine	-14.30	-15.80	-16.41	-16.64	-17.07	-16.71
7	A-T WC	-13.64	-15.32	-16.01	-16.29	-16.71	-16.37
Dispersion-dominant complexes							
8	(CH ₄) ₂	0.10	-0.31	-0.54	-0.63	-0.61	-0.53
9	(C ₂ H ₄) ₂	-0.15	-0.95	-1.33	-1.47	-1.65	-1.51
10	Benzene-CH ₄	0.11	-0.81	-1.27	-1.45	-1.78	-1.50
11	PD-benzene dimmer	2.20	-0.18	-1.86	-2.86	-2.89	-2.73
12	Pyrazine dimmer	0.73	-1.72	-3.39	-4.33	-4.18	-4.42
13	Stacked uracil dimmer	-3.29	-6.64	-8.78	-9.93	-9.98	-10.12
14	Stacked indole-benzene	2.55	-0.88	-3.28	-4.51	-4.57	-5.22
15	Stacked A-T	-2.14	-7.15	-10.33	-11.93	-11.90	-12.23
Mixed complexes							
16	Ethene-ethyne	-0.86	-1.30	-1.54	-1.63	-1.64	-1.53
17	Benzene-H ₂ O	-2.08	-2.95	-3.43	-3.66	-3.74	-3.28
18	Benzene-NH ₃	-0.88	-1.78	-2.27	-2.49	-2.68	-2.35
19	Benzene-HCN	-3.17	-4.17	-4.65	-4.87	-5.24	-4.46
20	T-shaped benzene dimmer	-0.05	-1.49	-2.20	-2.48	-3.02	-2.74
21	T-shaped indole-benzene	-1.95	-3.84	-4.74	-5.13	-5.79	-5.73
22	Phenol dimer	-4.29	-5.93	-6.75	-7.11	-7.39	-7.05
Overall							
MD ^c	(kcal/mol)	2.77	1.24	0.38	-0.04	-0.26	
MAD ^f	(kcal/mol)	2.80	1.35	0.58	0.27	0.38	
Range ^g	(kcal/mol)	10.42	6.24	3.44	2.34	2.62	
MPD ^h	(%)	61.7	27.7	8.2	-0.9	-5.7	
MAPD ⁱ	(%)	61.8	28.4	10.4	5.7	7.6	

^aWith C₆ terms.

^bWith C₆ and C₈ terms.

^cWith C₆, C₈, and C₁₀ terms.

^dFrom Ref. 112.

^eMean deviation from the CCSD(T) values.

^fMean absolute deviation.

^gThe largest positive minus the largest negative deviations.

^hMean percentage deviation.

ⁱMean absolute percentage deviation.

(MAPD) from the CCSD(T) ΔE 's, but still leaves large underestimations especially for the dispersion-dominated complexes. This is unlike the good performance with only C₆ terms in empirical DFT-D approaches,^{38,56,57} in which the strength^{56,57} and/or the damping^{38,55–58} of the C₆ interactions are optimized without higher-order terms. It is encouraging that inclusions of C₈ and C₁₀ terms steadily reduce the deviations from the CCSD(T) ΔE 's for all types of interactions. The MAD and MAPD for the full dataset obtained by the LC-BOP+LRD (implying inclusion of up to C₁₀ terms from here on) are only 0.27 kcal/mol and 5.7%, respectively. The accuracy is comparable to those reported for other recent approaches. For instance, among the work on empirical dis-

persion correction, MAD (MAPD) values obtained for the S22 set by wB97XD (Ref. 38) and B97D (Ref. 57) functionals have been reported³⁸ to be 0.22 kcal/mol (5.4%) and 0.50 kcal/mol (6.4%), respectively [with 6-311++G(3df,3pd) basis, counterpoise corrected]. The series of Minnesota hybrid meta-GGA functionals, e.g., M05-2X (Ref. 113) and M06-2X,⁴⁵ have shown similar performance.

We emphasize the notable agreement between LC-BOP+LRD and LC-BOP+NLF ΔE 's, especially for the stacking interactions (Nos. 11–15). This suggests the adequacy of the seemingly drastic assumption of the *local* atomic polarizability; see discussions above Eq. (16). The larger difference [relative to the CCSD(T) ΔE] between LRD and NLF dis-

TABLE V. Interaction energies (kcal/mol) of stacked adenine-thymine dimer calculated by the LC-BOP+LRD and the LC-BOP+NLF methods [with 6-311++G(3df,3pd) basis set], and CPU time (on power 6/4.7GHz machine) (second) for the LRD and NLF dispersion corrections, varying N in Eq. (28).

Method	N	ΔE	CPU time	
			Pol ^a	Sum ^b
LC-BOP+LRD	6	-11.63	193.2	0.3
	8	-11.82	193.2	0.3
	10	-11.90	193.4	0.4
	12	-11.93	193.6	0.4
	14	-11.95	193.8	0.5
	16	-11.95	194.0	0.5
	18	-11.96	194.2	0.6
LC-BOP+NLF		-11.90	192.4	1014.5

^aCPU time for calculating atomic polarizabilities of Eq. (27) for the LRD or preparing the integrand of Eq. (7) for the NLF.

^bCPU time for numerical evaluation of Eqs. (1), (24), and (28) for the LRD or that of Eq. (7) for the NLF.

persion corrections are found for so-called XH- π interactions (Nos. 19–21). The difference is mainly due to the different short-range damping: The damping has a stronger impact on calculated ΔE 's for these spatially closer interactions. On the other hand, the hydrogen-bonded complexes, which involve even shorter interactions, are described similarly with both methods, reflecting the minor importance of the dispersion interaction in these complexes.

Efficiency of the LRD method is highlighted in Table V, which summarizes the calculation of stacked adenine-thymine complex (No. 15). In the third column of the table, ΔE 's calculated by the LC-BOP+LRD (with various number N of Gauss–Chebyshev quadrature points) and the LC-BOP+NLF are listed. In increasing N , the LC-BOP+LRD ΔE 's come close to the LC-BOP+NLF one. The default value of $N=12$ is justified here. The fourth and fifth columns show central processor unit (CPU) times for two computational bottlenecks in the LRD and NLF computations, respectively. These two steps for the LRD procedure are the calculation of atomic polarizabilities of Eq. (27) [Pol] and evaluation of Eqs. (1), (24), and (28) [Sum], while those for the NLF are the preparation of the integrand [Pol] and the doubly numerical evaluation [Sum] of Eq. (7). Comparison of the “Sum” parts of CPU times for the LRD and NLF makes clear the benefit of replacing the computationally demanding double spatial integral with atomic pair summations. It is also noted that the “Pol” timings increase only marginally against N , which indicates that the cost for Eq. (27) is dominated by the N -independent procedure, i.e., the density evaluation at the spatial grid points. This numerically confirms the theoretical arguments made at the end of Sec. II D.

IV. CONCLUSIONS

In this article, we propose a new method for calculating system-dependent dispersion coefficients between atoms in a molecule, called the LRD method. Based on the local response approximation due to Dobson and Dinte,⁶⁷ the modi-

fied dispersion relation of Vydrov and van Voorhis,³⁶ and the Becke-type atomic partition function,⁸⁸ the multicenter multipole expanded expression of the second-order dispersion energy is derived. The distributed multipole polarizabilities for atoms in a molecule are first calculated from the local response model, from which the dispersion coefficients are obtained by an explicit frequency integral of the Casimir–Polder type. This procedure replaces the costly double spatial integral with the simpler double atomic summation without sacrificing accuracy. A new damping function is also introduced which possesses desirable features of both Fermi-type⁵⁵ and Tang–Toennis⁹³ functions, and takes into account the effective volume of atoms in molecular environment.

Thus formulated LRD method is combined with the LC-BOP functional via the damped atom-atom form and applied to calculations of weakly bound systems. Three empirical parameters included in the LRD method are first determined based on calculations for rare-gas diatoms. The method with the fixed parameters is then applied to interaction energy calculations of S22 database.¹¹² The mean absolute percent deviation of the calculated interaction energies from the CCSD(T) results is obtained as 5.7%, which is comparable to those obtained by other latest approaches. More importantly, it is confirmed that the LRD method performs similarly to the NLF approach with much less computational cost and no system fragmentation.

The present LRD method has a number of advantages in theoretical and practical points of view. It computes dispersion energy directly from the ground-state electron density. It is applicable to any geometries, free from outer sources of physical constants, and computationally no more demanding than the usual KS calculations.

The known problem is the overestimation of the higher-order dispersion coefficients observed in rare-gas interactions. This may indicate the need of further sophistication of the local response model. However, we are currently optimistic about this problem since the LRD method roughly corresponds to the multipole expansion of the parent NLF, which has been confirmed fairly accurate.^{31,33–35} A more fundamental defect of the LRD and any DFT-D type approaches is the need of damping functions. We manage to increase its transferability by introducing a system dependence to the damping. It is clear that such a prescription is far from satisfactory from a purely theoretical stand point; the seamless functional approaches^{36,37,68} or more rigorous treatments^{40–43} of the long-ranged electron correlation are desired. However, the LRD method has an opportunity to provide an ideal cost/performance balance in large-scale calculations, which we believe is one of the most important features of KS DFT.

Another strength of KS method is the ease of calculating analytical energy derivatives with respect to arbitrary perturbations. In particular, the geometry optimization with analytical gradients is probably the most common application of DFT. In this respect, the development of analytical derivatives for the LRD method based on the SCF treatment is indispensable, which should be our next work.

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