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Dispersion interactions from a local polarizability model

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A local approximation for dynamic polarizability leads to a nonlocal functional for the long-range dispersion interaction energy via an imaginary-frequency integral. We analyze several local polarizability approximations and argue that the form underlying the construction of our recent van der Waals functional [O. A. Vydrov and T. Van Voorhis, Phys. Rev. Lett. **103**, 063004 (2009)] is particularly well physically justified. Using this improved formula, we compute dynamic dipole polarizabilities and van der Waals C_6 coefficients for a set of atoms and molecules. Good agreement with the benchmark values is obtained in most cases.

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I. INTRODUCTION

Recently we developed [1] a nonlocal correlation energy functional that describes the entire range of van der Waals interactions in a general and seamless fashion, using only the electron density and its gradient as input. Improving upon its predecessors [2,3], the new van der Waals density functional [1], denoted VV09, has a simple analytic form, generalized to spin-polarized systems and well-behaved in some important limits. In the asymptotic long-range regime, VV09 reduces to a form similar to the models of Refs. [4] and [5], yet with some crucial differences. In this article, we examine this long-range behavior in detail and present some test results of dynamic dipole polarizabilities and asymptotic van der Waals C_6 coefficients.

II. FORMALISM

For two compact systems A and B separated by a large distance R, the nonretarded dispersion interaction energy [6] behaves asymptotically as $-C_6^{AB}R^{-6}$ with the C_6 coefficient given by the formula [7]

$$C_6^{AB} = \frac{3\hbar}{\pi}\int_0^\infty du\, \bar{\alpha}^A(iu)\,\bar{\alpha}^B(iu), \tag{1}$$

where $\bar{\alpha}(iu)$ is the average (isotropic) dynamic dipole polarizability at imaginary frequency iu. A simple but often sufficiently accurate approximation is to describe $\bar{\alpha}$ by a local model

$$\bar{\alpha}(iu) = \int d\mathbf{r}\,\alpha(\mathbf{r},iu). \tag{2}$$

The long-range dispersion interaction energy between systems A and B can then be written [8,9] in terms of local polarizabilities as

$$E_{\text{disp}} = -\frac{3\hbar}{\pi}\int_0^\infty du \int_A d\mathbf{r}\int_B d\mathbf{r}'\frac{\alpha(\mathbf{r},iu)\alpha(\mathbf{r}',iu)}{|\mathbf{r}-\mathbf{r}'|^6}, \tag{3}$$

where $\mathbf{r}$ is within the domain of system A and $\mathbf{r}'$ is within the domain of B.

In Refs. [4,5,9,10], a simple model for $\alpha(\mathbf{r},iu)$ was derived from the response properties of a uniform electron gas (UEG). The zero wave vector UEG dielectric function at frequency ω is given by

$$\epsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2}, \tag{4}$$

where $\omega_p = \sqrt{4\pi n e^2/m}$ is the plasma frequency for the electron density n. In nonuniform systems, the local analog of ω_p can be defined via $\omega_p^2(\mathbf{r}) = 4\pi n(\mathbf{r})e^2/m$. Then the local polarizability for $\omega = iu$ is found as [4,10]

$$\alpha(\mathbf{r},iu) = \frac{1}{4\pi}\left[1 - \frac{1}{\epsilon(\mathbf{r},iu)}\right] = \frac{1}{4\pi}\frac{\omega_p^2(\mathbf{r})}{\omega_p^2(\mathbf{r}) + u^2}. \tag{5}$$

Plugging Eq. (5) into Eq. (3) we arrive at the Andersson–Langreth–Lundqvist (ALL) formula [4]

$$E_{\text{disp}} = -\frac{3\hbar}{32\pi^2}\int_A d\mathbf{r}\int_B d\mathbf{r}'\frac{\omega_p(\mathbf{r})\omega_p(\mathbf{r}')}{\omega_p(\mathbf{r}) + \omega_p(\mathbf{r}')}\left|\mathbf{r}-\mathbf{r}'\right|^{-6}. \tag{6}$$

An immediately apparent problem with Eq. (5) is its treatment of static polarizability:

$$\bar{\alpha}(0) = \int d\mathbf{r}\,\alpha(\mathbf{r},0) = \int d\mathbf{r}\frac{1}{4\pi}. \tag{7}$$

$\alpha(\mathbf{r},0)$ is constant everywhere, therefore the above integral is divergent unless a cutoff is introduced. Equation (6), taken as it is, yields finite but severely overestimated E_{disp}. These difficulties are circumvented [4,10,11] by the introduction of sharp density-based integration cutoffs in Eqs. (2) and (6). Calculated polarizabilities and C_6 coefficients are admittedly [4,10] sensitive to the choice of the cutoff criterion, although the prescription of Refs. [4,10,11] appears to work well in many cases. Note that Ref. [10] gave separate cutoff criteria for the spin-compensated and the fully spin-polarized cases. To our knowledge, a prescription for a general spin-polarization case has never been put forth.

An integration cutoff discards density tail regions, which is not entirely satisfactory from the formal point of view. In the $u \to \infty$ limit, the f-sum rule requires [12] that

$$\bar{\alpha}(iu) \to \frac{Ne^2}{mu^2} = \int d\mathbf{r}\frac{\omega_p^2(\mathbf{r})}{4\pi u^2}, \tag{8}$$

where N is the number of electrons in the system. Omission of the density tails leads to the reduction of N, in violation of the f-sum rule.

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Another formal shortcoming of the ALL theory was pointed out by Nesbet [13,14], who argued that a more appropriate relation between α and ϵ is given by the Clausius–Mossotti formula

$$\alpha = \frac{3}{4\pi}\frac{\epsilon - 1}{\epsilon + 2}, \tag{9}$$

so that Eq. (5) should be replaced by

$$\alpha(\mathbf{r},iu) = \frac{1}{4\pi}\frac{\omega_p^2(\mathbf{r})}{\omega_p^2(\mathbf{r})/3 + u^2}. \tag{10}$$

It appears that Nesbet's articles went unnoticed because in the numerous practical applications [15–31] of the ALL formula, Nesbet's suggestion was never utilized.

The validity of Eq. (10) is corroborated by the example of interacting jellium spheres. For two identical spheres of uniform density and radius r_0 separated by distance R (such that $R \gg r_0$) the interaction energy is given by [32]

$$E_{\text{spheres}} = -\frac{\sqrt{3}}{4}\hbar\omega_p \frac{r_0^6}{R^6}. \tag{11}$$

The above result is exactly reproduced if Nesbet's model of Eq. (10) is plugged into Eq. (3), whereas the ALL formula (6) underestimates this result by the factor of $3\sqrt{3} \approx 5$. We note in passing that all three versions of the van der Waals density functional (vdW-DF) of Refs. [2,3,33] fail to reproduce Eq. (11) even on the qualitative level, yielding incorrect dependence on the electron density.

Local polarizability models of Eqs. (5) and (10) were derived using the UEG dielectric function of Eq. (4). UEG is rather dissimilar to our target systems—molecules. UEG has a continuous excitation spectrum and a zero band gap (i.e., it is a metal), whereas molecules have a discrete spectrum with a gap between the ground state and the fist excited state. The polarizability model could be made more realistic by introducing a gap. For a semiconductor with a band gap $\hbar\omega_g$, the zero wave vector dielectric function [34] is typically written as

$$\epsilon(\omega) = 1 + \frac{\omega_p^2}{\omega_g^2 - \omega^2}. \tag{12}$$

Using this $\epsilon(\omega)$ in the Clausius–Mossotti formula (9), we obtain

$$\alpha(\mathbf{r},iu) = \frac{1}{4\pi}\frac{\omega_p^2(\mathbf{r})}{\omega_p^2(\mathbf{r})/3 + \omega_g^2(\mathbf{r}) + u^2}, \tag{13}$$

where we introduced a "local gap" $\hbar\omega_g(\mathbf{r})$. The above $\alpha(\mathbf{r},iu)$ leads via Eq. (3) to the energy expression

$$E_{\text{disp}} = -\frac{3\hbar}{32\pi^2}\int_A d\mathbf{r}\int_B d\mathbf{r}' \frac{\omega_p^2(\mathbf{r})\omega_p^2(\mathbf{r}')|\mathbf{r}-\mathbf{r}'|^{-6}}{\omega_0(\mathbf{r})\omega_0(\mathbf{r}')[\omega_0(\mathbf{r}) + \omega_0(\mathbf{r}')]}, \tag{14}$$

where $\omega_0 = \sqrt{\omega_g^2 + \omega_p^2/3}$. A suitably chosen $\omega_g(\mathbf{r})$ obviates any need for an integration cutoff in E_{disp} and $\bar{\alpha}(iu)$. As a result, the f-sum rule on $\bar{\alpha}(iu)$ is obeyed.

An apt model for $\omega_g(\mathbf{r})$ can be deduced by examining the behavior of the electron density $n(\mathbf{r})$. In atoms, $n(\mathbf{r})$ can be approximated as piecewise exponential. In the density tails, the exact behavior [35] is known

$$n(\mathbf{r}) \sim \exp(-\alpha|\mathbf{r}|), \quad \text{with} \quad \alpha = 2(2mI/\hbar^2)^{1/2}, \tag{15}$$

where I is the ionization potential. Generalizing the result of Eq. (15), we can define a "local ionization potential" as [36,37]

$$I(\mathbf{r}) = \frac{\hbar^2}{8m}\left|\frac{\nabla n(\mathbf{r})}{n(\mathbf{r})}\right|^2. \tag{16}$$

Taking $\hbar\omega_g(\mathbf{r}) \propto I(\mathbf{r})$, in Ref. [1] we defined

$$\omega_g^2(\mathbf{r}) = C\frac{\hbar^2}{m^2}\left|\frac{\nabla n(\mathbf{r})}{n(\mathbf{r})}\right|^4, \tag{17}$$

where C is an adjustable parameter. We fitted C to a benchmark set of 17 van der Waals C_6 coefficients and obtained [1] the optimal value of $C = 0.0089$. It is instructive to consider the ratio $\omega_g(\mathbf{r})/I(\mathbf{r}) = 8\sqrt{0.0089} = 0.755$. This ratio seems reasonable since ω_g should be somewhat smaller than I. In the uniform density limit, Eq. (17) gives $\omega_g = 0$, so that our $\alpha(\mathbf{r},iu)$ of Eq. (13) reduces to Nesbet's $\alpha(\mathbf{r},iu)$ of Eq. (10).

Equations (13), (14), and (17) require only the *total* electron density as input and include no dependence on spin polarization. The question of the proper treatment of spin, not fully resolved in the ALL theory [10], does not arise in this model. We mention in passing that vdW-DF functionals of Refs. [2,3,33] were defined only for the spin-compensated case and their extension to spin-polarized systems is nontrivial. In VV09 [1], the dependence on spin polarization enters only at shorter range. In the long-range limit, the VV09 nonlocal correlation energy reduces to Eq. (14). In this regard, a clarification should be made: The coefficient before the double integral in Eq. (14) is twice the coefficient in Eq. (13) of Ref. [1] because these formulas compute different things. Equation (14) computes the interaction energy between systems A and B, hence the integral over $\mathbf{r}$ is limited to the part of space confining system A, while the integral over $\mathbf{r}'$ is limited to the domain of B. On the other hand, Eq. (13) of Ref. [1] gives the nonlocal correlation energy, which includes intermolecular and intramolecular contributions, hence both $\mathbf{r}$ and $\mathbf{r}'$ integrals are over the entire space.

III. BENCHMARK TESTS

All calculations reported in this section were performed at the LC-ωPBE08 [38] electron densities (using $\omega = 0.45\ a_0^{-1}$, as suggested in Ref. [38]), except for the H atom polarizability, computed at the Hartree-Fock (i.e., exact in this case) density. For the numerical integration, we use the Euler-Maclaurin-Lebedev unpruned (75,302) quadrature grid. The augmented correlation-consistent polarized-valence quadruple-zeta (aug-cc-pVQZ) basis set is used in all calculations. All the numbers in this section are given in atomic units (a.u.).

Using the VV09 model, given by Eqs. (13) and (17), we have calculated the isotropic dynamic dipole polarizabilities as functions of imaginary frequencies for several atoms and small molecules for which accurate reference data [39–42] are

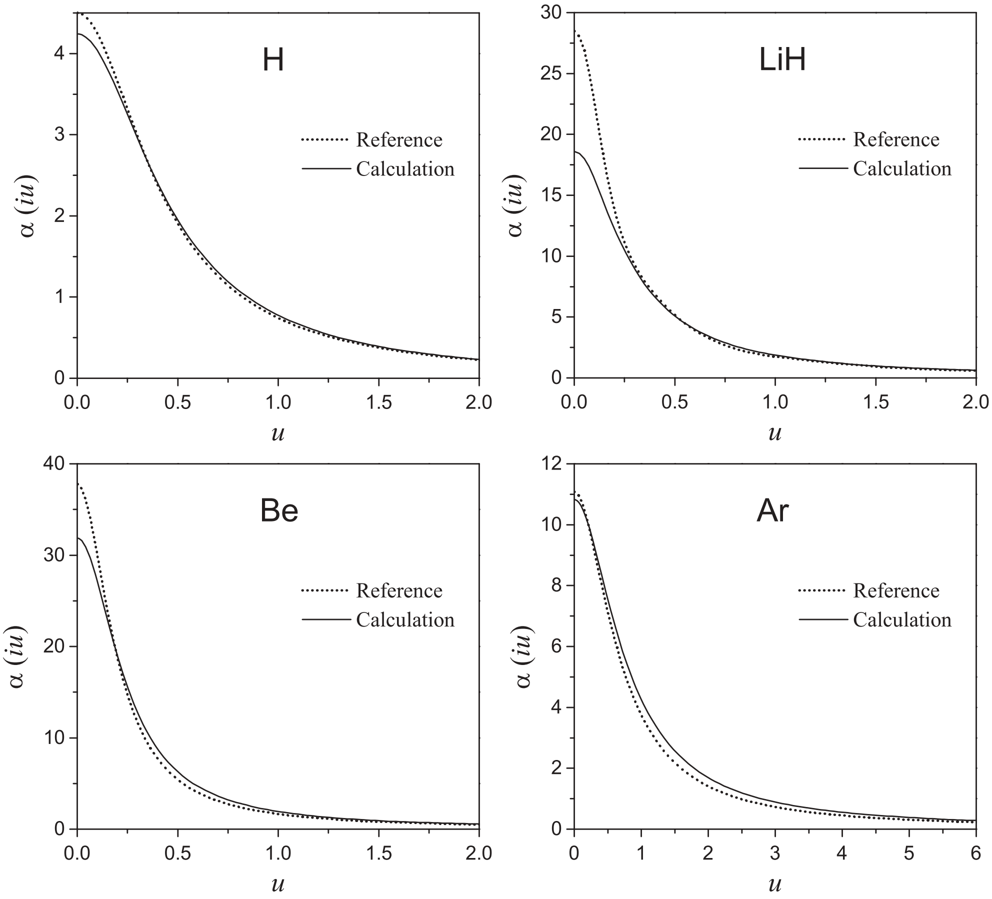

FIG. 1. Average dynamic dipole polarizabilities at imaginary frequencies calculated using the VV09 model [i.e., via Eqs. (2) and (13)]. Atomic units are used. The reference values are from Ref. [39] for LiH and from Ref. [40] for the atoms.

available. For LiH, BeH_2, and BH, we used the same bond lengths as in Refs. [39,41,42]. The results are given in Fig. 1 and Table I. The agreement between the calculated and reference values of $\bar{\alpha}(iu)$ is generally quite good, although this method has a tendency of underestimating static polarizabilities $\bar{\alpha}(0)$. The largest errors in $\bar{\alpha}(0)$ are observed for LiH (Fig. 1) and for alkali-metal atoms (not shown). Underestimation of $\bar{\alpha}(0)$ causes rather large errors in C_6 coefficients for alkali-metal atoms, as shown below.

TABLE I. Isotropic polarizabilities $\bar{\alpha}(iu)$ calculated via Eqs. (2) and (13) compared to the reference values for BeH_2 [41] and BH [42]. Atomic units are used.

	BeH_2		BH	
u	Ref.	Calc.	Ref.	Calc.
0.0	19.760	19.413	21.430	17.442
0.142 857	17.234	17.049	16.582	15.506
0.333 333	11.280	11.509	10.343	10.738
0.6	6.084	6.440	5.625	6.139
1.0	2.917	3.161	2.755	3.044
1.666 667	1.233	1.360	1.198	1.307
3.0	0.418	0.480	0.424	0.453
7.0	0.081	0.105	0.091	0.096

When the distance between species A and B is large compared to the size of these systems, $|\mathbf{r}-\mathbf{r}'|^{-6}$ in Eq. (14) can be taken out of the integral as R^{-6}, leading to the $-C_6^{AB}R^{-6}$ form with C_6^{AB} given by Eq. (1). To further assess the quality of the VV09 local polarizability model, we have calculated isotropic dispersion C_6 coefficients for a number of atoms and molecules. As expected from Eq. (1), any errors in the polarizability $\bar{\alpha}^A(iu)$ are reflected in C_6^{AA} and similarly in C_6^{AB}. It is sufficient to include only C_6^{AA} in our benchmark set since the accuracy for C_6^{AA} and C_6^{BB} determines the accuracy for C_6^{AB}. For example, VV09 strongly underestimates the C_6 coefficient for the Li–Li interaction, and as a result, all C_6 coefficients for Li interacting with other species are also underestimated. On the contrary, VV09 gives very accurate C_6 coefficients for He–He and Kr–Kr, and consequently, C_6 for He–Kr is also very accurate.

In Ref. [1] we reported the C_6^{AA} coefficients for a set of 17 closed-shell species, computed within the VV09 methodology. In fact, the value of $C = 0.0089$ in Eq. (17) was fitted to that set. In this study, we test whether this fit is transferable to atoms and molecules outside of the training set. In Table II we assembled a set of 34 closed-shell species for which accurate C_6^{AA} are known. Using this benchmark set, we compare the accuracy of VV09 [1] to the similar methods of Refs. [2,3,33]. In the asymptotic limit, all these methods reduce to the form of Eq. (14), but with different models for ω_0, as discussed in

TABLE II. C_6^{AA} coefficients (a.u.) for closed-shell species calculated by several methods. Experimental geometries [43] are used for all molecules. MPE stands for the mean percentage error and MAPE stands for the mean absolute percentage error.

Molecule	vdW-DF-04[a]	vdW-DF-09[b]	vdW-DF-10[c]	VV09[d]	Accurate	Ref.[e]
He	2.93	1.63	0.76	1.45	1.46	[40]
Ne	9.45	6.52	3.07	8.44	6.35	[44]
Ar	62.67	61.41	25.29	70.08	64.42	[44]
Kr	114.3	120.0	47.7	131.2	130.1	[44]
Be	269	330	102	186	214	[40]
Mg	649	835	246	425	627	[40]
Zn	269	240	87	163	284	[45]
H_2	16.82	12.53	5.09	10.28	12.09	[46]
N_2	78.76	77.59	31.96	88.70	73.43	[46]
Cl_2	289.3	336.8	131.4	366.7	389.2	[47]
HF	23.12	18.01	7.97	21.13	19.00	[48]
HCl	114.3	119.9	47.2	124.6	130.4	[48]
HBr	180.1	198.2	76.1	200.2	216.6	[48]
CO	87.56	86.34	35.01	93.51	81.40	[49]
CO_2	127.6	130.6	54.5	159.4	158.7	[49]
CS_2	586.3	731.7	274.3	739.4	871.1	[50]
OCS	316.8	370.1	143.4	395.6	402.2	[50]
N_2O	136.1	140.3	58.4	172.4	184.9	[51]
CH_4	122.0	130.1	50.8	129.6	129.6	[52]
CCl_4	1436	1882	715	2044	2024	[53]
NH_3	82.47	79.32	32.00	82.78	89.03	[51]
H_2O	46.96	40.83	17.17	44.95	45.29	[51]
SiH_4	338.0	406.1	147.2	344.6	343.9	[54]
SiF_4	360.9	382.7	158.6	455.8	330.2	[55]
H_2S	186.6	208.9	79.1	200.3	216.8	[56]
SO_2	239.5	265.1	106.5	305.2	294.0	[50]
SF_6	568.0	659.7	274.6	869.9	585.8	[57]
C_2H_2	191.3	210.3	81.0	210.3	204.1	[58]
C_2H_4	259.7	293.8	113.2	297.3	300.2	[59]
C_2H_6	330.4	386.1	148.8	396.6	381.8	[52]
CH_3OH	194.0	208.5	83.2	226.1	222.0	[60]
CH_3OCH_3	458.7	532.5	207.7	567.9	534.0	[61]
Cyclopropane	480.7	596.1	228.3	632.6	630.8	[52]
C_6H_6	1297	1715	647	1838	1723	[58]
MPE (%)	−2.8	−0.5	−60.9	1.2		
MAPE (%)	18.5	10.4	60.9	10.7		

[a] The method of Ref. [2].

[b] The method of Ref. [3].

[c] This method is denoted as vdW-DF2 in Ref. [33].

[d] The formalism proposed in Ref. [1] and described in this work.

[e] Literature references for the accurate benchmark C_6^{AA} values.

Ref. [3]. Deviations from the reference values are summarized in Table II as mean (signed) percentage errors (MPE) and mean absolute percentage errors (MAPE). VV09 and vdW-DF-09 exhibit very similar accuracy with MAPE of just over 10%. vdW-DF-04 is somewhat less accurate with MAPE of 18.5%. The latest reparameterization (denoted as vdW-DF2 in Ref. [33], but called vdW-DF-10 here for consistency) yields very poor C_6 coefficients: As compared to the reference values, vdW-DF-10 underestimates C_6^{AA} by a factor of 2.6 on average.

The good performance of vdW-DF-09 for C_6 coefficients motivated Sato and Nakai [62] to devise a pairwise atom-atom dispersion correction using the local polarizability model [3] underlying the construction of vdW-DF-09. We believe that the VV09 model of Eq. (13) can also be successfully employed in this scheme.

As mentioned previously, none of the three versions of vdW-DF [2,3,33] has been generalized for open-shell systems, whereas VV09 is defined for a general spin-polarized case. In Table III, we compare the C_6^{AA} coefficients predicted by VV09 to the accurate reference values for 20 open-shell species. The agreement is satisfactory in most cases. The largest errors are observed for the alkali-metal atoms Li and Na. The strong underestimation of the C_6 coefficients for alkali-metal atoms was also noted for the ALL formula [4]. It is likely that the local approximation of Eq. (2)

TABLE III. C_6^{AA} coefficients (a.u.) for open-shell species calculated using Eq. (14).

Molecule	VV09	Accurate	Ref.
H	6.75	6.50	[40]
Li	565	1389	[40]
B	87.6	99.5	[45]
C	47.0	46.6	[45]
N	27.65	24.10	[51]
O	18.19	14.89	[51]
F	12.21	9.52	[45]
Na	669	1556	[40]
Al	353	528	[45]
Si	253	305	[45]
P	179	185	[45]
S	130	134	[45]
Cl	94.7	94.6	[45]
Ga	255	498	[45]
Ge	251	354	[45]
As	222	246	[45]
Se	190	210	[45]
Br	158	162	[45]
O_2	66.18	61.57	[51]
NO	77.83	69.73	[51]
MPE (%)	−9.8		
MAPE (%)	18.7		

is inadequate for such highly polarizable systems as alkali metals.

IV. CONCLUSION

The ALL formula (6) for the long-range dispersion energy enjoys growing popularity [15–31], even though it has been superseded by more general [1–3,33] and more accurate [63,64] methods. A simple change from Eq. (6) to Eq. (14) improves the theory in several important ways: The sharp integration cutoff is obviated and consequently the f-sum rule is recovered; the model system of two distant jellium spheres is properly described; accurate C_6 coefficients are predicted for many atoms and molecules including open-shell species. Equation (14) describes the asymptotic limit and has to be damped at short range. To this end, empirical damping functions are often used (see, e.g., Ref. [62]).

The general and seamless van der Waals functional VV09 [1] reduces to Eq. (14) in the large separation limit. As our recent study [65] shows, VV09 performs well not only in the asymptotic limit, but also near equilibrium intermonomer separations, provided that an adequate exchange functional is used.

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