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.

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 $E_{\text{disp}}$ behaves asymptotically as $-C_6^{AB} R^{-6}$ with the $C_6$ coefficient given by the formula [7]

$$C_6^{AB} = \frac{3\hbar}{\pi} \int_0^{\infty} du \, \bar{\alpha}(iu) \bar{\alpha}(iu),$$  \hspace{1cm} (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:

$$\bar{\alpha}(iu) = \int \, dr \, \alpha(r, iu).$$  \hspace{1cm} (2)

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

$$E_{\text{disp}} = \frac{3\hbar}{2\pi^2} \int_0^{\infty} du \int_A \, dr \int_B \, dr' \frac{\alpha(r, iu) \alpha(r', iu)}{|r-r'|^6},$$  \hspace{1cm} (3)

where $r$ is within the domain of system $A$ and $r'$ is within the domain of $B$.

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

$$\epsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2},$$  \hspace{1cm} (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 $\omega_p$ can be defined via $\omega_p^2(r) = 4\pi n(r)e^2/m$. Then the local polarizability for $\omega = iu$ is found as [4, 10]

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

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

$$E_{\text{disp}} = -\frac{3\hbar}{2\pi^2} \int_A \, dr \int_B \, dr' \frac{\omega_p(r) \omega_p(r')}{\omega_p(r) + \omega_p(r')} |r-r'|^{-6}. $$  \hspace{1cm} (6)

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

$$\bar{\alpha}(0) = \int \, dr \, \alpha(r, 0) = \int \, dr \frac{1}{4\pi}. $$  \hspace{1cm} (7)

$\alpha(r, 0)$ is constant everywhere, therefore the above integral is divergent unless a cutoff is introduced. Eq. (5), taken as it is, yields finite but severely overestimated $E_{\text{disp}}$. These difficulties are circumvented [4, 10] 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

$$\bar{\alpha}(iu) \to N e^2/m u^2 = \int \, dr \frac{\omega_p^2(r)}{4\pi u^2}. $$  \hspace{1cm} (8)

In the domain of system $A$.
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.

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

\[
\alpha = \frac{3}{4\pi} \frac{\epsilon - 1}{\epsilon + 2},
\]

so that Eq. (5) should be replaced by

\[
\alpha(r, iu) = \frac{1}{4\pi} \frac{\omega_p^2(r)}{\omega_0^2(r)/3 + u^2},
\]

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

\[
E_{\text{spheres}} = -\frac{\sqrt{3}}{4} \hbar \omega_p \frac{r_0^6}{R^6}.
\]

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 vdW-DF functional 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 \[\epsilon(0)\] is typically written as

\[
\epsilon(\omega) = 1 + \frac{\omega_p^2}{\omega^2 - \omega_g^2}.
\]

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

\[
\alpha(r, iu) = \frac{1}{4\pi} \frac{\omega_p^2(r)}{\omega_0^2(r)/3 + \omega_g^2(r) + u^2},
\]

where we introduced a “local gap” \( \hbar \omega_g(r) \). The above \( \alpha(r, iu) \) leads via Eq. (3) to the energy expression

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

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

An apt model for \( \omega_g(r) \) can be deduced by examining the behavior of the electron density \( n(r) \). In atoms, \( n(r) \) can be approximated as piecewise exponential. In the density tails, the exact behavior \[32\] is known:

\[
n(r) \sim \exp(-\alpha |r|), \quad \text{with} \quad \alpha = 2 \left(2mI/h^2\right)^{1/2},
\]

where \( I \) is the ionization potential. Generalizing the result of Eq. (15), we can define a “local ionization potential” as

\[
I(r) = \frac{\hbar^2}{8m} \left| \frac{\nabla n(r)}{n(r)} \right|^2.
\]

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

\[
\omega_g^2(r) = C \frac{\hbar^2}{m} \left| \frac{\nabla n(r)}{n(r)} \right|^4,
\]

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

Eqs. (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 \[1\], 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. (13). 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. Eq. (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 inter- 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-\( \omega \)-PBE08 \[12\] electron densities (using \( \omega = 0.45 \alpha_0^{-1} \), as suggested in Ref. \[12\]), except for the H
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. [38] for LiH and from Ref. [39] for the atoms.

TABLE I. Isotropic polarizabilities $\bar{\alpha}(iu)$ calculated via Eqs. (2) and (13) compared to the reference values for BeH$_2$ [40] and BH [41]. Atomic units are used.

| $u$   | BeH$_2$ Ref. | BeH$_2$ Calc. | BH Ref. | BH Calc. |
|-------|--------------|---------------|---------|----------|
| 0.0   | 19.760       | 19.413        | 21.430  | 17.442   |
| 0.142857 | 17.234      | 17.049        | 16.582  | 15.506   |
| 0.333333 | 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    |
| 1.666667 | 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    |

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 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 [38–41] are available. For LiH, BeH$_2$, and BH, we used the same bond lengths as in Refs. [38, 40, 41]. 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.

When the distance between species A and B is large compared to the size of these systems, $|r - r'|^{-6}$ 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 $C_6^{BB}$. 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
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      | 39     |
| 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       | 39     |
| Mg       | 649            | 835            | 246            | 425      | 627       | 39     |
| 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$_2$O   | 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$_2$O   | 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$_2$S   | 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$_2$H$_2$ | 191.3      | 210.3          | 81.0           | 210.3    | 204.1     | 58     |
| C$_2$H$_4$ | 259.7      | 293.8          | 113.2          | 297.3    | 300.2     | 59     |
| C$_2$H$_6$ | 330.4      | 386.1          | 148.8          | 396.6    | 381.8     | 52     |
| CH$_3$OH | 194.0          | 208.5          | 83.2           | 226.1    | 222.0     | 60     |
| CH$_3$OCH$_3$ | 458.7 | 532.5          | 207.7          | 567.9    | 534.0     | 61     |
| Cyclopropane | 480.7 | 596.1          | 228.3          | 632.6    | 630.8     | 52     |
| C$_6$H$_6$ | 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. \[3\].
$^b$ The method of Ref. \[4\].
$^c$ 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.

$C_0^{AB}$. For example, VV09 strongly underestimates the $C_0$ coefficient for the Li–Li interaction, and as a result, all $C_0$ coefficients for Li interacting with other species are also underestimated. On the contrary, VV09 gives very accurate $C_0^{AA}$ coefficients for He–He and Kr–Kr, and consequently, $C_0$ for He–Kr is also very accurate.

In Ref. \[1\] we reported the $C_0^{AA}$ 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 \[11\] we assembled a set of 34 closed-shell species for which accurate $C_0^{AA}$ are known. Using this benchmark set, we compare the accuracy of VV09 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 $\omega_0$, as discussed in Ref. \[2\]. Deviations from the reference values are summarized in Table \[11\] 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 last reparametrization (denoted as vdW-DF2 in Ref. \[33\], but called vdW-DF-10 here for consistency) yields very poor $C_0$ coefficients: as compared to the reference values, vdW-DF-10 underestimates $C_0^{AA}$ by a factor of 2.6 on average.

The good performance of vdW-DF-09 for $C_0$ coeffi-
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     | [38] |
| Li       | 565    | 1389     | [39] |
| 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     | [39] |
| 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 (%) 18.7
MAPE (%) 9.8

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 above, 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) is inadequate for such highly polarizable systems as alkali metals.

IV. CONCLUSIONS

The ALL formula [6] for the long-range dispersion energy enjoys growing popularity [15–41], 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. Eq. (13) 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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[1] O. A. Vydrov and T. Van Voorhis, Phys. Rev. Lett. 103, 063004 (2009).
[2] M. Dion, H. Rydberg, E. Schröder, D. C. Langreth, and B. I. Lundqvist, Phys. Rev. Lett. 92, 246401 (2004); 95, 109902(E) (2005).
[3] O. A. Vydrov and T. Van Voorhis, J. Chem. Phys. 130, 104105 (2009).
[4] Y. Andersson, D. C. Langreth, and B. I. Lundqvist, Phys. Rev. Lett. 76, 102 (1996).
[5] J. F. Dobson and B. P. Dinte, Phys. Rev. Lett. 76, 1780 (1996).
[6] I. G. Kaplan, Intermolecular Interactions: Physical Picture, Computational Methods, and Model Potentials (Wiley, Chichester, England, 2006).
[7] C. Mavroyannis and M. J. Stephen, Mol. Phys. 5, 629 (1962).
[8] Electronic Density Functional Theory: Recent Progress and New Directions, edited by J. F. Dobson, G. Vignale, and M. F. Das (Plenum, New York, 1998).
[9] J. F. Dobson, B. P. Dinte, and J. Wang in Ref. [8], p. 261.
[10] Y. Andersson, E. Hult, H. Rydberg, P. Apell, B. I. Lundqvist, and D. C. Langreth in Ref. [3], p. 243.
[11] K. Rapcewicz and N. W. Ashcroft, Phys. Rev. B 44, 4032 (1991).
[12] G. D. Mahan and K. R. Subbaswamy, Local Density Theory of Polarizability (Plenum, New York, 1990).
[13] R. K. Nesbet Phys. Rev. A 56, 2778 (1997).
[14] R. K. Nesbet in Ref. [8], p. 285.
[15] Y. Andersson and H. Rydberg, Phys. Scr. 60, 211 (1999).
[16] M. Kamiya, T. Tsumeda, and K. Hirao, J. Chem. Phys. 117, 6010 (2002).
[17] T. Sato, T. Tsumeda, and K. Hirao, J. Chem. Phys. 123, 104307 (2005).
[18] T. Sato, T. Tsumeda, and K. Hirao, Mol. Phys. 103, 1151 (2005).
[19] T. Sato, T. Tsumeda, and K. Hirao, J. Chem. Phys. 126, 234114 (2007).
[20] T. Matsui, H. Miyachi, T. Sato, Y. Shigeta, and K. Hirao, J. Phys. Chem. B 112, 16960 (2008).
[21] T. Matsui, T. Sato, Y. Shigeta, and K. Hirao, Chem. Phys. Lett. 478, 238 (2009).
[22] T. Matsui, H. Miyachi, Y. Nakanishi, Y. Shigeta, T. Sato, Y. Kitagawa, M. Okumura, and K. Hirao, J. Phys. Chem. B 113, 12790 (2009).
[23] H. Miyachi, T. Matsui, Y. Shigeta, and K. Hirao, Phys. Chem. Chem. Phys. 12, 909 (2010).
[24] P. L. Silvestrelli, Phys. Rev. Lett. 100, 053002 (2008).
[25] P. L. Silvestrelli, K. Benyahia, S. Grubišić, F. Ancilotto, and F. Toigo, J. Chem. Phys. 130, 074702 (2009).
[26] P. L. Silvestrelli, J. Phys. Chem. A 113, 5224 (2009).
[27] P. L. Silvestrelli, Chem. Phys. Lett. 475, 285 (2009).
[28] P. L. Silvestrelli, F. Toigo, and F. Ancilotto, J. Phys. Chem. C 113, 17124 (2009).
[29] J. Gräfenstein and D. Cremer, J. Chem. Phys. 130, 124105 (2009).
[30] Y. Hagiwara and M. Tateno, J. Phys.: Condens. Matter 21, 245103 (2009).
[31] B. Rotenberg, M. Salanne, C. Simon, and R. Vuilleumier, Phys. Rev. Lett. 104, 138301 (2010).
[32] A. A. Lucas, A. Ronveaux, M. Schmeits, and F. Delelaine, Phys. Rev. B 12, 5372 (1975).
[33] K. Lee, É. D. Murray, L. Kong, B. I. Lundqvist, and D. C. Langreth, arXiv:1003.5255.
[34] Z. H. Levine and S. G. Louie, Phys. Rev. B 25, 6310 (1982).
[35] M. Levy, J. P. Perdew, and V. Sahni, Phys. Rev. A 30, 2745 (1984).
[36] G. Gutle, A. Savin, J. B. Krieger, and J. Chen, Int. J. Quantum Chem. 75, 885 (1999).
[37] C. Gutlé and A. Savin, Phys. Rev. A 75, 032519 (2007).
[38] G. L. Bendazzoli, V. Magnasco, G. Figari, and M. Rui, Chem. Phys. Lett. 330, 146 (2000).
[39] A. Derevianko, S. G. Porsev, and J. F. Babb, At. Data Nucl. Data Tables 96, 323 (2010).
[40] G. L. Bendazzoli, A. Monari, G. Figari, M. Rui, C. Costa, and V. Magnasco, Chem. Phys. Lett. 414, 51 (2005).
[41] G. L. Bendazzoli, A. Monari, G. Figari, M. Rui, C. Costa, and V. Magnasco, Chem. Phys. Lett. 450, 396 (2008).
[42] E. Weintraub, T. M. Henderson, and G. E. Scuseria, J. Chem. Theory Comput. 5, 754 (2009).
[43] CRC Handbook of Chemistry and Physics, 90th ed., edited by D. R. Lide (CRC Press, Boca Raton, FL, 2009).
[44] A. Kumar and A. J. Thakkar, J. Chem. Phys. 132, 074301 (2010).
[45] X. Chu and A. Dalgarno, J. Chem. Phys. 121, 4083 (2004).
[46] W. J. Meath and A. Kumar, Int. J. Quantum Chem. Symp. 24, 501 (1990).
[47] M. Kumar, A. Kumar, and W. J. Meath, Mol. Phys. 100, 3271 (2002).
[48] A. Kumar and W. J. Meath, Mol. Phys. 54, 823 (1985).
[49] B. L. Jhanwar and W. J. Meath, Chem. Phys. 67, 185 (1982).
[50] A. Kumar and W. J. Meath, Chem. Phys. 91, 411 (1984).
[51] D. J. Margoliash and W. J. Meath, Chem. Phys. 68, 1426 (1978).
[52] G. F. Thomas, F. Mulder, and W. J. Meath, Chem. Phys. 54, 45 (1980).
[53] A. Kumar, J. Mol. Struct. THEOCHEM 591, 91 (2002).
[54] A. Kumar, M. Kumar, and W. J. Meath, Chem. Phys. 286, 227 (2003).
[55] A. Kumar, M. Kumar, and W. J. Meath, Mol. Phys. 101, 1535 (2003).
[56] R. J. Pazur, A. Kumar, R. A. Thuraisingham, and W. J. Meath, Can. J. Chem. 66, 615 (1988).
[57] A. Kumar, G. R. G. Fairley, and W. J. Meath, J. Chem. Phys. 83, 70 (1985).
[58] A. Kumar and W. J. Meath, Mol. Phys. 75, 311 (1992).
[59] A. Kumar, B. L. Jhanwar, and W. Meath, Can. J. Chem. 85, 724 (2007).
[60] A. Kumar, B. L. Jhanwar, and W. J. Meath, Collect. Czech. Chem. Commun. 70, 1196 (2005).
[61] A. Kumar and W. J. Meath, Mol. Phys. 106, 1531 (2008).
[62] T. Sato and H. Nakai, J. Chem. Phys. 131, 224104 (2009).
[63] A. D. Becke and E. R. Johnson, J. Chem. Phys. 127, 154108 (2007).
[64] A. Tkatchenko and M. Scheffler, Phys. Rev. Lett. 102, 073005 (2009).
[65] O. A. Vydrov and T. Van Voorhis, J. Chem. Phys. 132, 164113 (2010).