Unified Treatment of Asymptotic van der Waals Forces

Erika Hult, Henrik Rydberg, and Bengt I. Lundqvist
Department of Applied Physics, Chalmers University of Technology and Göteborg University, S-412 96 Göteborg, Sweden

David C. Langreth
Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey 08854-8019

In a framework for long-range density-functional theory we present a unified full-field treatment of the asymptotic van der Waals interaction for atoms, molecules, surfaces, and other objects. The only input needed consists of the electron densities of the interacting fragments and the static polarization ability or the static image plane, which can be easily evaluated in a ground-state density-functional calculation for each fragment. Results for separated atoms, molecules, and for atoms/molecules outside surfaces are in agreement with those of other, more elaborate, calculations.

The ubiquitous van der Waals interaction needs an efficient and accurate description in many contexts such as interacting noble-gas atoms, van der Waals complexes, physisorption, interacting macroscopic neutral bodies, liquid-crystal interactions, solute-solvent interactions, and soft-condensed matter. For dense matter the density-functional theory (DFT) with its local-density (LD) [9] and generalized-gradient approximations (GGA) [10] is a clear success. Ground-state and thermodynamic properties of increasingly more complex systems are now being calculated with a practically very useful accuracy. As the world around contains far more objects than just hard solids, a generalization of these methods to also account for the van der Waals forces is in great demand. These forces are an inherent property of the exact DFT [9] and it is thus a question of providing an approximate van der Waals density functional that is generally applicable, efficient, and accurate, and that per definition is a functional of the density only.

Earlier works and others have proposed such functionals and shown them to give useful results in significant applications. For a review, see Ref. [13]. Until now, however, there has been a certain asymmetry in our treatment of “small” and “large” objects, respectively, which will be remedied in this paper.

The starting point for our functionals is the exact expression for the exchange-correlation energy \( E_{xc} \) as an integral over the coupling constant \( \lambda \), the so-called adiabatic connection formula (ACF)

\[
E_{xc}[\rho] = \frac{1}{2} \int d^3r d^3r' \frac{e^2}{|r - r'|} \times \int_0^1 d\lambda \left[ (\hat{n}(r)\hat{n}(r'))_{\rho,\lambda} - \delta(r-r')\langle n(r) \rangle \right],
\]

where \( \hat{n} = \hat{n} - n \), \( \hat{n} \) being the density operator, and \( \langle \cdots \rangle_{\rho,\lambda} \) means that the integration is performed with a potential \( V_\lambda \) present, keeping the density equal to \( n(r) \).

To second order perturbation theory in the interaction \( V_{ab} \) between two separated objects \( a \) and \( b \) the ACF can be cast into the form

\[
\Delta E_{xc}(R) = E_{xc}^\infty - \int \int \int d^3r_1 d^3r_2 d^3r_3 d^3r_4 \times V_{ab}(R + r_1 - r_2)V_{ab}(R + r_3 - r_4) \times \int_0^\infty du \frac{1}{2\pi} \Pi_0(r_1, r_3; iu)\Pi_0(r_2, r_4; iu). \tag{2}
\]

Our evaluation of this energy is based on two approximations. First we introduce a local dielectric function that depends on the local electron density. Second, we limit the volumes of the interacting objects by using a cutoff, an idea first introduced by Rapcewicz and Ashcroft [14] outside which the response to an electric field is defined to be zero. We thus have the dielectric function

\[
\epsilon(\omega; n(r)) = 1 - \kappa(n(r))\frac{\omega_p^2(n(r))}{\omega^2}, \tag{3}
\]

where

\[
\omega_p^2(n(r)) = 4\pi e^2 n(r)/m. \tag{4}
\]

The cutoff is implemented via the function \( \kappa(n(r)) \), which is either unity or zero, following the notion discussed earlier that the local approximation for dielectric response greatly exaggerates the response in the low-density tails, where it is better to assume no response at all.

These approximations are common for all of our three model systems – interacting atoms or molecules [12] an atom or molecule interacting with a planar surface [15] and finally two interacting surfaces. However, we have earlier treated the electrodynamics on different levels for “small” and “large” objects. Normally, local electrodynamics means a local relationship between the polarization \( P \) and the total electric field \( E \)

\[
P(r, \omega) = \frac{1}{4\pi} \left[ \epsilon(\omega; n(r)) - 1 \right] E(r, \omega), \tag{5}
\]

which we use for surfaces. For atoms, however, the calculations get somewhat more complicated than in the surface case when using Eq. (4). For instance, the electrodynamics must be solved numerically for each frequency.

Our earlier approach for atoms and molecules has approximated the local polarization by
\[ P(r, \omega) = \frac{1}{4\pi} \left( \epsilon(\omega; n(r)) - 1 \right) \frac{E_{\text{applied}}(r, \omega)}{\epsilon(\omega; n(r))}, \]

(6)

which implies the relation

\[ E(r, \omega) = \frac{E_{\text{applied}}(r, \omega)}{\epsilon(\omega; n(r))}, \]

(7)

which is certainly wrong for macroscopic objects, but gives surprisingly good results for atoms and molecules.[3] However, the optimum cutoff position defined by \( \kappa(n(r)) \) is somewhat larger for the approximate electrodynamics, and this fact seems to mitigate some of the deficiencies of this previous approximation. To obtain a unified treatment for different objects, and also to test our approximation for the dielectric function, this paper presents the electrodynamics using Eq. (6) also for atoms and molecules. We apply it to the asymptotic van der Waals interaction of separated atoms, molecules, and parallel surfaces,[4] and show the results to be in agreement with those of other, more elaborate, calculations.

For two widely separated atoms or molecules the van der Waals energy is given by \( E_{\text{vdW}} = -C_6/R^6 \), where the van der Waals coefficient is

\[ C_6 = \frac{3}{\pi} \int_0^\infty du \alpha_1(\nu) \alpha_2(\nu) \]

(8)

and \( \alpha_j(\nu) \) is the polarizability of atom \( j \). To calculate \( \alpha(\nu) \) we solve \( \nabla \cdot D(r) = 0 \), for each frequency in the presence of an applied constant electric field \( E_0 \). The displacement \( D(r) \) is given by \( \epsilon(\omega; n(r))E(r) \) and \( E(r) = -\nabla \phi(r) \). Thus we solve the equation

\[ \nabla \cdot (\epsilon(\omega; n(r)) \nabla \phi(r)) = 0, \]

(9)

where \( \epsilon(\omega; n(r)) \) is given by Eqs. (3) and (4), and \( \phi \) is the poloidal potential.

The cutoff function \( \kappa(n(r)) \) must however be defined. For surfaces the cutoff is found by taking the static displacement \( D \). In order to have a common cutoff scheme for both atoms, molecules, and surfaces, and in addition to implement the requirement introduced for surfaces that the static polarization response be accurate, it is expedient to simplify the scheme used previously for atoms and molecules. This is done by choosing the cutoff function \( \kappa \) according to

\[ \kappa(r) = \theta(n(r) - c), \]

(10)

where \( c \) is a constant.

For atoms and molecules, compared with the original scheme that uses both the density and its gradient, the practical effect of (10) is to eliminate any cutoff in the intra-shell regions. We have found that inclusion of the cutoff in the intra-shell regions as before results in a median reduction of the predicted values of the \( C_6 \) coefficients of 12% for the atom pairs calculated here. The extent to which these intra-shell corrections should be included even in principle is arguable, and since they are small, we have therefore opted for the simpler scheme (11). Adapting the analogue of the procedure used when the full-field scheme is applied to surfaces,[3] we fix the constant \( c \) in (11) so that the static polarizabilities are accurate. For a spherically symmetric species, this means that the volume \( V \) inside which the step function in (11) is nonvanishing is simply \( V = (4\pi/3) \alpha(0) \). For species without spherical symmetry, we choose \( c \) so that the isotropic polarizabilities, \( \alpha(0) \) [see Eq. (12)], are correct. This scheme seems to underestimate the anisotropy of the molecular polarizability; if an accurate anisotropy is important the cutoff function should be modified so that the elements of the diagonalized static polarizability tensor are reproduced.

The solution of Eq. (1) is done with a finite element method with an adaptive net.[23] In this way we have a general method for all geometries. To secure a reasonable numerical accuracy (5%) at small frequencies, we here represent \( \alpha(\nu) \) by the expression \( a + b/(1 + \nu^2/c^2) \), where \( a, b, c \) are fixed by a smooth continuation of high-frequency results. In Table I the van der Waals coefficients for a number of pairs of identical atoms are given, together with the static polarizability used when defining the cutoff. In Figure 2 calculated \( C_6 \) values both for identical and mixed pairs of atoms are plotted against results from more accurate calculations. The values compare very well with results from other calculations, with the close agreement indicated by the narrow spread of the points around the diagonal. Especially the results for alkali and alkaline earth atoms are much improved compared with our earlier calculations.[1] In Figures 2 and 3 the dynamic polarizability from our calculations are compared with reference calculations. Figure 2 for He is a worst-case example, with a 12% error in \( C_6 \), while Figure 3 for Be is a best-case example, with a \( C_6 \) right on the reference value.

Results for a few molecules are given in Table I with results agreeing very well with literature values. The largest molecule for which we have so far calculated the van der Waals coefficient is fullerene, \( C_{50} \). Recently the dispersion energy between two fullerenes has been computed from first principles in time-dependent DFT, which gives the van der Waals coefficient \( C_6 = 253 \text{ kRy } a_0^6 \). Earlier, simpler methods have been used to estimate the polarizability and the van der Waals coefficient. A summation of C–C interactions gives \( C_6 = 200 \text{ kRy } a_0^6 \), and for a calculation of dipole modes using a discrete dipole model the result is \( C_6 = 350 \text{ kRy } a_0^6 \). Using \( \alpha(0) = 570 a_0^3 \) (experimental value from Ref. [24]) we get \( C_6 = 302 \text{ kRy } a_0^6 \), a result which lies in the same range as those from the other calculations.

In Tables I and II the characteristic frequencies, \( u_0 \), corresponding to London’s empirical formula

\[ C_6 = \alpha^A(0) \alpha^B(0) \frac{3u_0^A u_0^B}{2(u_0^A + u_0^B)}, \]

(11)

where \( A \) and \( B \) denote the two fragments, are also given.
This formula provides an easy way of estimating isotropic van der Waals coefficients for mixed pairs of atoms and molecules. In Table II we have only given the isotropic dispersion coefficients for the molecules, that is, we have used the averaged polarizability $\overline{\alpha}(iu)$ in Eq. (8), where

$$\overline{\alpha}(iu) = \frac{1}{3} (\alpha_{xx}(iu) + \alpha_{yy}(iu) + \alpha_{zz}(iu)).$$

(12)

It is easy, however, to calculate the anisotropic corrections, in addition. A simple example is for two interacting identical linear molecules, where the anisotropic coefficients $C_6'$ and $C_6''$ control the orientation-dependent part of the long-range interaction according to Eq. (13)

$$E_{\text{vdW}}(R, \theta_A, \theta_B, \phi_A, \phi_B) =$$

$$- \left[ C_6 + C_6' \left\{ P_2(\cos \theta_A) + P_2(\cos \theta_B) \right\} + \frac{4\pi}{3} C_6'' \times$$

$$\sum_{m=-2}^{2} (3 - |m|) Y_m^2(\theta_A, \phi_A) Y_{-m}^2(\theta_B, \phi_B) \right] R^{-6},$$

(13)

where $\theta_A$ ($\theta_B$) is the angle between the vector $\mathbf{R}$ from the center of molecule $A$ to the center of $B$ and the axis of molecule $A$ ($B$). The other angle $\phi_A$ ($\phi_B$) describes the rotation of molecule $A$ ($B$) about $R$. With

$$\Delta \alpha(iu) = \alpha_{zz}(iu) - \alpha_{xx}(iu)$$

(14)

these coefficients can be written

$$C_6' = \frac{1}{\pi} \int_0^\infty du \overline{\alpha}(iu) \Delta \alpha_2(iu)$$

(15)

and

$$C_6'' = \frac{1}{3\pi} \int_0^\infty du \Delta \alpha_1(iu) \Delta \alpha_2(iu).$$

(16)

Calculating the anisotropic coefficients for $H_2$ we obtain $C_6'/C_6 = 0.08$ and $C_6''/C_6 = 0.017$. Accurate values are $C_6'/C_6 = 0.1$ and $C_6''/C_6 = 0.01$. The anisotropy is thus underestimated slightly with the simple cutoff scheme described above. In Figures 3 and 4 our calculated $\alpha_{zz}(iu)$ and $\alpha_{xx}(iu)$ for $H_2$ are compared with accurate results.

For an atom or molecule a distance $d$ outside a surface, the asymptotic van der Waals energy is given by

$$E_{\text{vdW}} = -\frac{C_3}{(d - Z_0)^6},$$

(17)

where the van der Waals coefficient is

$$C_3 = \frac{1}{4\pi} \int_0^\infty du \overline{\alpha}(iu) \frac{\epsilon_b(iu) - 1}{\epsilon_b(iu) + 1},$$

(18)

and with the van der Waals plane

$$Z_0 = \frac{1}{4\pi C_3} \int_0^\infty du \alpha(iu) \frac{\epsilon_b(iu) - 1}{\epsilon_b(iu) + 1} \frac{\epsilon_b(iu)}{\epsilon_b(iu) + 1} d(iu).$$

(19)

In these expressions, $\epsilon_b(iu)$ is the bulk dielectric function, and $d(iu)$ is the centroid of the induced surface charge caused by an electric field oriented perpendicular to the surface and varying in time like $e^{iu\theta}$. Our earlier calculations of $C_3$ and $Z_0$ have used the exact electrodynamics, Eq. (3), for the surface but the approximate treatment, Eq. (13), for the atom and molecule. In this paper we use Eq. (8) also for the latter. In Table I the calculated values for $C_3$ and $Z_0$ are given for He and $H_2$ outside jellium, showing a very good agreement with other more elaborate calculations.

Including the orientational dependence that results from the anisotropy of the molecular polarizability, the energy for a homonuclear diatomic molecule is to first order given by

$$E_{\text{vdW}}(\theta) = -\frac{1}{d^3} \left[ C_3^{(0)} + C_3^{(2)} P_2(\cos \theta) \right],$$

(20)

where $\theta$ is the angle between the molecule axis and the surface normal. $C_3^{(0)}$ is given by Eq. (18) and

$$C_3^{(2)} = \frac{1}{4\pi} \int_0^\infty du \Delta \alpha(iu) \frac{\epsilon_b(iu) - 1}{\epsilon_b(iu) + 1}.$$

(21)

In Table I the ratio $C_3^{(2)}/C_3^{(0)}$ is given for $H_2$ outside jellium. We find this ratio to be around 0.05 in agreement with Ref. 8.

We have in this paper refined the electrodynamical treatment of atoms and molecules within our previously presented density functional framework, thereby unifying our approaches for objects of different sizes. The calculated polarizabilities and van der Waals coefficients are in good agreement with results in the literature. This gives a possibility to easily calculate these quantities for complex systems with useful accuracy.

**ACKNOWLEDGMENTS**

Work at Rutgers supported in part by NSF Grants No. DMR 94-07055 and DMR 97-08499. Financial support from the Swedish Natural Science Research Council and the Swedish Foundation for Strategic Research through Materials Consortium no. 9 is also acknowledged.

1. P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).
2. W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
3. O. Gunnarsson and B. I. Lundqvist, Phys. Rev. B **13**, 4274 (1976).
4. D. C. Langreth and M. J. Mehl, Phys. Rev. Lett. **47**, 446 (1981).
5. A. D. Becke, Phys. Rev. A **30**, 3098 (1988).
TABLE I. Van der Waals coefficients $C_6$ for pairs of identical atoms (Ry atomic units). The static polarizabilities used for defining the cutoff are given in the second column (atomic units) and results from other calculations in the fifth one. The third column gives the frequency $\nu_0$ obtained from the London formula, Eq. (4).

| System | $\alpha(0)$ | $\nu_0$ | $C_6$ | $C_6^{\text{ref}}$ |
|--------|-------------|--------|-------|-----------------|
| He-He  | 1.38$^a$    | 1.81   | 2.58  | 2.92$^a$        |
| Ne-Ne  | 2.67$^a$    | 2.80   | 15.0  | 13.8$^c$        |
| Ar-Ar  | 11.1$^a$    | 1.56   | 143   | 134$^c$         |
| Kr-Kr  | 16.7$^a$    | 1.37   | 291   | 266$^c$         |
| Xe-Xe  | 27.3$^d$    | 1.15   | 663   | 597$^c$         |
| H-H    | 4.5$^b$     | 0.70   | 10.6  | 13$^b$          |
| Li-Li  | 164$^e$     | 0.14   | 2830  | 2780$^f$        |
| Na-Na  | 159$^e$     | 0.16   | 3000  | 3080$^f$        |
| K-K    | 293$^e$     | 0.13   | 8400  | 7890$^f$        |
| Be-Be  | 37.5$^g$    | 0.41   | 429   | 425$^g$         |
| Mg-Mg  | 70$^h$      | 0.34   | 1230  | 1240$^f$        |
| Ca-Ca  | 154$^f$     | 0.25   | 4430  | 4010$^f$        |

TABLE II. Van der Waals coefficients $C_6$ for pairs of identical molecules (Ry atomic units). The static polarizabilities used for defining the cutoff are given in the second column (atomic units) and values from the literature in the fifth one. The third column gives the frequency $\nu_0$ obtained from the London formula, Eq. (4).

| System  | $\alpha(0)$ | $\nu_0$ | $C_6$ | $C_6^{\text{ref}}$ |
|---------|-------------|--------|-------|-----------------|
| H$_2$-H$_2$ | 5.41$^a$   | 0.98   | 21.5  | 24.1$^a$       |
| N$_2$-N$_2$ | 11.77$^a$ | 1.44   | 149   | 147$^b$        |
| CO-CO   | 13.1$^c$   | 1.37   | 176   | 163$^c$        |
| HF-HF   | 5.52$^d$   | 1.77   | 40.4  | 38$^e$         |
| H$_2$O-H$_2$O | 9.64$^f$ | 1.40   | 97.4  | 93$^f$         |
| Cs$_6$-Cs$_6$ | 570$^g$  | 1.24   | 302 $^k$ | 200 $^k$, 253 $^k$, 350 $^k$ |

$^a$ Ref. 31, $^b$ Ref. 40, $^c$ Ref. 38, $^d$ Ref. 28, $^e$ Ref. 38, $^f$ Ref. 38, $^g$ Ref. 34, $^h$ Ref. 30, $^i$ Ref. 29.
TABLE III. The van der Waals coefficient $C_3$ and the van der Waals plane position $Z_0$ (Ry atomic units) for He and H$_2$ interacting with jellium. For H$_2$ also the ratio between the anisotropic coefficient $C_3^{(2)}$ and $C_3^{(0)}$ is given.

|       | $r_s$ | $C_3$  | $C_3^{\text{ref}}$ | $C_3^{(2)}/C_3^{(0)}$ | $Z_0$  | $Z_0^{\text{ref}}$ |
|-------|-------|--------|--------------------|------------------------|-------|-------------------|
| He    | 2     | 0.10   | 0.10$^a$           | 0.78                   | 0.74  |                   |
|       | 3     | 0.064  | 0.064$^a$          | 0.62                   | 0.64$^b$ |               |
|       | 4     | 0.045  | 0.045$^a$          | 0.53                   | 0.59$^b$ |               |
| H$_2$ | 2     | 0.31   | 0.32$^a$           | 0.90                   | 0.85$^b$ |               |
|       | 3     | 0.22   | 0.22$^a$           | 0.70                   | 0.71$^b$ |               |
|       | 4     | 0.16   | 0.16$^a$           | 0.59                   | 0.64$^b$ |               |

$^a$ Ref. [30], $^b$ Ref. [45]

FIG. 1. Calculated van der Waals coefficients $C_6$ (Ry atomic units) for all possible pairs of the atoms in Table I plotted against corresponding values from other calculations.

FIG. 2. Our calculated $\alpha(iu)$ for He, compared with a more accurate calculation.
FIG. 3. Our calculated $\alpha(iu)$ for Be, compared with a more accurate calculation.

FIG. 4. Our calculated $\alpha_{zz}(iu)$ for $H_2$, compared with a more accurate calculation.

FIG. 5. Our calculated $\alpha_{xx}(iu)$ for $H_2$, compared with a more accurate calculation.