Unified treatment of asymptotic van der Waals forces

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In a framework for long-range density-functional theory we present a unified full-field treatment of the asymptotic van der Waals density functional by doing the full, self-consistent electrodynamics for atoms, molecules, surfaces, and other objects. The only input needed consists of the electron densities of the interacting fragments and the static polarizability 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. [S0163-1829(99)00707-9]

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),[1] with its local-density[2,3] and generalized-gradient approximations,[4–7] 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 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,[8] 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 we[9,10] and others[11,12] have proposed such functionals and shown them to give useful results in significant applications. For a review of our approach, see Ref. 13. Until now, however, there has been a certain asymmetry in our treatment of ''small'' objects, e.g., atoms and molecules being described with an approximate electrodynamics,[9] and ''large'' ones, with the exact electrodynamics for, e.g., surfaces.[10,19] This will be remedied in this paper with a unified treatment of the asymptotic van der Waals forces, applying the exact electrodynamics to all the interacting objects.

The starting point for our functionals is the exact expression for the exchange-correlation energy $E_{\rm xc}$ as an integral over the coupling constant λe^2, the so-called *adiabatic connection formula*[3,14] (ACF)

$$E_{\rm xc}[n]=\frac{1}{2}\int d^3r d^3r' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\int_0^1 d\lambda[\langle \tilde{n}(\mathbf{r})\tilde{n}(\mathbf{r}')\rangle_{n,\lambda} - \delta(\mathbf{r}-\mathbf{r}')\langle n(\mathbf{r})\rangle], \quad (1)$$

where $\tilde{n}=\hat{n}-n$,$\hat{n}$ being the density operator, and $\langle\cdots\rangle_{n,\lambda}$ means that the integration is performed with a potential V_λ present, keeping the density equal to $n(\mathbf{r})$. 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[8,15]

$$\Delta E_{\rm xc}(\mathbf{R})=E_{\rm xc}^{\infty}-\int\int\int\int d^3r_1 d^3r_2 d^3r_3 d^3r_4 \times V_{ab}(\mathbf{R}+\mathbf{r}_1-\mathbf{r}_2)V_{ab}(\mathbf{R}+\mathbf{r}_3-\mathbf{r}_4)\int_0^\infty \frac{du}{2\pi} \times \Pi_a(\mathbf{r}_1,\mathbf{r}_3;iu)\Pi_b(\mathbf{r}_2,\mathbf{r}_4;iu). \quad (2)$$

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,[16] outside which the response to an electric field is defined to be zero. We thus have the dielectric function

$$\epsilon(\omega;n(\mathbf{r}))=1-\kappa(n(\mathbf{r}))\frac{\omega_p^2(n(\mathbf{r}))}{\omega^2}; \quad (3)$$

where

$$\omega_p^2(n(\mathbf{r}))=4\pi e^2 n(\mathbf{r})/m. \quad (4)$$

The cutoff is implemented via the function $\kappa(n(r))$, which is either unity or zero, following the notion discussed earlier[9] 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,[9,17] an atom or molecule interacting with a planar surface,[10,18] and finally two interacting surfaces.[19] However, we have earlier treated the electrodynamics on different levels for ''small'' and ''large'' objects. Normally, local electrodynamics means a local relationship between the temporal Fourier transforms of the polarization **P** and the total electric field **E**,

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

which we use for surfaces. For atoms, however, the calculations get somewhat more complicated than in the surface case when using Eq. (5). For instance, the electrodynamics must be solved numerically for each frequency. Our earlier approach for atoms and molecules has approximated the local polarization by

$$\mathbf{P}(\mathbf{r},\omega)=\frac{1}{4\pi}[\epsilon(\omega;n(\mathbf{r}))-1]\frac{\mathbf{E}_{\text{applied}}(\mathbf{r},\omega)}{\epsilon(\omega;n(\mathbf{r}))}, \tag{6}$$

which implies the relation

$$\mathbf{E}(\mathbf{r},\omega)=\mathbf{E}_{\text{applied}}(\mathbf{r},\omega)/\epsilon(\omega;n(\mathbf{r})), \tag{7}$$

which is strikingly wrong for macroscopic objects, but gives surprisingly good results for atoms and molecules.[9,17,20] 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. (5) also for atoms and molecules. We apply it to the asymptotic van der Waals interaction of separated atoms, molecules, and parallel surfaces[19] 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[21,22]

$$C_6=\frac{3}{\pi}\int_0^\infty du\,\alpha_1(iu)\alpha_2(iu) \tag{8}$$

and $\alpha_j(iu)$ is the polarizability at imaginary frequency $\omega=iu$ of atom j. To calculate $\alpha(iu)$ we solve $\nabla\cdot\mathbf{D}(\mathbf{r},iu)=0$, for each frequency in the presence of a spatially uniform applied electric field $\mathbf{E}_{\text{applied}}(\mathbf{r},iu)=E_0(iu)\hat{z}$. The displacement $\mathbf{D}(\mathbf{r},iu)$ is given by $\epsilon(iu;n(\mathbf{r}))\mathbf{E}(\mathbf{r},iu)$ and $\mathbf{E}(\mathbf{r},iu)=-\nabla\phi(\mathbf{r},iu)$. Thus we solve the equation

$$\nabla\cdot[\epsilon(iu;n(\mathbf{r}))\nabla\phi(\mathbf{r},iu)]=0, \tag{9}$$

where $\epsilon(iu;n(\mathbf{r}))$ is given by Eqs. (3) and (4) and with the boundary condition that $\mathbf{E}(\mathbf{r},iu)$ approaches $E_0(iu)\hat{z}$ at infinity.

Assume for simplicity that we have solved Eq. (9) for an atom, where the applied field is directed along the z axis with magnitude $E_0(iu)$. We then obtain $\alpha(iu)$ from the relation $p(iu)=\alpha(iu)E_0(iu)$, where the dipole moment $p(iu)$ is given by $p(iu)=\int d^3rP(\mathbf{r},iu)$. From Eq. (5) we get

$$\begin{aligned}\alpha(iu)&=\frac{1}{E_0(iu)}\int d^3rP(\mathbf{r},iu)\\&=-\frac{1}{4\pi E_0(iu)}\int d^3r[\epsilon(iu;n(\mathbf{r}))-1]\hat{z}\cdot\nabla\phi(\mathbf{r},iu),\end{aligned} \tag{10}$$

where for each frequency we first must solve numerically for ϕ. In the old scheme, using Eq. (6) we instead obtain the expression

$$\begin{aligned}\alpha(iu)&=\frac{1}{E_0(iu)}\int d^3rP(\mathbf{r},iu)\\&=\frac{1}{4\pi E_0(iu)}\int d^3r[\epsilon(iu;n(\mathbf{r}))-1]\frac{E_0(iu)}{\epsilon(iu;n(\mathbf{r}))}\\&=\frac{1}{4\pi}\int d^3r\frac{[\epsilon(iu;n(\mathbf{r}))-1]}{\epsilon(iu;n(\mathbf{r}))},\end{aligned} \tag{11}$$

which we can immediately evaluate using Eq. (3). The latter approach is thus computationally extremely simple, but it does not give very good results for large objects. In this paper we show that the exact electrodynamic treatment improves the results considerably.

The cutoff function $\kappa(n(\mathbf{r}))$ must however first be defined. For surfaces, the cutoff is found by taking the static limit of the surface response,[10] which implies that the cutoff should be defined by the static image plane $d(0)$. In order to have a common cutoff scheme for 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 κ according to

$$\kappa(\mathbf{r})=\theta(n(\mathbf{r})-c), \tag{12}$$

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 Eq. (12) is to eliminate any cutoff in the intrashell regions. We have found that inclusion of the cutoff in the intrashell 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 intrashell corrections should be included even in principle is arguable, and since they are small, we have therefore opted for the simpler scheme (12). Adapting the analogue of the procedure used when the full-field scheme is applied to surfaces,[10] we fix the constant c in Eq. (12) so that the static polarizibilities are accurate. For a spherically symmetric species, this means that the volume V inside which the step function in Eq. (12) is nonvanishing is simply $V=(4\pi/3)\alpha(0)$. For species without spherical symmetry, we choose c so that the isotropic polarizabilities $\bar{\alpha}(0)$ [see Eq. (14)] 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. (9) 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, here we represent $\alpha(iu)$ by the expression $a+b/(1+u^2/c^2)$, where a, b, and c are fixed by a smooth continuation of high-frequency results. In Table I calculated 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 Fig. 1 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 calcu-

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 sixth one. The third column gives the frequency u_0 obtained from the London formula, Eq. (13). For comparison, previous results (Ref. 9) using the approximate electrodynamics are included in the fifth column.

	$\alpha(0)$	u_0	C_6	C_6^{old}	C_6^{ref}
He-He	1.38 [a]	1.81	2.58	4	2.92 [b]
Ne-Ne	2.67 [a]	2.80	15.0	12	13.8 [c]
Ar-Ar	11.1 [a]	1.56	143	126	134 [c]
Kr-Kr	16.7 [a]	1.37	291	245	266 [c]
Xe-Xe	27.3 [d]	1.15	663	520	597 [c]
H-H	4.5 [b]	0.70	10.6	12	13 [b]
Li-Li	164 [e]	0.14	2830	1335	2780 [f]
Na-Na	159 [e]	0.16	3000	1849	3080 [f]
K-K	293 [e]	0.13	8400	5640	7890 [f]
Be-Be	37.5 [g]	0.41	429	582	425 [g]
Mg-Mg	70 [h]	0.34	1230	1513	1240 [f]
Ca-Ca	154 [f]	0.25	4430	4500	4010 [f]

[a]Reference 38.
[b]Reference 30.
[c]Reference 33.
[d]Reference 29.
[e]Reference 39.
[f]Reference 34.
[g]Reference 35.
[h]Reference 40.

lations, 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.[9] In Figs. 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 Fig. 3 for Be is a best-case example with a C_6 right on the reference value.

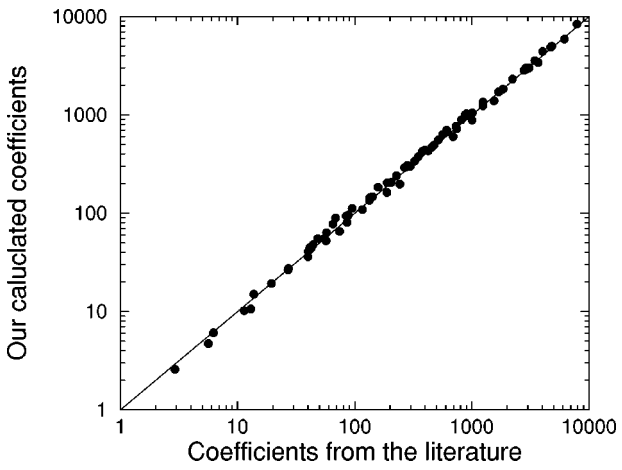

FIG. 1. Calculated van der Waals coefficients C_6 (Ry atomic units) for all possible pairs of the atoms in Table I plotted against corresponding values from other calculations (Refs. 30 and 33–36).

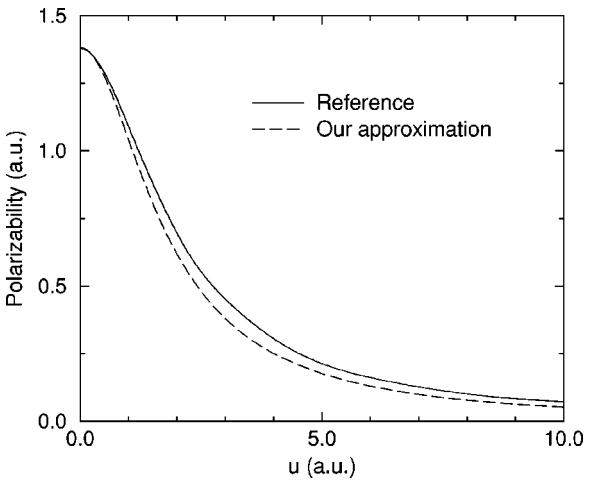

FIG. 2. Our calculated $\alpha(iu)$ for He, compared with a more accurate calculation (Ref. 37).

Calculated C_6 values for a few molecules are given in Table II 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_{60}. Recently the dispersion energy between two fullerenes has been computed from first principles in time-dependent DFT, which gives the van der Waals coefficient $C_6 = 253$ kRy a_0^6.[24] Earlier, simpler methods have been used to estimate the polarizability and the van der Waals coefficient. A summation of C-C interactions gives $C_6 = 200$ kRy a_0^6,[25] and for a calculation of dipole modes using a discrete dipole model the result is $C_6 = 350$ kRy a_0^6.[25] Using $\alpha(0) = 570 a_0^3$ (experimental value from Ref. 26) we get $C_6 = 302$ kRy a_0^6, a result that 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[27]

$$C_6 = \alpha^A(0)\alpha^B(0)\frac{3u_0^A u_0^B}{2(u_0^A + u_0^B)}, \tag{13}$$

where A and B denote the two fragments, are also given. This formula provides an easy way of estimating isotropic van der

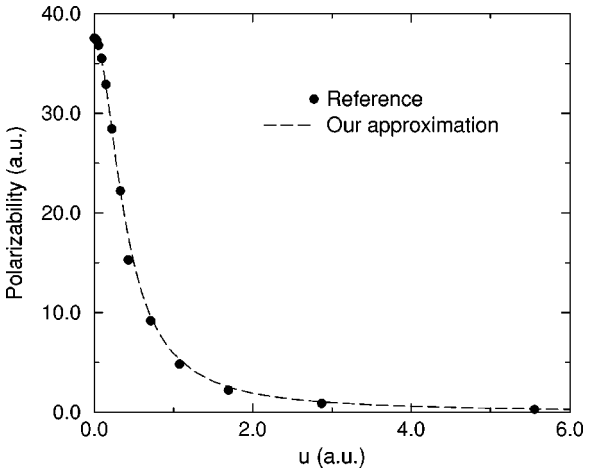

FIG. 3. Our calculated $\alpha(iu)$ for Be, compared with a more accurate calculation (Ref. 35).

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 u_0 obtained from the London formula, Eq. (13).

	$\alpha(0)$	u_0	C_6	C_6^{ref}
H_2-H_2	5.41 [a]	0.98	21.5	24.1 [a]
N_2-N_2	11.77 [b]	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_2O-H_2O	9.64 [f]	1.40	97.4	93 [f]
C_{60}-C_{60}	570 [g]	1.24	302 k	200 k, [h] 253 k, [i] 350 k [h]

[a]Reference 30.
[b]Reference 41.
[c]Reference 42.
[d]Reference 43.
[e]Reference 44.
[f]Reference 45.
[g]Mean value of estimates from Ref. 26.
[h]Reference 25.
[i]Reference 24.

Waals coefficients for mixed pairs of atoms and molecules.[28,29]

In Table II we have only given the isotropic dispersion coefficients for the molecules; that is, we have used the averaged polarizability $\bar{\alpha}(iu)$ in Eq. (8), where

$$\bar{\alpha}(iu)=\tfrac{1}{3}[\alpha_{xx}(iu)+\alpha_{yy}(iu)+\alpha_{zz}(iu)]. \tag{14}$$

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[30]

$$E_{\text{vdW}}(R,\theta_A,\theta_B,\phi_A,\phi_B) = -\left[C_6+C_6'\{P_2(\cos\theta_A)+P_2(\cos\theta_B)\}+\frac{4\pi}{5}C_6'' \times\sum_{m=-2}^{2}(3-|m|)Y_2^m(\theta_A,\phi_A)Y_2^{-m}(\theta_B,\phi_B)\right]R^{-6}, \tag{15}$$

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

$$\Delta\alpha(iu)=\alpha_{zz}(iu)-\alpha_{xx}(iu) \tag{16}$$

these coefficients can be written[30]

$$C_6'=\frac{1}{\pi}\int_0^\infty du\,\bar{\alpha}_1(iu)\Delta\alpha_2(iu) \tag{17}$$

and

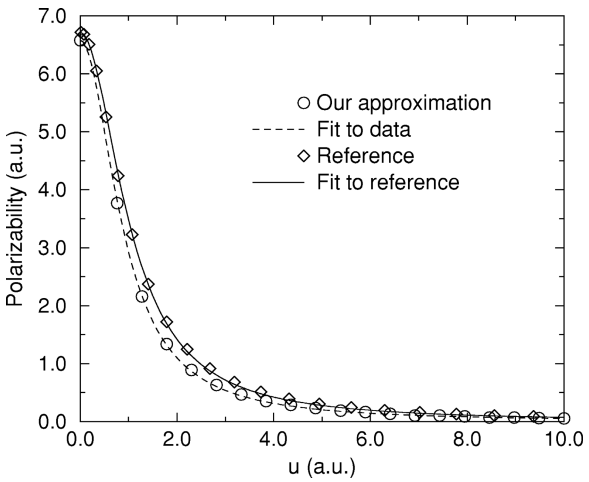

FIG. 4. Our calculated $\alpha_{zz}(iu)$ for H_2, compared with a more accurate calculation (Ref. 37).

$$C_6''=\frac{1}{3\pi}\int_0^\infty du\,\Delta\alpha_1(iu)\Delta\alpha_2(iu). \tag{18}$$

Calculating the anisotropic coefficients for H_2, we obtain $C_6'/C_6=0.08$ and $C_6''/C_6=0.007$. Accurate values are $C_6'/C_6=0.1$ and $C_6''/C_6=0.01$.[30] The anisotropy is thus underestimated slightly with the simple cutoff scheme described above. In Figs. 4 and 5 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[31]

$$E_{\text{vdW}}=-\frac{C_3}{(d-Z_0)^3}, \tag{19}$$

where the van der Waals coefficient is

$$C_3=\frac{1}{4\pi}\int_0^\infty du\,\bar{\alpha}(iu)\frac{\epsilon_b(iu)-1}{\epsilon_b(iu)+1}, \tag{20}$$

and with the van der Waals plane

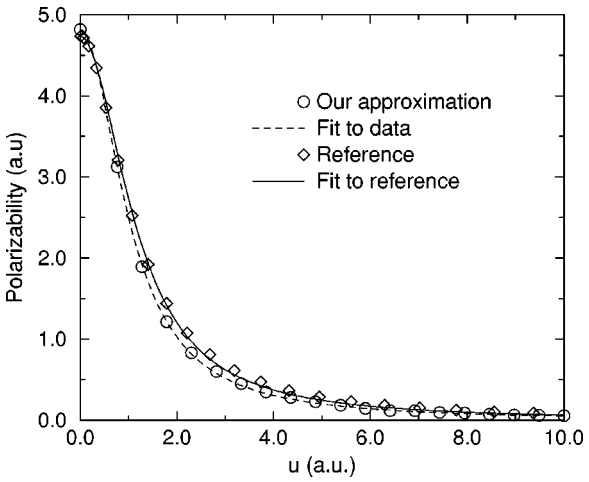

FIG. 5. Our calculated $\alpha_{xx}(iu)$ for H_2, compared with a more accurate calculation (Ref. 37).

TABLE III. 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^{ref}	$C_3^{(2)}/C_3^{(0)}$	Z_0	Z_0^{ref}
He	2	0.10	0.10 [a]		0.78	0.74 [b]
	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]	0.040	0.91	0.85 [b]
	3	0.22	0.22 [a]	0.044	0.70	0.71 [b]
	4	0.16	0.16 [a]	0.046	0.59	0.64 [b]

[a]Reference 31.
[b]Reference 46.

$$Z_0=\frac{1}{4\pi C_3}\int_0^\infty du\,\alpha(iu)\frac{\epsilon_b(iu)-1}{\epsilon_b(iu)+1}\,\frac{\epsilon_b(iu)}{\epsilon_b(iu)+1}\,d(iu). \tag{21}$$

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^{ut}. Our earlier calculations[10,18] of C_3 and Z_0 have used the exact electrodynamics, Eq. (5), for the surface but the approximate treatment, Eq. (6), for the atom and molecule. In this paper we use Eq. (5) also for the latter. In Table III 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[32]

$$E_{\text{vdW}}(\theta)=-\frac{1}{d^3}[C_3^{(0)}+C_3^{(2)}P_2(\cos\theta)], \tag{22}$$

where θ is the angle between the molecule axis and the surface normal. $C_3^{(0)}$ is given by Eq. (20) and

$$C_3^{(2)}=\frac{1}{4\pi}\int_0^\infty du\,\Delta\alpha(iu)\frac{\epsilon_b(iu)-1}{\epsilon_b(iu)+1}. \tag{23}$$

In Table III 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. 32.

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.

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[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 **38**, 3098 (1988).
[6] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, Phys. Rev. B **46**, 6671 (1992).
[7] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[8] B. I. Lundqvist, Y. Andersson, H. Shao, S. Chan, and D. C. Langreth, Int. J. Quantum Chem. **56**, 247 (1995).
[9] Y. Andersson, D. C. Langreth, and B. I. Lundqvist, Phys. Rev. Lett. **76**, 102 (1996).
[10] E. Hult, Y. Andersson, B. I. Lundqvist, and D. C. Langreth, Phys. Rev. Lett. **77**, 2029 (1996).
[11] J. F. Dobson and B. P. Dinte, Phys. Rev. Lett. **76**, 1780 (1996).
[12] W. Kohn, Y. Meir, and D. E. Makarov, Phys. Rev. Lett. **80**, 4153 (1998).
[13] Y. Andersson, E. Hult, H. Rydberg, P. Apell, B. I. Lundqvist, and D. C. Langreth, in *Electronic Density Functional Theory: Recent Progress and New Directions*, edited by J. F. Dobson, G. Vignale, and M. P. Das (Plenum, New York, 1997), p. 243.
[14] D. C. Langreth and J. P. Perdew, Solid State Commun. **17**, 1425 (1975); Phys. Rev. B **15**, 2884 (1977).
[15] J. F. Dobson, in *Topics in Condensed Matter Physics*, edited by M. P. Das (Nova, New York, 1994).
[16] K. Rapcewicz and N. W. Ashcroft, Phys. Rev. B **44**, 4032 (1991).
[17] Y. Andersson and H. Rydberg (unpublished).
[18] E. Hult and A. Kiejna, Surf. Sci. **383**, 88 (1997).
[19] Y. Andersson, E. Hult, P. Apell, D. C. Langreth, and B. I. Lundqvist, Solid State Commun. **106**, 235 (1998).
[20] One reason for the good results of the approach using the approximate electrodynamics is that the optimum cutoff position defined by $\kappa(n(r))$ is somewhat larger in that case than for the exact electrodynamics, and this fact seems to mitigate some of the deficiencies of the approximation.
[21] C. Mavroyannis and M. J. Stephen, Mol. Phys. **5**, 629 (1962).
[22] H. Margenau and N. R. Kestner, *Theory of Intermolecular Forces* (Pergamon Press, Oxford, 1969).
[23] H. Rydberg, Licentiate thesis, Chalmers University of Technology, 1998.
[24] J. M. Pacheco and J. P. Prates Ramalho, Phys. Rev. Lett. **79**, 3873 (1997).
[25] C. Girard, P. Lambin, A. Dereux, and A. Lucas, Phys. Rev. B **49**, 11 425 (1994).
[26] F. Alasia, R. A. Broglia, H. E. Roman, L. Serra, G. Colo, and J. M. Pacheco, J. Phys. B **27**, L643 (1994).
[27] F. London, Z. Phys. Chem. Abt. B **11**, 222 (1930).
[28] G. D. Mahan, J. Chem. Phys. **76**, 493 (1982).

[29] K. T. Tang and J. P. Toennis, Z. Phys. D **1**, 91 (1986).
[30] D. M. Bishop and J. Pipin, Int. J. Quantum Chem. **45**, 349 (1993).
[31] E. Zaremba and W. Kohn, Phys. Rev. B **13**, 2270 (1976).
[32] J. Harris and P. J. Feibelman, Surf. Sci. **115**, L133 (1982).
[33] J. M. Standard and P. R. Certain, J. Chem. Phys. **83**, 3002 (1985). Note that this paper is an update of the reference used in Ref. 9, using newer, more accurate, input data.
[34] F. Maeder and W. Kutzelnigg, Chem. Phys. **42**, 95 (1979).
[35] H. Koch and R. J. Harrison, J. Chem. Phys. **95**, 7479 (1991).
[36] K. T. Tang, J. M. Norbeck, and P. R. Certain, J. Chem. Phys. **64**, 3063 (1976).
[37] D. M. Bishop and J. Pipin, J. Chem. Phys. **97**, 3375 (1992).
[38] P. J. Leonard, At. Data Nucl. Data Tables **14**, 21 (1974).
[39] R. W. Molof, H. L. Schwartz, T. M. Miller, and B. Bederson, Phys. Rev. A **10**, 1131 (1974).
[40] H. Gollisch, J. Phys. B **17**, 1463 (1984).
[41] W. J. Meath and A. Kumar, Int. J. Quantum Chem., Symp. **24**, 501 (1990).
[42] A. Kumar and W. J. Meath, Chem. Phys. **189**, 467 (1994).
[43] G. H. F. Diercksen and A. J. Sadlej, J. Chem. Phys. **75**, 1253 (1981).
[44] A. Kumar and W. J. Meath, Mol. Phys. **54**, 823 (1985).
[45] G. D. Zeiss and W. J. Meath, Mol. Phys. **33**, 1155 (1977).
[46] A. Liebsch, Phys. Rev. B **33**, 7249 (1986).