

## Van der Waals Density Functional for General Geometries

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A scheme within density functional theory is proposed that provides a practical way to generalize to unrestricted geometries the method applied with some success to layered geometries [H. Rydberg *et al.*, Phys. Rev. Lett. **91**, 126402 (2003)]. It includes van der Waals forces in a seamless fashion. By expansion to second order in a carefully chosen quantity contained in the long-range part of the correlation functional, the nonlocal correlations are expressed in terms of a density-density interaction formula. It contains a relatively simple parametrized kernel, with parameters determined by the local density and its gradient. The proposed functional is applied to rare gas and benzene dimers, where it is shown to give a realistic description.

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Density functional theory (DFT) for molecules and materials is widely applied with approximate *local* and *semilocal* density functionals for the interaction effects. For largely homogeneous systems, for example, simple metals and semiconductors, the local-density approximation (LDA) for these effects is appropriate. For inhomogeneous systems, for example, transition metals, ionic crystals, compound metals, surfaces, interfaces, and some chemical systems, semilocal-density approximations, such as members of the family of generalized gradient approximations (GGA), work well. Today DFT describes cohesion, bonds, structures, and other properties very well for dense molecules and materials, as shown by recent studies for both single molecules [1] and dense solid-state [2] systems. However, sparse systems, including soft matter, van der Waals complexes, and biomolecules, are at least as abundant. They have interparticle separations, for which *nonlocal*, long-ranged interactions, such as van der Waals (vdW) forces, are influential.

The aim of this Letter is to develop and apply a van der Waals density functional (vdW-DF) for general geometries to supplement the planar vdW-DF that we recently applied with some success [3] to several layered materials. The simplest form for the nonlocal correlation-energy part to such a functional is

$$E_c^{\text{nl}} = \frac{1}{2} \int d^3r d^3r' n(\vec{r}) \phi(\vec{r}, \vec{r}') n(\vec{r}'), \quad (1)$$

where  $\phi(\vec{r}, \vec{r}')$  is some given, general function depending on  $\vec{r} - \vec{r}'$  and the densities  $n$  in the vicinity of  $\vec{r}$  and  $\vec{r}'$ . It is approximately derived here and applied to some key cases, with results that give promise for broader applications.

We start with the same approximation scheme used for layered systems [3,4], and divide the correlation energy into two pieces,

$$E_c[n] = E_c^0[n] + E_c^{\text{nl}}[n], \quad (2)$$

which are treated in different approximations. In particular, as discussed in Ref. [4], we treat the second term in the full potential approximation, which is exact at long distances between separated fragments, and therefore adopt Eq. (25) of Ref. [4]:

$$E_c^{\text{nl}} = \int_0^\infty \frac{du}{2\pi} \text{tr}[\ln(1 - V\tilde{\chi}) - \ln\epsilon], \quad (3)$$

where  $\tilde{\chi}$  is the density response to a fully self-consistent potential with long-range, interfragment spectator [5] contributions omitted [4].  $V$  is the interelectronic Coulomb interaction,  $\epsilon$  an appropriately approximated dielectric function, and  $u$  the imaginary frequency. While Eq. (3) is taken to be the definition of  $E_c^{\text{nl}}$ , we will show that Eq. (1) can be obtained with suitable approximations. The first term  $E_c^0$ , defined by Eqs. (2) and (3), is also nonlocal; however, with the long-range vdW terms treated separately, it seems a reasonable approximation to treat  $E_c^0$  in the LDA, and this is what we do. There is no double counting, because for a uniform system  $1 - V\tilde{\chi} = \epsilon$ , which implies that the LDA for  $E_c^{\text{nl}}$  vanishes. This is also the key to a seamless theory.

For layered systems, the scheme was made tractable by the use of the lateral average of the densities to calculate the interplanar contribution from Eq. (3) [6]. For general geometries, we make the scheme tractable by expanding Eq. (3) to second order in  $S \equiv 1 - \epsilon^{-1}$ , obtaining

$$E_c^{\text{nl}} \approx \int_0^\infty \frac{du}{4\pi} \text{tr} \left[ S^2 - \left( \frac{\nabla S \cdot \nabla V}{4\pi e^2} \right)^2 \right]. \quad (4)$$

This vanishes in the uniform limit as it must.

This  $S$  expansion replaces the exact solution to the Poisson equation for all possible external potentials, which was carried out for the planar functional [6]. It gives the correct asymptotic forms for fragments, parallel sheets, and parallel surfaces. For fields parallel to the density gradient, it includes the correct differential local field correction. For fields perpendicular to the density gradient, the response is correct to the extent that  $S$  can be

treated as a small quantity, as it can in good parts of the frequency and density integration range. In many-body perturbation theory, the  $S$  expansion corresponds to a well specified (infinite) set of terms, which will allow future corrections in cases where they should prove necessary. This approximation to the electrodynamics (proposed earlier [7,8]) was used to calculate the  $C_6$  coefficient successfully over a large set of atomic and molecular pairs [7,9], with some excerpts in the second data column of Table I. Comparison with the third data column, calculated with exact electrodynamics, shows that we may expect an error on the level of 20% to be introduced by the  $S$  expansion. However, the  $C_2$  coefficient for parallel surfaces is somewhat less accurately predicted than this, and the effect of possible anisotropic atomic polarizabilities on  $C_6$  is not included at all. Nevertheless, the functional apparently gives exemplary results for layered systems, for example, improving the results of the planar functional on graphite [3].

In order to evaluate Eq. (4), we need a simple approximation for  $S$ , as a functional of the density. This choice is constrained by a number of exact relationships. In a plane-wave representation,  $S_{\vec{q},\vec{q}'}$ , one has the requirements (i)  $S_{\vec{q},\vec{q}'}(\omega) \rightarrow -(4\pi e^2/m\omega^2)n_{\vec{q}-\vec{q}'}$  at large frequencies (the  $f$ -sum rule), where  $n_{\vec{k}}$  is the Fourier transform of the density; (ii)  $\int_{-\infty}^{\infty} du S_{\vec{q},\vec{q}'}(iu) \rightarrow 8\pi^2 N e^2/q^2$  for large  $q$ , where  $N$  is the number of electrons, to reproduce the exactly known self-correlation; (iii)  $S_{\vec{q},\vec{q}'} = S_{-\vec{q}',-\vec{q}}$  for time reversal invariance; (iv) a finite  $S_{\vec{q},\vec{q}'}(\omega)$  for vanishing  $q$  or  $q'$  at all nonzero values of  $\omega$ , to give an exchange-correlation hole with the correct volume (charge conservation).

An approximate  $S$  inspired by the plasmon-pole model successfully applied earlier [6] takes  $S_{\vec{q},\vec{q}'} = \frac{1}{2}[S_{\vec{q},\vec{q}'} + S_{-\vec{q}',-\vec{q}}]$ , where

$$\tilde{S}_{\vec{q},\vec{q}'} = \int d^3r e^{-i(\vec{q}-\vec{q}')\cdot\vec{r}} \frac{4\pi n(\vec{r})e^2/m}{[\omega + \omega_q(\vec{r})][-\omega + \omega_{q'}(\vec{r})]}. \quad (5)$$

We will take  $\omega_q(\vec{r})$  to be a function of the local density at point  $\vec{r}$  and its gradient. The above  $S$  satisfies all the constraints provided  $\omega_q \rightarrow q^2/2m$  for large  $q$ .

TABLE I.  $C_6$  values for dimers (Rydberg atomic units). Present: from Eq. (17). Similar: calculations from Ref. [7] using the same electrodynamics approximation. Unified: calculations from Ref. [10] using self-consistent electrodynamics. Reference: sources cited in Ref. [10].

Dimer	Present	Similar	Unified	Reference
He	4.8	4	2.58	2.92
Ne	14.6	12	15.0	13.8
Ar	124	126	143	134
Kr	238	245	291	266
Xe	516	520	663	597
Mg	1598	1513	1230	1240

To facilitate the numerical evaluation, we choose an  $\omega_q$  which depends on a single length scale  $l$ , and switches from its small- $q$  form  $\omega_q = 1/2ml^2$  to its large- $q$  form (above) when  $q \sim 1/l$ . We make an arbitrary choice for the switching function letting  $[1 - e^{-(ql)^2}]\omega_q = q^2/2m$ . The quantity  $l$  will be a function of position, and for convenience later we define  $q_0^2 = \gamma/l^2$ , where  $\gamma = 4\pi/9$ . Hence, letting  $h(y) = 1 - e^{-\gamma y^2}$ , we may write

$$\omega_q(\vec{r}) = \frac{q^2}{2m} \frac{1}{h[q/q_0(\vec{r})]}. \quad (6)$$

It would, of course, be preferable to use a form with a second length scale, as would be provided by a linear term  $\propto qv_F$  in the  $\omega_q$  dispersion [3,4,6], but this source of error is mitigated by a continuously variable choice of  $q_0$  based on the density. We make this choice so the exchange-correlation energy density  $\varepsilon_{xc}^0(\vec{r})$  defined by

$$E_{xc}^0 = \int d^3r \varepsilon_{xc}^0(\vec{r})n(\vec{r}) \quad (7)$$

produced by this choice of  $q_0(\vec{r})$  corresponds to that of a full calculation.

The expression for  $E_{xc}^0$  corresponding to the approximation (3) for  $E_c^{\text{nl}}$  is simply

$$E_{xc}^0 \approx \int_0^\infty \frac{du}{2\pi} \text{tr}(\ln \epsilon) - E_{\text{self}} \approx \int_0^\infty \frac{du}{2\pi} \text{tr} S - E_{\text{self}}, \quad (8)$$

where  $E_{\text{self}}$  subtracts off the internal Coulomb self-energy of each electron. As was done previously, we expand to lowest order in  $S$  in the second equality. Substituting for  $S$  using (5), integrating over  $u = -i\omega$ , and using Eq. (7) gives

$$\varepsilon_{xc}^0(\vec{r}) = \frac{\pi e^2}{m} \int \frac{d^3q}{(2\pi)^3} \left[ \frac{1}{\omega_q(\vec{r})} - \frac{2m}{q^2} \right], \quad (9)$$

where the second term in the brackets is the self-energy subtraction written explicitly. Upon substitution from (6), one finds

$$\varepsilon_{xc}^0(\vec{r}) = \frac{e^2 q_0(\vec{r})}{\pi} \int_0^\infty dy [h(y) - 1] = -\frac{3e^2}{4\pi} q_0(\vec{r}). \quad (10)$$

Approximations for  $\varepsilon_{xc}$  are conveniently expressed as their ratio to the LDA exchange value  $\varepsilon_x^{\text{LDA}} = -3e^2 k_F/4\pi$ , where  $k_F^3 = 3\pi^2 n$ . Equation (10) then implies that the local value of the parameter  $q_0$  is simply given by the local value of  $k_F$  modulated by an easily understood energy ratio; that is,

$$q_0(\vec{r}) = \frac{\varepsilon_{xc}^0(\vec{r})}{\varepsilon_x^{\text{LDA}}(\vec{r})} k_F(\vec{r}). \quad (11)$$

Equation (11) is used to determine the  $q_0$  value to be used in Eq. (6), continuously as a function of position. For this purpose we use LDA with gradient corrections,

$$\varepsilon_{xc}^0 \approx \varepsilon_{xc}^{\text{LDA}} - \varepsilon_x^{\text{LDA}} \left[ \frac{Z_{\text{ab}}}{9} \left( \frac{\nabla n}{2k_F n} \right)^2 \right], \quad (12)$$

where  $Z_{ab} = -0.8491$ . This is the contribution labeled “screened exchange” in the table in the review of Ref. [11], where the relationship to the original work of various authors, who obtained this quantity from first principles, is discussed. The remaining contribution  $Z_c$ , labeled “fluctuation” in Ref. [11], is part of  $E_c^{\text{nl}}$ , and, hence, inappropriate to include as part of  $E_{\text{xc}}^0$ . It comes from a term in perturbation theory that gives a long-range vdW-like interaction if taken at long range instead of in an expansion in gradients [12].

Writing Eq. (4) in a plane-wave representation gives

$$E_{\text{xc}}^{\text{nl}} = \int_0^\infty \frac{du}{4\pi} \sum_{\vec{q}, \vec{q}'} [1 - (\hat{q} \cdot \hat{q}')^2] S_{\vec{q}, \vec{q}'} S_{\vec{q}', \vec{q}}. \quad (13)$$

This may be straightforwardly, but tediously, expressed in the form of Eq. (1), where the kernel  $\phi$  is given by

$$\phi(\vec{r}, \vec{r}') = \frac{2me^4}{\pi^2} \int_0^\infty a^2 da \int_0^\infty b^2 db W(a, b) \times T(\nu(a), \nu(b), \nu'(a), \nu'(b)), \quad (14)$$

where

$$T(w, x, y, z) = \frac{1}{2} \left[ \frac{1}{w+x} + \frac{1}{y+z} \right] \left[ \frac{1}{(w+y)(x+z)} + \frac{1}{(w+z)(y+x)} \right], \quad (15)$$

and

$$W(a, b) = 2[(3 - a^2)b \cos b \sin a + (3 - b^2)a \cos a \sin b + (a^2 + b^2 - 3) \sin a \sin b - 3ab \cos a \cos b] / a^3 b^3. \quad (16)$$

The quantities  $\nu$  and  $\nu'$  are given by  $\nu(y) = y^2/2h(y/d)$  and  $\nu'(y) = y^2/2h(y/d')$ , with  $d = |\vec{r} - \vec{r}'|q_0(\vec{r})$  and  $d' = |\vec{r} - \vec{r}'|q_0(\vec{r}')$ , where  $q_0$  is given by Eq. (11). The kernel  $\phi$  thus depends on  $\vec{r}$  and  $\vec{r}'$  only through  $d$  and  $d'$ , so that  $\phi$  can be tabulated in advance in terms of these two variables, or better yet in terms of the sum and difference variables  $D$  and  $\delta$  defined by  $d = D(1 + \delta)$  and  $d' = D(1 - \delta)$ . Then  $0 \leq D < \infty$  and  $0 \leq |\delta| < 1$ . For large  $d$  and  $d'$ , the asymptotic form is

$$\phi \rightarrow -\frac{C}{d^2 d'^2 (d^2 + d'^2)}, \quad (17)$$

where  $C = 12(4\pi/9)^3 me^4$ . In Fig. 1, we show a plot of  $4\pi D^2 \phi$  vs  $D$  for several values of  $\delta$ . The integral of the  $\delta = 0$  curve vanishes as it must.

The numerical work uses Eq. (2) for the correlation functional coupled with the Zhang-Yang revPBE [13] exchange functional. This choice is motivated by the work of Wu *et al.* [14], which pointed out that a more standard GGA predicts substantial binding in rare gas dimers from exchange alone, a feature absent for exact Hartree-Fock (HF) exchange. We found [4] that revPBE exchange does not have this property, so by using it we

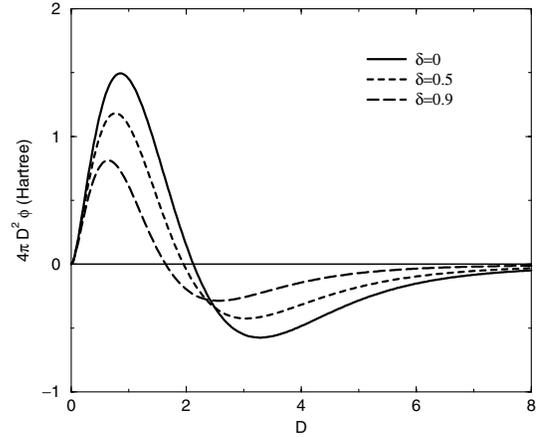


FIG. 1. The kernel  $\phi$  in Eq. (1) as a function of the dimensionless  $D$  parameter for several values of the asymmetry parameter  $\delta$ , as defined in the text.

ensure that vdW binding, a correlation effect, actually comes from the correlation term in our approximation scheme [15].

In Table I, our calculated values for the coefficient  $C_6$  in the asymptotic interaction  $-C_6/R^6$  between the elements of several dimers are compared with those from previous related calculations as well as reference values, which also have some uncertainty.

Figure 2 shows the calculated binding-energy curves as functions of separation for Ar and Kr dimers. The comparison with experimental values for the binding energy and distance [16] illustrate the promise of vdW-DF for such systems. The binding-energy curves for a benzene dimer in the atop-parallel configuration in

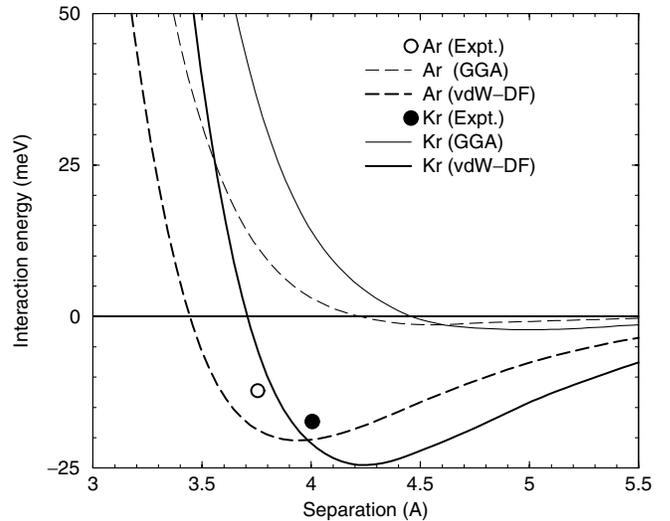


FIG. 2. Calculated interaction energy between two Ar atoms (dashed curves) and between two Kr atoms (solid curves). The experimental equilibrium data [16] are shown for comparison with the full vdW-DF, and the GGA predictions in the revPBE flavor are also shown.

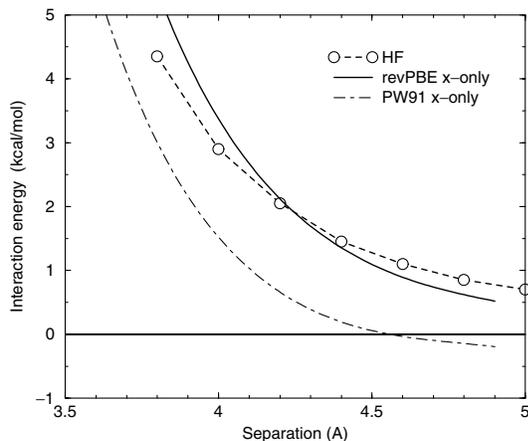


FIG. 3. Interaction energy between two benzene molecules in the atop-parallel configuration as predicted by the exchange-only part of two of the several GGA functionals tested. The full Hartree-Fock results [17] are shown for comparison.

Fig. 3 illustrate the importance of choosing the right GGA flavor, i.e., revPBE [13], to avoid erroneous attraction in exchange-only accounts, as discussed in Refs. [4,14]. Figure 4 illustrates the relative agreement between modern wave function based calculations [17] and our vdW-DF method, and the importance of not using the GGA alone. We have also studied the benzene dimer in the slipped-parallel and T-shaped geometries. Also, here our results compare well with those of wave function

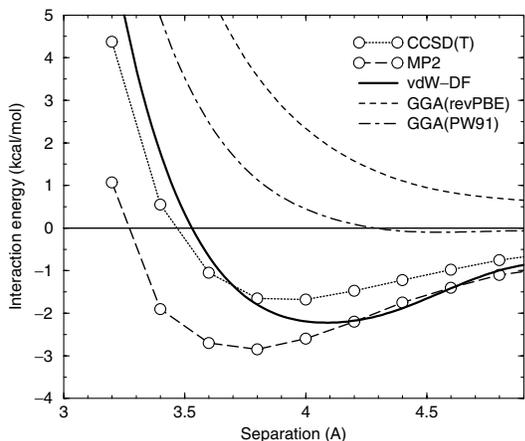


FIG. 4. Full interaction energy between two benzene molecules in the atop-parallel configuration using the vdW-DF functional. For comparison, we show recent results [17] using coupled-cluster [CCSD(T)] and perturbation-theoretic (MP2) methods, as well as the prediction of two flavors of GGA. Our vdW-DF would have given an equilibrium separation closer to those from the wave function calculations, if exact HF exchange (see Fig. 3) had been used instead of revPBE exchange.

based calculations. Preliminary tests on the water dimer also give similar qualitatively good results.

The above moderate successes of the vdW-DF proposed here suggest that its use, along with future improvements, may be a way to proceed for calculating properties of vdW bound molecules that are too large for wave function based methods to be useful.

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