Nonlocal van der Waals Density Functional Made Simple

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We derive a nonlocal correlation functional that adequately describes van der Waals interactions not only in the asymptotic long-range regime but also at short range. Unlike its precursor, developed by Langreth, Lundqvist, and co-workers, the new functional has a simple analytic form, finite for all interelectron separations, well behaved in the slowly varying density limit, and generalized to spin-polarized systems.

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Kohn-Sham density functional theory (DFT) [1] is the most prominent method for the electronic structure of molecules and solids, but commonly used semilocal correlation functionals completely miss nonlocal dispersion interactions [2]. This is a significant flaw, since dispersion (van der Waals) forces [3] are essential for the formation and properties of biological macromolecules, nanostructures, molecular crystals, polymers, liquids, and other types of sparse matter. The search for dispersion corrections amending common functionals is the subject of immense current interest. Considerable success has been achieved with empirical corrections in the form of force fields (see reviews in Refs. [2,4]). Among the *pure* DFT methods, the nonlocal correlation functional of Ref. [5] is unique, because it was derived from first principles, describes dispersion interactions in a general and seamless fashion, and yields the correct asymptotics (at least for nonconductors). Applications of this van der Waals density functional (vdW-DF-04) to various weakly bound systems are reviewed in Ref. [6]. vdW-DF-04 is known to be incompatible [7,8] with accurate exchange functionals, i.e., with Hartree-Fock (HF) or long-range corrected (LC) hybrid exchange models. Recently, we proposed [9] a modification, denoted vdW-DF-09, that was adjusted to work well with HF and LC exchange.

In this Letter, we derive a new correlation functional (which we call VV09) based on the vdW-DF methodology but incorporating different exact constraints. The VV09 nonlocal correlation energy is expressed in a straightforward analytic form, whereas its predecessors (vdW-DF-04 and vdW-DF-09) used numerically tabulated kernels. Furthermore, these predecessors were defined only for closed-shell systems, but VV09 can treat open-shell systems as well. VV09 correlation performs well in combination with HF or LC exchange.

The central quantity in the vdW-DF formalism [5,10] is the polarization operator $S(\omega)$, dependent on frequency ω and related to the dielectric function ϵ_λ via

$$S = \int_0^1 \frac{d\lambda}{\lambda}\left[1 - \frac{1}{\epsilon_\lambda}\right], \tag{1}$$

where λ is the coupling constant, multiplying every occurrence of e^2 inside ϵ_λ. To a good approximation, $\epsilon_\lambda \approx 1 + \lambda(\epsilon - 1)$, where ϵ with no subscript uses $\lambda = 1$. Then Eq. (1) gives

$$S \approx \int_0^1 d\lambda \frac{\epsilon - 1}{\lambda(\epsilon - 1) + 1} = \ln\epsilon. \tag{2}$$

The nonlocal correlation energy is most conveniently expressed [5] in terms of the Fourier transform of S:

$$E_c^{\mathrm{nl}} = \frac{\hbar}{4\pi}\int_0^\infty du \sum_{\mathbf{q},\mathbf{q}'} [1 - (\hat{\mathbf{q}}\cdot\hat{\mathbf{q}}')^2] S_{\mathbf{q},\mathbf{q}'}(iu) S_{\mathbf{q}',\mathbf{q}}(iu), \tag{3}$$

where $\hat{\mathbf{q}} = \mathbf{q}/q$ is a unit wave vector and $\sum_{\mathbf{q},\mathbf{q}'}$ stands for $\iint d\mathbf{q} d\mathbf{q}'(2\pi)^{-6}$. Using $S = \ln\epsilon$ in Eq. (3) proves intractable. By the mean value theorem, the integral in Eq. (2) can be replaced by

$$S = \frac{\epsilon - 1}{\nu(\epsilon - 1) + 1}, \tag{4}$$

where $0 \leq \nu \leq 1$.

It can be shown [9,10] that, in the limit of large distance R between two molecules A and B, E_c^{nl} of Eq. (3) gives the correct asymptote of the dispersion interaction: $-C_6^{AB}/R^6$. The C_6^{AB} coefficient can be written in the standard [3] form as

$$C_6^{AB} = \frac{3\hbar}{\pi}\int_0^\infty du\, \alpha^A(iu)\alpha^B(iu), \tag{5}$$

with the polarizability given by

$$\alpha^A(iu) = S_0^A(iu)/4\pi, \tag{6}$$

where S_0 denotes the $\mathbf{q} = \mathbf{q}' = \mathbf{0}$ limit of $S_{\mathbf{q},\mathbf{q}'}$. A connection between α and ϵ for $\mathbf{q} = \mathbf{q}' = \mathbf{0}$ is provided [11] by the Clausius-Mossotti relation $4\pi\alpha = 3(\epsilon - 1)/(\epsilon + 2)$, which corresponds to $\nu = 1/3$ in Eq. (4). Moreover, it can be shown that $\nu = 1/3$ is required to give the correct asymptotic limit for the interaction of two jellium spheres.

A good model for ϵ in the $\mathbf{q} = \mathbf{q}' = \mathbf{0}$ limit is [12]

$$\epsilon(\omega) = 1 + \frac{\omega_p^2}{\omega_g^2 - \omega^2}, \tag{7}$$

where $\omega_p = \sqrt{4\pi n e^2/m}$ is the plasma frequency for the total electron density n and $\hbar\omega_g$ is a band gap. Using

Eq. (7) in Eq. (4) with $\nu = 1/3$, we obtain

$$S_0(iu) = \int d\mathbf{r} \frac{\omega_p^2(\mathbf{r})}{\omega_p^2(\mathbf{r})/3 + \omega_g^2(\mathbf{r}) + u^2}. \qquad (8)$$

Equation (8) is written for nonuniform densities, and hence the local variants of ω_p and ω_g are used. The local band gap can be modeled [13] as $\hbar\omega_g \propto (\hbar^2/m)|\nabla n/n|^2$. Therefore we write

$$\omega_g^2(\mathbf{r}) = C \frac{\hbar^2}{m^2} \left| \frac{\nabla n(\mathbf{r})}{n(\mathbf{r})} \right|^4. \qquad (9)$$

We adjust the parameter C in Eq. (9) so that Eq. (5) gives accurate C_6 coefficients. For the test set of Table I, $C = 0.0089$ minimizes the average deviation from experiment. For C_6^{AA}, the present method (VV09) is comparable in accuracy to vdW-DF-09 [9], as Table I shows.

Generalizing S to the case of nonzero $\mathbf{q}$ and $\mathbf{q}'$ is highly nontrivial because the simple Clausius-Mossotti relation no longer holds and ν in Eq. (4) may be a function of $\mathbf{q}$ and $\mathbf{q}'$. Moreover, little is known about the dielectric function in inhomogeneous systems. Even in the uniform system of noninteracting electrons, the dielectric function depends on q and ω in a complicated and singular way. After some trial and error, we found that a successful model for $S_{\mathbf{q},\mathbf{q}'}$ is obtained when Eq. (8) is multiplied by two simple screening factors: $\exp(-q^2/k_s^2)$ and $\exp(-q'^2/k_s^2)$, where $k_s = \sqrt{4k_F/\pi a_0}$ is the Thomas-Fermi screening wave vector, written in terms of the Fermi wave vector $k_F = (3\pi^2 n)^{1/3}$ and the Bohr radius $a_0 = \hbar^2/me^2$. Finally, we write the full spin-dependent model for S as

$$S_{\mathbf{q},\mathbf{q}'}(iu) = \int d\mathbf{r} e^{-i\mathbf{r}\cdot(\mathbf{q}-\mathbf{q}')} \frac{\omega_p^2}{\omega_0^2 + u^2} \exp\left[-\frac{q^2 + q'^2}{k_s^2 \phi^2}\right], \qquad (10)$$

where $\omega_0^2 = \omega_g^2 + \omega_p^2/3$. In Eq. (10), the $\mathbf{r}$ dependence of ω_p, ω_0, k_s, and ϕ is implied but suppressed for brevity. Equation (10) depends on the relative spin polarization $\zeta = (n_\uparrow - n_\downarrow)/n$ via the spin-scaling factor $\phi(\zeta) = [(1+\zeta)^{2/3} + (1-\zeta)^{2/3}]/2$. The reason for including ϕ^2 alongside k_s^2 is explained below. Equation (10) satisfies the time-reversal invariance requirement: $S_{\mathbf{q},\mathbf{q}'} = S_{-\mathbf{q}',-\mathbf{q}}$. In the uniform density limit, $S(iu)$ reduces to

$$S_q^{\mathrm{uni}}(iu) = \frac{\omega_p^2}{\omega_p^2/3 + u^2} \exp\left(-\frac{2q^2}{k_s^2\phi^2}\right). \qquad (11)$$

TABLE I. C_6^{AA} coefficients (in a.u.) computed using Eqs. (5) and (6). The electron densities are obtained using LC-ωPBE with the aug-cc-pVQZ basis set and the EML-(99, 590) quadrature grid (see explanations of the terms in Ref. [9]).

Molecule	Ref.[a]	vdW-DF-04	vdW-DF-09	VV09
He	1.5	2.9	1.6	1.4
Ne	6.4	9.4	6.5	8.4
Ar	64.3	62.7	61.4	70.1
Kr	129.6	114.3	120.0	131.2
Be	213.1	268.7	329.5	186.2
Mg	629.5	648.8	835.3	425.1
Zn	282.0	268.9	239.8	163.1
H_2	12.1	16.8	12.5	10.3
N_2	73.4	78.8	77.6	88.7
HF	19.0	23.1	18.0	21.1
HCl	130.4	114.3	119.9	124.6
HBr	216.6	180.1	198.2	200.2
CH_4	129.6	122.0	130.1	129.6
CO	81.3	87.6	86.3	93.5
CO_2	158.7	127.6	130.6	159.4
Cl_2	389.2	289.3	336.8	366.7
CS_2	871.1	586.3	731.7	739.4
MPE (%)[b]		7.2	1.3	−2.7
MAPE (%)[b]		22.7	12.5	13.3

[a] Reference values collected in Ref. [9].
[b] Mean (signed) percentage error (MPE) and mean absolute percentage error (MAPE).

Let us consider the gradient expansion of E_c^{nl} in the $t \to 0$ limit, where $t = |\nabla n|/2\phi k_s n$ is the dimensionless density gradient. The second-order gradient term [14,15] can be written as $(ne^2/a_0)\beta^{\mathrm{nl}}\phi^3 t^2$, and the coefficient β^{nl} can be found from S_q^{uni} of Eq. (11) by the formula [9,10]

$$\beta^{\mathrm{nl}} = \frac{4k_F^4\hbar}{9\pi^6 e^2 \phi} \int_0^\infty du \int_0^\infty dq \left| \frac{\delta S_q^{\mathrm{uni}}}{\delta n} \right|^2 = \frac{9}{16\pi^{3/2}}. \qquad (12)$$

The important result is that β^{nl} is properly a constant, whereas in vdW-DF-04 and vdW-DF-09 the nonlocal gradient coefficient was erroneously strongly density-dependent. ϕ^2 was included in Eq. (10) to give the correct ζ dependence [14] of the gradient term, i.e., $\propto \phi^3 t^2$. The value of $\beta^{\mathrm{nl}} \approx 0.101$ appears to be somewhat too large, although the proper value for β^{nl} is debatable [16] and its recovery is of minor importance for real systems [17].

As stated above, the asymptotic form of E_c^{nl} is determined solely by S_0 via Eqs. (5) and (6). Equation (10) was constructed to have realistic small-q behavior, which we expect to be important for the intermediate and long range of van der Waals interactions. The older versions of vdW-DF (the 04 [5] and 09 [9] species) were markedly different in this regard: The $q \to 0$ limit was largely ignored in favor of the opposite $q \to \infty$ limit where S was constrained to behave as $\propto q^{-4}$. We argue that imposing this large-q constraint is not important for E_c^{nl} and even harmful: Correlation kernels $\Phi(\mathbf{r}, \mathbf{r}')$ in vdW-DF-04 and vdW-DF-09 diverge to $+\infty$ when $|\mathbf{r} - \mathbf{r}'| \to 0$. This divergence is eliminated in VV09, as shown below. We may further argue that the local real-space analogue of q^4 is $\propto |\nabla n/n|^4$ [18], and such a term is included in our model via ω_g^2.

With $S_{\mathbf{q},\mathbf{q}'}$ of Eq. (10), it is possible to perform integrations over u, $\mathbf{q}$, and $\mathbf{q}'$ in Eq. (3) analytically, yielding a rather simple form for E_c^{nl}:

$$E_c^{\text{nl-VV}} = \frac{3\hbar}{64\pi^2}\iint d\mathbf{r}d\mathbf{r}'\,\frac{\omega_p^2(\mathbf{r})\omega_p^2(\mathbf{r}')D(K)|\mathbf{r}-\mathbf{r}'|^{-6}}{\omega_0(\mathbf{r})\omega_0(\mathbf{r}')[\omega_0(\mathbf{r})+\omega_0(\mathbf{r}')]}, \tag{13}$$

where

$$K = \frac{|\mathbf{r}-\mathbf{r}'|}{2}\left[\frac{\kappa(\mathbf{r})\kappa(\mathbf{r}')}{\kappa(\mathbf{r})+\kappa(\mathbf{r}')}\right]^{1/2}, \tag{14}$$

with $\kappa(\mathbf{r}) = k_s^2(\mathbf{r})\phi^2(\mathbf{r})$. The function $D(K)$ in Eq. (13) is conveniently expressed as

$$\begin{aligned} D &= \frac{4}{3}K^2AB - B^2, \\ \text{with } A &= \frac{2K}{\sqrt{\pi}}e^{-K^2} \\ \text{and } B &= \mathrm{erf}(K) - A, \end{aligned} \tag{15}$$

where erf is the standard error function. It can be easily verified that

$$4\pi\int_0^\infty dK K^2\frac{D(K)}{K^6} = 0, \tag{16}$$

so that $E_c^{\text{nl-VV}}$ vanishes in the uniform density limit, just as Eq. (3) was designed to do. The integrand of Eq. (16), plotted in Fig. 1, is negative (attractive) for $K > 1.236$ and positive (repulsive) otherwise. For large K, $D(K) \to -1$ and Eq. (13) reduces to the $-C_6/R^6$ form. In the $|\mathbf{r}-\mathbf{r}'| \to 0$ limit,

$$\frac{D(K)}{|\mathbf{r}-\mathbf{r}'|^6} \to \frac{\kappa^3(\mathbf{r})}{288\pi} \quad (\mathbf{r}' \to \mathbf{r}), \tag{17}$$

so that the integrand in Eq. (13) is finite when $\mathbf{r}' = \mathbf{r}$.

We define the full correlation functional as

$$E_c^{\text{VV09}} = E_c^{\text{nl-VV}} + E_c^{\text{LSDA}}, \tag{18}$$

where E_c^{LSDA} is the local spin-density approximation (LSDA) for the correlation energy in the parametrization of Perdew and Wang [19]. Using E_c^{LSDA} in Eq. (18) avoids double counting of the same correlation effects. Typical gradient-corrected semilocal correlation functionals cannot be paired with $E_c^{\text{nl-VV}}$, because it already contains a gradient correction to LSDA.

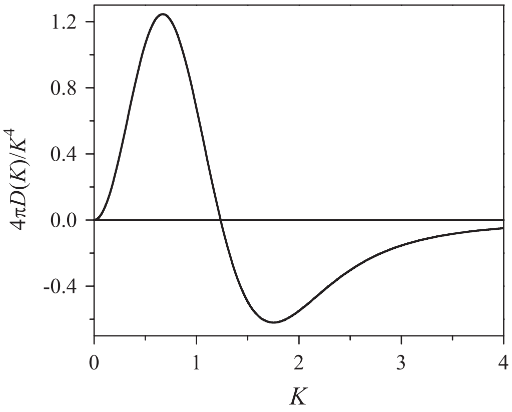

FIG. 1. The integrand of Eq. (16): $4\pi D(K)/K^4$.

We have implemented VV09 in the Gaussian-orbital software package Q-CHEM 3.1 [20]. All calculations reported in this work are fully self-consistent. Our code includes analytic gradients with respect to nuclear displacements, enabling efficient geometry optimizations. Implementational details will be reported elsewhere, but the general formalism is largely the same as in Ref. [8].

For molecular complexes bound exclusively by van der Waals forces, HF exchange provides adequate representation of the repulsive wall (''Pauli repulsion''), which most semilocal exchange functionals fail to reproduce. Using HF exchange with VV09 correlation of Eq. (18), we performed the full structural optimization of the benzene-Ar complex, which has C_{6v} symmetry with Ar on the main symmetry axis. Table II shows that HF-VV09 precisely nails the equilibrium distance between the Ar atom and the benzene plane (R_{Ar}) and gives a reasonable estimate of the binding energy. For covalent bonds, HF-VV09 inherits the poor performance of its parent functional HF-LSDA. We find that $E_c^{\text{nl-VV}}$ has little effect on covalent bond lengths. For the CC and CH bonds in benzene, HF-LSDA and HF-VV09 give nearly the same results. These bonds are predicted too short, as shown in Table II. HF-LSDA performs poorly for atomization energies, and HF-VV09 is even somewhat worse (see Table III).

The so-called ''long-range correction'' scheme [23] preserves the proper Hartree-Fock treatment of Pauli repulsion in van der Waals complexes but greatly improves the description of covalent bonds. In this method, the Coulomb operator $1/r$ is separated into the long-range (LR) part $\mathrm{erf}(\mu r)/r$ and the short-range (SR) counterpart $\mathrm{erfc}(\mu r)/r$. The exchange energy is then split as

$$E_x^{\text{LCS}} = E_x^{\text{SR-S}}(\mu) + E_x^{\text{LR-HF}}(\mu), \tag{19}$$

where the LR component is treated by HF. For the SR part, we use the attenuated Dirac/Slater exchange [24]. Pairing long-range corrected Slater (LCS) exchange with VV09 correlation, we fit the range separation parameter μ to the benchmark set of six atomization energies (the AE6 set

TABLE II. Equilibrium structures and binding energies of the benzene-Ar complex. The aug-cc-pVTZ basis set and (75, 302) grid are used. D_e values are counterpoise corrected.

Method	D_e (kcal/mol) Disp.[a]	Total	Distances (Å) R_{Ar}	R_{CC}	R_{CH}
PBE	···	0.24	3.97	1.397	1.091
vdW-DF-04[b]	2.20	1.38	3.74	1.402	1.088
vdW-DF-09[b]	2.20	1.40	3.68	1.389	1.086
HF-VV09	1.76	1.38	3.55	1.368	1.059
LCS-VV09	1.87	1.51	3.51	1.379	1.085
Reference[c]	2.05	1.15	3.55	1.391	1.080

[a] Contribution of dispersion interactions to D_e.
[b] The vdW-DF-04 and vdW-DF-09 results are taken from Ref. [9].
[c] Accurate values from Ref. [21].

TABLE III. Mean errors (ME) and mean absolute errors (MAE) in kcal/mol for the AE6 set of atomization energies and the BH6 set of barrier heights, computed using the aug-cc-pVTZ basis set, (75, 302) grid, and molecular geometries from Ref. [22].

	AE6		BH6	
Method	ME	MAE	ME	MAE
PBE	10.4	14.0	−9.5	9.5
PBEh	−1.5	5.6	−4.8	4.8
HF-LSDA	−40.0	45.9	8.9	8.9
HF-VV09	−57.2	60.3	10.2	10.2
LCS-LSDA[a]	14.5	17.1	−1.7	2.6
LCS-VV09[a]	−2.9	5.2	−0.2	1.9

[a] Using $\mu = 0.45a_0^{-1}$ optimized for LCS-VV09 (this value is suboptimal for LCS-LSDA).

of Ref. [22]) and six reaction barrier heights (the BH6 set of Ref. [22]). As shown in Table III, LCS-VV09 with $\mu = 0.45a_0^{-1}$ is incomparably more accurate for the AE6 and BH6 sets than HF-VV09. For these test sets, LCS-VV09 outperforms even such well-established functionals as Perdew-Burke-Ernzerhof (PBE) [15] and its global hybrid with 25% of HF exchange (PBEh).

As can be seen in Table II, LCS-VV09 gives more accurate covalent bond lengths in benzene, as compared to HF-VV09, while the dissociation energy of benzene-Ar and R_{Ar} are not significantly affected. Using LCS-VV09, we computed binding energy curves for Ar_2 and for Kr-Cl ($^2\Sigma^+$). As shown in Fig. 2, the positions of the potential energy minima are predicted rather well. Finally, we optimized the geometry of the methane dimer in the D_{3d} conformation using LCS-VV09 and computational details as in Table II. LCS-VV09 predicts the equilibrium C-C distance of 3.8 Å and the binding energy of 0.54 kcal/mol, which agree well with the reference values [25] of 3.6 Å and 0.54 kcal/mol.

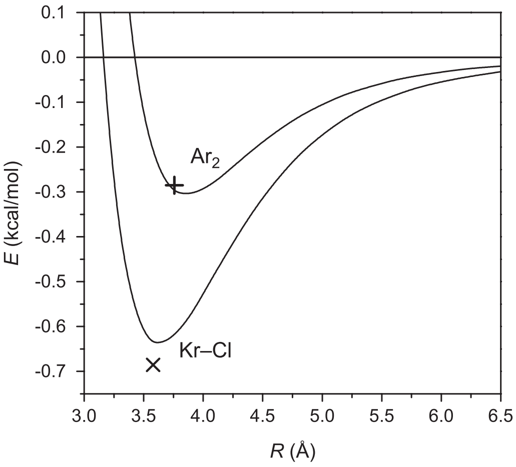

FIG. 2. LCS-VV09 binding energy curves for two diatomics, computed with the aug-cc-pVQZ basis set and (99, 302) grid. Experimental potential energy minimum for Ar_2 (+ symbol) is from Ref. [26] and for Kr-Cl (× symbol) from Ref. [27].

The VV09 correlation functional includes the proper physics of dispersion interactions with minimal empiricism. VV09 is straightforward to implement and relatively inexpensive: It is similar to vdW-DF-04 in terms of computational cost (see Sec. IV of Ref. [8]). This work was supported by an NSF CAREER grant (No. CHE-0547877) and the Packard Foundation.

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