Nonlocal van der Waals Density Functional Made Simple

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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, nanomaterials, molecular crystals, polymers, liquids, and other types of sparse matter. The search for dispersion corrections amending common functionals is the subject of intense 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 \( \omega \) and related to the dielectric function \( \epsilon(\omega) \) via

\[
S = \int_0^1 \frac{d\lambda}{\lambda} \left[ 1 - \frac{1}{\epsilon(\omega)} \right],
\]

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

\[
S = \int_0^1 d\lambda \frac{\epsilon - 1}{\lambda(\epsilon - 1) + 1} = \ln \epsilon.
\]

(2)

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

\[
E_{\text{nl}} = \frac{\hbar}{4\pi} \int_0^\infty du \sum_{q,q'} [1 - (\hat{q} \cdot \hat{q'})^2] S_{q,q'}(iu)S_{q,q'}(iu),
\]

(3)

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

\[
S = \frac{\epsilon - 1}{\nu(\epsilon - 1) + 1},
\]

(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 \( B \), \( E_{\text{nl}} \) 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

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

(5)

with the polarizability given by

\[
\alpha^A(iu) = S_0^A(iu)/4\pi,
\]

(6)

where \( S_0 \) denotes the \( q = q' = 0 \) limit of \( S_{q,q'} \). A connection between \( \alpha \) and \( \epsilon \) for \( q = q' = 0 \) 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 \( \epsilon \) in the \( q = q' = 0 \) limit is [12]

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

(7)

where \( \omega_p = \sqrt{4\pi n e^2/m} \) is the plasma frequency for the total electron density \( n \) and \( \hbar\omega_s \) is a band gap. Using
Eq. (7) in Eq. (4) with $\nu = 1/3$, we obtain

$$ S_0(iu) = \int dr \frac{\omega_p^2(r)}{\omega_p^2(r)/3 + \omega_s^2(r) + u^2}. $$

(8)

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

Therefore we write

$$ \omega_s^2(r) = C \frac{\hbar^2}{m^2} \left[ \frac{\nabla n(r)}{n(r)} \right]^4. $$

(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 $C_6^{4A}$, the present method (VV09) is comparable in accuracy to vdW-DF-09 [9], as Table I shows.

Generalizing $S$ to the case of nonzero $q$ and $q\prime$ is highly nontrivial because the simple Clusius-Mossotti relation no longer holds and $\nu$ in Eq. (4) may be a function of $q$ and $q\prime$. 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 $\omega$ in a complicated and singular way. After some trial and error, we found that a successful model for $S_{q,q'}$ is obtained when Eq. (8) is multiplied by two simple screening factors: $\exp(-q^2/k_F^2)$ and $\exp(-q'^2/k_F^2)$, where $k_F = \sqrt{4k_F/\pi \rho_0}$ 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 $a_0 = \hbar^2/\rho_0$.

Finally, we write the full spin-dependent model for $S$ as

$$ S_{q,q'}(iu) = \int dr e^{-i(q-q')\cdot r} \frac{\omega_p^2}{\omega_p^2/3 + u^2} \exp\left[-\frac{q^2 + q'^2}{k_F^2\Phi^2}\right]. $$

(10)

where $\omega_p^2 = \omega_p^2 + \omega_s^2/3$. In Eq. (10), the $r$ dependence of $\omega_p$, $\omega_s$, $k_F$, and $\Phi$ is implied but suppressed for brevity. Equation (10) depends on the relative spin polarization $\xi = (n_1 - n_2)/n$ via the spin-scaling factor $\Phi(\xi) = [(1 + \xi)^{1/2} + (1 - \xi)^{1/2}]/2$. The reason for including $\Phi^2$ alongside $k_F^2$ is explained below. Equation (10) satisfies the time-reversal invariance requirement: $S_{q,q'} = S_{-q,-q'}$. In the uniform density limit, $S(iu)$ reduces to

$$ S^{\text{uni}}_{q,q'}(iu) = \frac{\omega_p^2}{\omega_p^2/3 + u^2} \exp\left(-\frac{2q^2}{k_F^2\Phi^2}\right). $$

(11)

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

$$ \beta^{\text{nl}} = \frac{4k_F^4 \hbar}{9 \pi^6 e^3} \frac{1}{\Phi} \int_0^\infty d\nu \int_0^\infty dq \frac{\delta S^{\text{uni}}_q}{\delta \nu} \left[ \frac{8\delta S^{\text{uni}}_q}{\delta \nu} \right]^2 = \frac{9}{16 \pi^3 \nu^2}. $$

(12)

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

As stated above, the asymptotic form of $E^{\text{nl}}_d$ is determined solely by $S_q$ 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 $E^{\text{nl}}_d$ and even harmful: Correlation kernels $\Phi(r,r')$ in vdW-DF-04 and vdW-DF-09 diverge to $+\infty$ when $|r - r'| \to 0$. This divergence is eliminated in VV09, as shown below. We may further argue that the local real-space analogue of $q^2$ is $\propto |\nabla n|/n^4$ [18], and such a term is included in our model via $\omega_s^2$.

With $S_{q,q'}$ of Eq. (10), it is possible to perform integrations over $u$, $q$, and $q'$ in Eq. (3) analytically, yielding a rather simple form for $E^{\text{nl}}_d$.
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 C₆ᵥ 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 (Rₐ) 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 Eᵥᵥ⁻¹⁻⁻ 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 erf(μr)/r and the short-range (SR) counterpart erf(μr)/r. The exchange energy is then split as

\[ E^{\text{LCS}}_x = E^{\text{LR-HF}}_x + E^{\text{SR-S}}_x, \]

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

\[ E_{\text{c}}^{\text{LSSDA}} = E_{\text{c}}^{\text{LSSDA}} + E_{\text{c}}^{\text{LSSDA}}, \]

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

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<td>-1.7</td>
<td>2.6</td>
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<tr>
<td>LCS-VV09(a)</td>
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<td>5.2</td>
<td>-0.2</td>
<td>1.9</td>
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\(a\)Using \(\mu = 0.45a_0^{-1}\) optimized for LCS-VV09 (this value is suboptimal for LCS-LSDA).

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.