Efficient implementation of a van der Waals density functional: Application to double-wall carbon nanotubes

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(Dated: December 2, 2008)

We present an efficient implementation of the van der Waals density functional of Dion et al [Phys. Rev. Lett. 92, 246401 (2004)], which expresses the nonlocal correlation energy as a double spacial integral. We factorize the integration kernel and use fast Fourier transforms to evaluate the selfconsistent potential, total energy, and atomic forces, in \( N \log N \) operations. The resulting overhead in total computational cost, over semilocal functionals, is very moderate for medium and large systems. We apply the method to calculate the binding energies and the barriers for relative translation and rotation in double-wall carbon nanotubes.

PACS numbers: 31.15.ee, 71.15.-m, 61.46.Fg

Density functional theory (DFT) has become the method of choice for first-principles simulations of static and dynamical properties of complex materials with strong ionic, covalent, and metallic interactions. However, weak van der Waals (vdW) interactions are also added as plug-ins to ab initio calculations of simple molecules. Such potentials fitted to empirical data or to accurate quantum chemical [4] typically relied on atom-atom potentials with the conventional \( r^{-6} \) asymptotic behavior and with parameters fitted to empirical data or to accurate quantum chemistry calculations of simple molecules. Such potentials are also added as plug-ins to ab initio semilocal density functionals [2, 3]. Another approach includes vdW interactions through effective atom-electron pseudopotentials [3]. However, the accuracy and reliability of such approaches is limited because vdW energies arise from electron-electron correlations that depend not only on the atomic species but also on their chemical environment. More ab initio wavefunction-dependent approaches are more reliable but also much more expensive [8].

Thus, a key development has been the proposal by Dion et al. [9] of a universal nonlocal energy functional of the electron density \( n(\mathbf{r}) \) with the form

\[
E_{xc}[n(\mathbf{r})] = E_{xc}^{\text{GGA}}[n(\mathbf{r})] + E_{xc}^{\text{LDA}}[n(\mathbf{r})] + E_{xc}^{\text{nl}}[n(\mathbf{r})]
\]

(1)

where the exchange energy \( E_{xc}^{\text{GGA}} \) is described through the semilocal generalized gradient approximation (GGA) [10] and the correlation energy has a local part \( E_{xc}^{\text{LDA}} \), described in the local density approximation (LDA), and a nonlocal (nl) part \( E_{xc}^{\text{nl}} \) given by

\[
E_{xc}^{\text{nl}}[n(\mathbf{r})] = \frac{1}{2} \int \int d^3 \mathbf{r}_1 \ d^3 \mathbf{r}_2 \ n(\mathbf{r}_1) \ n(\mathbf{r}_2) \ \phi(q_1, q_2, r_{12})
\]

(2)

where \( r_{12} = |\mathbf{r}_1 - \mathbf{r}_2| \), and \( q_1, q_2 \) are the values of a universal function \( g_0(n(\mathbf{r}), |\nabla n(\mathbf{r})|) \), evaluated at \( \mathbf{r}_1 \) and \( \mathbf{r}_2 \). The kernel \( \phi \) has also a precise and universal form that in fact depends only on two variables \( d_1 = q_1 r_{12} \) and \( d_2 = q_2 r_{12} \), but it can obviously be written also as a function of \( q_1, q_2 \), and \( r_{12} \), what we will find convenient. The shape of \( \phi \) obeys that: i) \( E_{xc}^{\text{nl}} \) is strictly zero for any system with constant density; and ii) the interaction between any two molecules has the correct \( r^{-6} \) dependence for large separations \( r \). Using a direct evaluation of Eq. (2), this vdW functional has been applied successfully to a variety of systems, including interactions between pairs of atoms and molecules, molecules adsorbed on surfaces, molecular solids, and biological systems. [8, 11, 12, 13, 14]

If \( q_1 \) and \( q_2 \) in Eq. (2) were fixed values, independent of \( \mathbf{r}_1 \) and \( \mathbf{r}_2 \), \( E_{xc}^{\text{nl}} \) would be a simple convolution, like the Coulomb energy, that could be evaluated by Fourier methods. Therefore, our key step for an efficient implementation is to expand the kernel \( \phi \) as

\[
\phi(q_1, q_2, r_{12}) \simeq \sum_{\alpha \beta} \phi(q_\alpha, q_\beta, r_{12}) \ p_\alpha(q_1) \ p_\beta(q_2)
\]

(3)

where \( q_\alpha \) are fixed values, chosen to ensure a good interpolation of function \( \phi \). In order to illustrate how the factorization [3] can be performed in a systematic way, we consider first the interpolation of a function \( f(x) \) using a linear scheme, like those of Lagrange, Fourier, or splines:

\[
f(x) \simeq \sum_{\alpha} f_\alpha \ p_\alpha(x)
\]

(4)

where \( f_\alpha = f(x_\alpha) \) and \( p_\alpha(x) \) is the function resulting from the interpolation of the particular values \( f_\beta = f(x_\beta) \).
\(\delta_{\alpha\beta}\). In Lagrange interpolation, it is a polynomial of given order. In Fourier interpolation it has the form 
\[
sin(\pi(x-x_\alpha)/\Delta x)/(\pi(x-x_\beta)/\Delta x).
\]
We use cubic splines, in which \(p_\alpha(x)\) is a succession of cubic polynomials in every interval \([x_\alpha, x_{\beta+1}]\), matching in value and first two derivatives at every point \(x_\beta\). Notice that \(p_\alpha(x)\) depends on the interpolation scheme and on the (fixed) points \(x_\alpha\), but not on the interpolated function. In two-dimensional interpolation, one typically interpolates first in one variable and then in the other:
\[
f(x, y) \simeq \sum_\beta f(x_\beta, y_\beta) p_\beta(y) \\
\simeq \sum_\beta \left( \sum_\alpha f(x_\alpha, y_\beta) p_\alpha(x) \right) p_\beta(y) \tag{5}
\]
what shows that such an interpolation leads automatically to an expansion in terms of factored functions of \(x\) and \(y\). Thus, Eq. \(4\) is just the interpolation of a three-dimensional function in its first two variables. In this latter case, however, the interpolation points \(q_\alpha\) must be appropriate for every value of the third variable \(r_{12}\).

The fact that \(r_{12}\) acts as a scaling factor (i.e. increasing \(r_{12}\) merely “contracts” \(\phi\) as a function of \(q_1\) and \(q_2\), without changing its shape) suggests a logarithmic mesh of points \(q_\alpha\), in which \((q_{\alpha+1} - q_\alpha) = \lambda(q_\alpha - q_{\alpha-1})\), with \(\lambda > 1\). Such a logarithmic mesh is also suggested by the shape of \(\phi(d_1, d_2)\) shown in Fig. 1 of ref. \(3\). We have found that \(N_\alpha \sim 20\) interpolation points \(q_\alpha\) are sufficient for an accurate description of \(\phi\) up to a cutoff \(q_c\) at which we artificially “saturate” the original function \(q_0(n, |\nabla n|)\) by redefining
\[
q_0\text{sat}(n, |\nabla n|) = h[q_0(n, |\nabla n|), q_c]\tag{6}
\]
where \(h(x, x_c)\) is a smooth function such that \(h(x, x_c) \simeq x\) for \(x < x_c\) and \(h(x, x_c) \rightarrow x_c\) for \(x \rightarrow \infty\):
\[
h(x, x_c) = x_c \left[ 1 - \exp \left( - \frac{x_c}{m_c} \left( \frac{x}{x_c} \right)^m \right) \right] \tag{7}
\]
with \(m_c \sim 12\) and \(q_c \sim 5\) a.u. Higher \(q_0\) values are obtained only for very large \(n(r)\) (i.e. close to the nucleus, where \(E_{c}^{nl}\) is negligible compared to other terms in \(E_{xc}\), and for large \(|\nabla n|/n\) (in the electron density tails, where \(E_{c}^{nl}\) is negligible because of the factor \(n(r)\) in the integrand of Eq. \(2\)). In what follows, we will omit, but assume, superindex “sat” in \(q_0(n, |\nabla n|)\).

A minor but significant difficulty is that \(\phi(d_1, d_2)\) has a logarithmic divergence when \(d_1, d_2 \rightarrow 0\), which prevents its straightforward interpolation. Therefore, we interpolate and use instead a modified “soft” form
\[
\phi_s(d_1, d_2) = \begin{cases} 
\phi_0 + \phi_2 d^2 + \phi_4 d^4 & \text{if } d < d_s \\
\phi(d_1, d_2) & \text{otherwise.}
\end{cases} \tag{8}
\]
where \(d = \sqrt{d_1^2 + d_2^2}\). \(\phi_0\) and \(d_s\) are fixed parameters, and \(\phi_2, \phi_4\) are adjusted so that \(\phi_s(d_1, d_2)\) and \(\phi(d_1, d_2)\) match in value and slope at \(d = d_s\) (for given \(d_2/d_1\)). This modification leads to a change in \(E_{c}^{nl}\), which is corrected using a local density approximation:
\[
\Delta E_{c}^{nl} = \int d^3 r \ n(r) \Delta E_{c}^{nl}(r) \tag{9}
\]
where
\[
\Delta E_{c}^{nl}(r) = \frac{n(r)}{2} \int_0^{\infty} 4 \pi r^2 dr' \left[ \phi(q, q, r') - \phi_s(q, q, r') \right] \\
= \frac{n(r)}{2q^2} \int_0^{d_s} 4 \pi d^2 dd \left[ \phi(d, d) - \phi_s(d, d) \right] \tag{10}
\]
with \(q = q_0(n(r), \nabla n(r))\). The evaluation of \(\Delta E_{c}^{nl}\) and its derivatives is performed, like that of the semilocal terms in Eq. \(1\), as in ref. \(13\). In what follows, we will assume, but omit for simplicity, the subindex \(s\) in \(\phi_s\).

Substitution of \(3\) into \(2\) leads to
\[
E_{c}^{nl} = \frac{1}{2} \sum_{\alpha\beta} \int d^3 r_1 d^3 r_2 \theta_{\alpha}(r_1) \theta_{\beta}(r_2) \phi_{\alpha\beta}(r_{12}) \\
= \frac{1}{2} \sum_{\alpha\beta} \int d^3 k \theta_{\alpha}(k) \theta_{\beta}(k) \phi_{\alpha\beta}(k) \tag{11}
\]
where \(\theta_{\alpha}(r) = n(r) p_\alpha(q_0(n, \nabla n(r)))\) and \(\theta_{\alpha}(k)\) is its Fourier transform. Equally, \(\phi_{\alpha\beta}(k)\) is the Fourier transform of \(\phi_{\alpha\beta}(r) \equiv \phi(q_{\alpha}, q_{\beta}, r)\). It can be calculated in spherical coordinates, and stored in a radial mesh of points \(k\) for convenient interpolation. Thus, the heavier part of the calculation is the fast Fourier transforms of the \(N_\alpha\) functions \(\theta_{\alpha}(r)\), which still have a very moderate cost in a typical density functional calculation.

The evaluation of atomic forces requires the use of the Hellman-Feynman theorem, which holds only if the full energy functional is minimized self-consistently. In turn, this requires the nonlocal part of the correlation potential, i.e. the functional derivative of Eq. \(2\) \(16\). To handle the gradient dependency in \(q_0(n, \nabla n)\) we use the same technique as in ref. \(13\): approximating the spatial integrals by sums in a uniform grid of points, and the gradients by finite differences in the same grid. This makes \(E_{c}^{nl}\) an ordinary function of the densities \(n_i\) at fixed grid points \(r_i\), allowing to perform conventional partial derivatives, rather than functional derivatives. Besides its conceptual simplicity, this method ensures a perfect consistency between the calculated potential and the energy:
\[
E_{c}^{nl} = \frac{1}{2} \Delta \Omega^2 \sum_{\alpha\beta} \sum_{i j} \theta_{\alpha i} \theta_{\beta j} \phi_{\alpha\beta}(r_{ij}) \tag{12}
\]
where \(\Delta \Omega\) is the volume per grid point and \(\theta_{\alpha i} \equiv n_i p_\alpha(q_0(n_i, \nabla n_i))\). Notice that \(\phi_{\alpha\beta}(r_{ij})\) does not depend on \(n_i\), since the values \(q_{\alpha}\) are fixed. A straightforward
derivation then gives
\[ v_i^{nl} = \frac{1}{\Delta \Omega} \frac{\partial E^{nl}}{\partial n_i} = \sum_\alpha \left( u_{\alpha i} \frac{\partial \theta_{\alpha i}}{\partial n_i} + \sum_j u_{\alpha j} \frac{\partial \theta_{\alpha j}}{\partial \nabla n_j} \frac{\partial \nabla n_j}{\partial n_i} \right) \]
\[ \tag{13} \]
where \( \partial \nabla n_j/\partial n_i \) are fixed coefficients (determined by the finite difference formula used for \( \nabla n_j \)) that depend only on \( r_{ij} \) and that are nonzero only for small \( r_{ij} \). Also,
\[ u_{\alpha i} = \Delta \Omega \sum_\beta \sum_j \theta_{\beta j} \phi_{\alpha \beta}(r_{ij}) \]
\[ \tag{14} \]
is a convolution that can be obtained using fast Fourier transforms since (apart from \( \pi \) and volume factors)
\[ \int d^3 r_2 \theta_\beta(r_2) \phi_{\alpha \beta}(r_{12}) = \int d^3 k \, e^{i k r_1} \theta_\beta(k) \phi_{\alpha \beta}(k). \]
\[ \tag{15} \]
Thus, a self-consistency step requires \( N_\alpha \) direct transforms to find \( \theta_\alpha(k) \) and \( N_\alpha \) inverse transforms to obtain \( u_\alpha(r) \). The calculation of the atomic forces does not require any additional effort, since the nonlocal contribution \( v_i^{nl} \) is simply added to the semilocal terms \( v_i^{xc} \) and to the rest of the effective potential. Notice that the implementation is independent of the basis set, accepting \( n(r_i) \) in a uniform real space grid \( r_i \) and returning \( E^{xc} \) and \( v^{xc}(r_i) \) in the same grid. It has been checked that it reproduces accurately the results obtained by direct evaluation of Eq. \( \tag{2} \) (and, eventually, its functional derivative \( \tag{16} \)) for a variety of systems \( \tag{14} \).

We have applied the above method to study the interaction between the concentric layers of double-wall carbon nanotubes (DWNT). Such interactions are crucial for different nanodevices proposed recently \[ \tag{17} \] and with a local DFT functional \[ \tag{21} \] and with a local DFT functional \[ \tag{22} \] and with a local DFT functional \[ \tag{23} \] and with a local DFT functional \[ \tag{24} \]. We have used the SIESTA code \[ \tag{25} \] with an optimized \[ \tag{26} \] triple-\( \zeta \)+polarization basis set of pseudoatomic orbitals, correcting for basis set superposition errors (BSSE). The integration grids in real and reciprocal space had cutoffs of 300 Ry and 20 Å, respectively. The cutoff parameter for \( k \)-point sampling \[ \tag{27} \] was 20 Å, ensuring at least 34, 20 and 14 \( k \)-points for the armchair, zigzag and chiral DWNTs studied, respectively. The atomic forces were relaxed to less than 20 meV/Å.

Figure \[ \tag{1} \] shows the calculated interaction energy between two rigid SWNTs, relaxed independently, as a function of their interwall separation (difference of radii). It also shows the DWNT formation energies, defined as the difference between the total energy of the relaxed DWNT and that of the two SWNTs. The calculated tubes \( (m,m)@(n,n) \) (armchair), \( (m,0)@(n,0) \) (zigzag) and \( (8,2)@(16,4) \) (chiral) were chosen for their commensurability in the longitudinal direction, as well as for comparison with prior calculations. It can be seen that the interaction energy depends negligibly on chirality and curvature, being very well represented by the interaction between two flat graphene layers. On the other hand, the formation energy, that includes the relaxation of the radii induced by the interaction, shows a steeper repulsion than between flat graphene layers. In agreement with previous results for graphene and graphite, we find that the LDA works reasonably well. For sufficiently long tubes, in which the border effects can be neglected, the calculated vdW interaction energy gives a telescopic contraction force \[ \tag{18} \] \( F = 0.91 \text{N/m} \times d \), where \( d \) is the mean of the inner and outer tube diameters.

Next, the two concentric tubes of the DWNT were moved rigidly, relative to each other, in order to construct rotation-translation energy maps. To generate these maps, we first project the inner tube coordinates onto the outer tube surface, i.e. we multiply its \( x \) and \( y \) coordinates (the tube axis being \( z \)) by the ratio \( R_{out}/R_{in} \) between the two radii. We then unroll the coordinates of both tubes onto a flat surface, repeating them periodically also in the \( x \) axis. This gives two flat periodic lattices (commensurate in the cases considered) with reciprocal unit cell vectors \( a_i \) and \( b_i, i = 1, 2 \). The energy maps can then be represented, as a function of the position \( x \) on this surface, relative to the minimum, by an
expansion of the form

\[ U(x) = U_0 - \frac{1}{2} \sum_{G \neq 0} U_G \cos(G \cdot x) \]  

(16)

where \( G \) are the superlattice wavevectors, common to the reciprocal lattices \( a \) and \( b \), and \( U_G \) are the barrier heights for motion along \( G \). We have found that limiting this expansion to the first two wavevector stars, \( \pm G_1 \) and \( \pm G_2 \) (which, in the cases studied, are parallel and orthogonal to the axial direction), gives a good approximation to the cases studied, with the parameters given in Table I.

Overall, the relative values of these barrier heights are in qualitative agreement with previous calculations, i.e. larger barrier distances lead to larger barrier heights. Quantitatively, however, those calculations vary by an order of magnitude depending on the models used.\[20,21,22\]. The small discrepancies with ref.\[22\] may be due to the different basis sets and to our finer \( k \)-point sampling. Again, we find that the LDA does a rather good job for these systems, compared to the more complex vDW functional. Nevertheless, we find that LDA systematically underestimates the interaction energies and that it overestimates the barrier heights, relatively to the vDW results.

In conclusion, we have described an efficient algorithm to include van de Waals interactions through the self-consistent treatment of a nonlocal \( \textit{ab initio} \) functional proposed recently.\[5\]. Typical overheads in the total computation time, using the SIESTA code, over that required by LDA or GGA, are a factor \( \sim 5 \) in a two-atom system and \( \sim 10\% \) increase for \( \sim 150 \) atoms. Using this implementation, we have calculated the interaction energies, as well as the barriers for relative displacement, between concentric tubes in several armchair, zigzag, and chiral DWNTs.

We would like to thank E. Anglada, E. Artacho, and D. C. Langreth for many discussions and for their help in generating basis sets and testing our implementation. This work has been founded by grant FIS2006-12117 from the Spanish Ministry of Science.

\[ \text{TABLE I: Periodicities (} \Delta x_i = 2\pi/G_i, \text{ in Å) and energy barriers } U_i \text{ (in meV per outer tube atom) for translation (} i = z \text{) and rotation (} i = \phi \text{) of the outer tube, relative to the inner tube, in double wall carbon nanotubes.} \]

| DWNT (5,5)@(10,10) | (9,0)@18,0) | (8,2)@16,4) |
|---------------------|-------------|-------------|
| \( \Delta x_z \)   | 1.24        | 2.15        | 0.47        |
| \( \Delta x_\phi \) | 2.15        | 1.24        | 0.81        |
| \( U_{1LDA}^z \)    | 0.07        | 1.38        | 0.00        |
| \( U_{1LDA}^\phi \) | 0.48        | 0.16        | 0.00        |
| \( U_{2vdW}^z \)    | 0.04        | 1.22        | 0.00        |
| \( U_{2vdW}^\phi \) | 0.43        | 0.06        | 0.00        |