

## Van der Waals Interactions in DFT Made Easy by Wannier Functions

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Ubiquitous van der Waals interactions between atoms and molecules are important for many molecular and solid structures. These systems are often studied from first principles using the density functional theory (DFT). However, the commonly used DFT functionals fail to capture the essence of van der Waals effects. Most attempts to correct for this problem have a basic semiempirical character, although computationally more expensive first principles schemes have been recently developed. We here describe a novel approach, based on the use of the maximally localized Wannier functions, that appears to be promising, being simple, efficient, accurate, and transferable (charge polarization effects are naturally included). The results of test applications to small molecules and bulk graphite are presented.

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DFT represents a well-established tool to study the structural and electronic properties of molecules and condensed matter systems from first principles, and to elucidate complex processes such as surface adsorptions, catalytic reactions, and diffusive motions. Although current density functionals are able to describe well several systems, at much lower computational cost compared to other first principles methods, they fail to do so [1] for the description of long-range dispersion effects, generally denoted as van der Waals (VdW) interactions, particularly the leading  $R^{-6}$  term originated from correlated instantaneous dipole fluctuations; the cases where DFT [using, for instance, the Perdew-Burke-Ernzerhof (PBE) [2] functional] provides reasonable estimates for the interaction energy of weakly bound systems are actually due to favorable errors or cancellations and should therefore be considered accidental.

In order to overcome this severe deficiency of DFT, two basic strategies have been adopted: on one hand, new density functionals or/and relatively complex schemes have been proposed that allow for a first-principles treatment of the VdW interactions [1,3–9] (of particular importance is the seamless VdW-DF method [8], based on the calculation of the nonlocal correlation energy); on the other hand, several semiempirical approaches [10,11] have been developed where an approximately derived  $R^{-6}$  term, multiplied by a suitable short-range damping function, is explicitly introduced. Although both these approaches have been somehow successful, neither of them appears to be entirely satisfactory: in fact, the former is generally quite complex and computationally demanding, compared to a standard DFT calculation, while the latter, based on interatomic  $C_6$  coefficients (actually dependent on the molecular environment of the atoms involved) and empirical fits, turns out to be far from generally applicable because it neglects changes in the atomic polarizabilities (which, in general, are not additive) and should be tailored to the specific system considered.

Therefore, the development of a practical efficient scheme to include VdW interactions in DFT still represents an important issue.

In this Letter, we propose a novel method which allows the efficient calculation of the VdW interaction between nonoverlapping fragments, using as input only the ground state electron density and the Kohn-Sham (KS) orbitals computed in a conventional DFT approach.

Crucial to our analysis is the use of the Maximally Localized Wannier function (MLWF) formalism [12], that allows the total electronic density to be partitioned, in a chemically transparent and unambiguous way, into individual fragment contributions [13]. The MLWFs represent a generalization, for systems characterized by periodic boundary conditions, of the Boys’ localized orbitals [14] that are commonly used in quantum chemistry; they allow for an intuitive interpretation of the bonding properties of condensed matter systems [12] and are at the center of the modern theory of polarization [15]. The MLWFs,  $\{w_n(\mathbf{r})\}$ , are generated by performing a unitary transformation in the subspace of the occupied KS orbitals, obtained by a standard DFT calculation, so as to minimize the total spread:

$$S = \sum_n S_n = \sum_n (\langle w_n | r^2 | w_n \rangle - \langle w_n | \mathbf{r} | w_n \rangle^2). \quad (1)$$

Besides its spread,  $S_n$ , each MLWF is characterized also by its Wannier-function center (WFC); for instance, if periodic boundary conditions are used with a cubic supercell of side  $L$ , the coordinate  $x_n$  of the  $n$ -th WFC is defined [12] as

$$x_n = -\frac{L}{2\pi} \text{Im} \ln \langle w_n | e^{-i(2\pi/L)x} | w_n \rangle, \quad (2)$$

with similar definitions for  $y_n$  and  $z_n$ . If spin degeneracy is exploited, every MLWF corresponds to 2 paired electrons. Starting from these MLWFs, the leading  $R^{-6}$  VdW correction term can be evaluated using different possible recipes; one of them is described and applied in the follow-

ing. We make the reasonable (at least for insulating systems; clearly the present scheme is not appropriate if the generated MLWFs are not well localized, as it could happen in truly metallic systems) assumption [16] of exponential localization of the MLWFs in real space, so that each of them is supposed to be an hydrogen-like, normalized, function, centered around its WFC position,  $r_n$ , with a spread  $S_n$ :

$$w_n(|\mathbf{r} - \mathbf{r}_n|) = \frac{3^{3/4}}{\sqrt{\pi}S_n^{3/2}} e^{-(\sqrt{3}/S_n)|\mathbf{r} - \mathbf{r}_n|}. \quad (3)$$

Then, the binding energy of a system composed of two fragments is given by  $E_b = E_0 + E_{\text{VdW}}$ , where  $E_0$  is the binding energy obtained from a standard DFT calculation, while the VdW correction is assumed to have the form

$$E_{\text{VdW}} = - \sum_{n,l} f_{nl}(r_{nl}) \frac{C_{6nl}}{r_{nl}^6}, \quad (4)$$

where  $r_{nl}$  is the distance of the  $n$ -th WFC, of the first fragment, from the  $l$ -th WFC of the second one, the sum is over all the MLWFs of the two fragments, and the  $C_{6nl}$  coefficients can be calculated directly from the basic information (center positions and spreads) given by the MLWFs. In fact, using for instance the expression proposed by Andersson *et al.* (see Eq. (10) of Ref. [4]) that describes the long-range interaction between two separated fragments of matter,

$$\begin{aligned} C_{6nl} &= \frac{3}{32\pi^{3/2}} \int_{|\mathbf{r}| \leq r_c} d\mathbf{r} \int_{|\mathbf{r}'| \leq r'_c} d\mathbf{r}' \frac{\sqrt{\rho_n(r)\rho_l(r')}}{\sqrt{\rho_n(r)} + \sqrt{\rho_l(r')}} \\ &= \frac{3}{32\pi^{3/2}} \int_{|\mathbf{r}| \leq r_c} d\mathbf{r} \int_{|\mathbf{r}'| \leq r'_c} d\mathbf{r}' \frac{w_n(r)w_l(r')}{w_n(r) + w_l(r')}, \end{aligned} \quad (5)$$

where  $\rho_n(r) = w_n^2(r)$  is the electronic density corresponding to the  $n$ -th MLWF,  $C_{6nl}$  is given in a.u., and the  $r_c, r'_c$  cutoffs have been introduced [3,4] to properly take into account both the limit of separated fragments and of distant disturbances in an electron gas: by equating the length scale for density change to the electron gas screening length one obtains,

$$\frac{6\rho_n(r_c)}{|\vec{\nabla}\rho_n(r_c)|} = \frac{v_F[\rho_n(r_c)]}{\omega_p[\rho_n(r_c)]}, \quad (6)$$

where  $v_F = [3\pi^2\rho_n(r)]^{1/3}/m$  is the local Fermi velocity and  $\omega_p = [4\pi e^2\rho_n(r)/m]^{1/2}$  is the local plasma frequency. By using the analytic form [see Eq. (3)] of the MLWFs, it is straightforward to obtain the cutoff expressed in terms of the MLWF spread:

$$r_c = S_n\sqrt{3}[0.769 + 1/2\ln(S_n)], \quad (7)$$

and to evaluate very efficiently the multidimensional integral of Eq. (5). For instance, in the test case of two, distant

H atoms, using the well known (unperturbed) analytic H atom wave function, the above formula gives  $C_6 = 6.41$  a.u. to be compared to the reference literature value of 6.50 a.u. [17].

In Eq. (5), if the electronic density corresponding to every MLWF is multiplied by 2, the  $C_{6nl}$  coefficients increase by a  $\sqrt{2}$  factor; therefore, it appears reasonable to assume that, when each MLWF describes 2 paired electrons (spin degeneracy),  $C_{6nl}$  has to be multiplied by  $\sqrt{2}$ . This is also supported by the fact that, in the Slater-Kirkwood approximation for estimating the  $C_6$  coefficients, the effective number of electrons is smaller than the number of valence electrons, and it is  $1.42 \approx \sqrt{2}$  in the case of the He atom [18], whose DFT ground state is just given by 2 paired electrons in the lowest-energy KS orbital.

In Eq. (4),  $f_{nl}(r)$  is a damping function which serves to cut off the unreasonable behavior of the asymptotic VdW correction at small fragment separations. For it, we have chosen a form [11,19] with parameters directly related to the MLWF spreads:

$$f_{nl}(r) = \frac{1}{1 + \exp[-a(r/R_s - 1)]}, \quad (8)$$

where [19]  $a \approx 20$  (the results are almost independent on the particular value of this parameter), and  $R_s = R_{\text{VdW}} + R'_{\text{VdW}}$  is the sum of the VdW radii of the MLWFs, which, following Grimme *et al.* [19], are determined as the radii of the 0.01 electron density contour (in realistic systems the results are essentially unchanged even by reducing this value by an order of magnitude); using Eq. (3), one easily obtains that

$$R_{\text{VdW}} = [1.475 - 0.866\ln(S_n)]S_n. \quad (9)$$

The damping function effectively reduces the VdW correction to zero at short distances; at intermediate distances, a minimum in the VdW potential exists that usually lies around the sum of the corresponding VdW radii,  $R_s$ . Note that the above recipe resembles that proposed in Ref. [20], where the long-range electron-electron interaction is separated by the short-range one, using a single parameter describing the physical dimensions of a valence electron pair.

The  $E_0$  binding energy can be obtained from a standard DFT calculation (we have used the CPMD [21] and Quantum-ESPRESSO [22] *ab initio* packages), using the Generalized Gradient Approximation (GGA) in the revised PBE (revPBE) flavor [23]. This choice [8,19] is motivated by the fact that revPBE is fitted to the exact Hartree-Fock exchange so that the VdW binding, a correlation effect, only comes from the VdW correction term, as described above, without any double-counting effect (for instance, the Local Density Approximation or some GGA functionals, such as PBE, predict substantial binding in rare gas dimers, due to a severe overestimate of the long-range part of the exchange contribution [8]). The evaluation of the

VdW correction as a post-standard DFT perturbation, using the revPBE electronic density distribution, represents an approximation because, in principle, a full self-consistent calculations should be performed; however, recent investigations [24] on different systems have shown that the effects due to the lack of self-consistency are negligible (this is reasonable because one does not expect that the rather weak and diffuse VdW interaction substantially changes the electronic charge distribution).

The VdW correction scheme described above can be refined by considering the effects due to the anisotropy of the MLWFs, and distinguishing between contributions along (or orthogonal to) the fragment-fragment direction (details will be published elsewhere [25]). Moreover, also higher-order term VdW corrections, involving the  $C_8$ ,  $C_{10}$ , ... coefficients, could be easily included. Clearly, in the present method, the evaluation of the VdW corrections to the interfragment forces is trivial, thus allowing an easy implementation in standard geometry optimization calculations or Molecular Dynamics simulations. Remarkably, the whole procedure of generating the MLWFs and evaluating the VdW corrections represents a negligible additional computational cost, compared to that of a standard DFT calculation.

We have applied the new method to selected dimers among typical VdW-bonded systems:  $\text{Ar}_2$ ,  $\text{N}_2\text{-N}_2$  (“*T*-shaped”),  $\text{CH}_4\text{-CH}_4$ ,  $\text{C}_6\text{H}_6\text{-Ar}$ ,  $\text{CO}_2\text{-CO}_2$ , and also to a mixed (H-bonded–VdW-bonded) complex,  $\text{C}_6\text{H}_6\text{-H}_2\text{O}$ .

In Tables I and II, we report our computed binding energy and equilibrium characteristic interdimer distance. These values are compared to the most reliable (to our knowledge) experimental [26] and theoretical [24,27–29] literature data (when available, theoretical reference data obtained using the seamless VdW-DF scheme of Langreth *et al.* [8], which probably represents the best, DFT-based, first-principles approach derived so far, have been reported). As can be seen, the general performance of the method is quite satisfactory; in fact, the improvement achieved by including the VdW correction, with respect

to the pure revPBE results, is dramatic, even in the case of a mixed complex, such as  $\text{C}_6\text{H}_6\text{-H}_2\text{O}$ , where some fraction of the binding energy is already given by the standard DFT calculation. In Fig. 1, we show the effect of the inclusion of the VdW correction on the behavior of the binding energy of the  $\text{Ar}_2$  dimer, plotted as a function of the Ar-Ar distance, and compared to the experimental equilibrium value; in Ar, the 8 valence electrons of each atom are described by 4 MLWFs (spin degeneracy is exploited), whose WFCs are tetrahedrally located around the Ar ion.

In the case of the equilibrium characteristic distances, the more substantial deviation from the reference results can easily be explained by the fact that the potential energy curves for weakly-bonded systems are typically very shallow. Inspection of the Tables shows that anisotropy effects do not much affect the binding energy and equilibrium distance estimates. In Table I, by considering the MLWF anisotropy, the absolute values of the binding energies are always decreased, and most of the data are lower than the experimental corresponding values; this behavior is probably due to the neglect of higher-order contributions to the VdW correction, such as the  $-C_8/R^8$  term (dipole-quadrupole interaction), which should be included to have a very accurate estimate of the binding energy [30].

We have also applied our technique to an extended, semimetal system, such as bulk hexagonal graphite (*AB* stacking), using the WANNIER90 program [31], which allows the efficient generation of the MLWFs, by adopting a proper *k*-point sampling of the Brillouin Zone. As can be seen in the Tables, even in this more complex case, where the standard DFT-revPBE approach gives completely unphysical results, the performances of the present method are very satisfactory.

In conclusion, we have presented and applied in test cases a technique suitable to describe VdW effects in the framework of standard DFT calculations. The technique is based on the generation of the MLWFs and naturally describes changes in the electronic density distributions of the fragments due to the environment, for instance,

TABLE I. Binding energy (exfoliation energy per surface C atom, for graphite), in meV, computed using the standard DFT-revPBE calculation,  $E_0$  and including the VdW correction,  $E_0 + E_{\text{VdW}}$ , compared to available experimental [26] and theoretical [24,27–29] reference data; in parentheses, values computed taking anisotropy effects into account are reported.

system	$E_0$	$E_0 + E_{\text{VdW}}$	expt.	theor.
Ar-Ar	-1.7	-11.9 (-9.5)	-12.3	-23
$\text{N}_2\text{-N}_2$	-2.9	-11.1 (-10.8)	-13.3	-12
$\text{CH}_4\text{-CH}_4$	-2.1	-11.7 (-9.9)	-20 ↔ -14	-17
$\text{C}_6\text{H}_6\text{-Ar}$	-2.4	-65.7 (-53.5)	-49	-65
$\text{CO}_2\text{-CO}_2$	-16.2	-54.0 (-47.9)	...	-67
$\text{C}_6\text{H}_6\text{-H}_2\text{O}$	-40.4	-131.2 (-121.6)	-106 ± 4	-115
graphite	-1.9	-61.0	-52 ± 5	-53

TABLE II. Equilibrium characteristic interdimer distance (layer-layer separation for graphite), in Å, computed using the standard DFT-revPBE calculation,  $R_0$  and including the VdW correction,  $R_{\text{VdW}}$ , compared to available experimental [26] and theoretical [27,27–29] reference data; in parentheses, values computed taking anisotropy effects into account are reported.

system	$R_0$	$R_{\text{VdW}}$	expt.	theor.
Ar-Ar	4.67	4.03 (4.07)	3.76	3.9
$\text{N}_2\text{-N}_2$	5.05	4.37 (4.37)	4.03	4.2
$\text{CH}_4\text{-CH}_4$	4.70	4.23 (4.25)	3.8 ↔ 4.3	3.85
$\text{C}_6\text{H}_6\text{-Ar}$	4.79	3.57 (3.57)	3.68	3.41
$\text{CO}_2\text{-CO}_2$	3.86	3.49 (3.49)	4.04	3.1
$\text{C}_6\text{H}_6\text{-H}_2\text{O}$	4.23	3.17 (3.17)	3.32	3.6
graphite	5.10	3.35	3.34	3.59

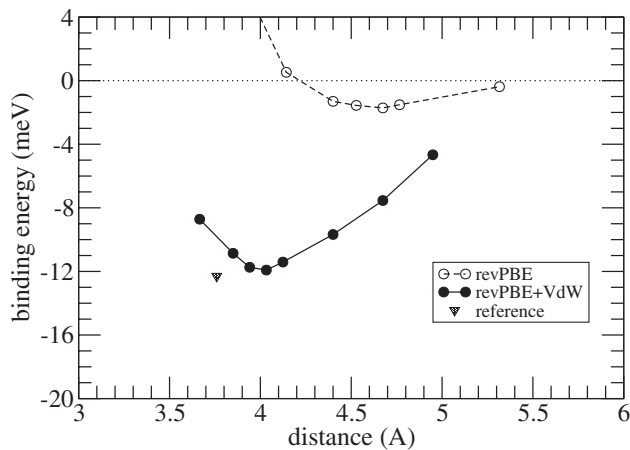


FIG. 1. Binding energy of the  $\text{Ar}_2$  dimer, as a function of the Ar-Ar distance, using the standard DFT-revPBE calculation and including the VdW corrections, compared to the reference, experimental value [26].

related to charge polarization effects: in fact, these changes are easily described in terms of changes in the location of the centers and in the spreads of the MLWFs. The results of the method, which is simple to be implemented and not expensive computationally, are quite satisfactory and promising, also considering that a large area for future improvements exists: in fact, more elaborate schemes to utilize the MLWFs could be developed and/or improved reference DFT functionals, with respect to revPBE, could be adopted.

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