



Wannier functions approach to van der Waals interactions in ABINIT

C. Espejo^{a,b,*}, T. Rangel^{c,e}, Y. Pouillon^{d,e}, A.H. Romero^{a,f}, X. Gonze^{c,e}

^a Programa de Nanociencias y Nanotecnología, Centro de Investigación y de Estudios Avanzados del I.P.N. (CINVESTAV), Libramiento norponiente # 2000, C.P. 76230, Querétaro, Mexico

^b Departamento de Ciencias Básicas, Universidad de Bogotá Jorge Tadeo Lozano, Carrera 4 # 22-61, Bogotá D.C., Colombia

^c Institute of Condensed Matter and Nanosciences (IMCN), Université Catholique de Louvain, Place Croix du Sud 1 bte 3, B-1348 Louvain-la-Neuve, Belgium

^d Centro de Física de Materiales, Universidad del País Vasco UPV/EHU, Donostia-San Sebastián, Spain

^e European Theoretical Spectroscopy Facility, ETSF

^f Materials Department, CINVESTAV, Unidad Querétaro, Mexico

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ABSTRACT

The method to calculate van der Waals interactions based on maximally localized Wannier functions (MLWFs), proposed by Silvestrelli [Phys. Rev. Lett. 100 (2008) 053002], has been implemented within the ab initio DFT program ABINIT. In addition to a brief review of the theoretical background behind this methodology, we present the details of the implementation, which will help users to assess van der Waals corrections in both molecular and periodic systems with a negligible additional computational cost. Some tests on argon dimer, argon FCC solid, benzene dimer and bilayer of graphene are presented. A discussion about the reliability of the method is also included.

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1. Introduction

Dispersion forces are the dominant molecular interaction driving self-assembling and a wide set of phenomena at the nanoscale, in particular biomolecular processes such as protein folding, physisorption, and hydrogen storage, in nanostructures.

Coming from quantum–mechanical fluctuations, dispersion interactions were elusive for quite some time, when typical exchange–correlation (XC) functionals were used in density functional theory (DFT). However, recent theoretical works have provided several approaches to include van der Waals (vdW) or dispersion forces in DFT at different levels of approximation [1–3].

DFT is widely used in electronic structure calculations on a large variety of systems, from atoms and molecules to solids and surfaces, due to its inherently low computational cost compared with other ab initio methods. Nevertheless, its recognized range of reliable applicability ends where soft condensed matter begins. In this kind of systems, there are large regions of almost vanishing electronic densities, giving special importance to dispersion or vdW interactions. The increasing interest in weakly coupled systems has recalled attention on improving the usual XC functionals as required to assess vdW forces, which are out of range for the

most common XC functionals, namely, the local density approximation (LDA) and the generalized-gradient approximation (GGA).

Efforts in the direction of including vdW interactions within the DFT frame in a seamless ab initio way [4–7] have proven quite successful. As a result, a new functional – also known as vdW-DF – has been reported and tested on several prototypical vdW systems [8]. In spite of this, the computationally demanding nature of the vdW-DF did not allow for first principles simulations on systems bigger than several tens of atoms, in which vdW interactions are important. Therefore, as pointed out by Sun et al. [9], a dilemma was then encountered: the improvement of computational resources and algorithms allowed for an increase of the system size treated within DFT to thousands of atoms, whenever the systems were not complex and did not involve vdW interactions. However, the latter statement can be reconsidered, since Román-Pérez and Soler [10] proposed recently an efficient implementation of the vdW-DF, showing an $O(N \log N)$ scaling.

Apart from the vdW-DF method, several computationally efficient, approximate, methods have also been suggested, with the main idea that the long-range vdW interactions, that are present in the exact correlation functional of the electronic density and are missing from most of the present XC functionals, can be added either *a posteriori* or by means of atom-centered modifications.

In a first group, corrected long-range forces are usually obtained from atom–atom (fragment–fragment) interactions mediated by pair contributions of the form:

$$E_{vdW} = -\frac{1}{2} \sum_{i,j} \frac{f_{i,j}(R_{i,j})C_6^{i,j}}{R_{i,j}^6}, \quad (1)$$

* Corresponding author at: Programa de Nanociencias y Nanotecnología, Centro de Investigación y de Estudios Avanzados del I.P.N. (CINVESTAV), Libramiento norponiente # 2000, C.P. 76230, Querétaro, Mexico.

E-mail addresses: cespejo@qro.cinvestav.mx (C. Espejo), aromero@qro.cinvestav.mx (A.H. Romero).

where $R_{i,j}$ is the interatomic distance, f is a damping function that prevents both double counting of correlation and singularities for short distances, and $C_6^{i,j}$ are the dispersion coefficients, which are fitted to benchmark calculations, or experimental data [11] when available. These coefficients can as well be calculated by using the electronic structure information obtained from a DFT calculation, in particular, from maximally-localized Wannier functions (MLWFs), as proposed by Silvestrelli [12,13], and from ground-state electronic density of isolated atoms [14].

In a second group there are proposals in the midway between ab initio and semiempirical approaches. As an example, we can cite the local atomic potential (LAP) [9] and the dispersion-corrected atom-centered (DCAC) [15,16] approaches, which partially take the electronic nature of vdW interactions into account. In both schemes, the vdW interaction is represented either by a local or by a non-local parameterized contribution added to atomic pseudopotentials. The associated parameters are determined by comparison of calculated interaction energy curves with those obtained from high-level calculations on simple vdW systems.

In what follows we present the implementation of the method based on MLWFs [12,13] into the ABINIT program. By means of some test cases we will both demonstrate its reliability and explain how to use it for practical purposes. In Section 2, a brief presentation of the theoretical background of the method is found, in Section 3 we show computational details together with the new defined variables in ABINIT. Section 4 is dedicated to test the implementation in several molecular and solid systems where vdW interactions are important. Finally, a discussion about the performance of this methodology and also some hints for the user are provided in Section 5.

2. Van der Waals interactions using MLWFs

An approximation introduced by Andersson et al. [17] to calculate the XC energy associated with two distant charge disturbances of a uniform electron gas, known as the ALL functional, leads to the expression of the correlation of two distant charge fragments in terms of the electronic density as:

$$E_{xc}^{l-r} = \frac{6e}{4(4\pi)^{3/2}m^{1/2}} \times \int_{V_1} d^3r_1 \int_{V_2} d^3r_2 \frac{\sqrt{n_1(\mathbf{r}_1)n_2(\mathbf{r}_2)}}{\sqrt{n_1(\mathbf{r}_1)} + \sqrt{n_2(\mathbf{r}_2)}} \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|^6}, \quad (2)$$

where V_1 and V_2 are chosen so that both the limit of two separated fragments and of distant disturbances in an electron gas are taken into account. If applied to the case of two distant subsystems, the term $|\mathbf{r}_1 - \mathbf{r}_2|^{-6}$ can be taken out from the integral. The latter implies that the XC energy of the system takes the form of Eq. (1), providing a way to evaluate the dispersion coefficients from electronic density only. Indeed, the results of C_6 calculations performed on H_2 , He, Ar, Xe, Ne and Kr obtained from this approach are in good agreement with reported ones from quantum chemistry calculations [17].

In a recent work, Silvestrelli proposed to decompose the electronic density in terms of maximally localized Wannier functions [18]. Here we follow the same arguments as discussed in [13]. Due to the exponential localization of MLWFs [19,20], these can be expressed with the following analytical expression [13]:

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

where \mathbf{r}_n and S_n are the center and spread of the n -th Wannier function (w_n), respectively. One can make the substitution $n(r) = w^2(r)$ into Eq. (2), to obtain the dispersion coefficients:

$$C_6^{nl} = \frac{3}{32\pi^{3/2}} \int_{|\mathbf{r}| \leq r_c} d\mathbf{r} \int_{|\mathbf{r}'| \leq r'_c} d\mathbf{r}' \frac{w_n(\mathbf{r})w_l(\mathbf{r}')}{w_n(\mathbf{r}) + w_l(\mathbf{r}')}. \quad (4)$$

By equating the length scale for density change to the electron gas screening length, the cutoff radius corresponding to the volumes V_1 and V_2 (r_c and r'_c) is obtained. From the analytical expression of MLWFs in Eq. (3), one deduces:

$$r_c^n = S_n \sqrt{3} [0.769 + 1/2 \ln S_n]. \quad (5)$$

As in Eq. (1), a damping function is needed. The total van der Waals energy is then evaluated as sum of pair-wise terms over Wannier functions rather than over atoms:

$$E_{vdW} = - \sum_{n,l} \frac{f_{n,l}(r_{n,l}) C_6^{n,l}}{r_{n,l}^6}, \quad (6)$$

where n and l are indices for Wannier functions on different fragments, and $r_{n,l}$ is the distance between their centers. After some algebra, the dispersion coefficients can be calculated as:

$$C_6^{nl} = \frac{(S_n S_l)^3}{2 \cdot 3^{5/4}} \int_0^{x_c} dx x^2 e^{-x} \int_0^{y_c} dy \frac{y^2 e^{-y}}{S_1^{3/2} e^{-x} + S_n^{3/2} e^{-y}}, \quad (7)$$

where,

$$x_c = \frac{\sqrt{3}r_c}{S_n}, \quad y_c = \frac{\sqrt{3}r'_c}{S_l}.$$

The following damping function is adopted:

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

where $a \sim 20$, and $R_s = R_{vdw}^n + R_{vdw}^l$ is the sum of the vdW radii of the MLWFs. Initially [12], the vdW radii were obtained from the electron density isosurface at 0.01 Bohr^{-3} . However, after some testing, it was realized that by letting $R_{vdw}^n = r_c^n$ from Eq. (5), the resulting damping function is usable for a wide range of systems [13].

Examining this approach, it is clear that it is a post-processing tool that allows one to estimate the vdW energy correction to a self-consistent field (SCF) calculated energy once the MLWF are obtained. Although it is a relatively drastic approximation, recent investigations within the vdW-DF method have shown that there is almost no difference with the results of fully self-consistent calculations including the vdW energy [21]. The latter is expected, as weak dispersive interactions should only change the electronic density to a small extent.

Finally, the XC functional of the vdW-corrected scheme is defined as:

$$E_{xc}[n] = E_{xc}^{revPBE}[n] + E_{vdW}. \quad (9)$$

The revPBE [22] exchange is preferred, as it is fitted to the exact exchange, thus preventing spurious binding due to exchange only.

3. Computational implementation

With the ABINIT software package [23], the electronic wave function can be expanded on different basis sets, namely plane waves and projector-augmented waves (PAW). Such expansion can be used to solve the Kohn–Sham equations for periodical systems. It can also be used for molecular dynamics simulations, structural relaxations, TDDFT calculations and the evaluation of GW corrections, among many other capabilities. For a detailed description of the program, please refer to the ABINIT web page [24] and Ref. [23].

The interface to the **Wannier90** [25] library allows for the calculation of MLWFs from the initial KS states. The call to the **Wannier90** library at the end of a SCF calculation is triggered by a simple variable `prtwant` in the main input file. Moreover, a secondary input file is required to setup the **Wannier90** options. An adequate knowledge of the procedure for generating MLWFs in **ABINIT** is required as it is a preliminary step in the evaluation of vdW corrections.

The previously-described Silvestrelli method to obtain the vdW energy by using MLWFs, can be envisaged as a post-processing tool. The input data is related to the Wannier functions only, namely their centers and spreads. However, as the vdW correction is obtained from MLWF pair-wise contributions, the first step is the identification of the MLWFs corresponding to each interacting fragment, either atomic, molecular or solid. vdW-interacting fragments are defined in terms of their constituting atoms. Two new input variables were defined to specify the fragments. `vdw_nfrag` is the number of interacting fragments in the unit cell, and the array `vdw_typfrag (natom)` points out to the fragment to which each atom belongs, where `natom` is the total number of atoms in the unit cell. The ordering of `vdw_typfrag` is the same as in other common arrays, such as `typat`, `xangst`, `xred` or `xcart`. Each MLWF is assigned to a given fragment. This designation is performed internally by computing the distance between each MLWF center to the unit cell atoms: MLWFs belong to the same fragment as their nearest atom. **ABINIT** reports the number of MLWFs in each fragment together with their coordinates in `xyz` format for an easy visualization of the interacting fragments.

After the wannierization procedure, the MLWF center positions calculated in reciprocal space are translated to real space by **Wannier90**. Nevertheless, MLWFs can end up at different unit cells. Hence, by default, **ABINIT** translates the Wannier functions to the original unit cell (the unit cell in which the atoms are defined). However, in some cases the positions reported by **Wannier90** are correct, whereas a translation to the original unit cell gives wrong relative positions between MLWFs and atoms. Such is the case if some atoms are placed at the corners or at limiting faces of the unit cell. In such circumstances, a negative value of `vdw_nfrag` will deactivate the translation procedure and MLWF centers will keep the positions obtained by **Wannier90**. The default value for `vdw_nfrag` is 0.

Other methodologies are currently being implemented in **ABINIT** for vdW calculations, therefore, we also defined the variable `vdw_xc` which selects among vdW schemes. The selection of the Wannier functions method is done with `vdw_xc = 10`. Its default value is 0, meaning no selection of any vdW method.

For periodic systems, the vdW correction could include contributions from MLWFs in neighboring cells. The integer array `vdw_supercell(3)` defines the vicinity around the unit cell for which vdW interactions will be accounted for, thus allowing for convergence studies of vdW interactions in solids. Each component of `vdw_supercell` indicates the maximum number of cells along both positive and negative directions of the corresponding primitive vector, i.e. the components of the array `rprimd` in **ABINIT**. Layered materials are a special case of crystals where vdW interactions occur only between layers made of tightly bound atoms. In such a case, the computation of vdW energy between MLWFs belonging to the same layer must be avoided. In the current implementation, layers can be defined only if they are normal to any primitive vector. A negative value for one component of `vdw_supercell` means that the corresponding primitive vector is normal to the layers. In this sense, one and only one component of `vdw_supercell` may be negative. On the other hand, for molecular systems, the default value (0, 0, 0) should be used, as vdW interactions occur only inside the unit cell.

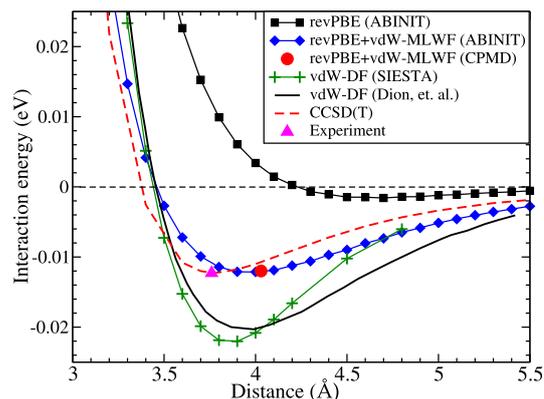


Fig. 1. Argon dimer interaction energy. Comparison of MLWFs method to reported data and vdW-DF as implemented in SIESTA. *Squares:* ABINIT revPBE calculation without vdW correction. *Diamonds:* ABINIT revPBE corrected with vdW-MLWF. *Circle:* vdW-MLWF by Silvestrelli [12]. *Crosses:* SIESTA implementation of vdW-DF. *Solid line:* vdW-DF taken from [6]. *Dashed line:* CCSD(T) [28]. *Triangle:* Experimental data from [26].

4. Tests on molecular systems

Here we present some tests calculations. Since some of these systems, namely argon dimer, benzene dimer, argon FCC and graphene bilayer, were previously studied by Silvestrelli [12,13], using an implementation in CPMD, the agreement with his results demonstrate that our implementation is reliable. The dihydrogen dimer was also studied to test the method on a simple molecular system and compare its results against DFT + LAP and CCSD(T).

4.1. Argon dimer

The argon dimer, as well as the other rare gas dimers, are considered valuable test systems and have been used not only in DFT but also in the quantum chemistry realm, to assess vdW methodologies [27,28]. In Fig. 1, the interaction energy as a function of interatomic distance is plotted. We obtain a very good agreement with experiment [26] and a quite similar result compared to Silvestrelli's original data. It should be stressed that revPBE without vdW correction shows a binding. However, the bond length is overestimated by 25% and the binding energy is underestimated by 86%. The differences obtained for the vdW-MLWF method are 6.4% and -1.18% , which indicate a large improvement over revPBE uncorrected calculations.

In order to test the performance of the MLWF method for Ar_2 , we have compared our results with that of the highly accurate CCSD(T) using `aug-cc-pV5Z + spd/fg` bond basis including core electrons of Slavíček et al. [28] and experimental data [26]. Results from vdW-DF, as implemented in the SIESTA code [29], are also included along with the reported results of Dion et al. [6], the authors of the vdW-DF. This calculation will also be used later, when testing the implementation of vdW-DF into ABINIT. We see that the Wannier-function-based method gives better results than vdW-DF with respect to experimental data and that the obtained agreement with CCSD(T) calculations is remarkable. Also, it should be noticed that some differences were found between the original results of [6] and the curve obtained with the implementation of the same functional in SIESTA.

4.2. Benzene dimer

The benzene dimer exists in at least three configurations, namely sandwich (S) with full hexagonal symmetry, parallel displaced, and T-shaped configuration. We have selected the S configuration to test our implementation. In this case, we compare

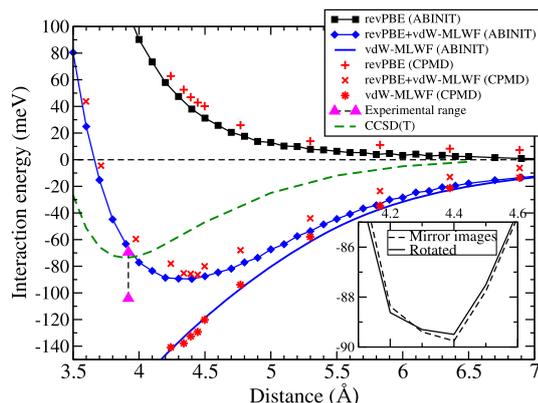


Fig. 2. Comparison between benzene dimer (S) interaction energies as obtained from ABINIT and CPMD. Squares: revPBE interaction energy from ABINIT. Diamonds: ABINIT corrected interaction energy. Solid line: ABINIT vdW-MLWF correction. Pluses: revPBE interaction energy from CPMD. Crosses: vdW-MLWF corrected interaction energy obtained in CPMD. Stars: CPMD vdW-MLWF correction. Triangles: Experimental values [30,31]. Dashed line: Estimated CBS CCSD(T)/aug-cc-pVQZ* [32]. Inset: Interaction energy for two different sets of MLWFs (see text).

our result within the vdW-MLWF approach [13] with those of the CPMD ab initio package [33]. In particular, we compare the binding energy and the bond distance for the interaction energy curve over a broad range of intermolecular distances. Experimental values [30, 31] for the binding energy are also displayed at the distance obtained as benchmark result from high-quality quantum chemistry calculations [34]. The wide experimental range for the binding energy is explained by the fact that the benzene dimer configuration was not precisely determined. It should be pointed out that the vdW energy is added to the GGA interaction energy, therefore, some discrepancies in the corrected energy could be found due to differences in the GGA calculations even though the vdW energy is correct, i.e. obtained from well-converged MLWFs. Moreover, the set of MLWFs for the benzene dimer is not unique: there are two possible configurations. Indeed, C_6 rotational symmetry of a single benzene molecule is broken if its corresponding MLWFs set is considered, as center positions resemble the Lewis view of chemical bonding, where double bonds (two MLWFs) are placed in alternating positions with single bonds (one MLWF) around the aromatic cycle. For the benzene dimer, in one of the configurations, Wannier functions of both benzene molecules are centered in the same positions (mirror images), while in the other configuration, the Wannier centers are rotated by 60° with respect to the other. The two configurations lead to different interaction energies, shown in the inset of Fig. 2. In this context, the agreement obtained in Fig. 2 between CPMD and ABINIT implementations is rather satisfactory and further confirms the reliability of the ABINIT implementation. The performance of vdW-MLWFs in this molecular system has been evaluated by comparison to the results from complete basis set (CBS) extrapolation of CCSD(T) calculations of Sinnokrot and Sherrill [32] using a modified aug-cc-pVQZ basis set. Although both interaction energy and bond length are overestimated, inclusion of vdW-MLWFs corrects the revPBE repulsive behavior and predicts a stable dimer.

4.3. H_2 dimer

Another prototypical vdW system is the dihydrogen dimer. We have performed calculations only for one of the possible geometries, in which the angle between the two molecular axes is 90° and the displacement occurs along a third axis which is simultaneously perpendicular to both H_2 molecules, as shown in inset of Fig. 3. In this case we have used revPBE [22] pseudopotentials obtained with APE [35] and the corresponding XC flavor in ABINIT.

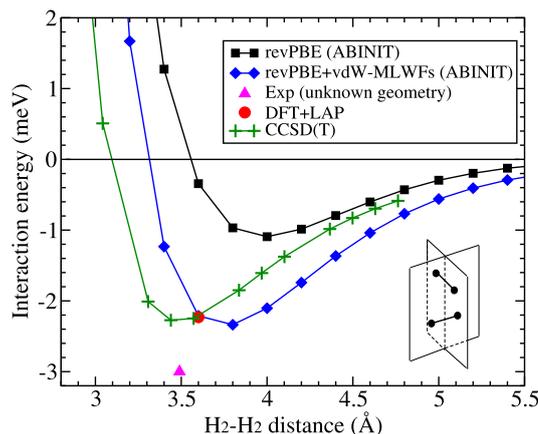


Fig. 3. H_2 dimer interaction energy. Squares: revPBE uncorrected calculation from ABINIT. Diamonds: revPBE corrected with vdW-MLWFs in ABINIT. Triangle: Experimental result for undetermined geometry [37]. Circle: DFT + LAP result from [9]. Pluses: Quantum chemistry CCSD(T) [36].

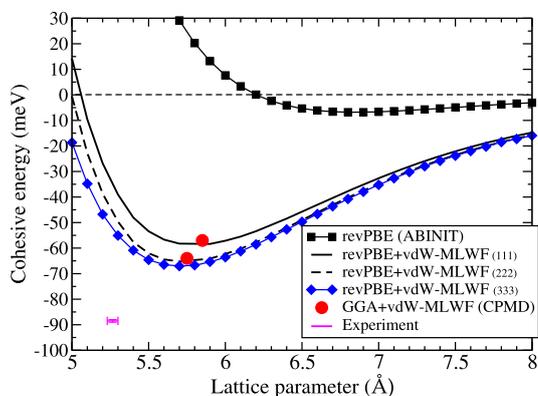


Fig. 4. Cohesive energy of Ar FCC as a function of the lattice parameter, and convergence of vdW correction. Squares: Non-corrected revPBE ABINIT calculation. Solid line: Corrected cohesive energy using $vdw_supercell = (1, 1, 1)$. Dashed line: Corrected cohesive energy using $vdw_supercell = (2, 2, 2)$. Diamonds: Converged cohesive energy obtained for $vdw_supercell = (3, 3, 3)$. Circles: Results from Ref. [13] obtained from supercell approach. Upper circle: cubic supercell with 32 Ar atoms and Γ point sampling of the BZ. Lower circle: cubic supercell with 4 Ar atoms and a $2 \times 2 \times 2$ BZ sampling. Error bars: Experimental data range [38–40].

The resulting curve is plotted in Fig. 3. A comparison to one of the most accurate CCSD(T) [36] and DFT-LAP [9] calculations available shows that our results overestimate the binding energy by only 0.084 meV (3.7%), while the bond length is 0.26 Å longer (7.55%). In this case, the revPBE binding is important if compared to the Ar_2 case, contributing 31.5% of the corrected binding energy. The latter shows that the interplay between the damping function and the correlation obtained by the present method is able to handle situations where bonding involves contributions coming not only from dispersion effects.

5. Tests on periodic systems

5.1. Ar FCC

Solid argon is one simple periodic system where atoms are held together by dispersion forces. We used our current implementation to study both the equilibrium structure and convergence of vdW energy as a function of the number of neighboring cells, see Fig. 4. In this case, accounting for the vdW interaction up to the third neighbor cells was enough for the vdW energy to converge. The agreement with Silvestrelli results, Ref. [13], is excellent. As opposed to the argon dimer where agreement with the experiment

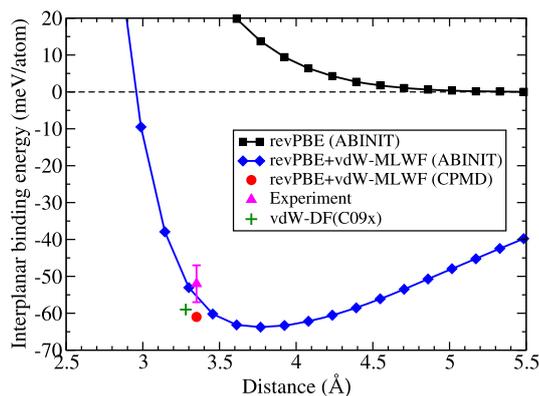


Fig. 5. Interlayer binding energy per surface atom in graphene bilayer. *Squares:* Non-corrected revPBE ABINIT calculation. *Diamonds:* Corrected binding energy using $\text{vdw_supercell} = (10, 10, 0)$. *Circle:* Result from [12], using Γ point only and full supercell approach (see text). *Triangle:* Experimental result from [43]. *Cross:* vdW-DF using the C09_x exchange [44].

is remarkable, the equilibrium lattice parameter of the crystal is found to be overestimated by 8.2%, while cohesive energy is underestimated by 24%. Even though dimer interactions might be well described within the MLWF approach, many-body components are not completely included in the latter, as it is well known that vdW correction do not come only from pairwise contributions [41,42].

5.2. Graphene bilayer

Sets of graphene sheets are good test cases for vdW interactions as well. Between graphene sheets as in other layered systems, vdW interactions are anisotropic. Layers interact weakly with each other by means of dispersion forces, while carbon atoms are tightly bound within each graphene layer. Traditional functionals have proven to be successful in these systems only for in-layer bond distances and formation energies, giving scattered (often wrong) results for interlayer interactions. In order to assess the interaction energy between two graphene layers, we have applied the MLWFs method using a large vertical supercell, $c = 12 \text{ \AA}$, in which interactions with vertical (top and bottom) neighbor cells are negligible. Horizontal parameters are the same as in normal AB graphite. For this case vdW convergence is reached for $\text{vdw_supercell} = 10 \text{ 10 0}$, pointing out the long range of dispersion interactions. Fig. 5 displays the resulting curve as a function of interlayer distance and some results from literature for comparison. The obtained difference with respect to the reference one [12] can be attributed to the fact that we are using a vertical supercell with the same horizontal periodicity as normal graphite, while the reference employed a complete supercell approach together with Gamma sampling of the Brillouin zone.

6. Concluding remarks

We have implemented the method for evaluating vdW energies by means of MLWFs into ABINIT. Three new variables were defined to set up the calculation, which allow to treat molecular systems and solids in the same framework, as well as test vdW spatial convergence. Reliability of the implementation has been shown by some test calculations and direct comparison to available data.

An important issue of the presented implementation is that it will work even though the set of Wannier functions is not the optimal one or if the interacting fragments are not properly defined. Although vdW-MLWFs is not a semiempirical method and there is no need to fit any parameter, a careful tracking of the whole process (SCF calculation and wannierization) should be adopted by potential users.

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