Intermolecular interaction in density functional theory:
Application to carbon nanotubes and fullerenes

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A theoretical study of weak interactions in graphitic materials such as carbon nanotubes (CNTs), fullerenes, and graphene is presented here. Based on a localized orbital density-functional theory formalism, our treatment which has already been applied for graphene-graphene interaction describes independently the weak chemical as well as the van der Waals interactions with high accuracy. The weak chemical interaction is described in the frame of the linear combination of atomic orbital S^2 model based on a weak overlap expansion, and the van der Waals interaction is treated in the dipolar approximation, taking into account virtual transitions of high energy. This formalism is applied here to the case of lateral interaction between CNTs, C_{60} dimers, adsorption of C_{60} on graphene and CNT, and encapsulation of C_{60} and CNT. The power law of the interaction is analyzed, and useful parameters such as C_6 coefficients and an exponential model for the "chemical" interaction are extracted. Beyond the study of graphitic materials, this work opens interesting perspectives in the analysis of weakly bonded metal/organics interfaces.

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I. INTRODUCTION

The study of van der Waals interaction and more generally noncovalent interactions[1] is becoming an active field in condensed matter physics as well as in biology or chemistry. Indeed, these interactions are really important in many different systems such as carbon nanostructures [graphene, carbon nanotubes (CNT), fullerenes (C_{60}), etc.],[2–5] π-conjugated systems such as organic molecules adsorbed on metallic surfaces,[6–8] rare gases dimers,[9,10] water molecules dynamics,[11,12] colloidal chemistry, interactions between biological membranes as protein folding, helicoidal structure of DNA through hydrogen bonding,[13] molecular recognition, etc.

Apart from being fundamental, these interactions present interesting properties. For example, in the emerging field of molecular electronics, molecules which are weakly connected to the electrodes present a higher conductance than the strongly bonded ones. Despite this high importance, the determination of weak interactions remains an important scientific challenge, especially in the case of extended system. Indeed, these interactions are weak (weak with respect to the covalent interaction; the corresponding energy ranges from some meV to hundreds of meV) and long range (up to some nanometers in some cases). Moreover these interactions are intrinsically really complex. Everyone knows of course the van der Waals interaction as a pure quantum-mechanical effect associated with virtual electronic excitations, and that can be viewed as an interaction between instantaneous fluctuating dipoles which leads to a long-range correlation energy. But another important contribution exists, which is often neglected or incorrectly approximated, which is due to the weak overlap between electronic densities of the interacting subsystems. This interaction, which we will call weak

"chemical" interaction, leading generally to a repulsion energy between the subsystems, needs, as well as the van der Waals interaction, to be described accurately, and this one is part of the present work.

Various models have already been proposed to describe such interactions. Among them we can quote the Lennard-Jones-type models,[3,14,15] where the van der Waals part is represented as a r^{-6} variation (due to its dipolar origin) and the chemical interaction as a r^{-12} term to fulfill the Pauli principle. This method presents a strong disadvantage: the parameters have to be adjusted for each considered material, and it cannot take into account structural modification of this material, at the atomic level, for example. Moreover, the validity of the fitted parameters is often questionable because the arbitrariness of the r^{-12} term has often to be compensated by the dipolar term, leading to a bad estimation of the r^{-6} term, the pure van der Waals energy.[3,16]

Other models have been proposed from the quantum chemistry, where the idea is to determine the two interacting subsystems accurately from first-principles methods, and then to treat the weak interaction in the frame of perturbation theory.[17] The problem lies in the fact that the total wave function of the system is not antisymmetric and one has to overcome this difficulty. Two models can be found which are symmetrized perturbation theory,[18–22] and symmetry adapted perturbation theory (SAPT).[23,24] Nevertheless, this approach presents the disadvantage, as in most of the quantum chemistry methods for weak-interaction determination, to be computationally very time and memory consuming, which limits its application to small molecular systems. Similarly, we have to mention second-order Møller-Plesset theory (MP2) (Refs. 25–31) where the zero-order Hamiltonian is the original one, minus the Fock Hamiltonian. This method is very accurate, and works quite well for small molecular systems.

Other *ab initio* methods such as density-functional theory (DFT) (Refs. [32] and [33]) have also been proposed to treat weak interactions. The main difficulty is that weak interactions are long range while the commonly used approximations like the local-density approximation (LDA) are short range and can obviously not handle these interactions. In this frame, all the calculation is based on the overlap of the electronic densities, and when this overlap becomes too small, it is not possible anymore to get an accurate result. Some way to overcome this problem is to add a semiempirical r^{-6} term such as in the DFT-*D* approach[34] (dispersion corrected DFT) but where a parameter has to be adjusted. A fully first-principles calculation is focused on the determination of a new functional, such as the work from Lundqvist and co-workers,[2,35] able to recover dispersion interactions like van der Waals.[36–39] Unfortunately the obtained functionals often present the disadvantage of being really expensive with respect to computational time and resources.

From the physical point of view, as the van der Waals interaction can be seen as a field interaction between virtual dipoles, these local approximations are not able to describe this process. Moreover, these dipole-dipole interactions can also be seen as exchange in virtual photons between the two systems, involving transitions with highly virtual states, whose description remains out of the range of standard DFT.[40,41]

In the present work, we use an approach previously developed for rare-gas dimers and graphene-graphene interaction,[40,42] based on DFT in a localized orbital basis set combined with intermolecular perturbation theory to describe both van der Waals and weak chemical interaction. This approach is now applied to the study of graphitic materials. It is not necessary nowadays to underline the importance of carbon nanotubes[43] but an accurate description of the weak interaction between these objects or the adsorption of molecules on their surface remains an important challenge. This work is a preliminary step to the comprehension of these interfaces. In Sec. II, we briefly review our theoretical approach, which combines DFT (in a local-orbital formalism), intermolecular perturbation theory, and an expansion in the overlap between the local orbitals in different subsystems. In Sec. III, we present the results obtained in the case of interactions between CNTs, C_{60} dimers, C_{60} adsorption on graphene and CNT, and C_{60} encapsulation in a CNT (10,10), as well as a double-walled CNT. Finally these results are discussed in Sec. IV in order to analyze the power laws and the so-called C_6 coefficients obtained within this approach. We will observe that this method is able to determine accurately the binding energies in graphitic systems, and is really promising for a general study of π-conjugated systems.

II. THEORETICAL FRAME: LCAO-S^2 METHOD AND VAN DER WAALS INTERACTION IN DFT

In this section, we briefly review our theoretical approach and main approximations for the calculation of weak interactions in graphitic materials. A detailed explanation of this approach can be found in Ref. [40], where as a first application

it has been used to analyze the interaction between two graphene layers.

The general theoretical framework is provided by the linear combination of atomic orbital-orbital occupancy (LCAO-OO) method,[44–46] which allows us to establish the connection between local-orbital DFT and intermolecular perturbation theory in second quantization formalism, ensuring that antisymmetry is properly included in the calculation of the intersystem interaction. The first step in our approach is the DFT solution for each isolated subsystem. This DFT solution is formally obtained within the LCAO-OO method, which is an alternative approach to DFT, in which instead of the traditional electronic density $\rho(\vec{r})$, we use the orbital occupation numbers $n_{\mu\sigma}$ as the central quantity:[44,47]

$$\rho(\vec{r}) \Rightarrow \{n_{\mu\sigma}\}. \qquad (1)$$

In conventional DFT, the Hohenberg-Kohn theorem states that the total energy of the fundamental state of an electronic system is a functional of the electronic density. In our formalism, this total energy is now a function of the orbital occupation numbers, $E=E[\{n_{\mu\sigma}\}]$. We can then rewrite Kohn-Sham-type equations to solve the new effective one-electron problem.[44,47]

In our work, for practical and simplicity reasons, we describe each isolated subsystem using the DFT code FIREBALL,[48–51] which can be viewed as an efficient simplified version of the more general LCAO-OO formalism. In similarity to the LCAO-OO method, self-consistency is achieved in FIREBALL in terms of the occupation numbers $n_{\mu\sigma}$, using a self-consistent version of the Harris functional[49] instead of the traditional Kohn-Sham functional based on the electronic density. In our approach to define these occupation numbers, we use an optimized atomiclike orbital basis set. In Ref. [52] an optimized minimal basis set for carbon was obtained, considering various carbon phases as well as several hydrocarbon molecules; this basis set was optimized for the covalent interactions in those systems (i.e., the basis set optimization did not take into account weak interactions). A comparison of the FIREBALL and LCAO-OO approaches has been made recently, using the same optimized basis set, and we have found that both yield similar results.[46] Finally, we mention that in the FIREBALL calculations pseudopotentials are used,[53] and the LDA exchange-correlation energy is calculated using the multicenter weighted exchange-correlation density approximation (McWEDA).[51]

As mentioned before, the weak interaction between two systems is mainly due to two contributions: an attractive van der Waals interaction and a repulsive "weak chemical interaction," which is often neglected or assimilated to the van der Waals interaction and which can be viewed as a residue of the strong covalent interaction occurring at smaller distances. This repulsion arises mainly from orthogonalization effects between the molecular wave functions of each subsystem, i.e., it is directly related to the overlap (S) between these wave functions. As these overlaps are very small for the case we are interested in, we use an overlap (S^2) expansion to obtain the corresponding interaction energy.[54–56] The main effect of this S^2 expansion, which includes a standard hybridization term also proportional to S^2 (in intermolecular

perturbation theory), is a shift of the molecular levels of each isolated systems, resulting in a net repulsive energy.

The van der Waals interaction can be seen as a long-range electronic correlation energy, which in our LCAO-OO formalism appears as a term proportional to the Coulombic integral $J_{i,j,\alpha,\beta}^{vdW}$, where i, j, α, and β are four different orbitals, with i and j belonging to the first subsystem, and α and β to the second. In our approach we use a pairwise atom-atom approximation, keeping only the interaction between two atoms from different subsystems, i.e., i and j belong to the same atom, and α and β also belong to the same atom in the other subsystem, and sum over all the atom pairs in the system. Then, considering the large interaction distances, we use the dipolar approximation to evaluate the Coulombic integral $J_{i,j,\alpha,\beta}^{vdW}$. This approximation is totally justified due to the standard equilibrium distances found in our analysis, around 3 Å. Finally, due to its relative weakness with respect to the covalent energy, the corresponding van der Waals contribution between the two subsystems is calculated using second-order perturbation theory, leading to the following expression[40]

$$E^{vdW} = 4 \sum_{i,j,\alpha,\beta} (J_{i,j,\alpha,\beta}^{vdW})^2 \frac{n_i(1-n_j)n_\alpha(1-n_\beta)}{(\bar{e}_i - \bar{e}_j + \bar{e}_\alpha - \bar{e}_\beta)}, \quad (2)$$

the factor 4 includes the spin degeneracy, and n_i are the orbital occupation numbers (per spin) defined by

$$n_i = \int_{occupied} \rho_i(\varepsilon) d\varepsilon. \quad (3)$$

Similarly, the average energies of occupied and unoccupied levels are defined by

$$\bar{e}_i = \int_{occupied} \varepsilon \rho_i(\varepsilon) d\varepsilon / \int_{occupied} \rho_i(\varepsilon) d\varepsilon, \quad (4)$$

$$\bar{e}_j = \int_{empty} \varepsilon \rho_j(\varepsilon) d\varepsilon / \int_{empty} \rho_j(\varepsilon) d\varepsilon, \quad (5)$$

where $\rho(\varepsilon)$ represents the local density of states.
$J_{i,j;\alpha,\beta}^{vdW}$ is calculated as

$$J_{i,j;\alpha,\beta}^{vdW} = \frac{1}{R^3}(\langle i|x|j\rangle\langle\alpha|x'|\beta\rangle + \langle i|y|j\rangle\langle\alpha|y'|\beta\rangle$$
$$- 2\langle i|z|j\rangle\langle\alpha|z'|\beta\rangle), \quad (6)$$

with $i \neq j$ on the same atom of one subsystem, and $\alpha \neq \beta$ on the same atom of the other subsystem; R is the distance between the two atoms, assumed to be in this expression along the z axis. This quantity depends on the different dipolar matrix elements in each atom. Of course, this approximation would not be valid anymore in the case of short distances but this is beyond the scope of the present work. Moreover, we have to underline the fact that this $J_{i,j;\alpha,\beta}^{vdW}$ represents the bare van der Waals interaction, without screening (which was neglected here; this point will be discussed later), as defined in this model.

To conclude this presentation of the model, we have to indicate here that a sum rule have been used to determine

dipole elements from high excited transitions (involving the d band of the carbon, for example). These virtual transitions represent in fact the main contribution to the van der Waals energy (more than a half), as explained in Ref. 40. Using these expressions and the DFT band structures of each subsystem obtained previously with FIREBALL, we can evaluate their van der Waals interaction energy. By combining this energy with the weak chemical repulsion obtained in the LCAO-S^2 approach, we determine the binding energy of the two subsystems.

III. RESULTS: APPLICATION TO CNT AND BUCKYBALLS (C_{60})

Now we will present the results of our calculations with the model presented above in some important graphitic systems, for example, CNT, fullerenes (C_{60}), or graphene. In particular, we will consider the case of weak lateral interaction between single-walled CNTs versus different radius, the case of C_{60} dimers, adsorption of C_{60} on graphene or CNT, and finally, double-walled CNTs and encapsulation of C_{60} in CNT. This work brings important results in this field and represents as well a step for such studies as many aspects still need to be improved or deeply studied. The starting point of the present work, which constitutes a reference for weak interactions in graphitic materials, is the interaction between two graphene planes. Corresponding results for this system and details can be found in Ref. 40.

A. Weak lateral interaction between CNTs: Influence of the radius

We study first the lateral interaction between two CNTs for various radiuses. This system is interesting on a methodological point of view because, for large radius, it can be compared directly with the interaction between two graphene sheets. Moreover, the lateral interaction is fundamental when one wants to understand how to build a crystal of standing up CNTs on a substrate for electronic emission, for example. We represent in Fig. 1 (left panel) the evolution of the lateral binding energy between two metallic CNTs, for CNT (4,4), (6,6), (8,8), (10,10), and (12,12). We only focused here on metallic CNTs as a first approach in order to observe the evolution for the same type of CNTs. Moreover, we do not expect, however, important physical differences in the result for the interaction between semiconductors CNTs. The main difference will be probably a slightly lower van der Waals interaction for the semiconductor case due to the larger gap which will increase the virtual energy transitions. We also represent the equilibrium position of two graphene planes, which should be reached for CNTs with infinite radius.

The various interaction energies per unit length are shown in Table I. The equilibrium positions determined here correspond to the closest distance between graphitic surfaces, depending obviously on the mutual orientation of the CNTs. Experimentally, the equilibrium distance is around 3.4 Å.[57] Our results give a little bit less but this is consistent with what we have obtained in the graphene-graphene case. Moreover, the metallic case leads to a stronger van der Waals
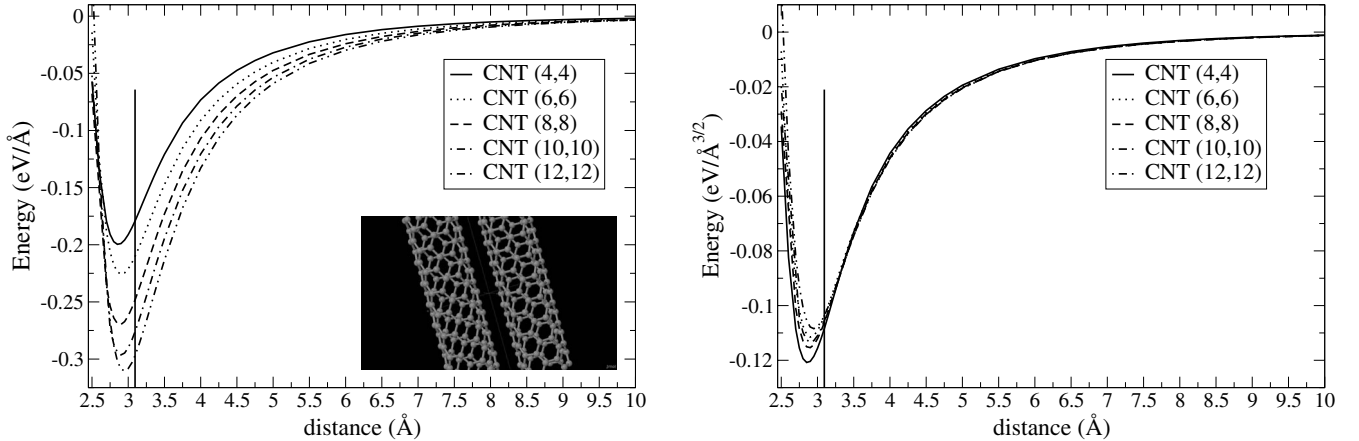
FIG. 1. Left panel: evolution of the lateral binding energy of CNTs as a function of the wall to wall distance, and for various CNT radii. We represent in inset the geometry of the interaction. Right panel: evolution of the lateral binding energy, normalized with the square root of the CNT radius, as a function of the wall to wall distance, and for various CNT radii.

energy which can affect a little the equilibrium position. For the sake of comparison, we mention that the LDA (Ref. 58) yields an equilibrium distance around 3.1 Å, similar to the ones calculated using the Lennard-Jones model from Girifalco *et al.*[16] for the same CNT series. However, a recent result from Kleis *et al.*[59] gives a slightly larger interdistance, around 3.45 Å.

We can also observe an increase in the binding energy per unit length with the diameter of the CNTs, from 5.46 to 16.39 Å, which is related obviously to the increase in the number of atoms in interaction. These binding energies are quite similar to what is obtained in a Lennard-Jones-type model.[16] Considering another van der Waals-DFT approach, let us mention that, for a semiconductor CNT (8,0), the binding energy calculated by Kleis *et al.*[59] is 75 meV/Å, to be compared with the binding energy of 220 meV/Å that we have calculated for a (5,5) CNT. We obtain a stronger binding energy (~220 meV/Å vs 75 meV/Å) considering the CNT diameter correspondence between a (8,0) and a (5,5). This behavior and these differences between the two models were also observed for the case of the graphene-graphene interaction. However, this comparison has to be taken with caution, as the CNT (5,5) is metallic, and the (8,0) is semiconductor. In our framework, one can expect more binding energy in the metallic case as explained before. On the other hand, if we consider an effective surface, for the interaction

between two CNTs, we can assume geometrically that, for quite large CNTs, this effective surface is proportional to the square root of the radius. In Fig. 1 (right panel), we represent as well the same lateral energies as before, divided by the square root of the CNT radius. We can observe that the normalized energetic curves are almost similar; deviations occur only in the case of small CNTs [(4,4), for example], where the radius is not large enough (2.73 Å) to validate the geometrical approximation.

Another interesting point to consider here is the mutual orientation of the CNTs. We have not studied in detail all the possible configurations but we just want to point out the main idea that the corrugation can be important at short range. We calculated the lateral energy between (12,12) CNTs, in an AA stacking and in an AB stacking, in analogy with the possible graphene-graphene configurations; this gives rise to a slight difference in binding energy and minimum (about 16 meV/Å for the binding energy and 0.05 Å for the equilibrium position), as the AA configuration here is more repulsive, similarly to the graphene case. This result is illustrated in Fig. 2.

Finally we have also calculated the binding energy of a bundle of (10,10) CNTs on a centered hexagonal lattice, in order to compare it to the pair interaction. We obtain a binding energy of 288 meV/Å for an equilibrium distance of 2.95 Å. This result indicates that the chemical repulsion is proportionally more important in a bundle than in a pair of CNTs, which is consistent with our small overlap description of this energy, leading to a slightly lower binding energy and a larger equilibrium position.

TABLE I. Evolution of the equilibrium positions and the energy minimum of CNT lateral interaction, as a function of the CNT dimensions (d being the diameter of the CNT).

CNT dimensions (Å)	Equilibrium position (Å)	Energy (meV/Å)
(4,4), $d=5.46$	2.85	199
(6,6), $d=8.19$	2.9	226
(8,8), $d=10.92$	2.9	269
(10,10), $d=13.58$	2.9	296
(12,12), $d=16.39$	2.95	310

B. Binding energy of C_{60} dimers

In this part, we are interested in the interaction between two fullerenes (C_{60}). We have to indicate that we consider in this work the neutral C_{60} dimer, which does not correspond to the case of cycloaddition, for example, $(C_{60})_2^+$, where there is one electron left in the system, leading to a much stronger (covalent) interaction energy. The study of this dimer is an interesting problem which has been already addressed by dif-
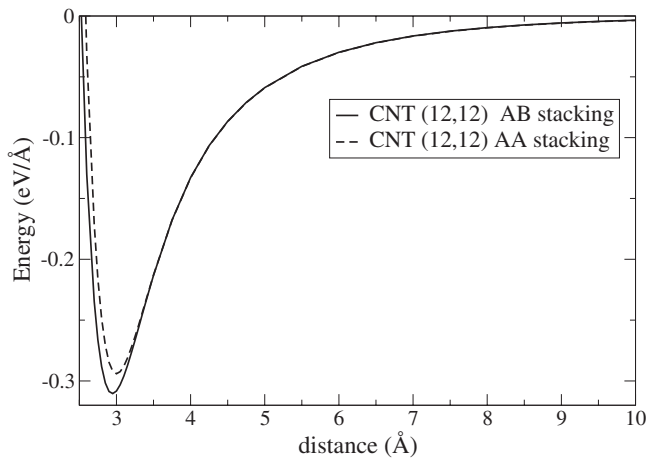
FIG. 2. Comparison of AB and AA stackings for the lateral interaction energy between two CNT (12,12).

ferent methods.[5,16,60] The binding energy of such system is still unclear, as we can find theoretical determinations ranging from 80 to 554 meV per dimer. Moreover, it is not well established if this binding energy is van der Waals type or if it is slightly covalent. In this work, following the formalism we have developed for graphene-graphene interaction, we consider that these two interactions coexist, and the balance between both is determined within our DFT +intermolecular perturbation theory.

We did not focus our discussion on the mutual orientation of the two C_{60}, as our goal is to get an idea of the binding energy of such system. Nevertheless, in a future work, we will look more precisely at this detailed structure. The point here is to see how our approach compares with previous theoretical determinations. Our result is represented in Fig. 3 as the total binding energy versus the distance between graphitic surfaces. We present as well the detail of the two contributions, which are the chemical repulsion and the van der Waals energy.

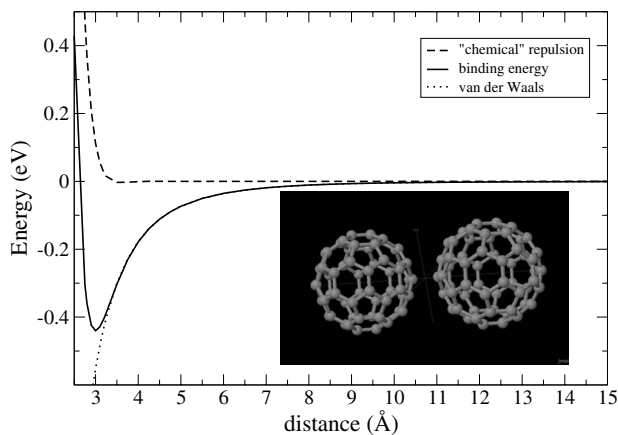We find a minimum energy of 440 meV for the whole dimer, at an equilibrium position of 3 Å. The equilibrium

FIG. 3. C_{60} dimer binding energy within our model. Chemical repulsion and van der Waals contribution are also represented. In inset we represent the atomic configuration corresponding to our calculation.

position is here also defined as the closest distance between graphitic surfaces, the diameter of a C_{60} molecule being 6.96 Å. This result constitutes an intermediate result between previous DFT-LDA calculations (which underestimates the binding energy because of the lack of van der Waals interaction), and the Lennard-Jones potential determination (which overestimates the van der Waals part to compensate an incorrect determination of the repulsive part).

It is also interesting to mention the case of C_{60} in a C_{60}-molecular crystal, in the simple-cubic crystalline form here, which is the stable phase at 0 K,[61,62] as in our calculations. In fact, the experimental results obtained for C_{60} dimers are extracted from C_{60} crystal structures. Obviously the comparison has to be taken with some caution since there is no direct relation between dimer and crystal (as is the case of a CNT crystal) but it gives at least the correct order of magnitude for the binding energy. We find a minimum binding energy of 1.74 eV per C_{60} molecule, for an equilibrium lattice parameter of 9.7 Å, which is in quite good agreement with the experimental data [around 1.7 eV at 9.93 Å (Refs. 61 and 63)] extracted from the study of a face-centered-cubic C_{60} crystal. The equilibrium distance between two C_{60} is about 3.06 Å (14.17 Å for lattice parameter in the fcc crystal),[63] and the binding energy (averaged on all the different C_{60} pairs of the crystal) is around 650 meV per dimer (1.7 eV for the whole crystal).[63] This result for the simple-cubic phase has to be taken with caution, as well-known rotational effects have not been considered here. Moreover a deeper study has to be achieved since the crystalline lattice is known to be simple cubic at low temperature and face-centered cubic at room temperature, above 90 K, from neutron and x-ray diffusive diffusion determinations.[64] These two forms are related by an orientational ordering transition,[61,62] which still has to be explored within our approach. This problem will be the subject of a future work where van der Waals forces will be introduced within a molecular-dynamics calculation.

C. Adsorption of C_{60} on graphene and CNT

In this part, we present the adsorption of C_{60} molecule on graphene and on a CNT (10,10). This work is also a step in the study of weakly adsorbed molecules on metallic surfaces as well as in the study of organic doped CNTs. The C_{60} adsorption on graphene has already given us elements to evaluate the equilibrium position of $C_{60}/Au(111)$ in order to determine interface dipole and charge transfer.[65]

The adsorption energy curve of C_{60} on graphene as well as the chemical repulsion and the van der Waals energy, calculated in our approach, are represented in Fig. 4.

In this case, we find an equilibrium position of 2.9 Å (i.e., the closest distance between graphitic surfaces), a bit less than for graphene-graphene interaction, and a minimum energy of about 1 eV per C_{60} molecule. This result is due to a lower repulsion between C_{60} and graphene because of the curvature of the molecule while the van der Waals interaction, which is long range, remains similar.

For C_{60} adsorption on CNT, we have considered the case of a (10,10) CNT. This CNT has been chosen for its relative
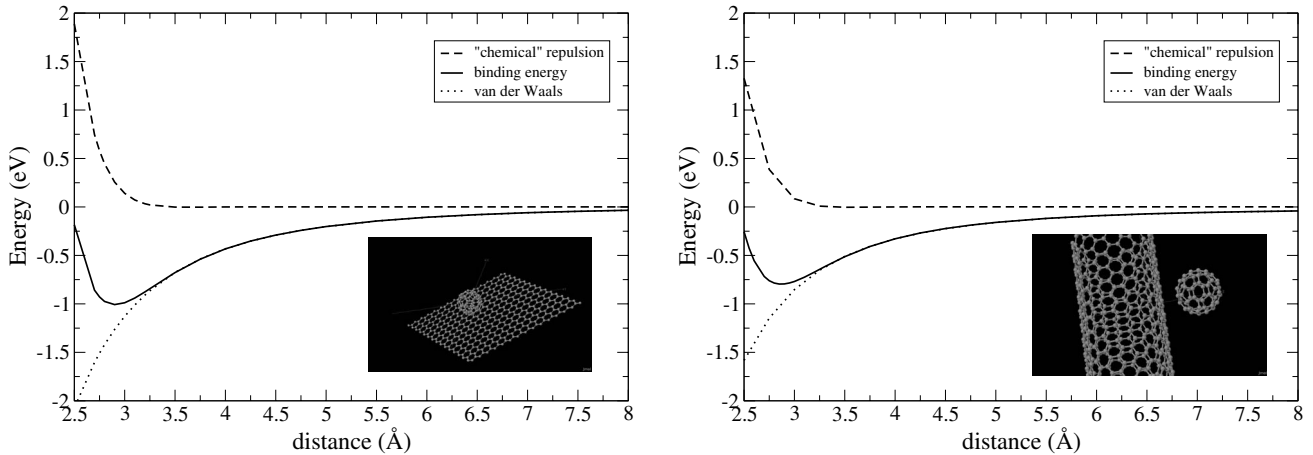
FIG. 4. Binding energy, chemical repulsion, and van der Waals energy of C_{60} adsorbed on graphene (left panel) and on a CNT (10,10) (right panel), calculated with our approach. The atomic configuration is represented in inset.

similar size to C_{60}, a bigger CNT would give a result really close to the one obtained for C_{60} on graphene. In Fig. 4, we represent the evolution of the binding energy per C_{60} molecule, with respect to the intersurface distance with the CNT.

Here we find an equilibrium position at 2.85 Å, and a minimum of energy of 796 meV per C_{60} molecule. In these two cases, more work has still to be done, for example, about mutual orientation between the two systems or about doped CNTs with organic molecules.[66] This will be explored in the future also.

D. Encapsulation of C_{60} in CNT and double-wall CNT

The problem of encapsulation of molecules and especially C_{60} is very important nowadays as these systems present interesting charge-transfer properties.[67,68] For example, it has been observed that a C_{60} encapsulated in a CNT, also called peapod,[69,70] presents an excess of electronic charge, resulting in a negative net charge. In the present formalism, such a charge transfer is complicated to evaluate. Nevertheless, as a first determination, we have assumed that such charge transfer does not change too much the binding energy and the equilibrium position. However, the present form of the van der Waals and weak chemical energy offers a way to introduce in a near future a reasonable potential able to describe weak interactions, taking into account charge transfer. These systems are really interesting for molecular electronics, and the study of various molecules inserted in CNT is a hot topic. However, even if the binding energy can be estimated experimentally, there is still an intense theoretical controversy to understand it with great precision, as the nature of the bond remains difficult to understand. Many attempts have been done to determine this interaction, mostly with Lennard-Jones calculations[71,72] which do not really bring a physical comprehension of this interaction as the repulsive part is adjusted empirically, which has an influence on the van der Waals part. We can also find a very recent paper where calculations have been performed in a pure DFT formalism,[73] without any inclusion of van der Waals interaction, which may be surprising.

We present here the result of our LCAO-S^2+van der Waals calculation for a C_{60} molecule inserted in a CNT (10,10) and in a CNT (12,12). We have then represented the binding energy of this C_{60} molecule as a function of the distance between the centers of the molecule with the axis of the CNT. The result is shown in Fig. 5.

From this result, we observe first that the minimum energy of C_{60} is not centered in the CNT but is situated at about 0.2 Å from the center for the CNT (10,10) and 1.9 Å for the CNT (12,12). This is due to the balance between the repulsive weak chemical interaction and the attractive van der Waals force. This result is not observed for a CNT (10,10) and the minimum remains close to the center for the CNT (12,12) in a Lennard-Jones-type model.[72] On another hand, these minima compare well to LDA calculation.[73] The curves here are really flat but we can clearly see these radial minima appearing when increasing the diameter of the tube from the (10,10) to the (12,12) (here there are only two positions, as we represent the evolution along a diameter). Regarding the minimum of energy, we observe total binding energies for
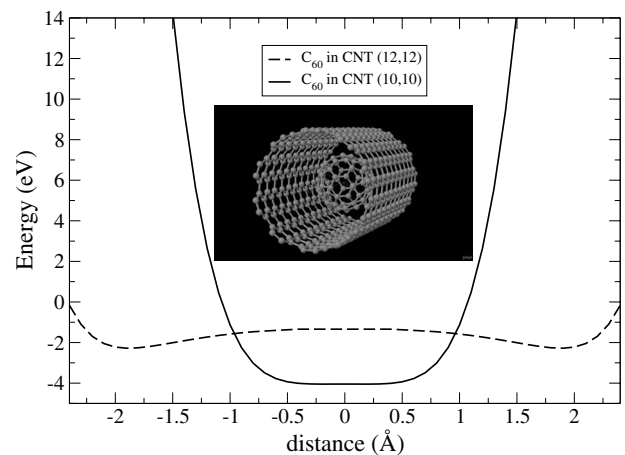

FIG. 5. Binding energy of C_{60} encapsulated in a CNT (10,10) and in a CNT (12,12) as a function of the distance between the center of the molecule and the CNT axis. Atomic configuration of C_{60} in a CNT (10,10) is represented in inset.
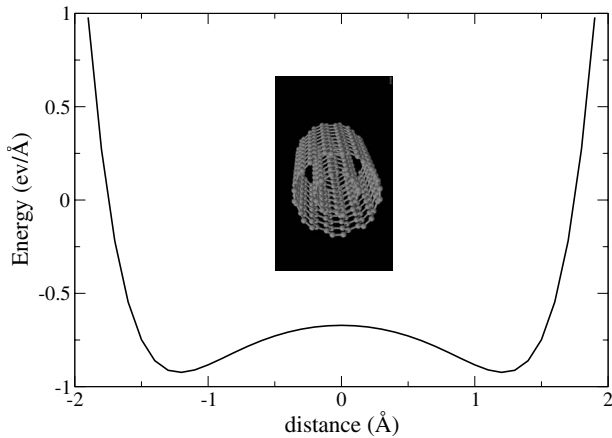
FIG. 6. Binding energy of CNT (4,4) inserted in a CNT (10,10) versus the interaxis distance. Atomic configuration is represented in inset.

TABLE II. Evolution of the average C_6 coefficients obtained for the different systems considered in this work.

System	C_6 coefficient $(eV/Å^6)$
Graphene-graphene	−13.8
CNT-CNT (all diameters)	−14.7
C_{60}-C_{60}	−15.1
C_{60}-graphene	−14.9
C_{60}-CNT	−14.9

the molecule of 4.05 eV [CNT (10,10)] and 2.28 eV [CNT (12,12)], which is in good agreement with previous calculations [3.26 eV/C_{60} in a CNT (10,10)] from Girifalco and Hodak[72] but reveals a stronger cohesion energy than the ones calculated in DFT. For example, a recent calculation on this system from Okada,[73] in a pure DFT-LDA formalism, gives a maximum binding energy of around 1 eV per C_{60} molecule in a CNT (12,12). This result clearly indicates the need to take the van der Waals interaction into account. From these results, we stress that the interaction of C_{60} with CNT is a weak one among which, one can find van der Waals which cannot be reproduced correctly in the frame of standard DFT. The different results we have obtained for the two sizes of CNTs are due to the number of effective interacting atoms contributing to the repulsive part that each CNT has with the molecule; this number is smaller for bigger CNT, and the situation tends to the case of C_{60} adsorbed on graphene. For the sake of comparison with experiments, the desorption energy of a C_{60} molecule from a CNT is estimated around 1.7 ± 0.2 eV by the mean of a kinetic model.[71,74] Another interesting quantity is the variation in energy for a translation of the C_{60} molecule along the axis of the CNT. We observe that there are only very small variations (about some meV) of the binding energy of C_{60} in the CNT due to the corrugation, which means that the translation is practically costless energetically. This kind of result has already been observed in bio-organic molecules, with covalent binding energy,[75] but it has not been demonstrated theoretically in the case of peapods until now.

We have proceeded to the same study with CNT (4,4) inserted in CNT (10,10). This system is comparable to the C_{60} considered before, as the diameters of both systems are similar. Moreover, this study opens the way to a more general study of multiwall CNT, which has still to be done since there is no clear interpretation of the binding energy in that case either. The energy of such system, per unit length, is represented in Fig. 6, in function of the interaxis distance.

Here also we can observe the same radial minimum (two positions represented, as we show the evolution along a diameter) previously seen with the C_{60} molecule, which is located at 1.3 Å from the central axis. Considering the respec-

tive radii of the two CNTs, this radial minimum corresponds to an equilibrium distance between CNT surfaces of 2.76 Å, a bit less than what is observed experimentally around 3.4 Å (Ref. 43) but which is consistent with the previous results of our calculations. In any case, our simple model of a CNT (4,4) in a CNT (10,10), which aimed to show how to use our LCAO-S^2+vdW formalism in this case, may be difficult to compare with experimental data, as it is really difficult to obtain such a specific chirality of the two CNTs in an experiment. Moreover, depending on the CNT diameter, we should take into account CNT deformations due to these weak interactions, which is complicated in the present approach. The binding energy is 0.92 eV/Å, which is totally comparable with the one obtained with C_{60} if we take around 6 Å length for the CNT (4,4).

These problems of encapsulations present many interesting applications, as underlined before, and these two model systems constitute a first step for future study of complex molecules inserted in CNTs.

IV. DISCUSSION: EXPONENTIAL MODEL FOR THE CHEMICAL REPULSION, C_6, AND POWER LAW ANALYSIS OF THE VAN DER WAALS INTERACTION IN GRAPHITIC MATERIALS

Here we would like to make a summary of the important results encountered in these materials. With such objective, we have represented in Table II the values of the C_6 coefficient (the van der Waals interaction between two atoms has a $1/r^6$ dependence, as we determined it from dipolar interaction) obtained from our calculations, for a pair of two Carbon atoms. These coefficients represent an average value obtained over all pairs of atoms.

The main observation we can make here is that the variation in our C_6 value is really small (about 1 eV/Å^6). This is due to the fact that, in our approach, the repulsive weak chemical energy as well as the van der Waals contribution are determined independently and with high accuracy from DFT data. In some other works, the van der Waals energy has to compensate the repulsive weak chemical energy to obtain good equilibrium positions and a correct binding energy, leading to strong variations in the C_6 coefficient (about 5 eV/Å^6).[16]

From our work, we have found that the chemical repulsion between two Carbon atoms can be approximated with reasonable accuracy by an exponential function such as

TABLE III. Evolution of the power law of the energy interaction tail obtained for the different systems considered in this work.

System	Power law
Graphene-graphene	$-1/d^4$
CNT-CNT (all diameters)	$-1/d^4$
C_{60}-C_{60}	$-1/d^4$
C_{60}-graphene	$-1/d^3$, $-1/d^4$
C_{60}-CNT	$-1/d^{\frac{7}{2}}$

$\alpha e^{-\beta(r-r_0)}$, where r is the interatomic distance, with $\alpha = 8$ meV, $\beta = 5.4$ Å^{-1}, and $r_0 = 3.1$ Å, being the equilibrium distance obtained for the graphene-graphene case. Of course this model is only valid for weak interacting systems, and cannot be considered to be valid for covalent bonds.

In Table III, we represent the evolution of the power law determined for the energy interaction in all these graphitic systems. These power laws were determined by geometric considerations over the $1/r^6$ interatomic potential and confirmed by fitting the tail of the energy curve obtained in our model. The aim of this section is to compare the present results with previous interpretations.[36,76]

As a general remark we can observe that this power law is around $1/d^4$, d being the wall to wall distance, corresponding essentially to the integration of the $1/R^6$ interaction between two atoms in two subsystems. This is true for graphene, CNT or C_{60}. In the case of C_{60} on graphene, we find a power law of $1/d^3$ at short distances, which goes to $1/d^4$ for distances bigger than the C_{60} diameter. Similarly, in the case of C_{60} on CNT, the power law is found to be $1/d^{\frac{7}{2}}$ for $d \ll R$ (R being the C_{60} radius), which is close to the result encountered for adsorption on graphene. In these last two cases, these geometrical considerations regarding the C_{60} dimensions are important due to the fact that the two interacting systems are not equivalent as in the three first cases.

We have to stress as well the main approximation of our approach, which is that the van der Waals interaction $J_{i,j;\alpha,\beta}^{\text{vdW}}$ is not screened, with respect to other approaches.[36,76] In metallic systems, and even in graphene-graphene interaction which has a metallic character due to the zero gap in the K point, the screening is usually important. However, in our case, as the van der Waals interaction comes mainly from virtual fluctuations associated with high energies (up to 50 eV for the $3d$ band),[40] the corresponding dielectric function $\varepsilon(\mathbf{r},\omega)$ goes to the unity and consequently the screening can be neglected. This approximation is of course only valid for the distances we are interested in this work, leading to a $-1/d^4$ behavior for graphene-graphene or CNT cases, for example. At larger distances, one would have to take into account collective effects such as plasmon frequency shift, associated with the dielectric screening of the system,[77] leading to a long-range $-1/d^3$ behavior as in the work of Dobson and co-workers.[36,76]

Let us remark that our approach, which obviously would not be appropriated in the case of two interacting metals, remains valid in the case of a semiconductor interacting with a metal, as is the case for metal/organics interfaces. This is due to the existence of the molecular gap, leading to high energy virtual transitions that justifies using an unscreened van der Waals interaction, $J_{i,j;\alpha,\beta}^{\text{vdW}}$.

To conclude this analysis, we will point out the main advantages of the method presented in this work. First, this approach constitutes a simple, fast, and efficient approach which allows to determine weak interactions in quite big systems (some of the supercells used in this work were composed of up to 500 atoms), from first principles. As a DFT-based method, there is no need to use parameters and therefore this can be generalized easily to other systems. The physics of these weak interactions is simple and well described by an overlap expansion, a dipolar approximation, and a perturbation theory, leading to a good comparison with previous models and experimental results. Finally, useful atomic potentials are extracted to perform molecular-dynamics simulations in order to treat these weak interactions in bigger systems out of the range of DFT.

V. SUMMARY

We have presented here a generalization to graphitic materials of the treatment previously tested to calculate weak interactions between graphene layers. We have studied the lateral interaction between two CNTs in function of their radii, the interaction in a C_{60} dimer, adsorption of C_{60} on graphene and CNT, and encapsulation of C_{60} and CNT (4,4) in a CNT (10,10). We could then observe that our approach gives very good results to determine an interaction which remains complicated to handle in standard DFT. We especially point out the accuracy of our determination of weak chemical interaction, which is often neglected or miscalculated. This weak chemical interaction, in combination with a determination of van der Waals interaction based on virtual dipolar transitions, allows us to determine with a high precision the equilibrium distances and binding energies in graphitic materials.

Still there are a lot of things to elucidate in such materials, but moreover this model can be extended to the study of π-conjugated systems such as metal/organics interfaces, in order to determine transport properties for molecular electronics applications.

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