Dynamical screening of van der Waals interaction between graphene layers

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(Dated: April 18, 2012)

Abstract

The interaction between graphene layers is analyzed combining local orbital DFT and second order perturbation theory. For this purpose we use the Linear Combination of Atomic Orbitals -Orbital Occupancy (LCAO-*OO*) formalism, that allows us to separate the interaction energy as a sum of a weak chemical interaction between graphene layers plus the van der Waals interaction [1]. In this work, the weak chemical interaction is calculated by means of corrected-LDA calculations using an atomic-like sp^3d^5 basis set. The van der Waals interaction is calculated by means of second order perturbation theory using an atom-atom interaction approximation and the atomic-like orbital occupancies. We also analyze the effect of dynamical screening in the van der Waals interaction using a simple model. We find that this dynamical screening reduces the van der Waals energy between graphene layers by 22 meV/atom , which represents a 40% reduction in the van der Waals interaction. Taking into account this dynamical screening, we obtain a graphene-graphene interaction of 64 meV/atom, in good agreement with the experimental evidence.

I. INTRODUCTION

Van der Waals (vdW) forces play an important role [2] in many physical, chemical or biological systems, like protein folding, polymers, membranes [3], colloid chemistry, water molecule dynamics [4, 5], carbon based technology [6–9], etc. However, an accurate calculation of those forces remains a great challenge due to its inherent non-local interaction and also to the complexity of the systems where their effects are important.

It is well known that the local density approximation (LDA) and the generalized gradient approximation (GGA) of density functional theory (DFT) completely miss to describe vdW for long distances (no electron density overlap) and do not describe it properly for shorter distances where the electron density overlap is important [6, 10, 11]. A fully first-principle calculation incorporating vdW in DFT has been introduced by Langreth, Lundquist and collaborators [12–15] who have developed new functionals, $E[\rho(\mathbf{r}))]$, that include properly the vdW interaction. These functionals seem to be, however, expensive with respect to computational time and resources. On the other hand, in a semiempirical approach a pair wise atom-atom vdW term has been added to a DFT (LDA or GGA) calculation of the whole system [16–20]. A third alternative consists on calculating each isolated subsystem using DFT, and then adding their interaction energy using perturbation theory [1, 21–23]. This last approach is deeply related to a line of research based on quantum chemistry techniques and the use of perturbation theory. In this case, the problem appears in the treatment of the antisymmetry of the wavefunction of the total system. Several methods have been developed to deal with this problem: the symmetrized perturbation theory [24, 25], and the symmetry adapted perturbation theory (SAPT) [26]. Unfortunately, these quantum-chemistry methods are very demanding in computational resources.

Finally, we can also mention a recent implementation in DFT of the RPA formalism for graphene-graphene interaction, as a promising method eventhough limited as well regarding computational resources [27].

In this paper we follow and extend the approach we presented in reference [1], combining local-orbital DFT with intermolecular perturbation theory to calculate the interaction between graphene layers. In this approach we use a linear combination of atomic orbitals-orbital occupancy (LCAO-OO) theoretical framework to establish the connection between local orbital DFT and intermolecular perturbation theory in second quantization formalism.

In the present work, we have extended this approach in several directions: (a) firstly, we have used a more complete basis set, namely, a sp^3d^5 instead of the optimized sp^3. (b) Second, we have introduced a corrected-LDA method to analyze the interaction between graphene layers, instead of the method based on the expansion of the interaction in the interlayer orbital overlap. (c) Finally, we have improved our calculation of the vdW-interaction by a more precise determination of the interaction term $J^{vdW}_{i,j,\alpha,\beta}$, without resorting to a dipole-dipole approximation, which yields the $(-C_6/R^6)$-behaviour for the vdW-potential between two atoms.

The results obtained with these changes are, however, very similar to the ones presented in [1], with an interaction energy per surface atom a little larger than the experimental evidence [28] : 86 meV/atom in our calculations and around 60 meV/atom from experiments [28]. This overestimation of the interaction energy (and other similar results from independent calculations [29, 30]) has prompted us to analyze the effect of introducing a kind of dynamical screening in the van der Waals interaction. This point is discussed in the final section, where we show that for the graphene-graphene interaction those dynamical screening effects reduce the interaction energy by around 20 meV/atom, yielding an excellent agreement between theory and experiments.

II. METHOD, BASIS SET AND SUM RULE

In this section, we present the general frame of our study, which lies on local-orbital Density Functional Theory (DFT) and intermolecular perturbation theory. The DFT calculations have been performed using the Fireball code which is a real-space local-orbital Molecular Dynamics implementation of DFT [31]. The LDA exchange-correlation potential is used for each system (graphene layer). We use a set of optimized numerical atomic orbitals (NAOs) [32] to represent the valence electron meanwhile the core electrons are represented by means of pseudopotentials [33].

For the C-atoms, we have considered, as mentioned above, a polarized sp^3d^5 basis, adding an additional empty d-state to the sp^3-basis used in ref [32]; the corresponding cut-off radii are $r_s = r_p = 4.5$ a.u., and $r_d = 3.5$ a.u. This allows us to introduce all the necessary transitions describing the Van der Waals interaction. This new orbital has also an important effect on the weak chemical interaction, since it yields a slightly attractive contribution in

agreement with other independent works [16, 17, 34], whereas for the simple basis set, the weak chemical energy is totally repulsive as we have seen in previous works on graphitic materials [1, 35, 36].

A. General frame : the LCAO-*OO* hamiltonian

The general frame of this work is the LCAO-*OO* method, which is a DFT formalism based on the occupation numbers, whereas the standard Kohn-Sham formulation considers the spatial electronic density $\rho(\vec{r})$ of the system. We start with the general Hamiltonian :

$$\hat{H} = \sum_{\nu,\sigma}(\epsilon_\nu + V^{ps}_{\nu\nu,\sigma})\hat{n}_{\nu,\sigma} + \sum_{\mu\neq\nu,\sigma}(t_{\mu\nu,\sigma} + V^{ps}_{\mu\nu,\sigma})\hat{c}^\dagger_{\mu\sigma}\hat{c}_{\nu\sigma} + \\ + \frac{1}{2}\sum_{\nu\omega\sigma\mu\lambda\sigma'} O^{\nu\mu}_{\omega\lambda}\hat{c}^\dagger_{\nu\sigma}\hat{c}^\dagger_{\mu\sigma'}\hat{c}_{\lambda\sigma'}\hat{c}_{\omega\sigma} \tag{1}$$

where the creation and annihilation operators $\hat{c}^+$, $\hat{c}$, as well as the occupation number operator $\hat{n} = \hat{c}^+\hat{c}$ are defined in a Löwdin orthonormal basis set $\{\phi_\mu\}$. This orthonormal basis set is defined from an original basis set of optimized atomic-like orbitals $\{\psi_\nu\}$ by the so-called Löwdin orthogonalization procedure :

$$\phi_\mu = \sum_\nu (S^{-1/2})_{\mu\nu}\psi_\nu; \tag{2}$$

where $S_{\mu\nu} =< \psi_\mu \mid \psi_\nu >$ is the overlap matrix.
In Eq. (1) $\epsilon_\nu + V^{ps}_{\nu\nu,\sigma}$ and $t_{\mu\nu,\sigma} + V^{ps}_{\mu\nu,\sigma}$ define the one-electron terms (with the pseudopotential (PS) contributions included), and

$$O^{\nu\mu}_{\omega\lambda} = \int \phi_\nu(\bar{r})\phi_\omega(\bar{r})\frac{1}{\mid \bar{r} - \bar{r}' \mid}\phi_\mu(\bar{r}')\phi_\lambda(\bar{r}')d\bar{r}d\bar{r}' = (\nu\omega|\mu\lambda) \tag{3}$$

are the electron-electron terms. In the LCAO-*OO* formalism, Hamiltonian (1) is rewritten as:

$$\hat{H} = \hat{H}_0 + \delta\hat{H} \tag{4}$$

$$\hat{H}_0 = \sum_{\nu\sigma}(\epsilon_\nu + V^{ps}_{\nu\nu,\sigma})\hat{n}_{\nu\sigma} + \sum_{\nu\neq\mu,\sigma}\hat{T}_{\nu\mu,\sigma}\hat{c}^\dagger_{\nu\sigma}\hat{c}_{\mu\sigma} + \sum_\nu U_\nu\hat{n}_{\nu\uparrow}\hat{n}_{\nu\downarrow} +$$

$$+\frac{1}{2}\sum_{\nu,\mu\neq\nu,\sigma}\left[J_{\nu\mu}\hat{n}_{\nu\sigma}\hat{n}_{\mu\bar{\sigma}}+(J_{\nu\mu}-J^{x}_{\nu\mu})\hat{n}_{\nu\sigma}\hat{n}_{\mu\sigma}\right], \tag{5}$$

$$\hat{T}_{\nu\mu,\sigma}=[t_{\nu\mu}+V^{ps}_{\nu\mu,\sigma}+\sum_{\lambda,\sigma'}h_{\lambda,\nu\mu}\hat{n}_{\lambda\sigma'}-\sum_{\lambda}h^{x}_{\lambda,\nu\mu}\hat{n}_{\lambda\sigma}].$$

In $\hat{H}_0$ the many-body terms are written explicitly showing the contributions depending on 1, 2 and 3 different orbitals. In particular, $U_\nu=(\nu\nu\mid\nu\nu)$, $J_{\nu\mu}=(\nu\nu\mid\mu\mu)$, $J^x_{\nu\mu}=(\nu\mu\mid\nu\mu)$, $h_{\lambda,\nu\mu}=(\lambda\lambda\mid\nu\mu)$, $h^x_{\lambda,\nu\mu}=(\lambda\nu\mid\lambda\mu)$, see Eq. (3). A deeper interpretation of the energy associated with each term can be found in Refs. 37–39. The vdW interaction $\hat{H}_{vdW}$ is included in $\delta\hat{H}$. Regarding our system of interest, the graphene-graphene interaction, $\hat{H}_0$ takes into account the covalent interaction inside each graphene plane, and the weak chemical interaction between graphene layers.

B. vdW formalism

We now present the general formalism developed here to determine the van der Waals energy in the system. This interaction is originated through quantum dipole-dipole interactions, due to charge fluctuations in the two subsystems. This energy is added perturbatively to the system. In the LCAO-*OO* method the van der Waals interaction is included in $\delta\hat{H}$:

$$\delta\hat{H}=\frac{1}{2}\sum_{\nu\omega\sigma\mu\lambda\sigma'}O^{\nu\mu}_{\omega\lambda}\hat{c}^{\dagger}_{\nu\sigma}\hat{c}^{\dagger}_{\mu\sigma'}\hat{c}_{\lambda\sigma'}\hat{c}_{\omega\sigma} \tag{6}$$

where μ, ν, ω and λ refer to four different orbitals. This term is of course really difficult to handle in a general way and includes, in particular, the van der Waals contribution, which in our approach corresponds to the following term

$$\hat{H}^{vdW}=\sum_{i,j,\alpha,\beta,\sigma_1,\sigma_2}J^{vdW}_{i,j;\alpha,\beta}\hat{c}^{+}_{i,\sigma}\hat{c}_{j,\sigma}\hat{c}^{+}_{\alpha,\sigma'}\hat{c}_{\beta,\sigma'} \tag{7}$$

with $J^{vdW}_{i,j;\alpha,\beta}=(ij\mid\alpha\beta)$, see Eq. 3, where i,j-orbitals ($i\neq j$) belong to the first graphene-layer and α,β ($\alpha\neq\beta$) to the second graphene-layer. In our work we have used an atom-atom approximation, keeping in Eq. (7) only the terms with i,j-orbitals in the same atom, and α,β in the same atom of the other layer, and have neglected all the other interlayer interactions from $\delta\hat{H}$. Also orbitals $\{\psi\}$ have been used for the calculation of $J^{vdW}_{i,j;\alpha,\beta}$, instead of orbitals

$\{\phi\}$ for simplicity. Notice that this term gives a zero contribution at the first order for the graphene-graphene interaction, since there are no permanent dipoles in graphene.

The van der Waals energy between the two subsystems is then calculated using second order perturbation theory. The van der Waals energy is weak with respect to the covalent energy, which justifies the use of this approximation. In that frame, we can now easily find the following van der Waals interaction energy (see ref [1]) :

$$E^{vdW} = 4 \sum_{i,j,\alpha,\beta} (J^{vdW}_{i,j,\alpha,\beta})^2 \int \frac{\rho_i(\varepsilon_1)\rho_j(\varepsilon_2)\rho_\alpha(\varepsilon_3)\rho_\beta(\varepsilon_4)}{(\varepsilon_1 - \varepsilon_2 + \varepsilon_3 - \varepsilon_4)} d\varepsilon_1 d\varepsilon_2 d\varepsilon_3 d\varepsilon_4 \tag{8}$$

where $i \neq j$ on the same atom of the first layer, and $\alpha \neq \beta$ on the same atom of the second layer. In Eq. (8), $\rho(\varepsilon)$ represents the local density of states per spin on each orbital; besides, the integrals in ε_1, ε_3 (ε_2, ε_4) run through the occupied (empty) states. This expression can be further simplified to express the result in terms of the occupation numbers of each state :

$$E^{vdW} \sim 4 \sum_{i,j,\alpha,\beta} (J^{vdW}_{i,j,\alpha,\beta})^2 \frac{n_i(1-n_j)n_\alpha(1-n_\beta)}{(\overline{e}_i - \overline{e}_j + \overline{e}_\alpha - \overline{e}_\beta)} \tag{9}$$

In this expression, n_i are the orbital occupation numbers (per spin)

$$n_i = \int_{occupied} \rho_i(\varepsilon) d\varepsilon \tag{10}$$

and

$$\overline{e}_i = \int_{occupied} \varepsilon \rho_i(\varepsilon) d\varepsilon \Big/ \int_{occupied} \rho_i(\varepsilon) d\varepsilon \tag{11}$$

$$\overline{e}_j = \int_{empty} \varepsilon \rho_j(\varepsilon) d\varepsilon \Big/ \int_{empty} \rho_j(\varepsilon) d\varepsilon \tag{12}$$

are average occupied and empty levels.

In our calculations we find: $n_s = 0.40e$, $n_p = 0.45e$ and $n_d = 0.05e$; whereas in the sp^3-basis set we had [1] :$n_s = 0.47e$, $n_p = 0.51e$. Using these numbers as well as the mean levels $\overline{e}_i$ and $\overline{e}_j$, as calculated from the graphene DFT band structure (see figure 1 for our calculated band structure, and figure 2 for the corresponding density of states decomposed in s, p and d contributions), we can evaluate the vdW-energy between the graphene layers.

Although in our calculations we are going to obtain $J^{vdW}_{i,j;\alpha,\beta}$ using the full integrals given in equation (3), it is worth mentioning that at long distances between the atoms, having the orbitals (ij) and $(\alpha\beta)$, $J^{vdW}_{i,j;\alpha,\beta}$ can be approximated by:

$$J^{vdW}_{i,j;\alpha,\beta} = \frac{1}{R^3}(< i|x|j >< \alpha|x'|\beta > + < i|y|j >< \alpha|y'|\beta > -2 < i|z|j >< \alpha|z'|\beta >) \quad (13)$$

which depends on the different dipolar matrix elements in each atom (R is the distance between the atoms assumed located along the z-axis). This equation shows the importance that the chosen basis set has in the calculation of the vdW interaction. In particular, a sp^3 minimal basis does not yield enough dipolar transitions to reproduce well that interaction [1]. This is better characterized by considering the following sum rules:

$$\langle s|z^2|s\rangle = \sum_i \langle s|z|i\rangle\langle i|z|s\rangle \quad (14)$$

$$\langle p_z|z^2|p_z\rangle = \sum_i \langle p_z|z|i\rangle\langle i|z|p_z\rangle \quad (15)$$

$$\langle p_x|z^2|p_x\rangle = \sum_i \langle p_x|z|i\rangle\langle i|z|p_x\rangle \quad (16)$$

in our sp^3d^5 basis set, these sum rules are approximated by:

$$\langle s|z^2|s\rangle \sim \langle s|z|p_z\rangle\langle p_z|z|s\rangle \quad (17)$$

$$\langle p_z|z^2|p_z\rangle \sim \langle p_z|z|s\rangle\langle s|z|p_z\rangle + \langle p_z|z|d_{z^2}\rangle\langle d_{z^2}|z|p_z\rangle \quad (18)$$

$$\langle p_x|z^2|p_x\rangle \sim \langle p_x|z|d_{xz}\rangle\langle d_{xz}|z|p_x\rangle \quad (19)$$

with $\langle s|z^2|s\rangle = 0.268$ Å^2; $< p_z|z^2|p_z >= 0.534$ Å^2; $< p_x|z^2|p_x >= 0.178$ Å^2; $< s|z|p_z >= 0.481$ Å; $< p_z|z|d_{z^2} >= 0.456$ Åand $< p_x|z|d_{xz} >= 0.395$ Å. The good quality of our basis set is shown by the fact that the previous approximated sum rules are satisfied with an accuracy of $\sim 85\%$. A sp^3 minimal basis set would yield a very poor approximation to the sum rules for $\langle p_z|z^2|p_z\rangle$, $\langle p_x|z^2|p_x\rangle$, indicating the necessity of introducing some corrections for calculating an appropriate vdW-interaction [1].

An important aspect to stress here is the $1/r^6$ behaviour of the van der Waals interaction due to the dipolar approximation, even when considering d orbitals through the sum rules. However, we will see in the four-center coulombic integrals approach that we develop in this article, that we can recover higher multipolar contributions leading to $1/r^8$ and $1/r^{10}$ contributions in the van der Waals interaction.

III. WEAK CHEMICAL INTERACTION AND VAN DER WAALS INTEGRALS

A. Weak chemical interaction

In the case of weakly interacting systems, the interaction energy is determined as a balance between short and long range interactions, namely a "chemical" interaction and the pure van der Waals energy. The short-range interaction can be calculated in an approximate way by means of a *corrected* LDA calculation, as follows : first, define the electron density for each subsystem (here, the two planes of graphene); then, approximate the exchange-correlation energy for the complete system as the sum of the exchange-correlation energies for each subsystem taken each one independently, neglecting in this way the effect of the overlapping densities in the exchange-correlation energy. In the following, we refer to the short-range interaction energy calculated in this way as the weak chemical interaction (WCI) [29]. This way of proceeding tries to avoid the double counting that would appear including both, Exchange provided by a conventional LDA and the correlation energy associated with the long range van der Waals potential discussed below: in particular, Lang [44] has clearly shown how the LDA exchange-correlation hole for rare-gas atoms on metal surfaces mimics partially the van der Waals polarization hole induced in the metal. We should also mention that other authors [45] have analyzed how to avoid this double counting by means of an approach similar to the one presented in this paper, using a short-range correlation energy. In the present approach, the exchange-correlation energy can be formally rewritten as :

$$E_{xc}(n_1 + n_2) = E_{xc}(n_1) + E_{xc}(n_2) \tag{20}$$

n_1 and n_2 representing symbolically the electronic occupancies of the orbitals of each subsystem. Using this approximation for the exchange-correlation energy, we proceed to the standard diagonalization of the system. In figure 3 we compare the graphene-graphene chemical interaction energy as obtained for the standard Fireball-LDA, the LCAO-S^2 approach of reference [1] and the WCI. In particular, notice the important effect introduced by the d-electrons that have increased that binding energy by around $30 - 40$ meV/atom; the effect of our WCI approximation on the LDA calculation is not, however, that important. Notice also the good agreement that our LDA-calculation shows with other independent LDA-results **??**.

B. Coulombic integrals and van der Waals interaction

The calculation of $J^{vdW}_{i,j;\alpha,\beta}$ has been performed by fitting the radial Fireball orbitals with spherical Gaussians functions. The spherical Gaussians are written as a proper combination of cartesian Gaussians; then, the analytical solutions of the electron repulsion integrals are expressed in terms of Boys functions [46].

In the pertubation treatment we use $(J^{vdW}_{i,j;\alpha,\beta})^2$. In Fig. 4, 5 and 6 we have represented the sum of $(J^{vdW}_{i,j;\alpha,\beta})^2$ for the different $sp-sp$, $sp-pd$ and $pd-pd$ transitions between a pair of C atoms; in these Figures we also show a fit of the long-range part of these sums as a combination of $1/r^6$, $1/r^8$ and $1/r^{10}$ terms. While we have an important $1/r^6$ contribution in all these integrals, in particular for the $sp-sp$ transitions, corresponding to the dipole-dipole interaction, we also observe contributions in $1/r^8$ and $1/r^{10}$ corresponding to quadrupolar contributions. Thus, in the present calculations we have used the calculated values of $(J^{vdW}_{i,j;\alpha,\beta})^2$, improving on the long-range dipole-dipole approximation, equation 13, used previously, yielding a better description of this interaction. Another important difference, is that in the sum rule calculation, contributions involving the d bands only appear as transitions from occupied p to unoccupied d bands. Now, with this more complete basis set, due to hybridization, we also recover transitions form occupied d bands to unoccupied p bands, as it can be seen from the DOS of the graphene.
In figure 7 we show the total van der Waals interaction energy between the graphene layers, and the different components $sp-sp$, $sp-pd$ and $pd-pd$ already presented in figures 4, 5 and 6.

C. Results : graphene-graphene interaction

The total interaction energy between graphene layers, calculated as the sum of the WCI energy and the van der Waals potential, is shown in figure 8. These results are rather similar to the ones presented in Ref. [1] : the interlayer equilibrium distance is $3.1-3.2\mathring{A}$ and the interlayer binding energy is 86 meV/atom (close to the value of 72 meV/atom given in that reference) although the WCI-energy has increased, the vdW-energy has decreased somewhat. This interlayer energy can be compared favourably with the 70 meV/atom of

independent calculations [16, 17]. Experimentally, this energy seems to be 52 meV/atom but, as commented by Hasegawa [16, 17], the value to compare with, due to thermal effects, should be a little larger, around 60 meV/atom. So, we conclude that our calculations seem to be rather satisfactory although probably a little too large. This fact and other independent works [30] has prompted us to consider, in the next section, the effect associated with the dynamical screening in the van der Waals interaction.

IV. DYNAMICAL EFFECTS IN THE VAN DER WAALS INTERACTION AND CONCLUSIONS

We analyze how dynamical processes affect the vdW-interaction by means of the simple model shown in figure 9 : here, atoms 1 and 2, represented each one by a two-level model, are coupled by means of the J interaction (in our previous notation J=$J^{vdW}_{i,j;\alpha,\beta}$). The van der Waals energy can be calculated as due to the interaction between the two bubbles of atoms 1 and 2, using the formalism of the causal Green-functions [47].

Bubble 1 contribution can be calculated as the following causal polarizability:

$$P_1^c(\omega') = \int \frac{d\omega}{2\pi} G^c(\omega) G^c(\omega - \omega') \tag{21}$$

while for bubble 2:

$$P_2^c(\omega') = \int \frac{d\omega}{2\pi} G^c(\nu) G^c(\nu - \omega') \tag{22}$$

Taking $G^c(\omega) = 1/(\omega - E_a - i\eta) + 1/(\omega - E_b + i\eta)$ and $G^c(\nu) = 1/(\nu - E'_a - i\eta) + 1/(\nu - E'_b + i\eta)$ we obtain the following polarizabilities:

$$P_1^c(\omega') = i\{1/(\omega' - \Delta E + i\eta) - 1/(\omega' + \Delta E - i\eta)\} \tag{23}$$

($\Delta E = E_b - E_a$) and

$$P_2^c(\omega') = i\{1/(\omega' - \Delta E' + i\eta) - 1/(\omega' + \Delta E' - i\eta)\} \tag{24}$$

$(\Delta E' = E'_b - E'_a)$

Then, the vdW-energy can be calculated up to second order in J, by the equation $E^{vdW} = 1/2J^2 \int \frac{d\omega'}{2\pi} P_1^c(\omega') P_2^c(\omega')$, that yields :

$$E^{vdW} = -J^2/[\Delta E + \Delta E'] \tag{25}$$

as corresponds to the virtual excitations, ΔE and $\Delta E'$ of atoms 1 and 2.

We introduce dynamical effects in this vdW-energy by means of the causal-response function, $\epsilon^c(\omega')$, that screens the interaction J, between the two bubbles. Using that dielectric function, the vdW-energy is given by:

$$E^{vdW} = 1/2 \int \frac{d\omega'}{2\pi} P_1^c(\omega')[J/\epsilon^c(\omega')] P_2^c(\omega')[J/\epsilon^c(\omega')] \tag{26}$$

For $\epsilon^c(\omega')$, we are going to assume that for the high frequencies of interest (the effect of the low frequencies in this vdW-screening is negligible) the dielectric function can be approximated by:

$$1/\epsilon^c(\omega') = 1 + \omega_p[1/(\omega - \omega_p + i\eta) - 1/(\omega + \omega_p - i\eta)] \tag{27}$$

where ω_p is a kind of plasmon frequency for the medium under consideration (graphite in our particular case). Then, equations 23, 24, 26 and 27 yield the following vdW-energy (assuming for simplicity that $\Delta E = \Delta E'$) :

$$E^{vdW} = -J^2/[\Delta E + \Delta E' + 2\omega_p] \tag{28}$$

This is the crucial result of this section; this equation shows how the dynamical screening of the bare vdW-interaction, reduces the vdW-energy by a factor $(\Delta E + \Delta E')/(\Delta E + \Delta E' + 2\omega_p)$ whose importance depends on the relative values of $(\Delta E + \Delta E')$ and $2\omega_p$).

For our present case, we consider the two graphene layers embedded in a graphite matrix and consider the plasmon frequency associated with this material. Electron energy-loss spectra from graphite [48] show two peaks at 7 and 27 eV; the 7 eV-peak is much smaller than the other one, and we are going to use eqn (27) for graphite with $\omega_p = 27$ eV. For the ΔE-energies we find three groups: the $sp - sp$, $sp - pd$ and the $pd - pd$ excitations with values of around 25, 40 and 60 eVs, respectively. Introducing these values in equation (28) leads to a vdW-potential reduction of about 40%. Then, for the graphene-graphene

equilibrium distance we find a reduction of the van der Waals energy of 22 meV/atom. With this value our graphene-graphene interaction energy is reduced to 64 meV/atom in very good agreement with the experimental evidence.

In conclusion, we have presented a combination of DFT with intermolecular perturbation theory, within the framework of the LCAO-*OO* approach, to analyze the graphene-graphene interaction. Our analysis is an extension of a previous work [1, 35], improving the basis set used in the calculation, the short-range chemical interaction between layers and the calculation of the van der Waals forces. In these calculations we have obtained an interaction energy between graphene layers of 86 meV/atom, slightly larger than the value afforded by the experimental evidence, 60 meV/atom. Then, we have analyzed the effect of introducing dynamical screening in the vdW-energy and have found that this dynamical effect reduces the vdW-energy by 40%. We conclude that this dynamical screening is not negligible and that it should be considered as an important effect to be introduced in many systems with a high plasmon energy, as is the case of many metals.

Acknowledgements

This paper has been written to the memory of Prof. D.C. Langreth for his outstanding scientific contributions.

P.G.B. is supported by the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) and Grant No. CAI+D PI-68-344 Universidad Nacional del Litoral.

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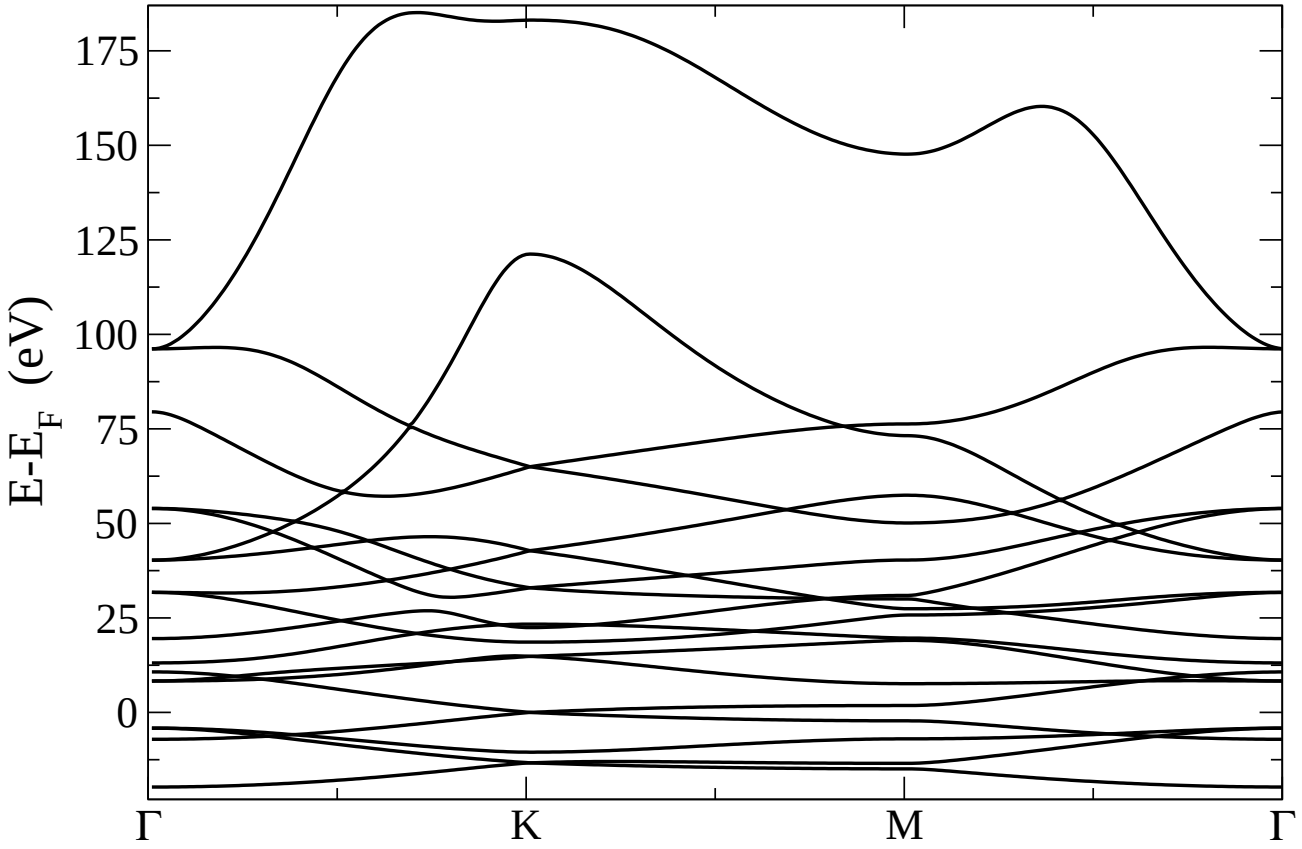

FIG. 1. Representation of the bandstructure of a graphene plane as calculated in our formalism.

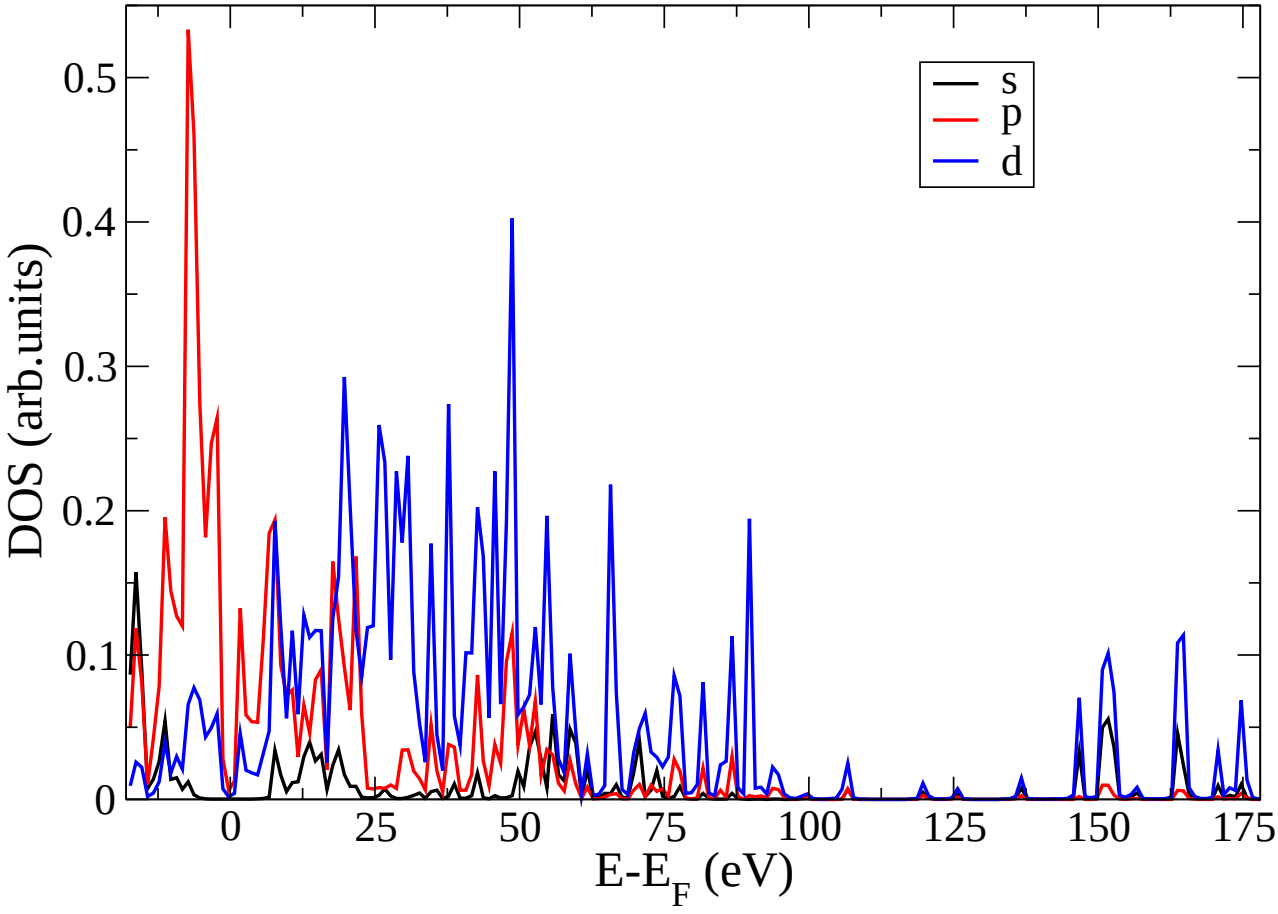

FIG. 2. Graphene Density of States (DOS) representing the major contributions of the s, p and d bands.

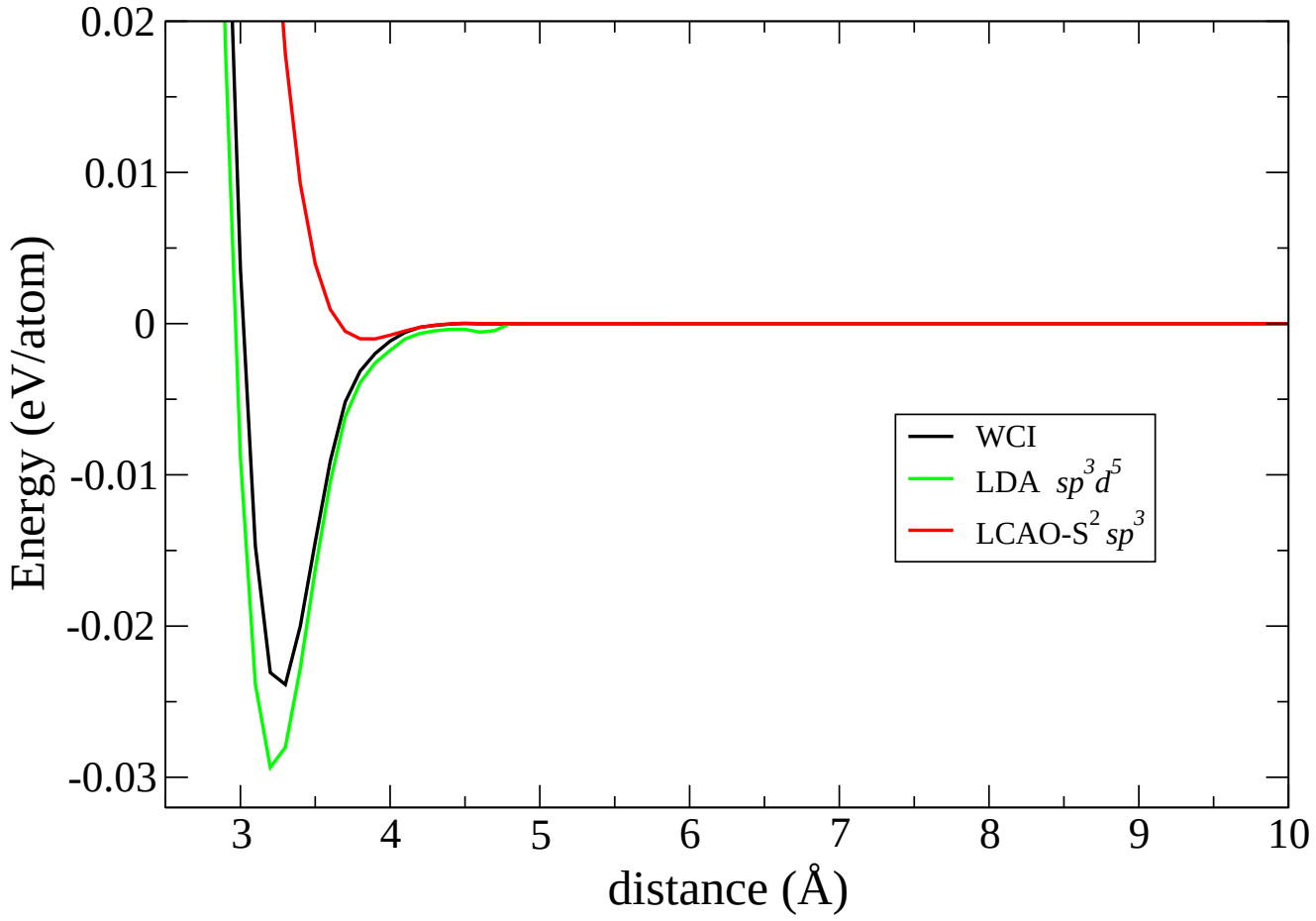

FIG. 3. Comparison of the chemical interaction between two graphene planes, obtained for the WCI, the standard fireball-LDA (sp^3d^5) and the LCAO-S^2 approach (sp^3)[1].

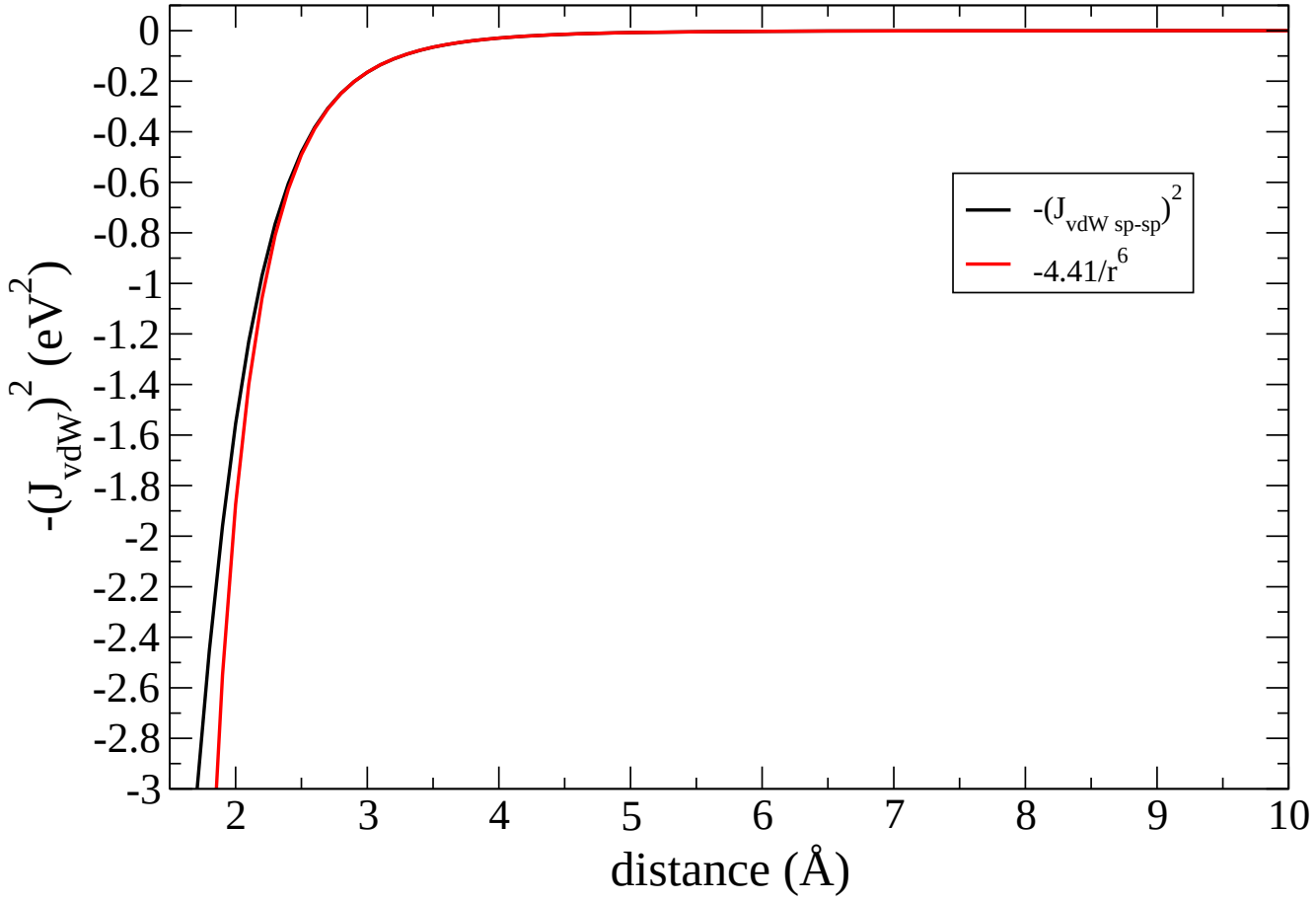

FIG. 4. Representation of the sum of all the $(J^{vdW})^2$ for $sp-sp$ transitions between two Carbon atoms. The fit of the interaction shows a $1/r^6$ behaviour.

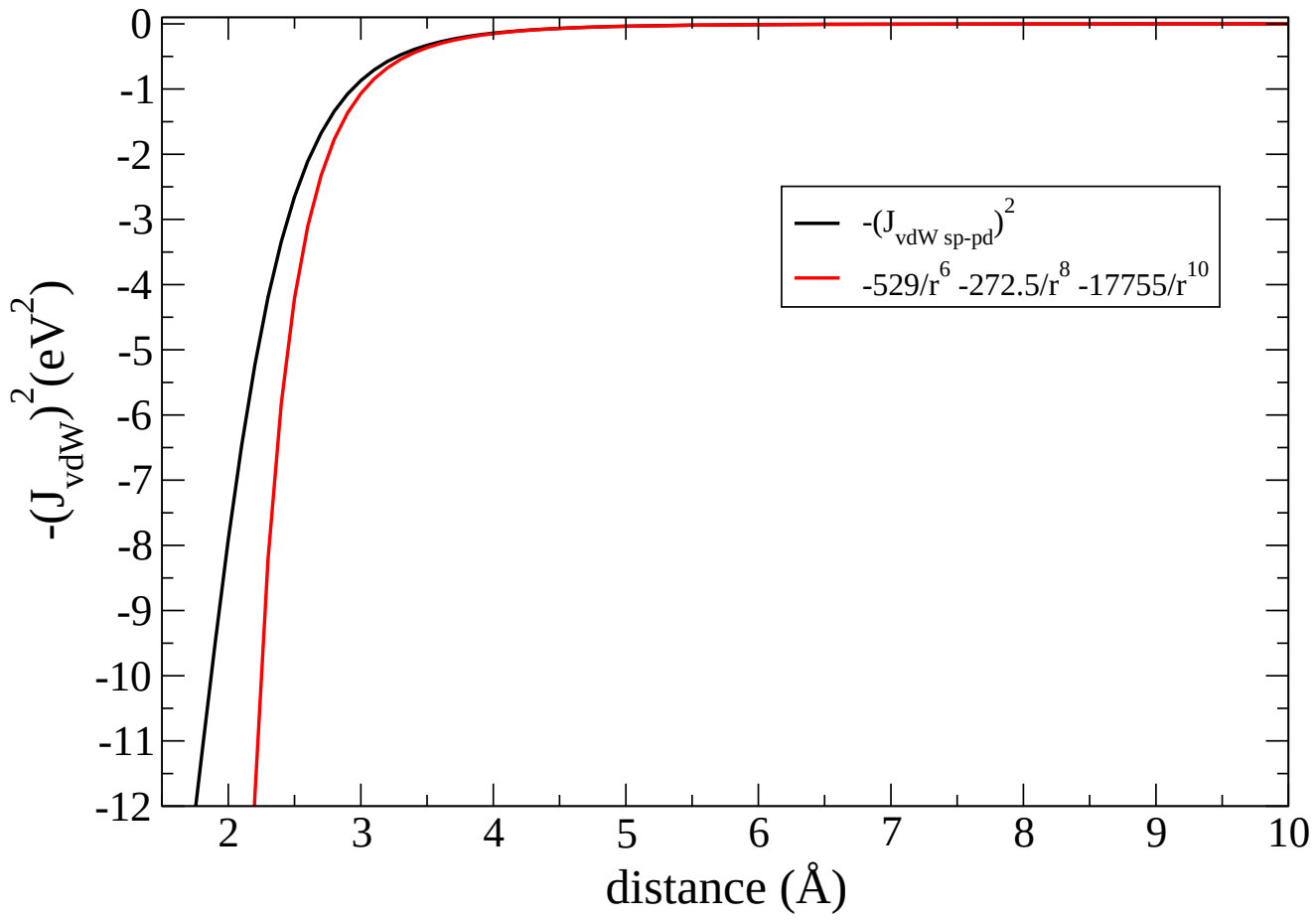

FIG. 5. Representation of the sum of all the $(J^{vdW})^2$ for $sp-pd$ transitions between two Carbon atoms. The fit of the interaction shows multipolar behaviours in $1/r^8$ and $1/r^{10}$ in addition to the expected $1/r^6$ behaviour.

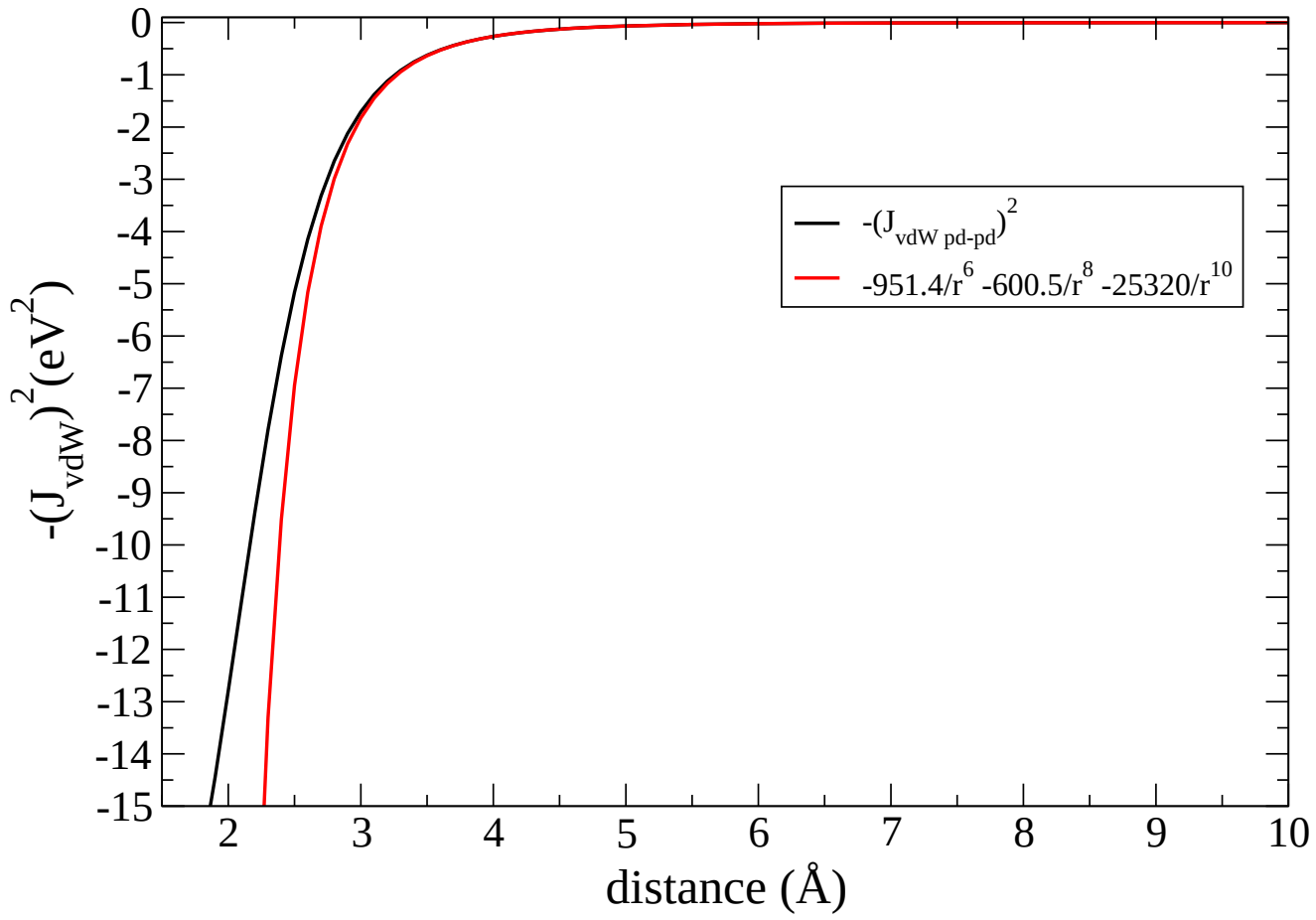

FIG. 6. Representation of the sum of all the $(J^{vdW})^2$ for $pd-pd$ transitions between two Carbon atoms. The fit of the interaction shows a multipolar behaviour of the interaction.

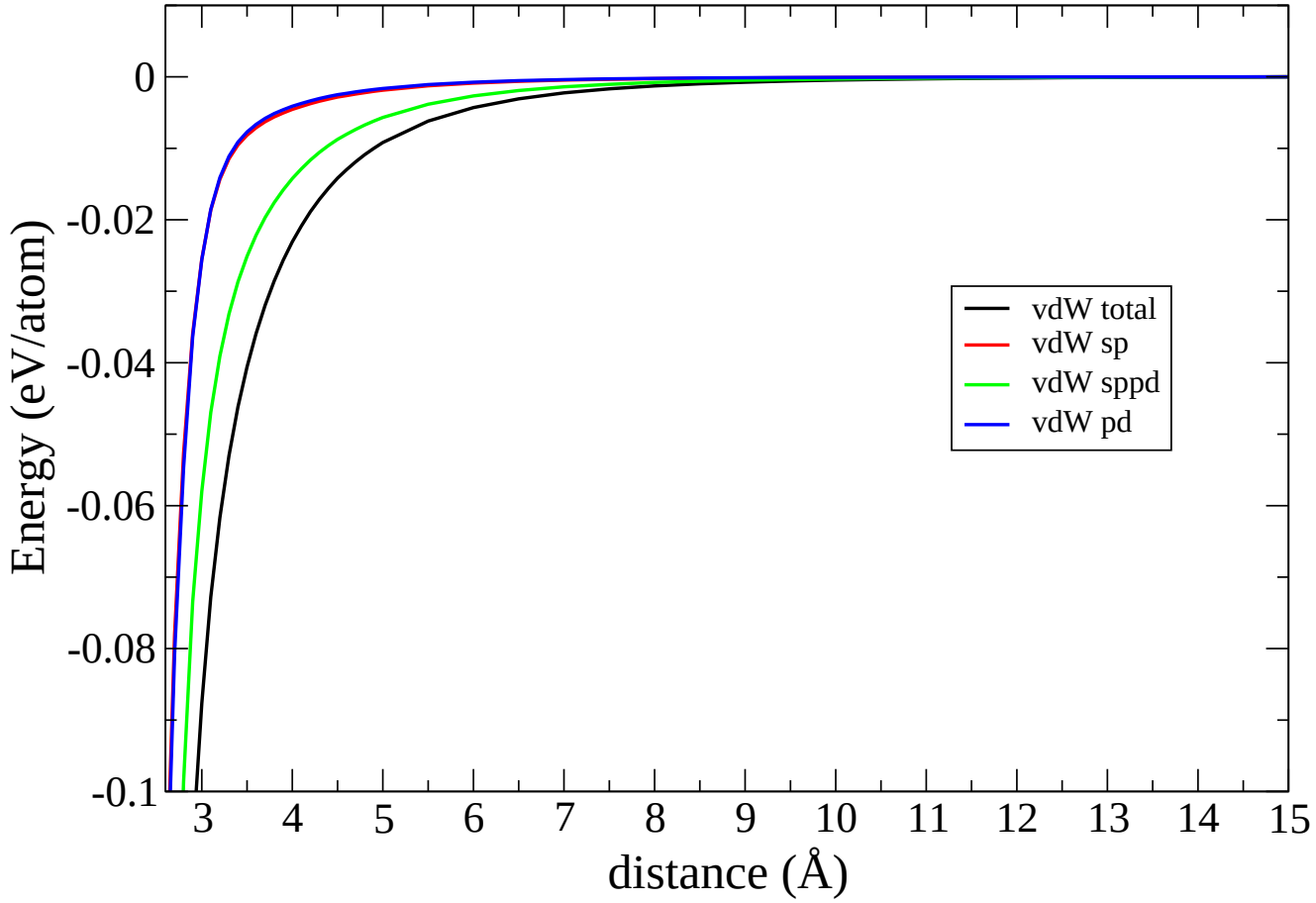

FIG. 7. Representation of the different transitions, namely $sp-sp$, $sp-pd$ and $pd-pd$, contributing to the van der Waals energy between two graphene planes.

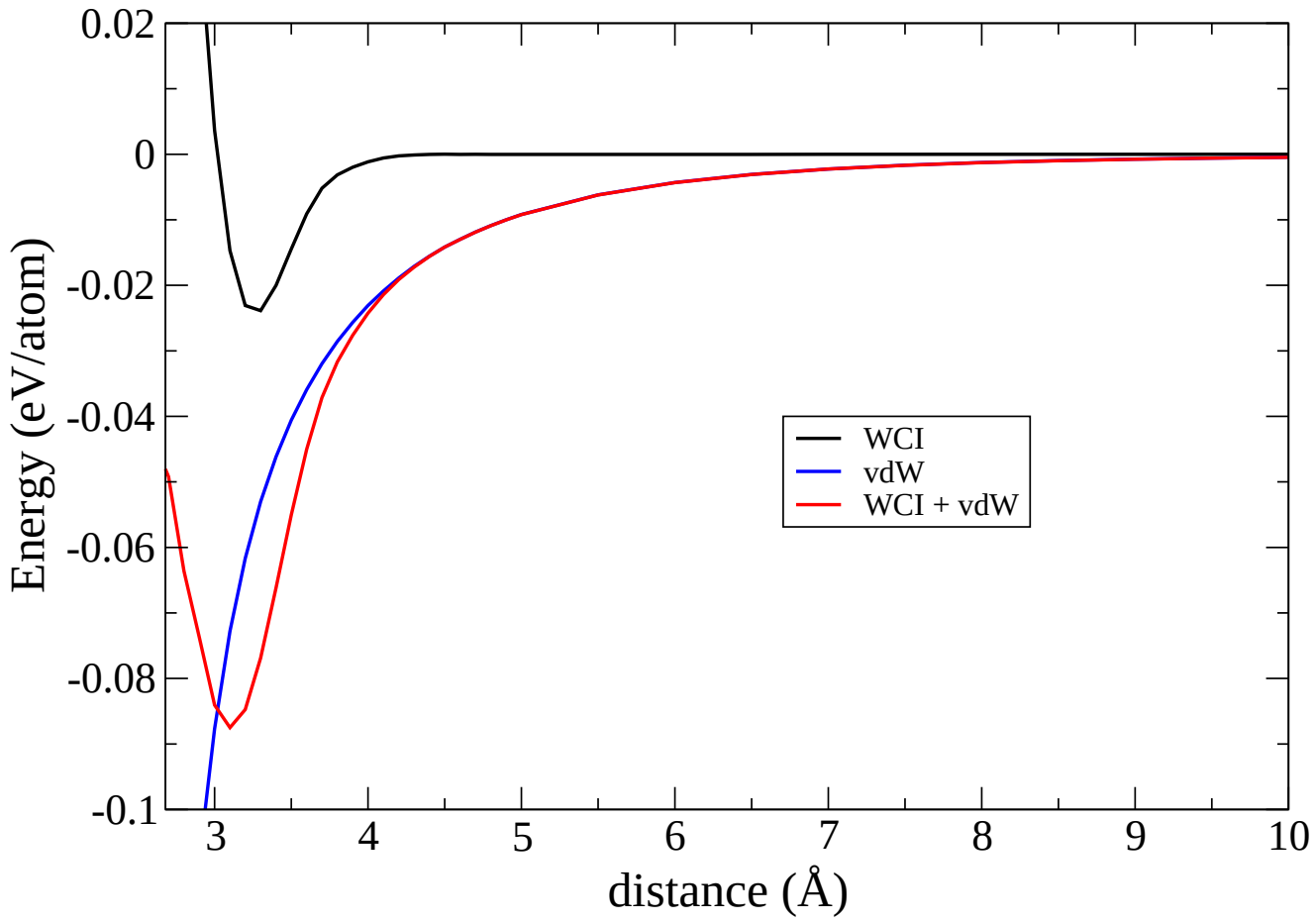

FIG. 8. Cohesion energy of the two graphene planes as the sum of the weak chemical interaction energy and the van der Waals energy.

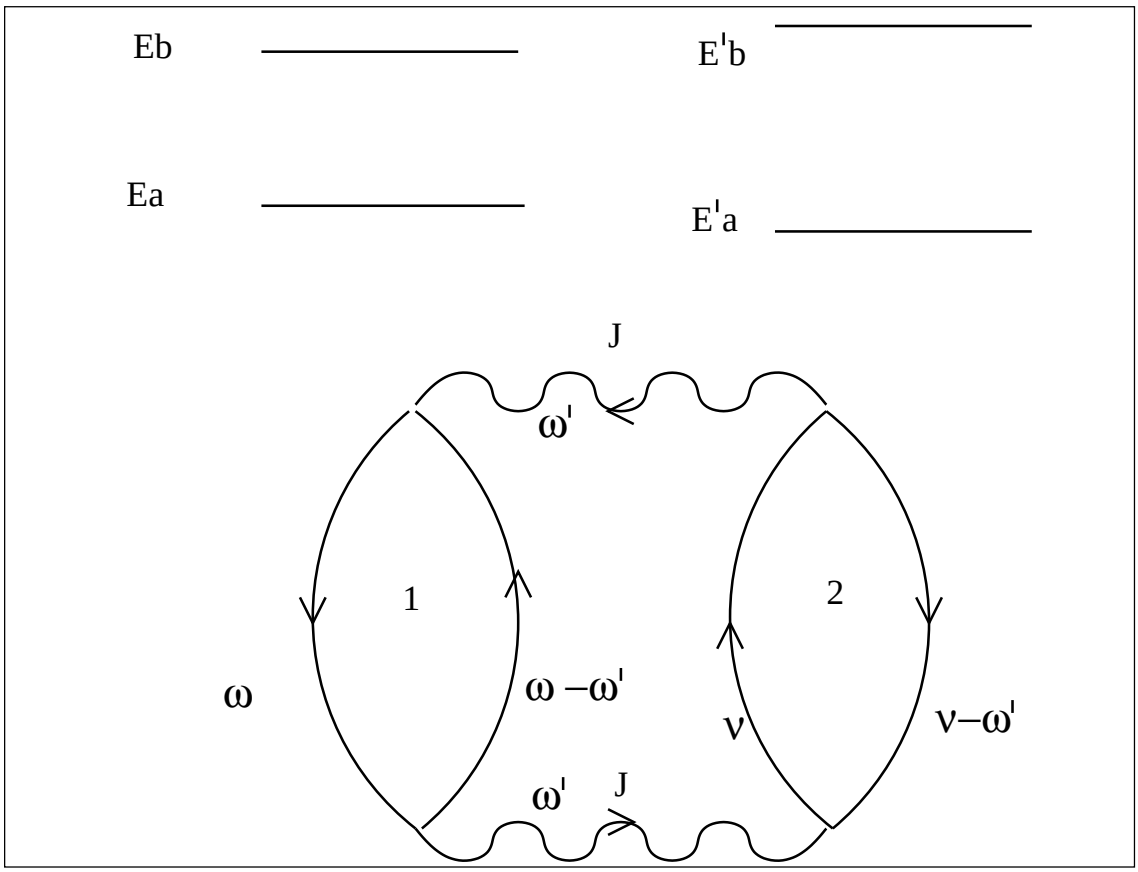

FIG. 9. Model representation of the van der Waals interaction