First-Principles Determination of the Dispersion Interaction between Fullerenes and Their Intermolecular Potential

J. M. Pacheco
Departamento de Física da Universidade, Apartado 94, 7001, Évora Codex, Portugal, and Departamento de Física da Universidade, 3000 Coimbra, Portugal

J. P. Prates Ramalho
Departamento de Química da Universidade, Apartado 94, 7001 Évora Codex, Portugal
(Received 27 May 1997)

We compute, from first principles, the dispersion interaction between two and three fullerenes, in time-dependent density functional theory. These results, complemented with total energy calculations at small and intermediate distances, lead to a parameter-free determination of the interaction between fullerenes. Agreement with experiment, within 4%, is found for all quantities, computed via Monte Carlo simulations of fullerite. Inclusion of the three-body term is found to increase by 6% the cohesive energy at equilibrium density. [S0031-9007(97)04509-2]

PACS numbers: 61.48.+c, 61.25.Em, 81.30.Dz

The interfullerene interaction plays a central role in the characterization of physical, chemical, and mechanical properties of fullerite, ultimately determining its phase diagram [1], which, in spite of the wealth of available experimental data [2], is not entirely known. In particular, the existence of a stable liquid phase of C_{60} remains a subject of controversy [1]: Experimentally an answer to this question is technically very involved; theoretically, one is faced with the remarkable sensitivity of the properties of fullerite to the details of the interfullerene potential [3]. Last but not least, the role played by three-body dispersive terms in the determination of these properties (which, on the basis of the large polarizability of the fullerene, may provide sizable effects [1]) has not been explicitly considered. Indeed, most of the theoretical work carried out so far takes as an interfullerene interaction that resulting from the superposition of carbon atom-atom classical interactions [4–6]. In spite of their success, these interactions have several drawbacks. Besides their intrinsic phenomenological nature, the interfullerene interaction is basically taken as a two-fullerene interaction only. Furthermore, each fullerene is usually treated as a superposition of noninteracting carbon atoms, disregarding the individual character and high stability of this quantal system. These are undesirable features which call for a more sound theoretical scheme to determine the interfullerene interaction. This is the purpose of the present Letter in which we derive for the first time a first-principles interfullerene interaction, not only its two-body part but also its dominant three-body term. This has been carried out in the local density approximation (LDA) to density functional theory (DFT) together with its extension for excited states, the time-dependent (TD) DFT [7]. It will be found that the interaction derived here leads systematically to a good and overall description of several properties of fullerite already determined experimentally. Indeed we obtain an essentially parameter-free theoretical curve which, besides reproducing the trends observed experimentally, will allow us to predict quantitatively the behavior of fullerite in situations which are difficult to realize experimentally such as those associated with the high-pressure and high-temperature regimes of fullerite, at which the issue of a stable liquid phase of C_{60} remains a challenge. As shown here, for such extreme conditions, other interfullerene potentials available at present fail to provide reliable estimates.

The LDA for exchange and correlation (XC) in DFT has been shown to provide an accurate description of structural and electronic properties of a wide variety of materials, including the different stable forms of carbon [2,8]. In spite of this, there is room for improvement, and refinements of the theory such as the self-interaction correction [9] (SIC), the generalized gradient approximation [10] (GGA), or the LB94 exchange-correlation potential [11] should not be overlooked, constituting potential sources for improvement of the accuracy in actual calculations. This is so for structural situations in which the electronic densities of the interacting molecules overlap. Each carbon atom is usually represented by means of a norm-conserving, transferable pseudopotential [12], leaving as active four valence electrons per atom. In this context, the calculation of Ref. [8] typifies a state-of-the-art LDA calculation of fullerite which we shall make use of below in order to extract information of the interaction energy between fullerenes at small and intermediate distances.

However, as is well known, LDA-DFT is unable to describe correctly the long-range behavior of, e.g., the interfullerene interaction energy, which is dominated by dispersion interactions. This feature, which constitutes one of the major drawbacks of the theory, can be circumvented if we consider its linear response extension—TDLDA or, in improved DFT descriptions, the corresponding extensions to the time-dependent domain [13–15]—for the description of excited states, and use this framework to

compute the polarizability tensor of one fullerene molecule, since this constitutes the key ingredient [16] for the determination of the two-body van der Waals and three-body Axilrod-Teller interactions. Indeed, the leading order van der Waals (C_6) and Axilrod-Teller ($C_{\rm AT}$) coefficients can be directly expressed as integrals of the dipole polarizability tensor $\alpha_d(iE)$ computed at purely imaginary energies iE,

$$C_6 = \frac{3}{\pi}\int_0^{+\infty} \alpha_d^2(iE)\,dE\,;$$
$$C_8 = \frac{15}{\pi}\int_0^{+\infty} \alpha_d(iE)\alpha_q(iE)\,dE\,; \qquad (1)$$
$$C_{\rm AT} = \frac{3}{\pi}\int_0^{+\infty} \alpha_d^3(iE)\,dE\,,$$

whereas the second van der Waals coefficient (C_8) requires the determination of the quadrupole polarizability tensor $\alpha_q(iE)$.

In keeping with this discussion, the van der Waals coefficients C_6 and C_8, together with the Axilrod-Teller coefficient $C_{\rm AT}$, were determined by direct integration of Eq. (1), in which we employed the dipole and quadrupole polarizability tensors of C_{60} computed in TDLDA. The method we utilized extends to imaginary frequencies the linear-response method in coordinate space developed in Ref. [17], which is well suited when applying the TDLDA to isolated molecules. In short, we start by solving the Kohn-Sham equations via the expansion of the solutions in a spherical basis. Subsequently, and for each value of iE, we employ the well-known sum-over-states (SOS) technique [18] to compute the unscreened density-density correlation function. This proves useful to check the convergence of this function which, in our case, is achieved by including $\approx 2 \times 10^4$ one-electron states in the calculation, corresponding to a cutoff at 40 eV. Unlike Ref. [18], no approximations are introduced in the incorporation of screening, since we compute it self-consistently by solving the integral equation for the induced density via a discretization of its multipole components in coordinate space. The result is equivalent to that obtained via an iterative solution in Ref. [15], which also includes screening in a numerically exact way. The results obtained with this formulation for the linear dynamic polarizability of the fullerene molecule [17] have been recently quantitatively corroborated in the state-of-the-art calculations of Ref. [15]. In our present calculations we utilized the same pseudopotentials [12] used in the plane-wave calculations of Ref. [8], as well as the same XC functional, for which we took the Ceperley and Alder results [19] as parametrized by Perdew and Zunger [9]. We took advantage of the high (icosahedral) symmetry associated with the fullerene and computed the polarizability tensors with respect to the principal axes of the molecule in which both the dipole and quadrupole tensors are diagonal. As usual, the polarizability is a smooth function of its purely imaginary argument such that the integrals in Eq. (1) converge nicely. The results obtained for the dispersive two- and three-body coefficients are given in Table I and have been used in generating the solid squares displayed in Fig. 1.

The long-distance behavior has been complemented with the data drawn with solid circles in Fig. 1, corresponding to the interaction between two fullerenes at small and intermediate distances, at which there is still an overlap of the charge densities of each fullerene. In Ref. [8] the cohesive energy of fullerite in an fcc primitive cell, as a function of the cell size parameter a, has been computed via efficient self-consistent pseudopotential plane-wave calculations (cf. Ref. [8] for details). From the cohesive energy, we extracted the two-body interaction energy by assuming that the interfullerene interaction is pairwise additive, and takes place only between nearest neighbors [20]. We shall come back to this approximation later. In this way, we consistently computed the short distance repulsive potential, the long distance dispersive interaction, as well as we have the potential behavior near equilibrium. In Fig. 1, the dashed line corresponds to the Girifalco potential [4] used in most of the high-temperature Monte Carlo and/or molecular dynamics simulations of fullerite, and which results from the superposition of atom-atom potentials of the Lennard-Jones type. The solid line corresponds to the fit to the *ab initio* data which we discuss in the following.

The *ab initio* results clearly establish the asymptotic behaviors at short and long distances, evidencing a stiff repulsive wall at short distances together with the appropriate van der Waals tail. In order to parametrize this interaction we considered two functions which display, individually, the expected limiting behavior [21] of a two-body interaction at short and long distances: A Morse potential $M(x) = M_0 \exp[\tau(1 - x/d_0)]\{\exp[\tau(1 - x/d_0)] - 2\}$ for the short-range part [22], and a van der Waals expansion $W(x) = -C_6/x^6 - C_8/x^8 - C_{10}/x^{10} - C_{12}/x^{12}$ at long distances. The crossover of these two regimes has been obtained via a third function of the Fermi-type, namely, $F(x) = \{1 + \exp[(x - \mu)/\delta]\}^{-1}$. The final form of the potential then reads

$$V_{\rm 2body}(x) = F(x) \times M(x) + [1 - F(x)] \times W(x)\,. \quad (2)$$

In the nonlinear fitting procedure, we varied freely the parameters $\mu, \delta, M_0, \tau, C_{10}, C_{12}$. The results obtained are

TABLE I. Values for the van der Waals coefficients C_6 and C_8, and for the Axilrod-Teller coefficient $C_{\rm AT}$ obtained using TDLDA (see main text for details). $N_{\rm at}$ is the number of atoms in a single fullerene (60). In TDLDA, the polarization of the electron cloud in the presence of an external field is included at the level of linear response. The values used in the production of the data plotted with solid squares in Fig. 1 correspond to the results tabulated here.

C_6 (eV Å^{-6})	C_8 (eV Å^{-8})	$C_{\rm AT}$ (eV Å^{-9})
21 $N_{\rm at}^2$	2534 $N_{\rm at}^2$	22 $N_{\rm at}^3$

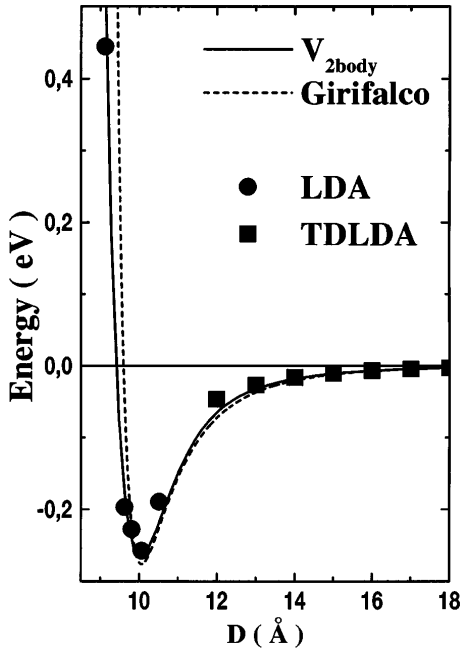

FIG. 1. Results of the present calculation for the interaction energy between two fullerenes, compared with other results. The LDA results extracted from the plane-wave bulk calculations are drawn with solid circles; the long-range van der Waals interaction obtained using the C_6 and C_8 parameters of Table I are drawn with solid squares. This leads to the two-fullerene interaction fit, $V_{2\text{body}}$, drawn with a solid line. The dashed line corresponds to the Girifalco potential (for details, see main text).

given in Table II, whereas in Fig. 1 $V_{2\text{body}}(x)$ is displayed (with a solid line) together with the *ab initio* data (solid circles and squares) and the Girifalco potential (dashed line). The quality of the fit is good, following the *ab initio* data rather closely. Moreover, $V_{2\text{body}}(x)$ is deeper than the pure van der Waals expansion (solid squares in Fig. 1) as one approaches the region of overlap between the fullerene densities, in agreement with the general properties expected for this type of potential [21].

In order to test the quality of our potential we have carried out several Monte Carlo (MC) simulations in a canonical ensemble. We computed the equilibrium pressure as a function of fullerite density, the equilibrium density of fullerite, as well as the energy per particle at room temperature and at zero pressure. The simulations were performed at different densities for a 256 C_{60} molecule system, using the usual periodic boundary conditions and starting from a perfect fcc lattice. More details will be published elsewhere [23]. Values of the equilibrium pressures calculated from the simulations for different densities are shown in Fig. 2 (with solid circles) compared with experimental data. The results displayed show that the trend observed experimentally (represented with solid squares and taken from Ref. [24]) is nicely reproduced with the present potential, in sharp contrast to the results obtained by performing the same simulations using the Girifalco potential, displayed with solid triangles.

The good agreement obtained at high pressure is due to the relative softness of our potential compared with previous potentials including the Girifalco [4] and the 12-6 carbon-carbon interaction [5]. As these potentials consider rigid molecules, one could think that the use of a "soft" model for the molecule could be more effective at high pressures. Nevertheless, there are experimental [25] and theoretical [8] evidences that the C_{60} molecules are extremely resilient to pressure and the geometric structure of the molecule remains stable upon hydrostatic compression, at room temperatures, up to about 20 GPa, suggesting that the interaction is too complex to be well described by such classical site-site models.

For the equilibrium density and the cohesive energy of fullerite (per mole) at equilibrium density and zero pressure, we obtain 1.40 10^{21} cm^{-3} and 160.7 kJ/mol, respectively, with $V_{2\text{body}}$, whereas experimentally one finds 1.44 10^{21} cm^{-3} and 167.9 kJ/mol, respectively.

Finally, we assessed the role of the Axilrod-Teller interaction in the determination of the same properties, for which we repeated the same simulations using not only $V_{2\text{body}}(x)$ but also the Axilrod-Teller term. We found essentially no changes as the equilibrium density or the density-pressure behavior were concerned, but we found a 6% contribution to the cohesive energy. As usual, the role of these three-body terms is mostly repulsive, so we obtained an overall increase of 6% in the cohesive energy of fullerite.

In summary, we obtained a parametrized two-body interfullerene interaction derived from a parameter-free LDA calculation of the cohesive energy of fullerite, which exhibits a long-range behavior governed by a dispersive interfullerene interaction computed consistently at the level of TDLDA. The major drawback of our method is the assumption that the fullerene-fullerene interaction in fullerite is pairwise and additive, thereby neglecting short-range n-body ($n > 2$) interactions. Although this effect has been argued to be small [20], it is included in an average way in our two-body interaction by means of our assumption, and therefore our interaction should not

TABLE II. Values for the quantities defined in main text, obtained as a result of the nonlinear fit of $V_{2\text{body}}$ to the *ab initio* data. The resulting interaction, $V_{2\text{body}}$, is plotted in Fig. 1.

M_0 (eV)	τ	d_0 (Å)	C_{10} (eV Å^{-10})	C_{12} (eV Å^{-12})	μ (Å)	δ (Å)
0.3	9.75	10.3	2.09×10^8	7.78×10^{10}	10.05	1.04

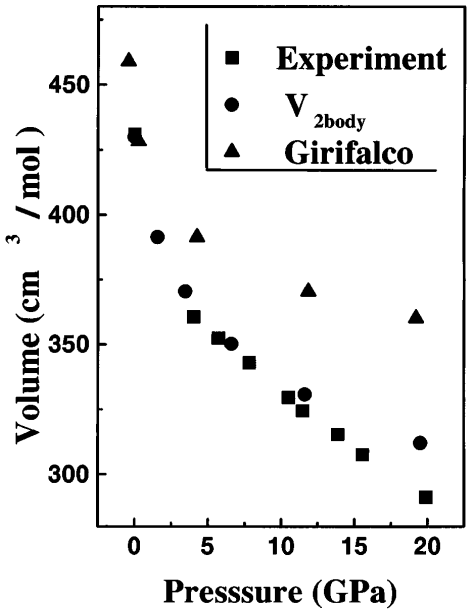

FIG. 2. Molar volume of fullerite as a function of pressure. The solid squares display the experimental data taken from Ref. [24]. The solid circles show the results of our Monte Carlo simulations carried out with $V_{2\text{body}}$ (see main text for details), whereas the solid triangles display the corresponding results when the simulations were carried out with the Girifalco potential.

be considered as a pure two-body term. Yet, this effective interaction has provided results which not only reproduce the trends observed experimentally, but also provide an overall agreement with experimental data which is good. Three-body dispersive interactions (not to be confused with the many-body correlations included in an average way before) are found to provide a repulsive contribution to the configurational energy of the order of 6%. This can be considered a "normal" contribution, in the sense that it lies in the range which one usually obtains for van der Waals fluids. This value, again, is directly related to the polarizability of the fullerenes, which, as pointed out in Ref. [1], have a high static value. However (and this is particularly clear if one uses the real-frequency expressions for the van der Waals and Axilrod-Teller coefficients), the charge density waves in the fullerenes occur at very high energies (≈20 eV), a feature which acts to reduce the effective value of the dispersion coefficients, thereby determining the 6% contribution obtained. Yet, we believe that three-body terms may prove important in the quest for a stable liquid phase of C_{60}. Indeed, following the results of Ref. [3], which are based on Morse potentials, and performing a Morse fit to the *ab initio* data, we obtain a potential which, again, is just on the borderline for meeting the criteria which ensures the existence of a stable liquid phase. Therefore, the three-body Axilrod-Teller interaction should not be overlooked when simulating the liquid-vapor and solid-vapor coexistence lines in fullerite. Work along these lines is in progress.

We thank José Luís Martins for useful discussions, as well as for providing us the data for the interfullerene interaction at short distances. Financial support from PRAXIS XXI under Contract No. PRAXIS/XXI/2/2.1/FIS/473/94 is gratefully acknowledged.

[1] N. W. Ashcroft, Nature (London) **365**, 387 (1993).
[2] M. S. Dresselhaus, G. Dresselhaus, and P. C. Eklund, *Science of Fullerenes and Carbon Nanotubes* (Academic Press, New York, 1995).
[3] J. P. K. Doye and D. J. Wales, J. Phys. B **29**, 4859 (1996).
[4] L. A. Girifalco, J. Phys. Chem. **95**, 5370 (1991); **96**, 858 (1992).
[5] M. Sprik, A. Cheng, and M. L. Klein, J. Phys. Chem. **96**, 2027 (1992).
[6] Ch. Girard, Ph. Lambin, A. Dereux, and A. A. Lucas, Phys. Rev. B **49**, 11 425 (1994).
[7] E. K. U. Gross, J. F. Dobson, and M. Petersilla, in *Density Funtional Theory*, edited by R. F. Nalewajski, Springer Series Topics in Current Chemistry (Springer-Verlag, Berlin, 1996), p. 71.
[8] N. Troullier and José Luís Martins, Phys. Rev. B **46**, 1754 (1992).
[9] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
[10] J. P. Perdew *et al.*, Phys. Rev. B **46**, 6671 (1992).
[11] R. van Leeuwen and E. J. Baerends, Phys. Rev. A **49**, 2421 (1994).
[12] N. Trouiller and José Luís Martins, Phys. Rev. B **43**, 1993 (1991).
[13] J. M. Pacheco and W. Ekardt, Ann. Phys. (Leipzig) **1**, 254 (1992).
[14] V. P. Osinga *et al.*, J. Chem. Phys. **106**, 5091 (1997).
[15] S. J. A. van Gisbergen *et al.*, Phys. Rev. Lett. **78**, 3097 (1997).
[16] G. D. Mahan and K. R. Subbaswamy, in *Local Density Theory of the Polarizability* (Plenum, New York, 1990), Chap. 4.
[17] F. Alasia, H. E. Roman, R. A. Broglia, Ll. Serra, G. Colò, and J. M. Pacheco, J. Phys. B **27**, L643 (1994).
[18] E. Westin *et al.*, J. Phys. B **29**, 5087 (1996).
[19] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).
[20] This seems to be a reasonable assumption, in view of the estimates in Ref. [4], in which the contribution from second and third nearest-neighbor interactions does not exceed 4%.
[21] Jacob N. Israelachvili, *Intermolecular and Surface Forces* (Academic Press, London, 1985).
[22] We point out that a Morse fit alone is rather inefficient, due to its inability to provide accurate results at long distances. Such an approach has been exploited in Ref. [3] in connection to the Girifalco potential, where further details can be found.
[23] J. M. Pacheco and J. P. Prates Ramalho (to be published).
[24] S. J. Duclos *et al.*, Nature (London) **351**, 380 (1991).
[25] M. Núñez-Regueiro, Mod. Phys. Lett. B **6**, 1153 (1992).