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Van der Waals binding energies in graphitic structures

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Two types of methods are commonly used to describe the van der Waals cohesive properties of graphitic systems: one is based on density functional theory and the other on empirical model potentials. This paper examines the relation between the two and finds that, when properly done, both methods give the same results. The local density approximation (LDA) method can describe cohesion when graphitic molecules are close together, but must be supplemented with the theory of dispersion forces when the intermolecular distance increases. It is found that LDA dispersion force calculations reproduce the empirical potentials, which are thereby validated by fundamental theory. A recent disparity between two types of calculations in determining binding energy of C_{60} molecules inside a (10,10) nanotube is also examined.

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Calculations of the van der Waals cohesive energies of graphitic structures are performed by *ab initio* methods and by using model potentials. The model potentials are based on empirical functions whose parameters are obtained from experiment and are restricted to computations that involve only physical forces. Given their simplicity, it is remarkable that they have been so successful in providing a unified, consistent description of the properties that depend on the weak interactions between and among graphene sheets, fullerene molecules, and nanotubes.[1–13] The local density approximation (LDA) of density functional theory (DFT) has given excellent results[14–19] for the total energies and band structures for graphite, fullerites, and nanotubes. Some of the studies that include calculation of the van der Waals interactions between graphitic structures give results that agree with experimental data. [Note that we define the van der Waals energy to include both the repulsive (from electron repulsions) and attractive (from dispersion) parts, as in the van der Waals gas equation, rather than just London dispersion forces, as used by some modern authors.]

The model potentials are convenient when the object of research is material properties, such as the equation of state or phase transformations, but *a priori* calculations are essential for analysis of the fundamental physics giving rise to these properties. Since both approaches are in use and both give valuable results, it is important to understand the relationship between them. We therefore examined the DFT-LDA and the van der Waals binding energies between graphene sheets, two C_{60} molecules and between two nanotubes, as well as those for the binding energy of a C_{60} molecule inside a nanotube. It is found that the important factors for the representation of cohesion between graphitic structures are the following:

(1) Empirical model potentials can adequately describe the cohesive properties of graphitic structures arising from van der Waals interactions.

(2) Appropriate *ab initio* calculations reproduce empirical potentials in detail to an adequate level of accuracy, provided dispersion interactions are added to DFT-LDA results.

(3) DTF-LDA calculations of the van der Waals cohesive properties are sensitive to the choice of pseudopotential, the exchange-correlation functional, the basis set, and the number of basis functions used in wave function expansions.

(4) Most *ab initio* calculations of van der Waals energies do not give results that agree with experiment, but some have been successful. There are indications that success depends on some cancellation of errors as well as on the specifics of the calculation.

(5) The repulsive part of the interaction results from the overlap of electrons on adjacent molecules.

(6) The attractive part is an electron correlation effect with two components: the decrease in kinetic energy arising from electron delocalization and the dispersion interaction between fluctuating dipoles on the two molecules.

(7) The delocalization energy has a shorter range than the exchange-correlation energy. When the molecules are far apart, the exchange-correlation energy is just the dispersion energy. The LDA underestimates these at large distances.

(8) DFT-LDA calculations that can be directly compared to multipole-polarization theory, and to the empirical models, show that, in graphitic structures, their accuracy decreases rapidly for distances greater than about 15% beyond the equilibrium distance.

These conclusions are supported by existing calculations.

It is recognized in the theory of rare gas interactions that the DFT-LDA does not describe dispersion forces correctly. Sandor and Pulay[20] and Perez-Jorda and Becke,[21] for example, performed calculations for rare gas interactions using a variety of LDA functionals and different basis sets. In only two cases was there any binding at all, and both the binding energy and equilibrium separations for two molecules were far from the experimental values. Their conclusion was that the DFT-LDA fails to describe the dispersion interaction, but does a good job for the repulsive part of the potential. Incidentally, this work shows that the nonlocality of the exchange energy can also contribute to errors of the LDA.[21] In fact, it has been shown that using a nonlocal exchange functional improves the calculated exchange energy in helium and neon by 1.3 atomic units.[22]

The inadequacy of the DFT-LDA for computing dispersion energies was stressed by Kohn, Meir, and Makarov[23] who pointed out that the DFT-LDA fails for long-range interactions. They proposed a method in which traditional

DFT-LDA methods are modified by treating long-range interactions separately in terms of the susceptibility. In the limit of large distances, they get the usual R^{-6} form for the van der Waals attraction, and the interaction constant is computable from electron densities calculated in the LDA. An alternate approach is typified by the work of Rapcewicz and Ashcroft[24] and by Andersson *et al.*[25] in which an effective "local" electron density for the interaction of two electron distributions is defined as some average of the densities in the two distributions. This effective density is then used in the LDA and works reasonably well because the densities for electrons that are far apart are included in the theory indirectly by the averages in the effective density. This approach has correctly reproduced the van der Waals attractive coefficients for a dozen atom-atom interactions.[25]

An early calculation by Santos and co-workers[26,27] using an extended Thomas-Fermi jellium model showed that nonhomogeneity corrections as well as exchange and correlation effects were needed to get binding between graphite sheets. The first application of noncontinuum DFT to a graphitic structure was that of DiVincenzo, Mele, and Holzwarth.[28] They computed the electron density for an isolated graphene sheet and assumed that the electron density in three-dimensional graphite was a superposition from different planes. They then used this density in DFT. Their kinetic energy was a gradient-corrected Thomas-Fermi functional, while for exchange correlation they used the homogeneous electron gas result, plus a correction containing the gradient of the density. Their interplanar binding energy is larger than experiment by a factor of 5. Actually, the disagreement is greater than this because their equilibrium interlayer spacing is 2.80 Å, which is much less than the experimental value of 3.35 Å. Their theoretical result for the energy should therefore be compared to the binding energy of highly compressed graphite, which at 2.8 Å is repulsive, so there is no binding. These studies are nevertheless important. They show that the DFT-LDA is sensitive to the choice of electron density by using a superposition of atomic densities, with a result for the binding energy that is almost an order of magnitude larger than experiment. Note that the superposition of planar densities does not allow for electron delocalization, which makes an important contribution to binding. The authors also recognized the importance of dispersion forces and performed a calculation of the van der Waals (VDW) attractive potential from the polarizability of graphite planes. While the shapes of the VDW and exchange-correlation potentials were similar at short distances, they were quantitatively different by 0.1–0.15 eV. We note that at large distances both the kinetic energy and the exchange-correlation energy should be included in a comparison of the DFT-LDA with dispersion energies. The binding energy based on the exchange-correlation potential was less attractive than that from the polarizability. An important point is that the deviation increased for distances greater than 4 Å, and at a distance of 4.5 Å the exchange-correlation result was small. Since the kinetic energy contribution is also small at these distances, we conclude that the total DFT-LDA interaction decreases rapidly with distance beyond the equilibrium separation. It should be noted that including dispersion forces would not eliminate all problems with this calculation since they would decrease the calculated equilibrium spacing which was already to low.

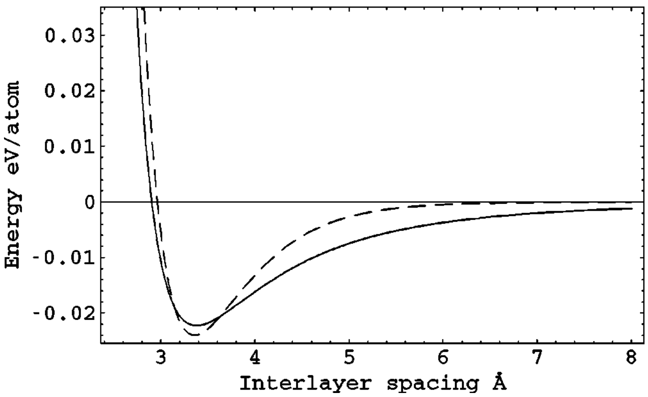

FIG. 1. Comparison of empirical (solid line) and LDA (dashed line) potentials for graphene-graphene interaction. Note the rapid falloff of the LDA potential at long distances.

Other work on graphite showed the high sensitivity of results to details of the calculation. Trickey *et al.*, first in 1989 and then in 1992,[14] performed DFT-LDA studies of the binding between two graphene sheets. As stated in their later paper, the first calculation gave spurious results. With an improved code, they obtained an interlayer binding energy that was 50% larger than experiment. Also, an LDA calculation by Jansen and Freeman[29] gave a fairly good answer for the interlayer spacing (3.41 versus 3.35 Å) but their result for the interlayer binding energy was larger than experiment by a factor of 4.

Schabel and Martins,[30] however, found an interlayer spacing and binding energy in excellent agreement with experiment. Their delocalization energy was about one-third of the exchange-correlation energy. Figure 1 shows the energy of graphite as a function of interlayer distance calculated both from the Schabel-Martins results and the empirical model potential for interacting graphene sheets.[1] At close distances, up to just beyond the minimum, the two curves are nearly the same. But the Schabel-Martins potential falls off exponentially rather than as R^{-6} as shown by their analytic representation. It is significantly less attractive than the model potential at distances 15% greater than the equilibrium distance and is close to zero at an interlayer spacing only 30% larger than the equilibrium value. This is consistent with DiVincenzo *et al.*[28] Since the attractive part of the model potential explicitly has its origin in dispersion forces, this supports the idea that the DFT-LDA does not describe the attraction when molecules are far apart and the electron density is low, but can give good results in the vicinity of the energy minimum. It is interesting to note that, in the Schabel-Martins calculation, choosing a different number of grid points in a DFT of the local potential operator gives a variation in the total cohesive energy of 0.03 eV. This is small relative to the total cohesive energy, but is of the same magnitude as the interlayer binding energy. The calculated binding energy varies little with changes in the number of grid points, suggesting that there is a significant cancellation of errors.

A DFT study of graphite by Charlier *et al.*[17] identified the various contributions to the interlayer binding and gave the correct interlayer spacing and binding energy. They confirmed that the attractive part of the binding energy had two origins: the exchange-correlation energy and a decrease in kinetic energy because of delocalization. The exchange correlation is critically important. Without it, the calculated equilibrium interlayer distance is 4.15 Å rather than 3.30 Å. The distance at which the interaction energy was negligible agreed with the Schabel-Martins work, being about 4.5–5 Å. In a study that compared bonding in graphite to that in graphitic silicon, Wang *et al.*[31] obtained similar results.

While some DFT-LDA calculations gave good results for the interlayer binding energy and spacing in graphite, they all failed to reproduce the experimental compressibility accurately. Compressibility depends on the curvature of the potential energy as a function of interlayer distance and this is difficult to obtain accurately from the LDA. This was recognized by Palser,[32] who used a tight-binding calculation along with an empirical dispersion potential. The dispersion contribution was necessary because the tight-binding results by themselves did not give binding. The dispersion potential was chosen to reproduce the experimental interlayer spacing and binding energy, so Palser could not independently give numerical results for these quantities, but he did find that ABA stacking was favored over AAA stacking, and he did get the correct compressibility. This illustrates the need to include long-range forces in calculations of cohesive properties.

First-principles studies of C_{60} interactions are consistent with the statements (1)–(8) listed above. The Saito-Oshiyama[15] DFT-LDA calculations for C_{60} crystal gave a cohesive energy that agreed with experiment. But this agreement is spurious because the cohesive energy was obtained for the lattice spacing that minimized the calculated energy. This corresponds to a highly compressed crystal, so the calculated energy should be compared to that of the compressed crystal. The energy of the compressed crystal can be estimated from either pressure-volume data or the Girifalco potential[2] which both show that the cohesive energy is positive at this compression.

Troullier and Martins,[18] on the other hand, got excellent results for the cohesive energy, lattice parameter, and compression equation of state for C_{60} crystal. They used a plane-wave, pseudopotential DFT-LDA method with the Ceperley-Alder[33] and Perdew-Zunger[34] forms for the exchange correlation. This is the same exchange correlation used by Saito and Oshiyama,[15] whose results were unsatisfactory. However, Troullier and Martins used a plane-wave, rather than a Gaussian basis set, and a pseudopotential different from that of Saito-Oshiyama. Also, they included a very large number of plane waves in their expansions (17 000–110 000). This again illustrates the sensitivity of calculated van der Waals energies to the details of the calculation. Compression increases the electron density between molecules, so one would expect that the calculation of the exchange correlation, and therefore the equation of state, would be more accurate at higher pressures. But the Troullier-Martins calculation of the bulk modulus shows that their method also correctly reproduces the curvature near the minimum of the energy-lattice parameter curve.

The dispersion energy was first calculated for C_{60} interactions from multipole expansions by Lambin *et al.*,[35] who used a polarizable shell model for the fullerene molecule. They compared their results to those obtained by summing an empirical Lennard-Jones potential for the interaction of carbon atoms on two different C_{60} molecules. Their attractive dispersion energy, at a distance equal to the equilibrium distance in C_{60} crystal, was in fair agreement with that calculated from the empirical potential. Their work also showed that the repulsive part of the binding energy is much more sensitive to atomic corrugation than the attractive part.

The importance of the long-range dispersion energy was also recognized by La Roca[36] who combined the results of Lambin *et al.* with a Gordon-Kim (GK) method[37] to study the $C_{60}-C_{60}$ potential. His result for the equilibrium lattice parameter was good (14.17 versus 14.0 Å) and his calculated energy of 1.4 eV/molecule was not too far from the experimental value. An important point is that the calculation gave no binding unless the dispersion energy was included in the theory. Because the GK method uses a superposition of molecular densities, the delocalization contribution to the attractive energy is missing. If the entire difference between the calculated and experimental values were attributed to this effect, then the delocalization energy would be about 0.25 eV/molecule.

The calculation for the dispersion potential was improved by Girard *et al.*[38] by treating each C_{60} molecule as a set of 60 polarizable carbon atoms. This resulting dispersion potential matched the attractive part of the Girifalco potential very well, provided the attractive constant was decreased by about 15%. The close agreement of the shape of the potential between the polarization theory and the model potential is additional support for the validity of the latter.

Detailed confirmation of this was obtained by Pacheco and Ramalho (PR).[39] They point out the failure of the LDA to account for long-range interactions, so they use the LDA for distances near, and less than, the equilibrium separation and a multipole expansion for the longer-range interaction. They constructed a pairwise potential from these results by using a Fermi-type function to join a Morse function representation of the short-range results with a dispersion inverse power function for the long-range results. Their potential is shown in Fig. 1 of their paper along with the Girifalco C_{60}-C_{60} potential. The two potentials are close together for distances in the vicinity of the minimum and beyond. For close distances, the PR potential is less repulsive. Both potentials reproduce the experimental equation of state up to at least 20 000 atmospheres, but the Girifalco potential predicts a compression that is too small at higher pressures. The inaccuracy of the model potential at close separation distances is understandable. The attractive part of the potential is based on the correct leading term for the form of the distance dependence, but the form of the repulsive part of the Lennard-Jones potential is arbitrary. This work provides the most convincing evidence for the agreement of the empirical approach with fundamental theory for the calculation of cohesive properties, provided the pressure is not too high.

TABLE I. Binding energy of a fullerene molecule interacting with other graphitic structures.

Interacting with	Reference	Binding energy (eV/molecule)	No. of relevant interactions
fullerene	2	0.277	364
on top of a (10,10) tube	4	0.537	732
graphite	11	0.968	1001
mouth of a (10,10) tube	4	1.63	2270
inside a (10,10) tube	4	3.26	4112
at a spherical cap	4	4.40	5416

The analytic representation of the PR potential permits the calculation of the contribution of the DFT-LDA calculation to the total potential as a function of distance. This calculation shows that the DFT-LDA contribution is less than 15% at a separation 20% greater than the equilibrium distance. This is similar to the conclusion for graphite from the Schabel-Martins[30] work. Further support for this agreement comes from the calculation of intertube binding energy of a (6,6) rope (radius $=4.07$ Å) by Charlier *et al.*[19] using a DFT-LDA method. The equilibrium distance between two nanotubes was found to be 3.14 Å at which the binding energy was 9.76 meV/atom. These compare well with the universal model potential[4] results which give 3.14 Å and 8.65 meV/atom.

All of these results support statements (1)–(8) listed above and the conclusion that the empirical model potentials correctly describe the VDW cohesive properties that are not sensitive to the atomic corrugation of interacting graphitic structures. This model provides a unified physical picture of the binding energies in graphitic structures, as displayed in Table I, which lists the binding energy of a C_{60} molecule interacting with other graphitic structures.

From the Table I, we note that the binding energies for a C_{60} molecule on top, at the mouth of, inside a tube, and at a spherical cap of the tube form a consistent series in which the energy increases with the number of carbon atoms close enough to each other to contribute to the binding energy. The last column in Table I gives the number of atoms within the ‘‘interaction distance’’ from atoms on a fullerene molecule with atoms on the other graphitic structure. The interaction distance is defined as the distance between two atoms for which the magnitude of the interaction energy is 5% or greater than that at the minimum of the Lennard-Jones potential. There is an obvious trend. The interaction of C_{60} with another fullerene molecule is the weakest because only a few atoms are close to each other, the distance between other atoms increasing rapidly as we move away from the point of contact. When fullerene is on top of a tube, its atoms see more other atoms that are close enough to interact because the cylinder curves away from the fullerene only tangentially to the tube rather than in all directions, as is the case for the interaction between two fullerenes. The interaction between C_{60} and graphite includes more atoms that are close to atoms on the fullerene molecule, so the binding is greater. At the mouth of a tube, the atoms on C_{60} are closer to an even larger number of atoms, and within the tube there are yet more atoms interacting. The largest number of interactions is between fullerene and the inside of the spherical cap in a (10,10) tube, so the binding energy is the largest. The binding energy is an almost linear function of the number of interacting atoms.

Recently, DTF-LDA calculations have been performed for the van der Waals interactions in a chain of C_{60} molecules inside a (10,10) nanotube[16] by Okada *et al.* Their result does not fit into the trend shown in Table I. They report a peapod formation energy of 0.51 eV/molecule. The fullerene molecules were constrained to be 9.824 Å apart. Since this is close to the equilibrium distance between two isolated fullerene molecules, an energy about equal to that of the equilibrium C_{60}-C_{60} interaction must be subtracted from this, which gives about 0.2 eV/molecule for the interaction of the C_{60} molecule with the inside of the tube. This result is less than that for the interaction of fullerene with any other graphitic structure. Given the success of the other calculations, especially for the cases of graphite and C_{60} crystal, it must be concluded that the result of Okada *et al.* is much too low. Furthermore, any large deviation for the ball-tube interaction from the trend in binding energies in graphitic structures must imply a significant difference in the nature of the binding. But any change in the type of binding would increase the binding energy, not decrease it. An examination of this discrepancy can shed light on the influence of errors and approximations on calculated results.

For a chain of C_{60} molecules inside a (10,10) nanotube, there are two factors that are not accounted for by the continuum approximation potential in the empirical model. The first is the effect of atomic corrugation, and the second is the nonlinear superposition of delocalization. An estimate of the first effect can be obtained from studies that examine corrugation energies. According to Savin *et al.*,[40] who analyzed the angular-dependent potential between two fullerene molecules, atomic corrugation results in a rotational barrier of about 42 meV. La Rocca[36] obtained a rotational barrier between two fullerenes of 23–40 meV. Also, Gravil *et al.*,[41] in a study of adsorption, found a barrier of 30 meV for fullerene on a graphite surface. These results suggest that the corrugation energy introduces a variation of about 5% around the mean which is not enough to account for the discrepancy between the empirical model and the results of Okada *et al.*

The second effect that can introduce a difference between the VDW model and the DTF-LDA results is that the result from the empirically based potential was not for a chain, but for a single molecule inside a tube. The models for the molecule-molecule interaction and the molecule-tube interaction each take all pairwise effects, including electron delocalization, into account. But when interpreting the result for a chain inside a tube as if it is a sum of interactions of individual molecules with the tube and with each other, it is presumed that the molecule-molecule and molecule-tube potentials are unchanged by the proximity of nearby molecules. More likely, the chain of molecules results in a greater charge transfer than for individual molecules, so there is more delocalization than for a single molecule in a tube. The delocalization of electrons can contribute a substantial amount to cohesion[17] but we need an estimate of how much this changes in a chain versus individual molecules in a nanotube. Such calculations have not been done, but the analysis by Pacheco and Ramalho[39] shows that three-body interactions contribute only 6% to the cohesive energy of C_{60} crystal and we would expect a similarly small effect for the three-body interactions in peapods. In any case, increased delocalization would increase binding and therefore cannot account for the low value of Okada *et al.*

Some important experiments exist that are relevant. The formation of encapsulated C_{60} in nanotubes has been observed and studied by Smith and Luzzi[42] by high-resolution transmission electron microscopy. They found that C_{60} crystallites coexisted with nanotubes in material that was chemically cleaned and baked at 225 °C. After acid reflux and reannealing at 4500 °C, chains of C_{60} molecules were found in the nanotubes (peapods). Their experiments provide strong evidence that peapods are more stable than C_{60} crystal, as predicted by the empirical model calculations and in direct contradiction to the result of Okada *et al.* Furthermore, diffraction experiments[43] yield a distance between adjacent encapsulated molecules that is almost identical with that in fullerite. This argues against the idea that there is a serious change in the nature of the binding when C_{60} molecules are placed inside a nanotube. Clearly, we must conclude that the value of the binding energy in a (10,10) tube from the VDW model potentials is to be preferred and that these potentials provide a valid method of studying the van der Waals interactions among graphitic structures.

This analysis shows that first-principles calculations for graphitic structures can be carried out quite successfully, but they are sensitive to the details of calculation and the long-range dispersion interaction must be included. Without the long-range interaction, DFT-LDA calculations are inaccurate for separation distances greater than 1.15 of the equilibrium separation. It also shows that model potentials, in which the van der Waals interactions between graphitic structures are treated as sums of carbon-carbon interactions, give valid results for the van der Waals cohesive properties. The fact that the empirical potentials can be reproduced by first-principles calculations for distances near to and less than the equilibrium separation for graphite, and over a large range of distances for C_{60} crystal, provides a good theoretical base for the former.

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[1] L.A. Girifalco and R.A. Lad, J. Chem. Phys. **25**, 693 (1956).

[2] L.A. Girifalco, J. Phys. Chem. **96**, 858 (1992).

[3] L.A. Girifalco, Phys. Rev. B **52**, 9910 (1995).

[4] L.A. Girifalco, M. Hodak, and R.S. Lee, Phys. Rev. B **62**, 13 104 (2000).

[5] K. Kniaz, L.A. Girifalco, and J.E. Fischer, J. Phys. Chem. **99**, 16 804 (1995).

[6] K. Kniaz, J.E. Fischer, L.A. Girifalco, A.R. McGhie, R.M. Strogin, and A.B. Smith, Solid State Commun. **96**, 739 (1995).

[7] V.I. Zubov, N.P. Tretiakov, T. Rabelo, and J.F. Sanchez-Ortiz, Phys. Lett. A **194**, 223 (1994).

[8] J.P.K. Doye and D. Wales, Chem. Phys. Lett. **247**, 339 (1995).

[9] S. Tamaki, N. Ide, I. Okada, and K. Kojima, J. Appl. Phys. **37**, 2608 (1998).

[10] R.S. Ruoff and A.P. Hickman, J. Chem. Phys. **97**, 2494 (1993).

[11] J. Song and R.L. Cappelletti, Phys. Rev. B **50**, 14 678 (1994).

[12] C. Rey, J. Garcia-Rodeja, L.J. Gallego, and J.A. Alonso, Phys. Rev. B **55**, 7190 (1997).

[13] L. Henrard, E. Hernandez, P. Bernier, and A. Rubio, Phys. Rev. B **60**, R8521 (1999).

[14] S.B. Trickey, F. Muller-Plathe, G.H.F. Diercksen, and J.C. Boettger, Phys. Rev. B **45**, 4460 (1992).

[15] S. Saito and A. Oshiyama, Phys. Rev. Lett. **66**, 2637 (1991).

[16] S. Okada, S. Saito, and A. Oshiyama, Phys. Rev. Lett. **86**, 3835 (2001).

[17] J.C. Charlier, X. Gonze, and J.-P. Michenaud, Europhys. Lett. **28**, 403 (1994).

[18] N. Troullier and J.L. Martins, Phys. Rev. B **46**, 1754 (1992).

[19] J.C. Charlier, X. Gonze, and J.-P. Michenaud, Europhys. Lett. **29**, 43 (1995).

[20] K. Sandor and P. Pulay, Chem. Phys. Lett. **229**, 175 (1994).

[21] J.M. Perez-Jorda and A.D. Becke, Chem. Phys. Lett. **233**, 134 (1995).

[22] J.A. Alonso and L.A. Girifalco, Solid State Commun. **24**, 135 (1977).

[23] W. Kohn, Y. Meir, and D.E. Makarov, Phys. Rev. Lett. **80**, 4153 (1998).

[24] K. Rapcewicz and N.W. Ashcroft, Phys. Rev. B **44**, 4032 (1991).

[25] Y. Andersson, D.C. Langreth, and B.I. Lundqvist, Phys. Rev. Lett. **76**, 102 (1996).

[26] E. Santos and A. Villagra, Phys. Rev. B **6**, 3134 (1972).

[27] M. Leal and E. Santos, Nuovo Cimento D **1**, 716 (1982).

[28] D.P. DiVincenzo, E.J. Mele, and N.A.W. Holzwarth, Phys. Rev. B **27**, 2458 (1983).

[29] H.J.F. Jansen and A.J. Freeman, Phys. Rev. B **35**, 8207 (1987).

[30] M.C. Schabel and J.L. Martins, Phys. Rev. B **46**, 7185 (1992).

[31] Y.C. Wang, K. Scheerschmidt, and U. Gosele, Phys. Rev. B **61**, 12 864 (2000).

[32] H.R. Palser, Phys. Chem. Chem. Phys. **1**, 4459 (1999).

[33] D.M. Ceperley and B.J. Alder, Phys. Rev. Lett. **45**, 566 (1980).

[34] J.P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[35] P. Lambin, A.A. Lucas, and J.P. Vigneron, Phys. Rev. B **46**, 1794 (1992).

[36] G.C.L. Rocca, Europhys. Lett. **25**, 5 (1994).

[37] R.G. Gordon and Y.S. Kim, J. Chem. Phys. **56**, 3122 (1981).

[38] C. Girard, P. Lambin, A. Dereux, and A.A. Lucas, Phys. Rev. B **49**, 11 425 (1994).

[39] J.M. Pacheco and J.P. Prates Ramalho, Phys. Rev. Lett. **79**, 3873 (1997).

[40] S. Savin, A.B. Harris, and T. Yildirim, Phys. Rev. B **55**, 14 182 (1997).

[41] P.A. Gravil, M. Devel, P. Lambin, X. Bouju, C. Girard, and A.A. Lucas, Phys. Rev. B **53**, 1622 (1996).

[42] B.W. Smith and D.E. Luzzi, Chem. Phys. Lett. **321**, 169 (2000).

[43] B. W. Smith and D. E. Luzzi (private communication).