Oxygen adsorption on graphite and nanotubes

P. Giannozzi,[a)] R. Car, and G. Scoles
*Chemistry Department and Princeton Materials Institute, Princeton University, Princeton,
New Jersey 08544*

We study the binding of molecular oxygen to a graphene sheet and to a (8,0) single walled carbon nanotube, by means of spin-unrestricted density-functional calculations. We find that triplet oxygen retains its spin-polarized state when interacting with graphene or the nanotube. This leads to the formation of a weak bond with essentially no charge transfer between the molecule and the sheet or tube, as one would expect for a physisorptive bond. This result is independent on the approximation used for the exchange-correlation functional. The binding strength, however, depends strongly on the functional, reflecting the inability of current approximation functionals to deal correctly with dispersion forces. Gradient-corrected functionals yield very weak binding at distances around 4 Å, whereas local density functional results yield substantially stronger binding for both graphene and the nanotube at distances of less than 3 Å. The picture of oxygen physisorption is not substantially altered by the presence of topological defects such as 5–7 Stone–Wales pairs. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1536636]

There is currently a strong interest on the phenomenology of gas adsorption by carbon nanotubes. Recent experimental data[1,2] have shown that the transport properties of single-wall nanotubes (SWNT) change dramatically upon exposure to gas molecules such as O_2, NO_2, NH_3, and many other gases, at ambient temperature. Practical applications to the production of better gas sensors ("thermoelectric nano-nose")[3] have been envisioned.

Several mechanisms may explain such phenomena. The gas molecules could affect transport properties indirectly, by binding to donor or acceptor centers in the substrate[2] or at the contacts (as recently suggested in Ref. 4), or directly, by binding to the nanotube.[5] In the latter case, the gas could be physisorbed (bound by dispersive van der Waals forces) or chemisorbed (bound by formation of a chemical bond), and adsorption could take place either on perfect nanotube walls or at defect sites. If the gas is chemisorbed, a key factor affecting the transport properties would be the charge transfer from the gas molecule to the nanotube, or vice versa.

Experimentally, a way to distinguish physisorbed from chemisorbed species is to check for a linear relation between the thermoelectric power and the additional resistivity induced by gas adsorption. According to such criterion, O_2 is chemisorbed.[3] However, a recent experimental study of the kinetics of O adsorption and desorption on SWNT and on graphite, finds that O is physisorbed on SWNT in molecular form,[6] with an estimated binding energy $E \sim 0.19$ eV. This would be consistent with the well-established fact that molecular oxygen physisorbs on graphite, with a binding energy $E \sim 0.1$ eV.[6,7]

On the theoretical side, contradictory results have been reported. Calculations based on the local-density approximation (LDA) find[8] that O_2 binds to a semiconducting (8,0)

nanotube with a binding energy $E = 0.25$ eV at a distance $d = 2.7$ Å from the nanotube. A weak hybridization between oxygen and carbon states occurs, with a charge transfer estimated at about $0.1e$, suggesting that the corresponding variation in the density-of-states (DOS) at the Fermi energy E_F is responsible for the observed behavior of the transport properties.[5,8] Similar results were reported by other groups as well.[9,10] Calculations based on gradient-corrected approximation (GGA) functionals, on the other hand, yield virtually no binding and no charge transfer for O_2 on both graphite and SWNT,[11] and so does an earlier set of calculations for O_2 on graphite.[12] A very recent quantum chemistry calculation at the MP2 level[13] also finds very weak binding, due to physisorption, and minimal charge transfer.

With the exception of Refs. 11 and 13, whose calculations take into account the spin state of the O_2 molecule, and of Ref. 12, which states that the calculation is spin-restricted, it is not clear how spin-polarization is accounted for in all these calculations. Since oxygen molecules have a triplet ground-state and since spin-polarization effects have been shown to be important in surface oxidation processes,[14] we believe that the spin state of O_2 should be taken into account in the calculations.

To help clarifying this issue, we report in this paper a density functional theory (DFT) study of the binding of O_2 molecules to a planar graphene sheet and to semiconducting ultrathin SWNTs. To assess the influence of the approximation adopted for the exchange and correlation functional, we perform both LDA and GGA spin-unrestricted calculations.

Calculations were performed using the PWSCF package[15] in a plane-wave supercell approach using ultrasoft (Vanderbilt) pseudopotentials.[16] Both LDA[17] and the PBE flavor[18] of the GGA were used. Unless explicitly specified, all calculations where an O_2 molecule is present use spin-polarized functionals. A kinetic energy cutoff of 25 Ry for the wavefunctions was used. For the charge density, a cutoff

---
[a)]Present address: NEST-INFM, Scuola Normale Superiore di Pisa, Piazza dei Cavalieri 7, I-56126 Pisa, Italy.
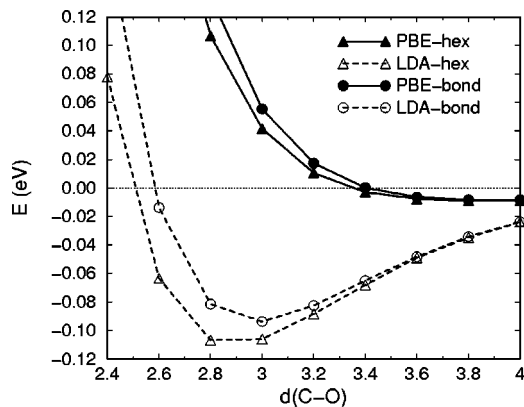
FIG. 1. Energy vs distance curves for O_2 on a graphene plane. (Solid lines) PBE results; (Dashed lines) LDA results; (Triangles) O_2 molecule over a C–C bond; (Circles) O_2 molecule over a hexagon center. d is the distance between the center of the molecule and the graphene plane. The molecular axis is parallel to the graphene plane.

FIG. 2. Electronic states for O_2 on a graphene plane. Point Γ corresponds to $\mathbf{q}=0$, point X to $\mathbf{q}=(\pi/a,0,0)$. (Solid lines) majority spin states; (Dashed lines) minority spin states; (Dotted line) Fermi energy.

of 100 Ry was found to be sufficient in LDA calculations, while a cutoff of 300 Ry gave accurate results in PBE calculations. In the triplet state of the O_2 molecule we obtain a O–O equilibrium distance $d=1.22$ Å with LDA, $d=1.23$ Å with PBE (experimental value: $d=1.207$ Å), and a binding energy $E=7.2$ eV with LDA, $E=5.68$ eV with PBE (experimental value: $E=5.12$ eV). The large overestimate of the binding energy is a well-known drawback of LDA. The energy difference between the triplet and the singlet state is $\Delta E=1.07$ eV with LDA, $\Delta E=1.23$ eV with PBE (experimental value: 0.98 eV). The spin-splitting between the highest occupied majority state and the lowest unoccupied minority states is $\Delta E=2.15$ eV with LDA, $\Delta E=2.48$ eV with PBE.

The first system we studied is O_2 on a graphene sheet, at various distances and for different approaching geometries. The goal of this calculation is twofold. On the one hand, it is a test of the accuracy of different DFT approximations, since experimental data for O_2 binding on graphite are available. On the other hand, it also serves as a reference to estimate the effect of the curvature in the case of nanotube binding. The graphene is simulated by a relatively small orthorhombic supercell of 8 atoms, with lattice parameters $a=5.041$ Å, $b=4.3656$ Å in the xy planes, $c=12$ Å in the z direction (where periodicity is fictitious). A uniform grid in the xy plane of 8 k-points in the irreducible Brillouin zone is used. Since the Fermi surface in graphene reduces to a single point, there is no need to use Gaussian broadening or tetrahedra for k-point integration of the charge density.

In Fig. 1 we report the calculated energy versus distance curve, at fixed geometry for both O_2 and graphene, for O_2 approaching the graphene plane with the molecular axis parallel to the plane at several lattice sites. LDA yields a shallow minimum at $d=3.0$ Å with a binding energy $E=0.1$ eV, while PBE yields a very shallow minimum at $d\simeq3.8$ Å with an almost negligible binding energy $E\simeq0.01$ eV, in agreement with Refs. 11 and 12. In all cases a spin-polarized ground state is found, corresponding to triplet oxygen.

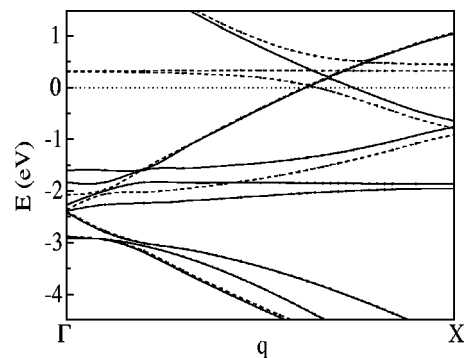Results obtained by leaving the atoms free to relax differ

very little from the above picture, as the final configurations differ only marginally from results with fixed geometry. If one repeats the calculations with the O_2 molecule in the singlet state using LDA, one finds for the equilibrium C–O distance $d=2.7$ Å and for the binding energy $E=0.23$ eV, in agreement with Refs. 8–10. A Gaussian broadening of 0.01 Ry is used to cope with the degeneracy of the singlet state of O_2.

Electronic states calculated at the LDA equilibrium geometry along the $\Gamma-X$ direction (referred to the supercell Brillouin zone) is shown in Fig. 2. The unperturbed bands of graphene cross the Fermi surface at a single point along this direction, at $\mathbf{q}=(2\pi/3a,0,0)$. Figure 2 shows that even for $d=3.0$ Å there is very little interaction between the graphene bands and O_2 triplet states and the induced DOS at the Fermi energy is small. A denser grid of 32 k-points and the tetrahedron method were used for this calculation. We have verified that there is very little differences between LDA and PBE results for the same geometry.

The amount of charge transfer from the graphene to the O_2 molecule can be estimated by projecting the charge density on atomic orbitals. Let us define the charge transfer as the difference between Löwdin charges for isolated O_2 and O_2 in presence of the graphene. We find a charge transfer of $0.03e$/molecule. Such value is quite dependent on the details of the calculations. If a large Gaussian broadening is used, the charge density has a sizable contribution from the spin minority states of oxygen lying just a few tenths of an eV above the Fermi energy, thus artificially inflating the value of the charge transfer. It seems unlikely that the presence of a triplet O_2 molecule at $d=3.0$ Å from a graphene sheet could significantly affect its transport properties.

Although the LDA and the GGA lead to qualitatively very similar electronic structures, large quantitative differences between the two approximations are apparent in the potential energy curves of Fig. 1. These differences reflect the difficulty of current approximated DFT functionals to deal with dispersion forces. The latter do not originate from charge overlap, which is well accounted for in local or semilocal DFT approximations, but from charge fluctuations, whose description is beyond current DFT approximations. The LDA is known to substantially overestimate the binding energy and underestimate the bonding distance in phys-

isorbed systems. GGA functionals tend instead to strongly underestimate the binding energy, or yield no bonding at all. Our results are fully consistent with the above general trends. The experimental values for binding energies and distances[7] are somehow intermediate between the GGA and the LDA results.

It is interesting to see whether adding dispersion forces to the GGA results may bring the O_2-graphene interaction curve in better agreement with experiment. We point out that a better starting point for adding dispersion contributions would be the Hartree–Fock energy.[19] As the GGA energies calculated using functionals of the PBE type are less repulsive than the Hartree–Fock energies[19] we expect that the potential energy curve obtained adding DFT and dispersion should be somewhat too attractive.

We have calculated the dispersion contribution using the O_2–benzene C_6 coefficient, divided by 6,[20] and estimating higher terms up to C_{14} using Ref. 21 and the usual recursion relationship.[22] The O_2-carbon atom interaction parameters used are: $C_6 = 53.38$, $C_8 = 7.203 \times 10^2$, $C_{10} = 1.191 \times 10^4$, $C_{12} = 2.478 \times 10^5$, $C_{14} = 6.334 \times 10^6$, in atomic units. The adimensional parameter ρ appearing in the damping functions derived in Ref. 22 is $\rho = 0.8433$. The O_2 molecule is assumed to be spherical. The dispersion contribution for O_2 over a hexagon center is calculated by summing over 54 carbon atoms. Following this procedure we obtain a well depth of about 0.18 eV located at 3.1 Å above the surface, to be compared with an experimental value of 0.1 eV.[7]

We have performed calculations of the behavior of O_2 molecules interacting with perfect nanotubes. We have chosen a (8,0) nanotube, whose diameter (6.24 Å) is definitely smaller than the diameters (~ 15 Å) of typical SWNT samples. The effect of the curvature, if any, is likely to be overestimated with this choice of a nanotube. The same system was studied in Refs. 8 and 11. We have used a simple tetragonal supercell, with cell parameters $a = 13.23$ Å, $c = 4.366$ Å, containing one nanotube with the axis in the c direction. The supercell contains 32 nanotube atoms. A uniform grid of 4 k-points in the z direction was found to adequately describe the electronic structure of the isolated nanotube. LDA calculations on the nanotube yield C–C bond lengths of 1.432 and 1.442 Å and bands along the $\langle 001 \rangle$ direction with a direct gap of $\simeq 0.5$ eV. PBE yields 1.443 and 1.444 Å for the bond lengths and a band structure that differs only marginally from that obtained with the LDA.

We have searched for the equilibrium position of an O_2 molecule initially placed over a C–C bond with its axis parallel to the nanotube axis. LDA calculations yield a binding energy $E = 0.08$ eV with C–O distances $d = 2.92$–2.93 Å. The relaxation of C–C distances does not exceed 0.005 Å. PBE yields almost no binding (binding energy $E = 0.004$ eV) at C–O distances $d = 3.68$–3.70 Å. The ground state is always spin-polarized. The same overall picture as in the case of O_2 on graphene emerges, indicating that the effect of the curvature on the binding properties is small.

To discuss the effect of oxygen physisorption on the electronic structure, we consider the electronic states at the geometry corresponding to the minimum of the LDA energy. The band structure along the $\Gamma - X$ direction (Fig. 3) is insu-
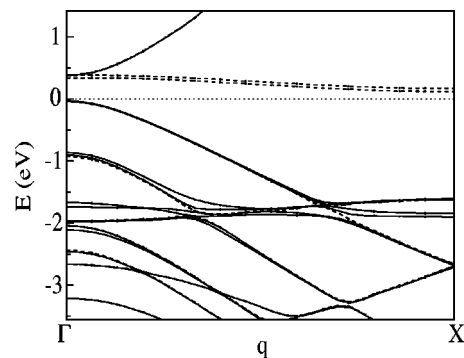

FIG. 3. Electronic states for O_2 adsorbed on a (8,0) nanotube. Point Γ corresponds to $\mathbf{q} = 0$, point X to $\mathbf{q} = (0,0,\pi/c)$. (Solid lines) majority spin states; (Dashed lines) minority spin states; (Dotted line) top of valence bands.

lating as in the case of an isolated nanotube. The O-derived states are superimposed to the nanotube bands with little interaction. O-derived majority spin states appear in the valence bands as a doubly-degenerate narrow band between -1.5 and -2 eV below the top of the valence band, while the corresponding minority states lie empty in the gap. Again, there is no evidence that the presence of an O_2 molecule induces any sizable change of the DOS at the Fermi level. A semiconducting nanotube remains semiconducting—at the DFT level—upon adsorption of O_2. A small but finite dispersion can be seen in the O_2 derived energy bands, leading to a small indirect gap between the top of the carbon-derived valence band and the bottom of the unoccupied oxygen-derived states. This band dispersion is an artifact of the supercell and no physical meaning should be attributed to it.

In Ref. 8, a charge transfer of 0.1 e from the nanotube to the O_2 molecule was estimated. We have calculated the charge transfer in analogy to case of O_2 on a graphene sheet. We find a charge transfer of $< 0.02e$/molecule for PBE, $0.02e$/molecule for LDA, at their respective equilibrium geometries. Again, the results is rather dependent in the details of the calculations. Test calculations on larger supercells with only the Γ point yield even smaller charge transfers ($< 0.01e$/molecule).

The difference between our results and those of Refs. 8–10 originates from the different treatment of spin-polarization. Indeed, with spin-restricted LDA calculations we find a larger binding energy ($E = 0.22$ eV) and a smaller C–O distance ($d = 2.70$–2.71 Å), in agreement with Refs. 8–10 and very similar to what we obtain in absence of spin-polarization for O_2 on graphene. The non-spin-polarized band structure for (singlet) O_2 adsorbed on a (8,0) nanotube is very similar to that reported in Ref. 8, with a degenerate O-derived state crossing the Fermi energy.

The possibility that O_2 may bind to defect sites should be considered. All nanotubes have a large number of defects of various kind: topological defects (such as pentagons and heptagons instead of hexagons), kinks, vacancies, impurities, and of course, ends. We have examined the binding of O_2 to one of the simplest topological defects: a Stone–Wales defect, consisting of two pentagon–heptagon pairs, in both a

graphene sheet and a nonanotube. In both cases, our results differ very little from those obtained for a perfect graphene or nanotube wall.

In conclusion, although we have considered only a limited set of structures, defects, and geometries, our calculations indicate that an O_2 molecule in the triplet state is only physisorbed on a nanotube or a graphene sheet, either perfect or with a Stone–Wales defect. Thus, we find no evidence that triplet O_2 absorbed at the walls of SWNTs can affect their transport properties in a way that could explain the experimental observations.

It has been found in recent calculations[11,13,23] that singlet oxygen can form a chemical bond with a nanotube. This occurs at O_2-nanotube distances ($d \sim 1.5$ Å) that are considerably smaller than those considered here. Chemisorbed oxygen is accompanied by a significant amount of charge transfer between the molecule and the nanotube.[11] A large activation barrier has to be overcome to access the chemisorbed state. Moreover, in the case of a perfect nanotube, this is only metastable having a significantly higher energy than the physisorbed state.[11] Clearly additional investigations are required to elucidate the origin of the observed phenomenology. An alternative explanation, suggested in Ref. 4 and further pursued in Ref. 24, is that the observed effects are not due to doping by oxygen absorbed at the nanotube walls, but are instead the result of oxygen absorbed at the contacts.

[1] P. G. Collins, K. Bradley, M. Ishigami, and A. Zettl, Science **287**, 1801 (2000).

[2] J. Kong, N. R. Franklin, C. Zhou, M. G. Chapline, S. Peng, K. Cho, and H. Dai, Science **287**, 622 (2000).

[3] C. K. W. Adu, G. U. Sumanasekera, B. K. Pradhan, H. E. Romero, and P. C. Eklund, Chem. Phys. Lett. **337**, 31 (2001).

[4] V. Derycke, R. Martel, J. Appenzeller, and Ph. Avouris, Appl. Phys. Lett. **80**, 2773 (2002).

[5] K. Bradley, S.-H. Jhi, P. G. Collins, J. Hone, M. L. Cohen, S. G. Louie, and A. Zettl, Phys. Rev. Lett. **85**, 4361 (2000).

[6] H. Ulbricht, G. Moos, and T. Hertel, Phys. Rev. B **66**, 075404 (2002).

[7] G. Vidali, G. Ihm, Y-J. Kim, and M. W. Cole, Surf. Sci. Rep. **12**, 133 (1991).

[8] S.-H. Jhi, S. G. Louie, and M. L. Cohen, Phys. Rev. Lett. **85**, 1710 (2000).

[9] J. Zhao, A. Buldum, J. Han, and J. P. Lu, Nanotechnology **13**, 195 (2002).

[10] S. Peng and K. Cho, Nanotechnology **11**, 85 (2000).

[11] D. C. Sorescu, K. D. Jordan, and P. Avouris, J. Phys. Chem. B **105**, 11227 (2001).

[12] D. Lamoen and B. N. J. Persson, J. Chem. Phys. **108**, 3332 (1998).

[13] A. Ricca and J. D. Drocco, Chem. Phys. Lett. **362**, 271 (2002).

[14] K. Kato, T. Uda, and K. Terakura, Phys. Rev. Lett. **80**, 2000 (1998).

[15] S. Baroni, A. Dal Corso, S. de Gironcoli, and P. Giannozzi: http://www.pwscf.org

[16] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990). The pseudopotential generation code can be downloaded from: http://www.physics.rutgers.edu/~dhv/uspp/

[17] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980); J. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[18] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[19] X. Y. Wu, M. C. Vargas, S. Nayak, V. Lotrich, and G. Scoles, J. Chem. Phys. **115**, 8748 (2001), and references quoted therein.

[20] A. Kumar and W. J. Meath, Mol. Phys. **75**, 311 (1992).

[21] A. Kumar, W. J. Meath, P. Bündgen, and A. J. Thakkar, J. Chem. Phys. **105**, 4927 (1996).

[22] C. Douketis, G. Scoles, S. Marchetti, M. Zen, and A. J. Thakkar, J. Chem. Phys. **76**, 3057 (1982).

[23] T. Savage *et al.* (unpublished).

[24] S. Heinze, J. Tersoff, R. Martel, V. Derycke, J. Appenzeller, and Ph. Avouris, Phys. Rev. Lett. **89**, 106801 (2002).