Electronic properties of O_2-doped DNA

H. Mehrez,* S. Walch,† and M. P. Anantram‡
Center for NanoTechnology and NASA Advanced Supercomputing Division, NASA Ames Research Center, Mail Stop 229-1, Moffett Field, California 94035-1000, USA
(Received 14 September 2004; revised manuscript received 8 February 2005; published 15 July 2005)

Based on recent experimental transport measurements, it has been suggested that DNA electronic properties can be modified by molecular oxygen hole doping. To explore the possibility of controlling the electronic properties of DNA by oxygen doping, we have carried out *ab initio* electronic structure calculations of O_2-doped DNA systems. We have found that O_2 is weakly bonded to DNA with negligible charge transfer. The highest occupied molecular orbital-lowest unoccupied molecular orbital gap is much larger than the room temperature energy scale, k_BT, making it unlikely that O_2 can dope DNA. To explain the experimental results we suggest other possible underlying mechanisms and further experiments to test their validity.

DOI: 10.1103/PhysRevB.72.035441 PACS number(s): 73.63.−b, 87.14.Gg, 87.15.Aa

I. INTRODUCTION

The ability to engineer arbitrary sequences of DNA and place them between electrodes has given rise to the possibility of DNA based electronic devices. This has resulted in intensive efforts in experimental[1,2] and theoretical[3–9] work exploring the electronic properties of these systems. As DNA is at best semiconducting, due to a fully filled valence band, doping is essential from a device application point of view. A significant recent experiment showed that the conductance of DNA can be drastically modified upon exposure to molecular oxygen.[10] The conductance of PolyG-PolyC (*G-C*) increased by orders of magnitude while that of PolyA-PolyT (*A-T*) decreased by a smaller factor. These results were interpreted in terms of oxygen hole doping in which electrons are transferred from DNA to O_2. However, interpreting experimental measurements at the nanoscale level is difficult and can even be controversial.[11] This is because ambient conditions, intrinsic effects, and the location of the Fermi energy are notoriously difficult to determine. As a result there can be many possible explanations for the same experiment. It is the aim of this work to perform *first principle* analysis and investigate for the first time if oxygen can intrinsically dope DNA. We address the following questions: Can O_2 bind to DNA? How can O_2 affect the electronic properties of DNA? Where are the O_2 eigenstates with respect to the highest occupied molecular orbital lowest unoccupied molecular orbital (HOMO)-(LUMO) states of DNA? Can the results depend on the DNA-counterion environment?

To answer these questions we have performed structural, electronic, and transport calculations of an oxygen-doped DNA system. We have optimized the geometry of O_2 and counterions in the vicinity of B-DNA at the MP2 level. Following this we have simulated short double stranded DNA, 1–3 base pairs (BP), within B3LYP[12] density functional theory (DFT) to investigate the electronic properties of O_2 doped DNA. These calculations are performed within the GAUSSIAN98 (G98) framework,[13] and the 6-31*G* basis set was employed. Using DFT calculations, as a starting point, transport properties through longer strands consisting of *ten* BP, as well as 500 BP, were studied within the Landauer-Büttiker formalism.[14] Our results are presented in the rest of the paper, which is organized as follows: Initially we describe our model in Sec. II. In Sec. III we present our results for hydrogen terminated DNA as well as for full DNA system with Back-Bone (B-B) and counterions. Following this, we discuss our results and their relevance to the experiment in Sec. IV, and finally we give a brief conclusion.

II. METHODOLOGY

We have carried out simulations on O_2-doped dry DNA in the B-configuration. Our calculations are performed on both hydrogen terminated DNA as well as full DNA with counterions. At first, we present our methodology for a H-terminated system in detail. Calculations on full DNA follow a similar approach and will be briefly described.

Coordinates for double strand B-DNA are generated using the Nucleic Acid Builder (NAB) software package.[15,16] The B-B of the structure generated by NAB is replaced by hydrogen atoms [see Figs. 1(a) and 1(b)]. The position of the H atom terminating each basis at N5 is optimized at the MP2 level within GAUSSIAN98 framework.[13] Using this atomic configuration of DNA basis, we have optimized the position of the O_2 dimer in the triplet state while in close contact with DNA. To determine an initial configuration for the O_2 dimer in the vicinity of DNA, we have calculated the electrostatic potential due to bare DNA bases. We find low electrostatic potential near oxygen and N5 atoms of the DNA bases shown in Figs. 1(a) and 1(b). Since O_2 is electrophilic, it is expected to bond to electron dense regions, such as nitrogen lone pairs. Hence we choose the initial O_2 position to be close to the N5 atom of either purine and then search for the configuration with minimum energy at the MP2 level. Following this we have simulated short double stranded DNA (1–3 BP) within B3LYP[12] DFT to investigate the electronic properties of O_2-doped DNA. Our results presented in this paper are derived from calculations performed on *two* BP systems.

The self-consistent Hamiltonian of oxygen-doped *two* DNA BP, along with the overlap matrix, are determined using B3LYP DFT in the quintet state. To describe the *two* O_2

 ©2005 The American Physical Society

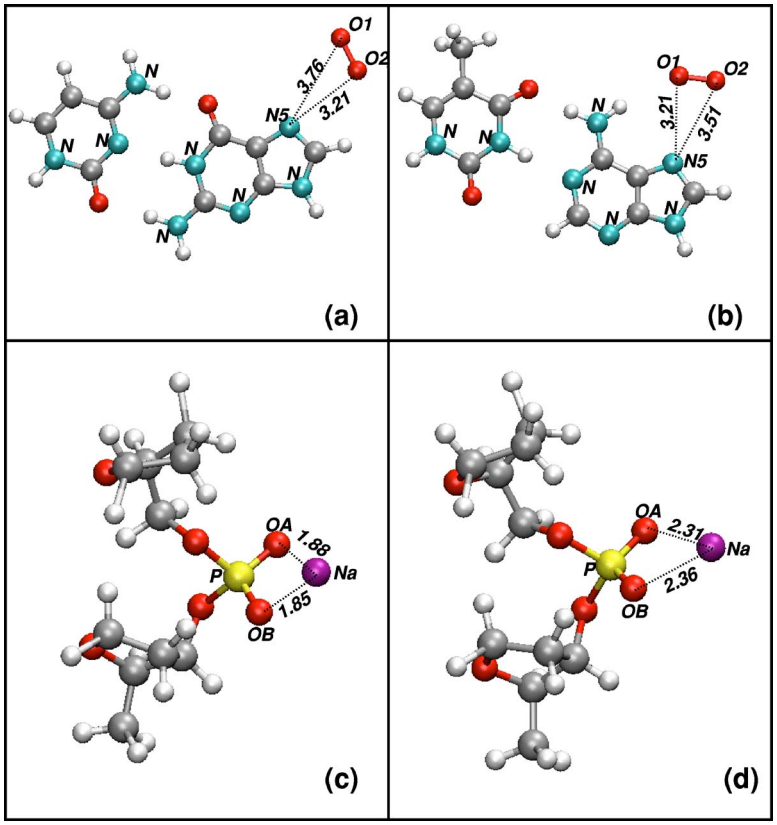


FIG. 1. (Color online) Atoms are either labeled or represented with a light gray color for H, dark gray for C, and black (or red) for oxygen. (a) and (b) show optimized structures of O_2 (O1, O2)-doped *G*-*C* and *A*-*T* base pairs with hydrogen termination, respectively. The nitrogen atom closest to O_2 dimer is labeled as *N*5. (c) The structure of the Na counterion near B-B (bases are removed) before optimization and (d) its equilibrium configuration.

dimers correctly, we use the unrestricted open shell scheme. This results in *two* Hamiltonians to describe electrons in the up (↑ spin) and down (↓ spin) states, referred to as $\mathbf{H}_\alpha$ and $\mathbf{H}_\beta$, where the α spin state has *four extra electrons*. The *ab initio* self-consistent Hamiltonians and overlap matrices are used to construct a *ten* BP system, in the B-DNA configuration, assuming nearest neighbor interaction between bases.[17] These results are further used to carry out transport calculations through O_2-doped DNA within the Landauer-Büttiker formalism.[14] However, we note that DNA-contact coupling is crucial and difficult to determine. Experimentally, it is also difficult to control this interaction. Hence we have parameterized the coupling strength, Γ, of the DNA bases at the ends to the contact.[18] We have simulated conductance calculations for different strengths ranging from 0.05 to 2.0 eV. In this regime, the results are qualitatively identical and we present results corresponding to $\Gamma=0.5$ eV.

Extensive calculations have also been carried out on a full DNA system to take into account the effect of B-B. Since the PO_4 group of DNA B-B is negatively charged, counterions are expected to be present in the vicinity of the phosphorus group. To model this system, we have considered H and Na as counterions. However, in this paper we focus on the Na results. Initially, we optimize the counterion positions by considering a single strand B-B structure with the sugar molecule terminated by a H atom, instead of being connected to a DNA basis. The initial configuration of such a system is shown in Fig. 1(c), and we fully relax the counterion at the MP2 level. Using the equilibrium configuration for the counterions with respect to the B-B and the position of O_2 dimers with respect to DNA bases, we generate a *two* BP structure of full DNA. The electronic and conductance calculations on this system are carried out following the same procedure described earlier for the H-terminated DNA. Now we present our results in detail and discuss the possibility of doping DNA with oxygen.

III. RESULTS

A. Results for H-terminated DNA

The final optimized structure of O_2 dimer in the triplet state, while in close contact to DNA bases, is shown in Figs. 1(a) and 1(b). The separation distance between O_2 and *N*5 on the DNA bases is 3.2–3.8 Å. This configuration indicates that O_2 is weakly bonded (physisorbed) to the DNA. Charge transfer between O_2 and DNA is also found to be insignificant ($<0.01e$). This has resulted in small binding energy at the MP2 level, which is ~50 and ~70 meV for O_2 in the vicinity of *G*-*C* and *A*-*T*, respectively.

To search for other possible minimum energy configurations for O_2 in the vicinity of DNA and to confirm that indeed this is the "global" minimum, we have relaxed various structures of O_2 dimer surrounding a two BP of *G*-*C* and *A*-*T* DNA with B-B and H as a counterion at the PM3 level.[19] Starting from 14 different initial conditions: *six* in the major groove, *six* in the minor groove, and *two* outside the DNA and close to B-B, O_2 is fully relaxed. Following this, single point energy calculations at the DFT level are carried out on the lowest energy configuration of each path. These results indicated that indeed the O_2 configuration, close to *N*5 and presented in Figs. 1(a) and 1(b), has the lowest total energy.

Using this optimized geometry of DNA with O_2, we have

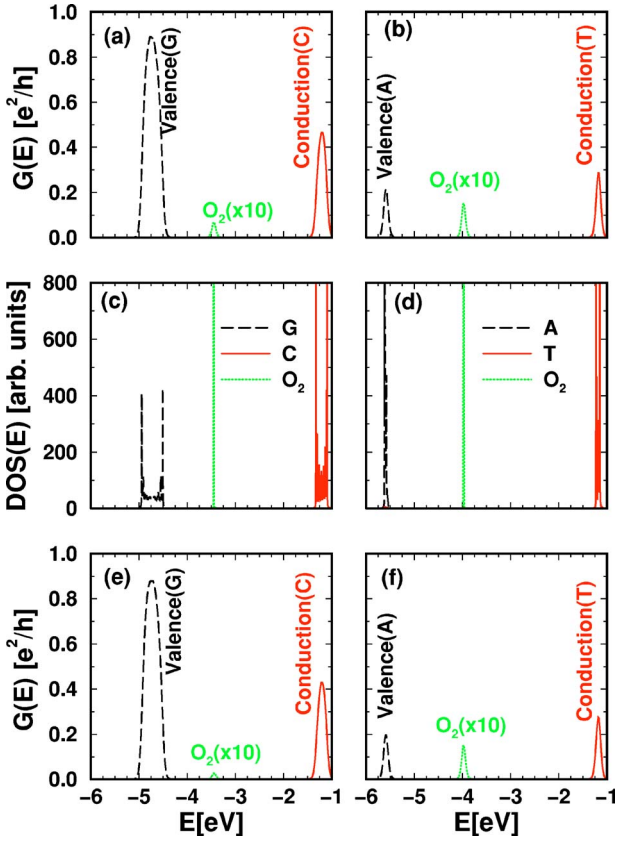


FIG. 2. (Color online) Conductance (calculated at 300 K) and DOS (arbitrary units) of *ten* base pairs of oxygen-doped *G-C* [(a) and (c)] and *A-T* [(b) and (d)]. (e) and (f) are conductance results for 500 base pairs (~169 nm long) of oxygen-doped *G-C* and *A-T*, respectively. Transport through HOMO (LUMO+1) is carried along *G* (*C*) in (a), (c), and (e) and *A* (*T*) in (b), (d), and (f) bases of DNA. Transport through O_2 is magnified by a factor of 10 in (a), (b), (e), and (f) for clarity. The essential point here is that the O_2 level is separated from the valence band (residing on *G* and *A*) by more than $10k_BT$, and hence cannot dope DNA at room temperature.

constructed a *two* BP system and determined the self-consistent Hamiltonian and the overlap matrix within the unrestricted open shell scheme. Analysis of the eigenvalues (orbital energies) of $\mathbf{H}_\alpha$ and $\mathbf{H}_\beta$ show that the HOMO (valence band) and LUMO (conduction band) levels lie on purine and O_2 in the β configuration, respectively. The HOMO level and the lowest unoccupied level primarily residing on the DNA are approximately the same in both α and β matrices. Hence we will present our results for $\mathbf{H}_\beta$ and they are almost indistinguishable from $\mathbf{H}_\alpha$, except for O_2 LUMO level. In Fig. 2 we show the conductance and density of states (DOS) of O_2-doped *G-C* and *A-T* systems at energies in the HOMO-LUMO vicinity. The HOMO (LUMO+1) level is pure *G* (*C*) for *G-C* and *A* (*T*) for *A-T*. Doped DNA has a new transport state due to O_2 dimers, at ~−3.5 eV for *G-C* and ~−4.0 eV for *A-T*. The band width of this state is only ~35 meV because of weak coupling between O_2 on subsequent base pairs. We have also found that the rotational barrier for O_2 bonded to DNA is smaller than k_BT, which will introduce further scattering to charge transport. Hence we expect transport along O_2 to be unimportant. DNA length effect on transport results has also been verified by repeating the same calculations on a DNA system consisting of 500 BP (~169 nm in length) and conductance is presented in Figs. 2(e) and 2(f). It is clear that these calculations are in qualitative as well as quantitative agreement with Figs. 2(a) and 2(b).

Now we would like to address the possibility of *p*-type/*n*-type doped *G-C*/*A-T* DNA in an O_2 environment. Can the new O_2 state act as a dopant level? Our analysis showed clearly that O_2 is weakly coupled to DNA and that charge transfer between O_2 and DNA is negligible, suggesting that doping is unlikely to occur in these systems. In addition to this, in the semiconductor picture,[20] dopant levels should be within a few k_BT away from the valence (conduction) band for *p*-type (*n*-type) semiconductors. In our calculations, the O_2 state is found at ~1.0 and ~1.5 eV (~2.2 and ~2.7 eV), above (below) the HOMO (LUMO) level of bare *G-C* and *A-T*, respectively. This energy difference is much larger than the room temperature energy scale, $k_BT \sim 26$ meV. This again strongly suggests the absence of intrinsic doping of DNA by O_2.

We note that these results are based on a hydrogen terminated DNA model, where B-B and counterions are neglected. To overcome this issue, we present in the following section our calculations on the full DNA model, which take into account the B-B and counterions effects.

B. Results for full DNA system

Counterion effect has been investigated for both H and Na. However, in this paper we focus on the Na results. The initial configuration of Na in the vicinity of a PO_4 group is shown in Fig. 1(c). We fully relax the counterion at the MP2 level. The final equilibrium configuration of the Na counterion is roughly symmetric with respect to oxygen atoms (*OA* and *OB*), as shown in Fig. 1(d). However, we note that for the H counterion, we find two equilibrium configurations. They correspond to one local minimum and one global minimum in which H is close to *OA* and to *OB*, respectively.

Using the equilibrium configuration of Na counterions in the vicinity of B-B and the same positions of O_2 dimers with respect to DNA bases, we generate *two* BP structures of the oxygen-doped full DNA system and determine its electronic properties. Our conductance calculations, performed for these systems, follow the same procedure described earlier for the H-terminated DNA structure. Conductance results for *G-C* and *A-T*, with Na counterions are shown in Fig. 3. We first note that in the full DNA system, B-B and Na counterions introduce new states whose band width is ~200 meV in the HOMO-LUMO gap of the corresponding H-terminated DNA. These results are consistent with earlier calculations.[7,8,17] We have also checked that these states have $NaPO_4$ character. Hence the corresponding current carrying state is formed along the DNA helix and its path is substantially different from states extended over purines and/or pyrimidines. However, the consequence of oxygen doping on the full DNA system is similar to its effect on the H-terminated DNA model. The O_2 dimers introduce new

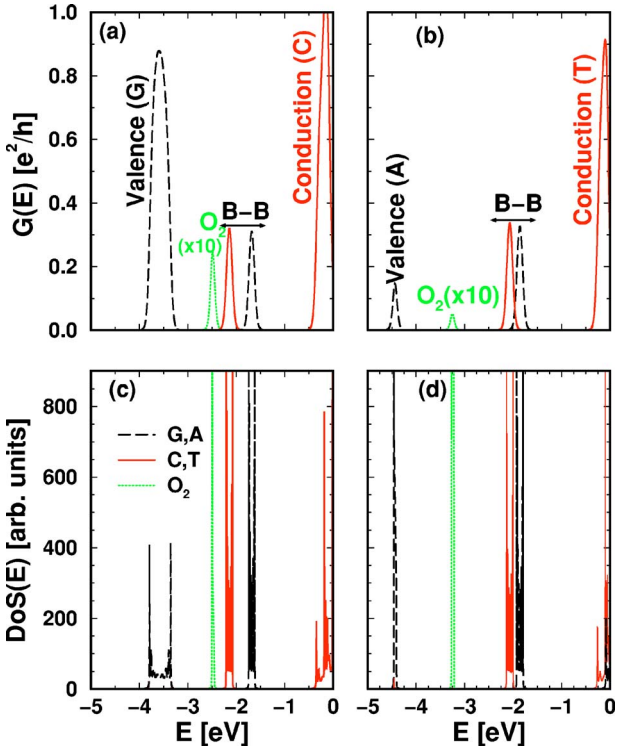


FIG. 3. (Color online) Conductance (calculated at 300 K) and DOS of *G-C* and *A-T* DNA with Na counterions. We use the same representation as Fig. 2. The new states occurring at $E \sim -2.0$ eV and indicated by B-B have $NaPO_2$ character. While the counterions decrease the energy separation between the O_2 levels and the valence band, the energy separation with counterions is still too large to dope DNA.

states in the HOMO-LUMO gap. These states are ~0.8 eV (~1.1 eV) above the HOMO state of *G-C* (*A-T*). While this is smaller than the gap found in the H terminated case, the energy scale is still too large to enable doping of DNA at room temperature.

IV. DISCUSSION

Our structural relaxation of O_2 at the MP2 level shows very weak bonding between O_2 and DNA. In addition to this, electronic properties calculations within B3LYP DFT indicate that the HOMO-LUMO gap of the O_2-doped DNA system is much larger than k_BT. The energy gaps for various systems are summarized in Table I. Although this gap depends on the counterion, it is always greater than 800 meV. Due to this large energy gap and small charge transfer, arising from the weak bond between DNA and O_2, intrinsic oxygen doping of DNA is impossible within our model. However, before describing the possible underlying mechanisms for the experimental results we will discuss the limitations of our model and possible effects on our results.

We first note that we have disregarded the presence of hydration shells while determining the effect of oxygen doping of DNA. Such a model simplification is performed because: (i) the orientation and optimum number of water molecules on dry DNA is still an unresolved topic and needs further attention, (ii) water molecules do not interact strongly with either DNA and/or O_2, hence water is not expected to influence doping effects, and (iii) our calculations are performed at the MP2 level with an open shell scheme to accurately model the interaction of DNA and O_2, as a result we cannot simulate large system sizes that include water molecules. The second limitation of our *first principles* approach is due to kinetic effects and long range van der Waals interactions, which cannot be fully incorporated. To overcome this limitation, we have displaced the O_2 dimer from its equilibrium position and performed single point energy calculations at different configurations, such that total energy increases by <100 meV. The smallest HOMO-LUMO gap, found from various higher energy configurations of O_2 in the vicinity of DNA, is 689 (968) meV for *G-C*(*A-T*), which is still much larger than room temperature thermal energy.

TABLE I. Energy gap, ΔE (eV), between the O_2 LUMO state and HOMO state localized on nearest purine. *Two*-bases results are obtained from G98 and *ten*-bases gap is calculated from the constructed Hamiltonian of the system, as described in the text. H term, Full+H, and Full+Na stand for hydrogen terminated, full DNA with H counterion, and full DNA with Na counterion. Note that ΔE is environment dependent but always much larger than k_BT.

System	ΔE (*two* bases)	ΔE (*ten* bases)
G-C (H term)	1.24	1.02
G-C (Full+H)	1.38	1.18
G-C (Full+Na)	1.05	0.82
A-T (H term)	1.59	1.54
A-T (Full+H)	1.59	1.42
A-T (Full+Na)	1.21	1.13

Our analysis indicates clearly that O_2 cannot intrinsically dope DNA. Determining the exact underlying mechanism for the experimental behavior is not possible at this stage, due to lack of information on the experimental details. Hence we attempt to give possible explanations and suggest further experiments to pin down the origin of this behavior.

Impurities, doping, and defects surrounding and/or within DNA can result in completely different electronic properties and hence would change the O_2 binding energy to DNA and its charge transfer. Doping DNA with iodine molecules, for example, is found by the same group of this experimental work[10] to substantially effect its electronic transport characteristics.[21] However, it is possible to eliminate these effects from the experiment and transport measurement could be carried out through an ideal system. The experimental results of Ref. 10 can also be related to contact doping.[22,23] In this regime, O_2 increases the work function of gold by more than 0.1 eV and hence changes the alignment of Fermi energy (E_F) with respect to valence-conduction bands. Such a possible scenario to interpret the experimental measurements is the focus of the rest of our paper.

In the experiment of Ref. 10, the distance between the contacts (100–200 nm) is smaller than DNA screening length,[24] and E_F of the *unoxygenated* Au contact is closer to the valence and conduction bands for *G-C* and *A-T*, respectively, consistent with the experimental work of Ref. 2. The

origin of this E_F alignment can be due to impurity effects and/or the ionization potential (IP) difference. While the former effect is an extrinsic property and can be controlled by the dopant properties, the IP difference between *G-C* and *A-T* is an intrinsic character of DNA.[25] Theoretical calculations[6,26,27] performed on short DNA strands, using different models, have determined the IP of *G-C* to be at least 500 meV smaller than the IP of *A-T*. Based on these assumptions, a band diagram could be deduced for both *G-C* and *A-T* sandwiched between Au contacts. Upon contact oxygenation, the hole barrier ($q\Phi_h$) for *G-C* decreases and hence current is enhanced. However, the electron barrier ($q\Phi_e$) for *A-T* increases and conductance decreases. Although this model describes the experimental results of Ref. 10, the barrier can either be bulk-type for $IP_{\mathrm{DNA}} < IP_{\mathrm{Au}}$ or Schottky barrier[22,23] at the DNA-Au contact region for $IP_{\mathrm{DNA}} > IP_{\mathrm{Au}}$. To test our interpretation experimentally, transport measurements need to be carried out when the distance between the electrodes is longer than DNA screening length. The bulk-type barrier height remains unchanged upon oxygenation for long strands (a direct result of charge neutrality in the bulk), and so the conductance does not change. However, if the barrier is Schottky-type, its height decreases for $q\Phi_h$ (and increases for $q\Phi_e$) upon oxygenation and is independent from length. In this regime, a further experiment needs to be performed. Negative gate voltage could be applied to deplete the Schottky barrier and hence current through this gated device will not be modified upon oxygenation.

Finally we note that these suggested experiments serve as an important test to validate our interpretations. However, they can also be used as a tool to determine the IP of DNA with respect to contacts, $\mathrm{IP}_{\mathrm{DNA}} < (>) \mathrm{IP}_{\mathrm{contact}}$ for bulk (Schottky) barrier.

V. CONCLUSION

We find that O_2 cannot intrinsically dope DNA. This result is based on the extensive *ab initio* calculations presented, which show that the HOMO-LUMO gap is much larger than room temperature energy scale, k_BT. Further, we also find that O_2 is weakly bonded to DNA with negligible charge transfer. While intrinsic doping of DNA with oxygen is impossible, we presented other possible explanations for the experiment of Ref. 10, which observed a large change in DNA conductance upon oxygenation.

ACKNOWLEDGMENTS

We acknowledge useful discussions with A. Ricca and T. Yamada on oxygen doping of a carbon nanotube, and with Ch. Bauschlicher on computational issues. H.M. and S.P.W. were supported by a NASA contract to ELORET. M.P.A. was supported by a NASA contract to UARC, UCSC. H.M. also thanks NSERC of Canada for support.

*Also at ELORET, Mail Stop 229-1, Moffett Field, CA 94035.
†Present address: Department of Mechanical Engineering, Terman Engineering, Room 557, Stanford University, Stanford, CA 94305.
‡Also at UARC-UCSC, Mail Stop 229-1, Moffett Field, CA 94035.

[1] H. W. Fink and C. Schönenberger, Nature (London) **398**, 407 (1999); D. Porath, A. Bezryadin, S. de Vries, and C. Dekker, *ibid.* **403**, 635 (2000); P. J. de Pablo, F. Moreno-Herrero, J. Colchero, J. Gómez Herrero, P. Herrero, A. M. Baró, Pablo Ordejón, José M. Soler, and Emilio Artacho, Phys. Rev. Lett. **85**, 4992 (2000).
[2] K.-H. Yoo, D. H. Ha, J.-O. Lee, J. W. Park, Jinhee Kim, J. J. Kim, H.-Y. Lee, T. Kawai, and Han Yong Choi, Phys. Rev. Lett. **87**, 198102 (2001).
[3] B. Gazdi, M. Seel, and J. Ladik, Chem. Phys. **86**, 41 (1984).
[4] Y. J. Ye and L. L. Shen, J. Comput. Chem. **21**, 1109 (2000).
[5] Y. A. Berlin, A. L. Burin, and M. A. Ratner, J. Phys. Chem. A **104**, 443 (2000); D. M. Basko and E. M. Conwell, Phys. Rev. Lett. **88**, 098102 (2002).
[6] R. N. Barnett, C. L. Cleveland, A. Joy, U. Landman, and G. B. Schuster, Science **294**, 567 (2001).
[7] R. N. Barnett, C. L. Cleveland, U. Landman, E. Boone, S. Kanvah, and G. B. Schuster, J. Phys. Chem. A **107**, 3525 (2003).
[8] Francesco Luigi Gervasio, Paolo Carloni, and Michele Parrinello, Phys. Rev. Lett. **89**, 108102 (2002).
[9] Yu Zhu, Chao-Cheng Kaun, and Hong Guo, Phys. Rev. B **69**, 245112 (2004).
[10] Hea-Yeon Lee, Hidekazu Tanaka, Yoichi Otsuka, Kyung-Hwa Yoo, Jeong-O Lee, and Tomoji Kawai, Appl. Phys. Lett. **80**, 1670 (2002).
[11] H. Mehrez and Hong Guo, in *Nanowires and Nonobelts* (Kluwer Academic Publishers, Netherlands, 2003).
[12] A. D. Becke, J. Chem. Phys. **98**, 5648 (1993); J. A. Pople, M. Head-Gordon, D. J. Fox, K. Raghavachari, and L. A. Curtiss, *ibid.* **90**, 5622 (1989); L. A. Curtiss, C. Jones, G. W. Trucks, K. Raghavachari, and J. A. Pople, *ibid.* **93**, 2537 (1990).
[13] GAUSSIAN 98 (Revision A.7), M. J. Frisch *et al.*, Gaussian, Inc., Pittsburgh, PA, 1998.
[14] R. Landauer, IBM J. Res. Dev. **1**, 223 (1957); M. Büttiker, *ibid.* **32**, 317 (1988), S. Datta, *Electronic Transport in Mesescopic Systems* (Cambridge University Press, New York, 1995).
[15] NAB program (Version 4.5), Tom Macke, W. A. Svrcek-Seiler, and David A. Case. In NAB program, the atomic position of B-DNA structure is based on x-ray diffraction data information to a resolution of ~2 Å, where heavy atoms are already tabulated in Ref. 16. Hydrogen atoms are added to the system based on AMBER94 force field.
[16] S. Arnott, P. J. Campbell-Smith, and R. Chandrasekaran, in *Handbook of Biochemistry and Molecular Biology*, 3rd ed., *Nucleic Acids V. II* edited by G. P. Fasman (CRC Press, Cleveland, 1976), p. 411.
[17] Ch. Adessi, S. Walch, and M. P. Anantram, Phys. Rev. B **67**, 081405(R) (2003).
[18] H. Mehrez and M. P. Anantram, Phys. Rev. B **71**, 115405 (2005).
[19] J. J. P. Stewart, J. Comput. Chem. **10**, 209 (1989).
[20] S. M. Sze, *Physics of Semiconductor Devices*, 2nd ed. (Wiley,

New York, 1981).
[21] M. Taniguchi, H. Y. Lee, H. Tanaka, and T. Kawai, Jpn. J. Appl. Phys., Part 2 **42**, L215 (2003).
[22] Xiaodong Cui, Marcus Freitag, Richard Martel, Louis Brus, and Phaedon Avouris, Nano Lett. **3**, 783 (2003).
[23] S. Heinze, J. Tersoff, R. Martel, V. Derycke, J. Appenzeller, and Ph. Avouris, Phys. Rev. Lett. **89**, 106801 (2002).
[24] Typical screening length in semiconducting carbon nanotubes is found to be more than a micron in the undoped case [François Léonard and J. Tersoff, Phys. Rev. Lett. **83**, 5174 (1999); *ibid.* **89**, 179902(E) (2002)], and DNA is more insulating.
[25] Note that even though the IP of DNA depends strongly on the model, counter ion, and hydration level (Refs. 6 and 7), it is found that the IP of *G-C* is smaller than the IP of *A-T* within the same conditions. This IP difference results in Au Fermi energy alignment which is closer to (farther from) the valence (conduction) band of *G-C* compared to *A-T*.
[26] A. A. Voityuk, J. Jortner, M. Bixon, and N. Rosch, Chem. Phys. Lett. **324**, 430 (2000).
[27] Stephen P. Walch, Chem. Phys. Lett. **374**, 496 (2003).