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Charge Control in a Model Biphenyl Molecular Transistor

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ABSTRACT. We study charge control in a gated $4,4'$-biphenyl diradical molecular transistor using *ab-initio* density-functional theory calculations. I-V curves and intrinsic gate capacitances were derived. We find charge control in this transistor to be strongly affected by polarization of the σ-states of the molecule, leading to strong electrostatic coupling of the internal potentials to the source and drain electrodes, and relatively weak coupling to the gate. We suggest that this spatially dependent and anisotropic polarization is an essential element in the operation of molecular transistors.

Conceptually, the molecular transistor has been approached much as an ordinary transistor where the function of the gate voltage is to translate some internal conducting states, e.g. band edges in an

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ordinary FET or resonant energy levels in a resonant tunneling transistor[1], with respect to the source and drain Fermi levels. The present work attempts to examine some of the assumptions of those treatments by using a more realistic model which is capable of solving *ab initio* the quantum transport problem posed by a small organic molecule in contact with source and drain electrodes, and in close proximity to a gate electrode.[2] The molecule we choose here as an example is $4,4'$-biphenyl diradical (biphenyl molecule with hydrogens removed from the 4 and $4'$ carbons[3]), which we will refer to as BPH. For purposes of our calculation, we take the two benzene rings to be co-planar[4], and we assume that the geometry is field-independent. Despite these approximations, our approach takes into account a number of aspects not included in the simpler models, such as the non-rigid shift of the energy levels, and the dependence of the level widths on gate voltage. Another aspect found to be important is the charge redistribution in the molecule caused by polarization of the deeper energy states. Usually only the π states of our molecule are assumed to participate in transport and charge control, since the deeper-lying σ states are completely filled. However, these σ states, which extend throughout the molecule, are easily polarizable, and we will show that they play a significant role in determining the potential distribution within the molecule.

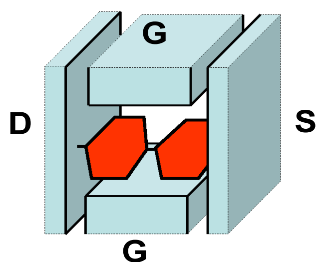

Fig 1. The BPH molecule is inserted between two metallic contacts (S & D) and gates are placed above and below it, with an inter-gate distance of 12.4 *b* (1*b*=0.053nm).

The configuration we want to consider is shown in Fig. 1. The left and right electrodes are semi-infinite, and are represented using the uniform-background model.[5,6] The gates are treated as equipotential slabs having no interaction with the molecule other than electrostatic.[7] With this geometry we expect relatively good electrostatic control by the gate. The energy levels, charge distribution and current are determined as a function of gate and drain voltage[8]; the structure of the density-functional calculation used is described in Ref. 9.

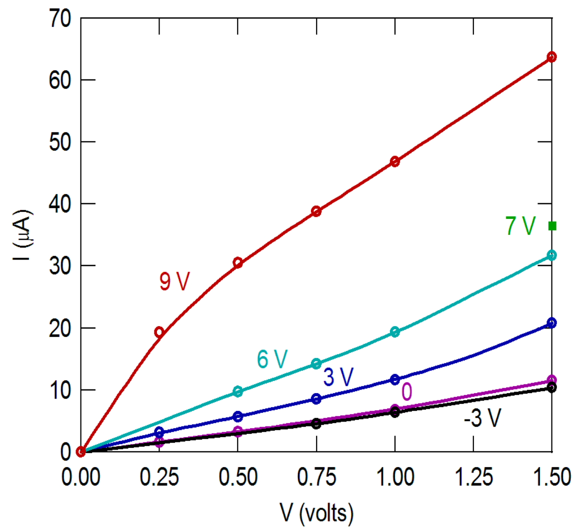

Fig. 2. Drain current vs. drain voltage at indicated gate voltages.

In contrast to our expectations, the I-V curves in Fig. 2, up to gate voltage $V_G = 6V$, do not show the saturation usually seen with macroscopic FET's, and exhibit poor control by the gate compared with the drain. This improves markedly at $V_G = 9V$, but in this case the gate voltage is large enough to create a sufficient potential depression near the gates[10] such that the conduction is in part through these regions rather than through the molecule.

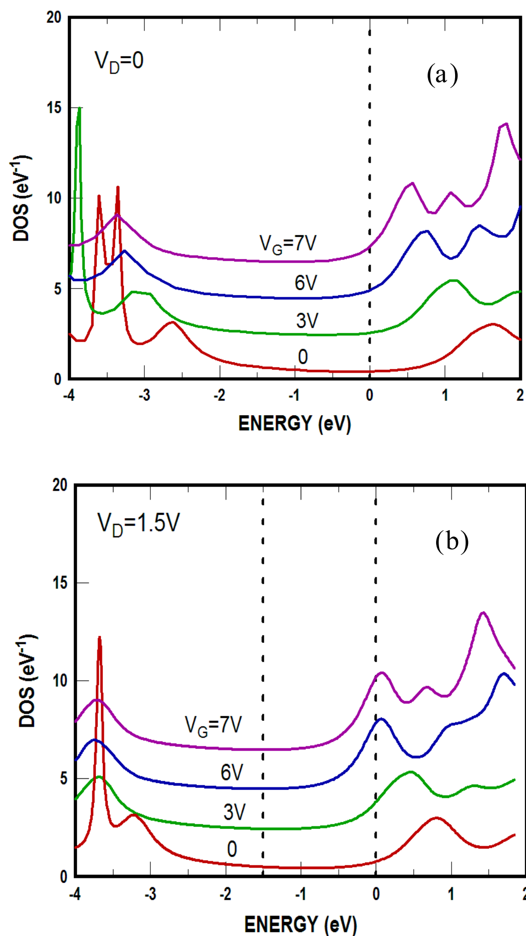

Fig 3. Total density of states near the Fermi level at (a) V_D=0 and (b) V_D=1.5V.Gate voltages are as indicated. Vertical dashed lines represent the source and drain Fermi levels. Curves are offset vertically for clarity.

The total DOS [11] vs. gate and drain voltage is shown in Fig. 3. We do not show the 9V curve here or in subsequent figures. The states shift with gate and drain voltage roughly as predicted by the simple model of Ref. 1, which we will refer to as the SK model, in that the unperturbed energy levels (V_D=V_G=0) are pulled down approximately by about half the drain voltage and a fraction of the gate voltage. Conduction occurs for positive gate bias as the LUMO levels are pulled down to the source Fermi level, and the scale of the conductance is of the order of the quantum of conductance. The I-V curves predicted by the SK model, based on our total DOS as in Fig. 3, differ from the present set in some important respects. The maximum SK currents were higher than the present simulations due to the SK assumption of unity transmission coefficients, and the SK results for negative V_G were higher than our simulations due to the overestimation of the importance of the gap states. While not being the subject of this work, it is important to note the difference between total state density and density of current-carrying states, with the latter only including states which connect the source with the drain.

Table I. Intrinsic Gate Capacitance (e/V)

	V_G=0 to 3V	**3 to 6V**	**6 to 7V**
V_D = 0	.090	.125	.126
V_D = 1.5V	.087	.129	.182

The intrinsic gate capacitance was evaluated by integrating the charge on the surface of the gate facing the molecule, and subtracting that for the no-molecule case; the result is shown in Table I. As a reference, the parallel-plate vacuum capacitance of a conducting plate of 10x15b^2 placed midway between the two gates is 0.14 *e*/*V*. We see that the gate capacitance can best be represented by a simple vacuum gap! The larger capacitance, when both gate and drain voltages are high (bottom right cell in Table) is because, aided by both gate and drain voltage, extra charge is induced near the gate (see also Fig. 7b). The intrinsic switching delay calculated from $C_G dV_G / dI_D$ is ~ 4fs although the capacitance, of course, will be dominated by the parasitics.

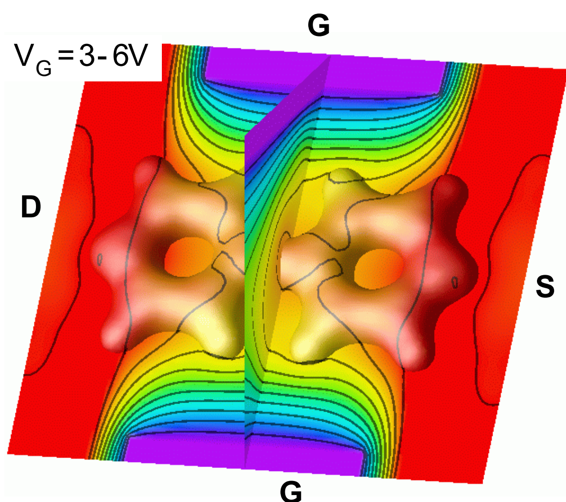

Fig. 4. Change in spatial electrostatic potential, normalized to change in gate voltage, in contours of {0 0.1 0.2 …1} at V_D=0, for V_G changing from 3 to 6V. The potentials are mapped onto symmetry planes, and onto an isosurface, representing the molecule, at an electron density of 0.1 e/b^3.

We attempt to understand more fully the source of the screening of the gate voltage. The simplest situation is when zero drain bias is applied so that the molecule is in thermal equilibrium, since quantum-mechanical interactions with the gate are not included in our model. Fig 4 shows a perspective view of our molecule where potential contours are mapped onto planes in and perpendicular to the plane of the molecule, and also onto an envelope of the molecule given by a charge density of 0.1e/b^3 (1 b = 0.053*nm*). Compared with the case where there is no molecule (not shown) the potential is very well screened in the plane of the molecule, about 5x better than when no molecule is present.

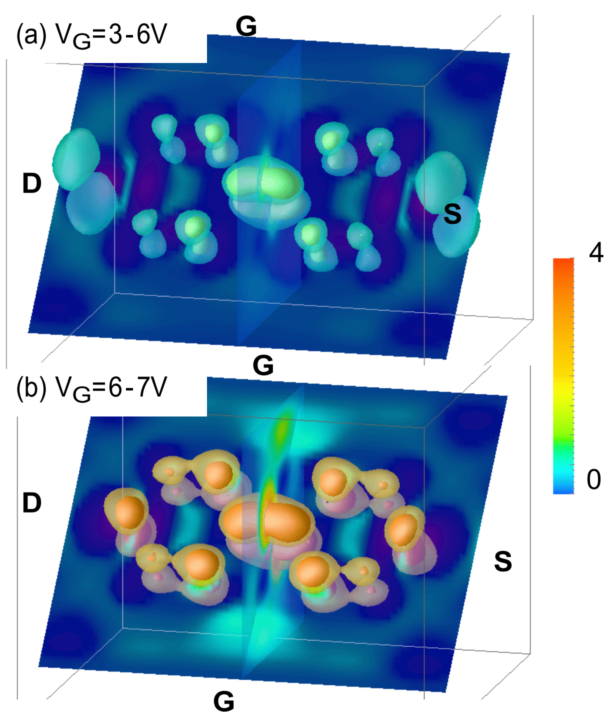

Fig. 5. Conduction charge isosurfaces for low gate voltages (a) and high gate voltages (b). The values of the isosurfaces are {0.05, 0.1} (a) and {2, 4} for (b) in units of 10^{-4} e/b^3–V. Scale is in units of 10^{-4} e/b^3–*V.*

To cause such strong screening, substantial charge dipoles are set up, in response to the gate voltage, between the center of the molecule and the contacts. The magnitude of the dipole, per unit change in gate voltage, was observed not to be strongly dependent on the gate voltage. [10] This dipole could result either from injection from the contacts or from polarization of the deeper molecular states. To separate these effects, we first plot the change of charge within 1 eV of the Fermi level (at $V_D = 0$); this will be called the conduction charge. (Our procedure is not as arbitrary as the '1 eV band' might suggest, since we are at the edge of the LUMO resonance (see Fig. 3) where the lower bound of the integral is not critical.) The results, normalized to the change in gate voltage, are shown in Fig. 5, where it is seen that the conduction charge is localized in the π states (off-plane) of the molecule and the injection increases strongly with gate voltage.

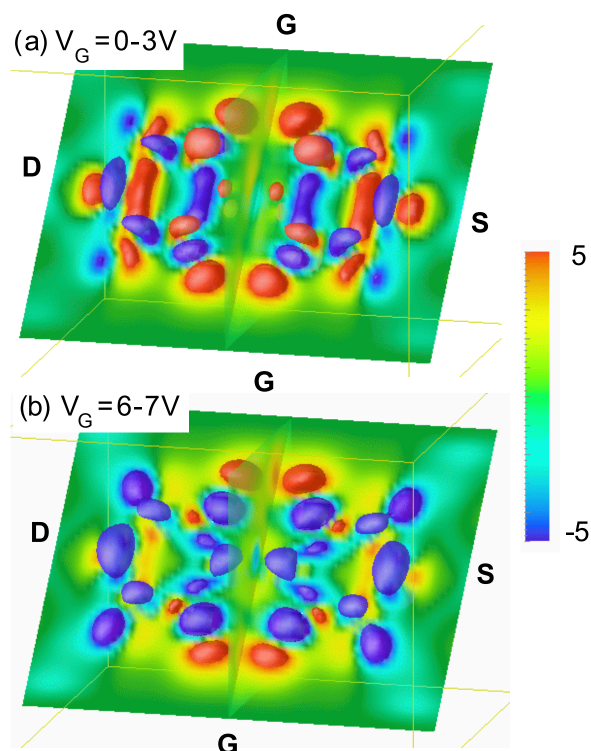

Fig. 6. Polarization charge isosurfaces, per unit gate voltage change, for low gate voltages (a) and high gate voltages (b). The values of the isosurfaces are $\pm 5\times10^{-4}$ e/b^3–V.

The polarization charge is defined as the difference between the total charge and the conduction charge, and is plotted in Fig. 6 at high and low gate bias. The polarization charge distribution is characteristic of the σ states of the molecule (in the plane), and shows a characteristic dipolar pattern at low gate bias. At high gate bias, the pattern shifts to a net deficit over the plane. The polarization

therefore adjusts itself to compensate for the increase in conduction charge, which is why the gate capacitance is relatively independent of gate voltage.

At a large drain bias ($V_D = 1.5V$) it is not easy to separate the charge components in this way, and instead we look at changes in the charge distribution, with gate voltage, in a narrow energy strip close to the source and drain Fermi levels. The change in charge near the drain Fermi level is uninteresting because there is little charge injection from the drain over this voltage range (see Fig. 3b). The results for source injection are shown in Fig. 7. At low gate bias (Fig. 7a), the two halves of the molecule seem to act independently (as also confirmed by looking at the potential), while at high gate bias, charge from the source is injected throughout the molecule. Extra charge injection is also seen near the gate , as indicated by the arrow.

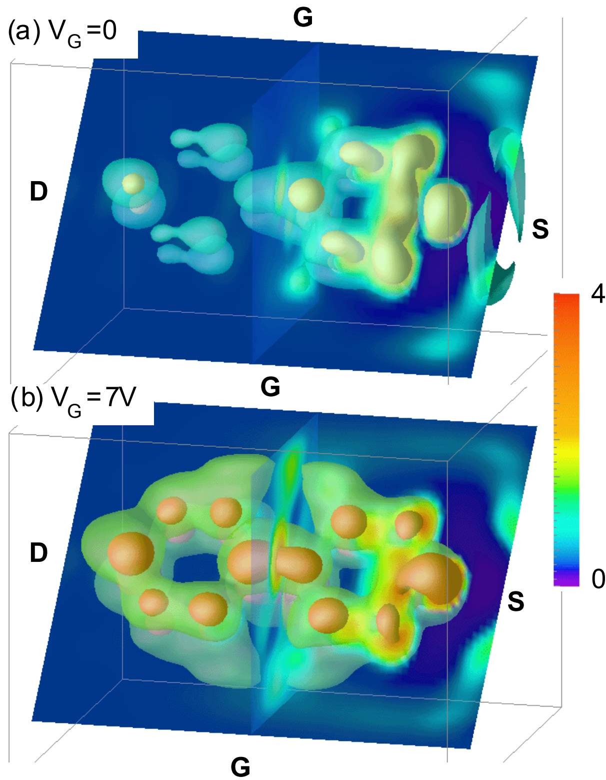

Fig. 7. Charge within 1meV of source Fermi-level, at V_D=1.5V, and V_G = 0 (a) and 7V (b). The values of the isosurfaces are {0.05, 0.2} (a) and {1, 4} for (b) in units of 10^{-3} e/b^3–eV. Scale is in units of 10^{-3} e/b^3–eV.

The large gate voltages required to turn on our molecular transistor are a direct consequence of the strong screening in the plane of the molecule. In effect we have here a plane of high permittivity (the molecule) separated from the gate by a vacuum dielectric. This is in strong contrast to models such as SK[1], where a uniform permittivity was assumed for the inter-gate region. This anisotropic and spatially

varying permittivity also has a deleterious effect on the output conductance and voltage gain of the transistor, since it enhances coupling to the drain at the expense of the gate.

We further investigated the in-plane polarizability by applying a constant field (0.33*V*/*b*) to an isolated BPH molecule, in the direction of the long axis, resulting in a dipole moment of 4.9 *a.u*. The internal field was reduced by a factor of ~15x. The high and anisotropic polarizability of the linear oligophenylene molecules is well known[12], since they form the basis for liquid-crystal displays, yet this fact seems not to be widely appreciated in discussions of molecular transistors.

Having achieved greater understanding of the charge control process within a molecular transistor, how might one engineer a better transistor? The voltage gain of a transistor is given by the electrostatic coupling ratio of the gate vs. drain to the control region of the transistor. Identifying the control region with the central region of our molecule, we see that the long-range polarizability along the chains is a disadvantage when it couples the drain more strongly to this region. Possibly that may be turned into an advantage if it is used to couple the gate to this central region. The engineering of molecular transistors is in its infancy, and as we have shown, there are many interesting pitfalls and opportunities.

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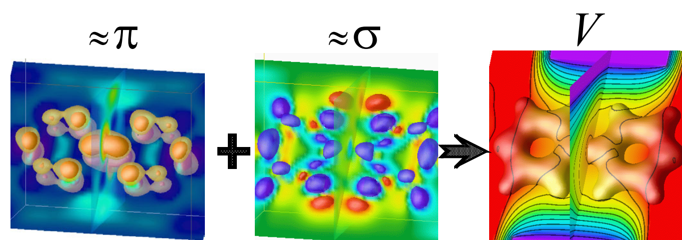

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[1] Solomon, P.; Kagan, C. R. in *Future Trends in Microelectronics: The Nano, the Giga, and the Ultra*; Luryi, S., Xu, J., Zaslavsky, A., Eds.; Wiley: New York, 2004; p. 168.

[2] Other recent discussions of this have been given by Ghosh, A. W.; Rakshit, T.; Datta, S. *Nano Lett.* **2004**, *4*, 565. Di Ventra, M.; Pantelides, S. T.; Lang, N. D. *Appl.Phys. Lett.* **2000**, *76*, 3448. Lang, N. D. *Phys. Rev. B* **2001**, *64,* 235121. Yang, Y.; Lang, N. D.; Di Ventra, M. *Appl. Phys. Lett.* **2003**, *82*, 1938. Experimental studies of gating of carbon nanotubes are given e.g. by Lin, Y.-M.; Appenzeller, J.; Avouris, Ph. *Nano Lett.* **2004**, *4*, 947. Javey, A.; Guo, J.; Farmer, D. B.; Wang, Q.; Wang, D.; Gordon, R. G.; Lundstrom, M.; Dai, H. *Nano Lett.* **2004**, *4*, 447. Biercuk, M. J.; Mason, N.; Marcus, C. M. *Nano Lett.* **2004**, *4*, 1. Li, S.; Yu, Z.; Yen, S.-F.; Tang, W. C.; Burke, P. J. *Nano Lett.* **2004**, *4*, 753. Martel, R.; Schmidt, T.; Shea, H. R.; Hertel, T.; Avouris, Ph. *Appl. Phys. Lett.* **1998**, *73*, 2447. Tans, S.; Verschueren, A.; Dekker, C. *Nature (London)* **1998**, *393*, 49

[3] These H atoms are expected to be removed when the molecule bonds to a metal.

[4] It has been shown by Baudour, J. L. [*Acta Cryst. B* **1991**, *47*, 935] that in solid biphenyl, the equilibrium configuration has a twist angle of 13.3° between the two carbon rings, but that at room temperature, the average configuration is planar. For the gas phase, electron diffraction measurements [Almenningen, A.; et al. *J. Mol. Struct.* **1985**, *128*, 59] show a twist angle of 44.4°. Ronald Breslow (private communication) has pointed out that another way to ensure that the rings are in fact co-planar is to consider instead dihydrophenanthrene.

[5] This model is described by e.g. Lang, N. D. in *Theory of the Inhomogeneous Electron Gas*; Lundqvist, S., March, N. H., Eds.; Plenum Press: New York, 1983; p. 309. We take $r_s = 2\,b$, typical of a high-electron-density metal, where $(4/3)\pi r_s^3 \equiv n^{-1}$, with n the mean interior electron number density in the metal.

[6] The various bond distances used are given in reference 16 of Lang, N. D.; Avouris, Ph. *Phys. Rev. B* **2001**, *64*, 125323.

[7] The separation of the two electrodes that comprise the gate was taken to be 12.4 *b*; the width of the electrodes was taken to be 9.85 *b*.

[8] Following common usage, drain and gate voltage, V_D or V_G, are referenced to the source.

[9] Lang, N. D. *Phys. Rev. B* **1995**, *52*, 5335. Di Ventra, M.; Lang, N. D. *Phys. Rev. B* **2002**, *65*, 045402.

[10] This was seen clearly in figures showing changes in the spatial distribution of total charge in response to changes in gate voltage. These figures are not reproduced here for lack of space.

[11] By state density we mean the difference in density of energy eigenstates between two systems: the electrodes together with the molecule, and the same electrodes (with the same spacing) without the molecule. The eigenstates are those of the single-particle equations of the density-functional formalism.

[12] Tsiper E.V., and Soos Z.G., *Phys. Rev. B* **2001***, 64*, 195124; Cheng, C.L., Murthy, D.S.N., Ritchie, G.L.D., *Aust. J. Chem*., **1972**, *25*, 1301; Le Fevre R.J.W., Radom, L., Ritchie, G.L.D., J. Chem. Soc. B, **1968**, 775.