Gating of a Three-Leg Molecule

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ABSTRACT We study the use of a simple three-leg molecule, triphenylene, as a transistor. This configuration allows increased voltage gain to be achieved. We analyze control of the transport between electrodes attached to two of the legs by a gate closely coupled electrostatically to the third leg, using self-consistent density functional calculations. In spite of the close coupling, the maximum voltage gain was less than unity, and this was attributed to efficient screening of the internal potential due to polarization of the molecular states. The transistor current vs. voltage characteristics were able to be reproduced using a simple electrostatic model.

KEYWORDS: molecular transistor · gate · triphenylene · density functional · transport

One of the goals in molecular electronics is to use a three-leg molecule as a transistor, with one leg each attached to source, drain, and gate. We consider here the triphenylene molecule, shown in Figure 1 together with the attachment groups we will use. The source and drain electrodes will be attached to the molecule with isocyanide groups. The gate electrode will be treated purely electrostatically. The advantage of this arrangement over a 2-leg configuration that we and others have considered previously[1−10] is that the protruding branch in the direction of the gate permits the convenience of a more distant placement of the gate while maintaining a close electrostatic coupling of the gate to the principal wave function to be modulated. The pure electrostatic coupling to the gate is an idealization which neglects leakage current that would arise with true quantum mechanical coupling. To reduce the voltage drop across the gap between the gate and the molecule, we have replaced the two H atoms nearest the gate by Ag atoms, and placed the electrostatic gate boundary very close to the centers of the Ag atoms (1 bohr). The actual physical configuration we study is shown in Figure 2. We consider a source−drain bias V_{SD} of 0.25 V. The theoretical method used, a self-consistent density-functional procedure, is the same as that described in ref 1. As in that work, we use a uniform-background (jellium) model to represent the source and drain electrodes. The geometry we use for the molecule is that computed for the free molecule;[11] the H atoms attached to the CN groups are then replaced by the source and drain electrodes.[12]

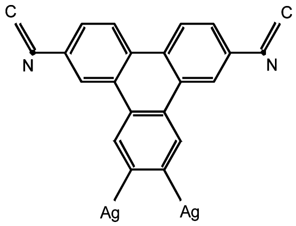

Figure 1. Structural formula for the molecule considered here (triphenylene with CN or Ag attachment groups substituting for H's as indicated).

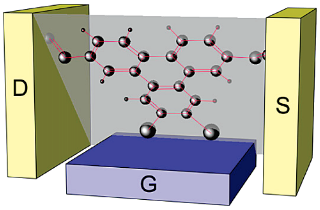

Figure 2. The molecule of Figure 1 is inserted between two metallic contacts, source S and drain D, and a gate G is placed below it. The molecular plane is oriented at 45° to the gate surface. Metallic spheres show atomic positions, with the large spheres representing the Ag atoms and the smallest spheres representing the H atoms.

Figure 3 shows the total density of states (DOS)[13] for the cases when the gate bias V_G is 0 and 2.5 V. In the self-consistent transport calculation, states in the energy window between the right- and left-electrode Fermi levels are only occupied by electrons incident from the right, while states above the right-electrode Fermi level are not occupied (we take the temperature to be zero).

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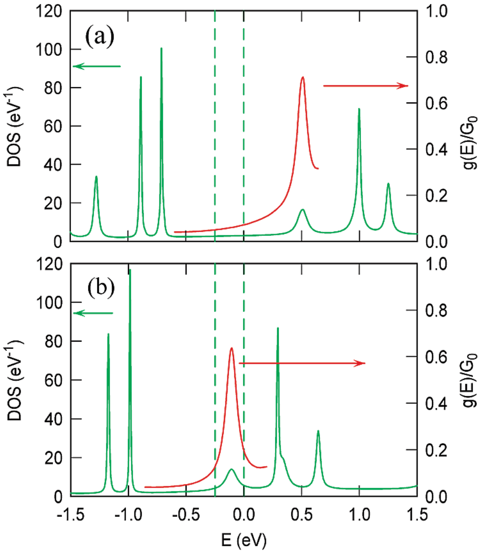

Figure 3. Total density of states in the vicinity of the source and drain Fermi levels (dashed lines) and energy-resolved conductance in units of G_0, the quantum of conductance, at (a) $V_G = 0$ and (b) $V_G = 2.5$ V. The source−drain bias V_{SD} is 0.25 V, as shown.

The first state above the source Fermi level (0 eV) at $V_G = 0$ is brought below this level when $V_G = 2.5$ V, thus opening a source/drain conduction path. The energy-resolved conductance of this path is shown on the right-hand scale. The large conductance of this state, approaching the quantum of conductance, indicates high transmission from source to drain *via* this state. Note that the whole state spectrum is shifted more or less rigidly by the gate voltage by a factor of ~30% of the gate voltage change. This close-to-rigid shift is in contrast to the strong dispersion seen in our previous results on the biphenyl molecule; we believe this is because we are able to place our gate contact farther away, resulting in more uniform induced potentials, as we will discuss below.

Figure 4 shows the conductance of the molecule as a function of the gate bias. This conductance can be correlated with the motion of the peaks in and out of the window defined between the source and drain Fermi levels as indicated by the marker lines (a−c). Figure 4 shows that the modulus of rate of change of conductance is maximized as the first unoccupied state crosses the source (a) and then the drain (b) Fermi levels and is maximized again as the second peak crosses the source Fermi level (c). This simple picture is not seen for the valence (normally occupied) states, which are much narrower (more localized), and so do not contribute much to the conduction for negative gate voltages.

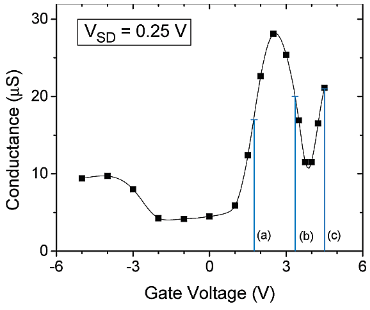

Figure 4. Conductance as a function of gate bias (V_{SD} = 0.25 V). The marker lines show where the peak of the first unoccupied state crosses the source Fermi level (a) or the drain Fermi level (b) or where the second unoccupied state crosses the source Fermi level (c).

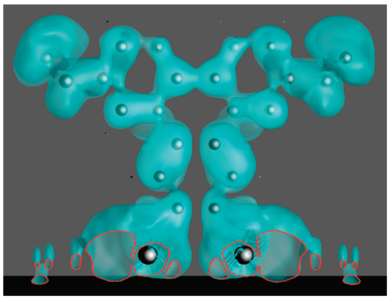

Figure 5. Local density of states isosurface for energy at center of first peak above the source Fermi level for $V_G = 0$ (see Figure 3a). The red contours show the intersection of the gate plane (cut away) with the isosurface.

We examine the effectiveness of our design with the aid of Figures 5 and 6. The local density of states (LDOS) for the first peak above the source Fermi level is shown in Figure 5. This figure is drawn in the same orientation as Figure 2 but tilted so that the plane of the molecule is presented face on. This illustrates a principal design feature whereby this state allows transport between source and drain while at the same time being strongly coupled, electrostatically, to the gate. The change in local potential resulting from a 2.5 V change in gate voltage is plotted in Figure 6a. This shows that the potential is fairly well screened over the entire view; that is, most of the gate voltage is dropped close to the gate electrode. Strong dipoles adjacent to the gate electrode (Figure 6b) are responsible for this. As the state in question is pulled below the source Fermi energy by the gate voltage, one might have expected to see the added charge distributed over the entire LDOS spatial range for that state, yet, as we see, the added charge is much more localized. This is due to the polarization of other states in the system, as well as polarization of the state itself as seen in Figure 6c, resulting in the strong screening seen in panels a and b.

The drain characteristics of the transistor are shown in Figure 7a. Fairly complex behavior is seen with saturating characteristics at large gate bias and a drain threshold-like increase in conductance at smaller gate voltages. Despite the improved gate coupling of our design, the maximum voltage gain of the transistor is still less than unity (0.63), but much better than our previous design.[1,2] This is indicated by the length of the horizontal line in Figure 7a which gives the change in drain voltage for a 1 V change in gate voltage, at constant drain current. The well-behaved movement of the states under bias shown in Figure 3 suggests that these

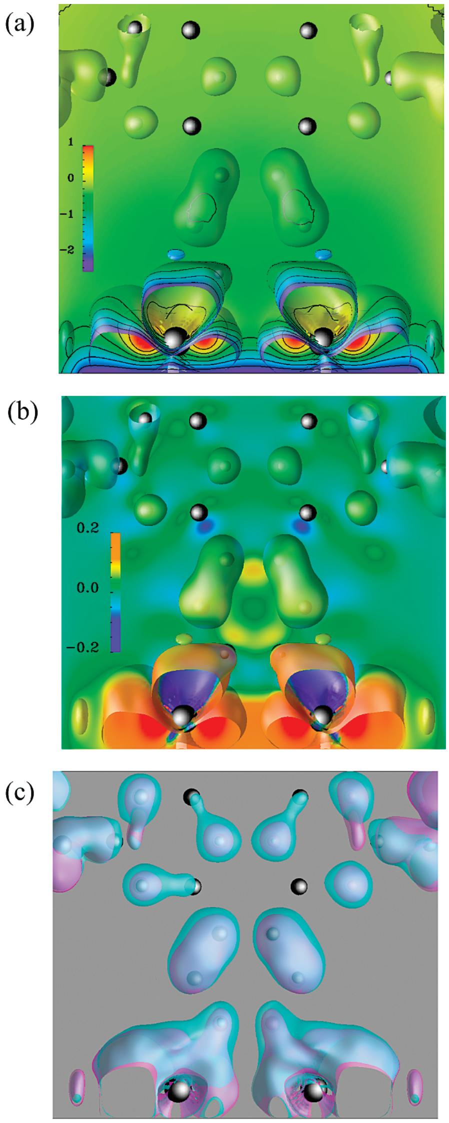

Figure 6. (a) Contours indicating change in molecule potential and (b) change in charge on change of gate voltage from 0 to 2.5 V, projected onto the principal plane of the molecule and onto an isosurface of LDOS at an energy corresponding to the conductance peak in Figure 3a. (c) Two isosurfaces of LDOS at this energy, with the light blue isosurface corresponding to $V_G = 0$ and the magenta isosurface to $V_G = 2.5$ V

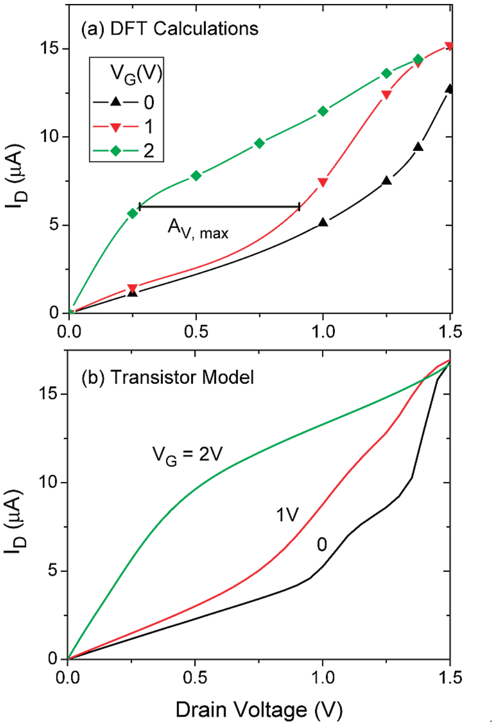

Figure 7. (a) Drain current vs drain voltage at indicated gate voltages. Horizontal bar shows maximum voltage gain. (b) *I*−*V* curves generated from transistor model,[14] using a gate coupling factor of 0.33 and a space-charge factor of 0.1 eV (see Fits to a Simple Model section).

characteristics can be explained with the aid of a simple model such as the Solomon−Kagan (SK[1,14]) model (see Simple Model section later), where transistor action is represented by a single gate-coupling factor, η, and space charge factor, V_{sc0}. The characteristics predicted by the model (Figure 7b) show good agreement with the full quantum calculations, showing that even quite complex behavior can be derived from a simple set of assumptions. The role played by the highest valence states is interesting. Even though not directly contributing much to the current, because of their narrow width, they can still modulate the drain current due to their change in occupancy as they are swept through the drain Fermi level by a change in drain voltage. As the drain voltage increases, the highest occupied state will be uncovered and will lose part of its electronic charge, resulting in an additional excursion of the central molecular potential that mimics an increase in gate voltage, causing an increase in conductance of the transistor in the regime where conductance increases with gate voltage. For example, in Figure 7b the conductance increase at the drain voltages of ∼1 and ∼1.3 V and at $V_G = 0$ are associated with the two upper valence peaks.

Our present design is a promising approach to increase gate coupling in a molecular transistor, but even while maximizing electrostatic coupling as best we can, it is still difficult to achieve high voltage gains. Furthermore, the closeness of the gate electrode to the silver atoms (see Figure 2) raises the question of how large the gate leakage would be had full quantum-mechanical treatment of the gate-molecule coupling been considered. The nature of the coupling of the external gate to the internal molecular potential goes to the heart of the design. As we have seen above, pure electrostatic coupling is inefficient, requiring an extreme closeness of the gate to the part of the wave function being controlled, and even then the potential is not applied uniformly to the whole wave function but only to the part nearest to the gate, while the energy of that state is modulated by the average potential. To achieve a stronger coupling, one should transport the potential from the gate to the active region of the molecule using a molecular link (as discussed below). In this case, the link is coupled quantum mechanically to the gate, and the coupling should be strong enough to supply charge to the link faster than it can be drained away to the rest of the molecule. Pure electrostatic coupling would not work, since then the charge lost cannot be resupplied and the potential of the link would tend to equilibrate with the rest of the molecule, negating the gate modulation. To some extent this happens in our present design. The lack of quantum mechanical coupling to the gate electrode is a restriction of our present approach which must be removed in order to make further progress.

We propose that a high-gain transistor can be achieved using the design of Figure 8. In this arrangement all electrodes (G, S, D) are strongly coupled quantum-mechanically to the internal wave functions, *s/d* and *gate*. The potential of the gate wave function closely follows the external gate voltage and it is coupled electrostatically to the *s-d* wave function, while the two wave functions are designed to be isolated quantum mechanically from each other. It is the quantum contact to the gate wave function that allows the transfer of the gate potential, by transfer of charge, into the molecule's interior, in contrast to the present design where the pure electrostatic transfer limits the achievable modulation.

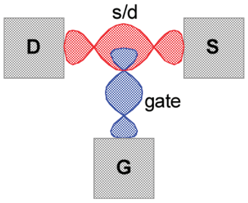

Figure 8. Proposed design for a molecular transistor where a *gate* wave function modulates an *s/d* (source/drain) wave function.

In conclusion we have introduced and analyzed a new design for a three-leg molecular transistor that has increased gate coupling and which shows a much higher voltage gain than previous (non-three-leg) designs. It was found that a strong dipole adjacent to the electrostatically coupled gate still limited the voltage gain to be less than unity. A new design having a quantum mechanically coupled gate was proposed to overcome this limitation.

FITS TO A SIMPLE MODEL

We use the SK model[1,14] to explain the characteristics obtained with our detailed calculations using density-functional theory. The SK model assumes a rigid shift of the molecular states due to an internal potential shift (the "Hartree" potential) caused by both gate and average of source and drain voltages in the ratio of $\eta/(1-\eta)$ where η is the coupling factor. In addition there is a space charge factor which represents the self-consistent contribution to the internal potential caused by changes in occupancy of the states under bias. The space charge factor V_{sc0} is expressed as the potential change caused by the addition of a single electron to the molecule so that e/V_{sc0} is the effective capacitance between the internal states and the external **S**, **D**, and **G** electrodes. The states are modeled as a collection of Lorentzian peaks each with its own width and transmission factor. The model was calibrated by fitting the density of states in Figure 3 with 8 Lorentzian peaks where each peak contained 2 electrons and had a transmission factor of 0.4. The η and V_{sc0} factors were adjusted to reproduce the shift in Figure 3b for the lowest unoccupied state. In addition the nonzero background in the DOS spectrum was modeled by a broad peak containing 20 electrons, but with a small transmission factor and space charge contribution.

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12. The width of the gate electrode was taken to be 16 bohr; the separation between the C in the CN attachment group and the background edge of the model source and drain electrodes was taken to be 1.75 bohr (the same, to within 0.02 bohr, as the distance between the 4 and 4′ carbons and their respective electrodes used in ref 1).
13. The DOS we consider here is 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 (and without a gate field). The eigenstates are those of the single-particle equations of the density-functional formalism.
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