

Comment on “First-Principles Calculation of Transport Properties of a Molecular Device”

In a recent Letter, Di Ventra, Pantelides, and Lang [1] presented intriguing results of first principles calculations of electrical conduction through a benzene-dithiolate (BDT) molecule bridging a pair of gold nanocontacts. The shape of the calculated conductance vs voltage curve was similar to that measured in the seminal experiment of Reed *et al.* [2], but as in simpler semiempirical tight-binding calculations [3–5], the magnitude of the calculated conductance (and current) was much larger than in the experiment. The discrepancy ranged from a factor of 20 to several hundred [1] depending on the bonding configuration of the sulfur atoms of the molecule and the gold atoms of the contacts. Because of the sophistication of the calculations of Di Ventra *et al.* [1], it seems very unlikely that further technical improvements within the same conceptual framework will change the outcome of the calculations by a factor of 20, and therefore the reason for the discrepancy between theory and experiment should be sought elsewhere. In this Comment we suggest that the source of the discrepancy may be the use of an inadequate model of the system. Our calculations based on an alternate model agree very well with the experimental data, including both the shape of the conductance curve and the magnitude of the conductance.

In the experiment [2] two gold nanocontacts were both coated with dense monolayers of BDT molecules, and they were then brought together until electrical contact was established between them. One possibility is that a *single* molecule bonded chemically to *both* contacts and carried most of the current between them as was assumed by Di Ventra *et al.* [1]. However, because most of the bonding sites on both contacts were occupied with molecules before the contacts were brought together, a more likely possibility is that no molecule could find bonding sites on *both* contacts and the main current path from contact to contact was through one (or more) overlapping pair(s) of molecules such as that depicted in the inset of Fig. 1. Since in the experiment the contacts were in the form of nanoscale tips, we have explored the implications of the second possibility theoretically assuming that the current flows through a single overlapping pair. Our transport calculations [6] were based on a semiempirical extended-Hückel Hamiltonian and Landauer theory and assumed the planes of the two carbon rings to be roughly orthogonal to each other, an electrostatically favored configuration that results in herringbone patterns in benzene-thiol monolayers adsorbed on gold [7]. The differential conductance characteristic that we obtained by averaging over 20 configurations of the pair of molecules to simulate thermal fluctuations at room temperature is shown in Fig. 1. Considering the simplicity of our model and theoretical approach, the agreement between our results and the experiment [2] is excellent: As in the work of Di Ventra *et al.* [1] the rises in conductance occur at values of the bias close to those in the experiment.

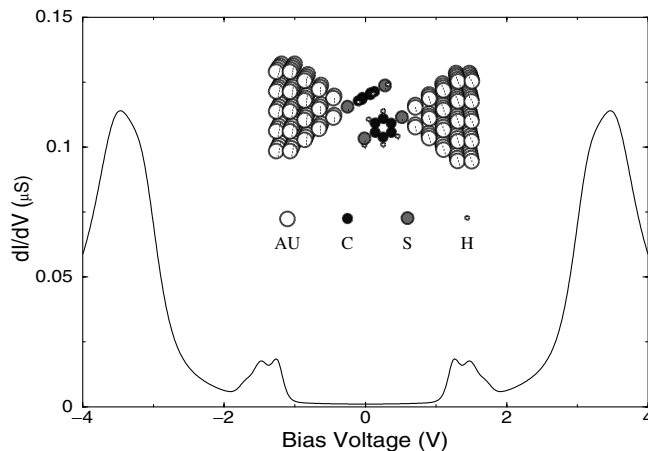


FIG. 1. Differential conductance vs bias of pair of BDT molecules connecting Au contacts as in inset.

This similarity between our results and those of Di Ventra *et al.* (and with previous theoretical work [3–5]) is due to the fact that in both models most of the current is carried through hybridized highest occupied and lowest unoccupied molecular orbital states of the BDT molecule(s). But unlike all preceding theoretical work the *magnitude* of the differential conductance (and current) that we find is also close to that observed in the experiment [2]: There is no chemical bond between the molecules, and the weak link between them limits the conductance. The present model may be tested further experimentally by repeating the experiment [2] with the BDT replaced by dense monolayers of a similar molecule that is designed so that it can bond chemically to only one contact; we predict that conductances having a similar form and (low) magnitude will be observed.

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