Distributed response analysis of conductive behavior in single molecules

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The *ab initio* computational approach of distributed response analysis is used to quantify how electrons move across conjugated molecules in an electric field, in analogy to conduction. The method promises to be valuable for characterizing the conductive behavior of single molecules in electronic devices.

If Moore's law (every 12–24 months the number of transistors on a silicon chip doubles) is to continue to apply until the year 2020, transistor features will have to shrink to molecular scale. This small size will lead to problems that spell the end of Moore's law in classical system architecture. These problems are related to the way dopants are distributed in each device. As transistor size decreases, dopants may aggregate, or statistical deviations in dopant density from device to device may become important. Equally serious is that very small transistors must have very small insulator gates. As dimensions decrease, quantum mechanical tunneling across the gate becomes important. At very small scales, this tunneling acts to decrease device efficiency, presenting a significant limitation: as processing power increases, computationally intensive fields such as virtual reality, complex image recognition, nanorobotics, and real-time holography develop and demand increases in step.

In recent years, this need for new transistor architecture has stimulated the emerging field of molecular-scale electronics (1–10). It has been demonstrated that these impediments can be overcome by using a nonclassical device architecture that does not rely on doping or inversion layer–conduction channel formation. Thorough overviews of the concepts, prospects, and expected impact of molecular electronic devices have been given in the literature (7, 11–14).

The work of Tour, Reed, and colleagues (5) on two-terminal self-assembled monolayer (SAM) devices has advanced the technology of molecular electronic devices. Their nanoscale device uses charge flow in the conjugated molecule 2'-amino-4-ethynylphenyl-4'-ethynylphenyl-5'-nitro-1-benzenethiol, which has polar functional groups that can be used to switch the device. Applying a voltage to the gate electrode sets up an electric field, to which the polar groups respond by changing their orientation, breaking the effective conjugation between adjacent carbon atoms and hence limiting current flow, corresponding to switching from the ON to the OFF state (1, 3–5, 15, 16). Current-voltage measurements at 60 K showed an ON–OFF peak-to-valley ratio of 1,030:1 (5).

Three-terminal molecular devices, such as the SAM organic field effect transistor (SAMFET) as reported by Schön *et al.* (9, 10), in contrast to two-terminal devices have the ability to modulate the conductance and achieve gain in logic circuits. A schematic of the SAMFET device using the molecule 4,4'-biphenyldithiol (BPDT) as reported in refs. 9 and 10 is shown in Fig. 1, with a SAM connected to source and drain electrodes. It is reported that the drain current can be modulated by ≈ 5 orders

of magnitude by an applied gate voltage. The gate voltage affects only the molecules close to the gate (ON current), whereas the OFF current samples all of the molecules in the SAM. This switching results in a conductance change of ≈ 7 orders of magnitude at room temperature. Schön *et al.* estimated a conductance of $\approx 5 \mu\text{S}$ per molecule.

In the present paper, we show that the recently developed *ab initio* computational approach of distributed response analysis (17) can be used to quantify the conduction behavior of single molecules. In principle, this technique can be used to identify superior active molecules for electronic devices. We are currently exploring how well the conductive behavior calculated in this paper predicts experimental results on molecular conductance like those reported in refs. 9 and 10.

Distributed Response Analysis. Since its earliest days, molecular electronics has been concerned with electrical conduction, rectification, and switching in single molecules (18). Much progress has now been made in studying these processes both experimentally and theoretically, and it is apparent that for a single molecule, the perturbation caused by the electrical contacts is significant (19–21). Nevertheless, it is desirable to explore means of characterizing separately the propensity of molecules to conduct or switch. The distributed polarizability (22) quantifies (among other things) the tendency for charge to flow between different regions of a molecule, which is analogous to conduction, whereas the distributed hyperpolarizability (23) quantifies how the distributed polarizability depends on electric field, which is analogous to switching. Distributed response can be calculated rigorously for both linear (17, 24) and nonlinear (23) coefficients. Hence, although they characterize charge flow within rather than through molecules, distributed linear polarizability and quadratic hyperpolarizability appear suitable means to assess molecules for use as conductors and switches.

Distributed molecular response is calculated by using *ab initio* techniques described in detail in ref. 17. The distributed polarizability components $\alpha_{\alpha\beta}^{AB}$ relate the change in electron density in an atomic region *A* to the electrical potential in atomic region *B*. This approach allows us to calculate various atomic and molecular properties such as dipole moment and (hyper)polarizability.

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Abbreviations: SAM, self-assembled monolayer; SAMFET, SAM organic field effect transistor; pNA, *para*-nitroaniline; mNA, *meta*-nitroaniline; FB, fluorobenzene; CN, conduction number; BPDT, 4,4'-biphenyldithiol.

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Fig. 1. Schematic representation of SAMFET, according to Schön *et al.* (9). The self-assembled monolayer consists of BPDT molecules.

In addition, charge flow into an atomic region can be calculated rigorously.

The distributed multipole polarizability components are calculated according to ref. 17.

$$\alpha_{\alpha\beta}^{AB} = 4 \sum_{i\sigma} \sum_{j\tau} \langle i | \hat{Q}_{\alpha} | \sigma \rangle_A (\mathbf{G}^{-1})_{i\sigma, j\tau} \langle j | \hat{Q}_{\beta} | \tau \rangle_B, \quad [1]$$

where $\hat{Q}_{\alpha}$ is a multipole moment operator, i and j denote occupied molecular orbitals, and σ and τ are virtual molecular orbitals obtained through closed-shell Hartree–Fock calculations. The quantities $\langle i | \hat{Q}_{lm} | \sigma \rangle_A$ are transition multipole moment matrix elements in an atomic basis, as defined in the atoms in molecules context (25, 26) with $\mathbf{r}^A$ as origin. The matrix $\mathbf{G}$ is defined in terms of two-electron integrals,

$$G_{i\sigma, j\tau} = 4(\sigma i | j \tau) - (\sigma j | i \tau) - (\sigma \tau | i j) + \delta_{ij} \delta_{\sigma\tau} (\varepsilon_{\sigma} - \varepsilon_i), \quad [2]$$

where ε_{σ} and ε_i are orbital energies.

Charge flow into an atomic region A is calculated from the distributed polarizability components according to ref. 17,

$$\Delta Q_q^A = \sum_B \sum_i \alpha_{qi}^{AB} X_i^B, \quad [3]$$

where $i = q, x, y, z$. Thus $X_q^B = V = V'$ is the electrostatic potential at the origin of an atomic basin B and $X_x^B = E_x^B = V'$ is the x component of the electric field at the origin of atomic basin B .

Results

We define the charge flow number for atomic region A as ΔQ_q^A per unit field magnitude V' , both in a.u.. Fig. 2 shows the calculated values for *para*-nitroaniline (pNA) across the symmetry axis, for *meta*-nitroaniline (mNA) across the equivalent

axis from the center of the ring to the amino, and for fluoro-benzene (FB) across the symmetry axis. We further define the total conduction number (CN) as the sum of the charge flows on one side of the molecular axis perpendicular to the field direction, taking advantage of the molecular symmetry in pNA and FB, which fixes a nodal plane across which the charge flow numbers change sign. For mNA, with no symmetry axis, we calculate CN similarly as the sum of the positive charge flow numbers, allowing the molecular response itself to determine the surface across which the charge flow numbers change sign; in this case, the charge flow is not rigorously parallel to the field. For pNA, we find CN = 11.7, whereas mNA and FB yield 11.1 and 8.3, respectively.

Now the distributed polarizability components yield the usual molecular polarizability according to refs. 17 and 22,

$$\alpha_{\alpha\beta} = \sum_A \sum_B (r_{\alpha}^A \alpha_{qq}^{AB} r_{\beta}^B + r_{\alpha}^A \alpha_{q\beta}^{AB} + \alpha_{\alpha q}^{AB} r_{\beta}^B + \alpha_{\alpha\beta}^{AB}), \quad [4]$$

where $\alpha, \beta = x, y, z$, and hence CN and the average polarizability $\text{Tr} \alpha$ share a common origin. The calculated values of CN and the average polarizability are collected in Table 1, which reveals for the three molecules investigated the new empirical result that 1 unit of CN is approximately equivalent to 1/6 a.u. of polarizability.

The ability of an electron to move across a molecule in the direction of an external field is analogous to conduction. Current flow refers to flow of positive charge, so that current is opposite in direction to electron flow. Our method allows us to study the ease of conduction as a function of the direction of the external field; in particular, charge flow is not permitted if the external field is perpendicular to the molecular plane. Distributed response analysis yields atomic polarizabilities (17) and atomic charge flow numbers. These can be combined to calculate polarizabilities and charge flow numbers for

Fig. 2. Charge flow numbers for (A) pNA, (B) FB, and (C) mNA. The numbers are dimensionless representations of the reorganization of charge per unit field among the atomic regions.

functional groups, such as the donor, π -bridge, and acceptor parts of pNA and mNA, but Table 2 shows that these functional group properties are not related in the same way as their whole-molecule counterparts. The complete distributed response analysis of pNA, mNA, and FB is described elsewhere (M.i.h.P., S. O'Flaherty, P.L.A.P., R.W.M. and W.J.B., unpublished work).

Table 1. Calculated average polarizability $\alpha_{av} = 1/3\text{Tr}\alpha$ and conduction numbers CN for pNA, mNA, and FB

Molecule	CN	$\alpha_{av}/\text{a.u.}$	CN/ α_{av}
pNA	11.7	70.5	0.166
mNA	11.1	68.8	0.161
FB	8.3	48.7	0.170

The new result that 1 CN is equivalent to 1/6 a.u. of polarizability can be used to predict the CNs from the polarizability for molecules for which the conductance has been measured experimentally to explore the relationship between CN and conductance. As already noted, the experimental conductance has been estimated for BPDT (9). We therefore calculated the average molecular polarizability for four molecules related to BPDT (see Table 3), using the same level of *ab initio* calculation as for pNA, mNA, and FB. Benzenedithiol has recently been studied in detail between nanoscale metal contacts (27). The thiol groups (used to connect to source and drain) increase the polarizability along the molecular axis, and we predict that the dithiols each have a CN over 40% larger than the parent molecules benzene and biphenyl, with the CN for BPDT reaching 25.6.

We observe that introducing side groups such as amino or nitro and increasing the number of phenyl rings both increase the CN. On the basis of these observations, we predict that SAMFETs based on 2'-amino-4-ethynylphenyl-4-ethynylphenyl-5'-nitro-1-benzenethiol [as used by Tour, Reed, and colleagues (5)] should have a much higher CN than those based on BPDT [as used by Schön *et al.* (refs. 9 and 10)]. The best materials known today to serve as active molecules are carbon nanotubes. The static polarizability of single walled carbon nanotubes has been estimated around 800 a.u. (28), which would lead us to predict a CN of approximately 150, far superior to any other conjugated molecule. If conductance were proportional to CN, then from the BPDT conductance of 5 μS , we would predict a conductance of some 30 μS for single walled carbon nanotubes, compared with the quantum of conductance e^2/h of about 77 μS . The conductance for multi-walled carbon nanotubes (with only the outer shell contributing to conduction) has been measured as 77 μS (1 unit of quantum conductance) (29). However, these predictions remain to be validated by making a connection between calculated CNs and experimentally measured conductance.

Conclusion

In conclusion, we have shown that the *ab initio* computational technique of distributed response analysis can, in principle, be used to quantify the conduction behavior of a single molecule acting as a switching region in a nanoscale field effect transistor design. In an analogy to conduction, it is shown that once an electron is introduced on one side of the molecule, it has the ability to move across the molecule. The calculations demonstrate in detail how charge flow occurs in pNA, mNA, and FB.

On the basis of our calculations, we predict that pNA has a more efficient conductive behavior than mNA and FB. We

Table 2. Calculated average polarizability $\alpha_{av} = 1/3\text{Tr}\alpha$ and conduction numbers CN for the functional groups in pNA

Functional group	CN	$\alpha_{av}/\text{a.u.}$
Acceptor ($-\text{NO}_2$)	0.64	16.8
Bridge ($-\text{C}_6\text{H}_4-$)	7.46	33.9
Donor ($-\text{NH}_2$)	3.60	19.8

Table 3. Calculated average polarizability $\alpha_{av} = 1/3\text{Tr}\alpha$ and predicted CN for benzene, 1,4-benzenedithiol (BDT), biphenyl, and BPDT

Molecule	$\alpha_{av}/\text{a.u.}$	Predicted CN
Benzene	49.8	8.3
BDT	86.6	14.5
Biphenyl	108.3	18.1
BPDT	155.1	25.6

established the empirical result that 1 unit of molecular CN is approximately equal to 1/6 a.u. of (static) molecular polarizability. This result has been used to estimate the conductive behavior of similar conjugated molecules by using the average molecular polarizability. It was predicted that BPDT has a CN

of 25.6 and therefore should have the most effective conduction behavior of the molecules investigated (see Tables 1 and 3).

We are currently investigating how accurately our CN predicts the results of experiments on molecular conductance such as those reported by Schön *et al.* (9, 10). We envisage that distributed response analysis could then be used to identify superior molecular switches from molecular CN before the molecules are experimentally investigated.

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