

## Electron Transport in Molecular Wire Junctions

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Molecular conductance junctions are structures in which single molecules or small groups of molecules conduct electrical current between two electrodes. In such junctions, the connection between the molecule and the electrodes greatly affects the current-voltage characteristics. Despite several experimental and theoretical advances, including the understanding of simple systems, there is still limited correspondence between experimental and theoretical studies of these systems.

One of the major themes in electronics is the construction, measurement, and understanding of the current-voltage response of an electronic circuit in which molecular systems act as conducting elements. Traditional metal-molecule-metal junctions comprise thin molecular films between macroscopic metal electrodes. Here we focus on single-molecule transport junctions that are currently the subject of substantial experimental, theoretical, and technological interest. These nanoscale molecular interconnects act as novel chemical environments and may help minimize computer circuit dimensions and enhance performance. They can act as switches, gates, or transport elements, providing new molecular functions that need to be characterized and understood.

A main challenge is understanding the coupling of individual molecular structures to macroscopic electrodes under nonequilibrium conditions. Although early measurements go back to the work of Kuhn (1), real progress depended on the development of assembly schemes for addressing single molecules and layers and of scanning probe methodologies for preparing, characterizing, and measuring such junctions. Two transport junctions that have been considered most often are (i) a single molecule coupled to noble metal electrodes through thiol linking groups (Fig. 1A) and, more commonly, (ii) a self-assembled monolayer (SAM) prepared on a metallic surface and measured with a scanning probe tip. Measurements in both of these systems record a current between the electrodes due to an applied voltage  $V$ , with conductance  $g$  defined as

$$g(V) = \partial I(V)/\partial V \quad (1)$$

Poor contacts limit junction transport, and contacts must be present in any persuasive model of  $g(V)$ .

Reliable single-molecule transport measure-

ments were first reported on rigid structures, in particular (2) on single-walled carbon nanotubes. In another approach, a single molecule junction is prepared using feedback-controlled lithography to place molecular structures (such as phthalocyanines) on a hydrogen passivated silicon surface (3). In most scanning probe measurements of such structures, small (nanoampere) currents are recorded because at least one of the electrodes, the measuring tip, is not chemically bonded to the molecule; a relatively large vacuum gap separates it from the adsorbed molecule. More recently, electromigration methods have been used to prepare small gaps ( $\sim 1$  nm) (4, 5) in a gold wire. Single molecules can be placed across the gap.

Perturbation theory based on the Tersoff-Hamann approach (6) is commonly used to interpret transport in the highly asymmetric, vacuum gap-type measurements. In this approach, current is proportional to the density of states at the Fermi energy, evaluated at the position of an atom on the tip end.

In an efficient molecular transport system, actual contact of the molecule to both electrodes is required (Fig. 1, A and B). The simplest theoretical view, therefore, is based on a tight binding-type one-electron picture. As illustrated in Fig. 1C, the structures on the left and on the right are the noble metal electrodes, and the atomic basis functions within the molecule are represented by line segments. The interaction potentials or tunneling matrix elements are shown by double headed arrows; there can be interactions among all atomic levels, and any of them can couple to the electrode.

More commonly, one thinks of the molecular orbitals of the molecule within the junction. The Fermi level of a noble metal is around  $-5$  eV, whereas the highest occupied molecular orbital (HOMO) (7) of a characteristic molecule is roughly  $-9$  volts. These numbers relate to the so-called "vacuum level"—the lowest energy level of a free electron in a vacuum—as zero. Upon allowing the interaction between the molecule and the metal electrodes indicated in Fig. 1, A and B,

some charge flow, charge rearrangement, and geometric reorganization will occur. After this process, the simplest viewpoint is expressed by the level scheme depicted in Fig. 1D. Here the Fermi level of the electrodes lies within the HOMO-LUMO (lowest unoccupied molecular orbital) gap of the molecule. Were this not true, charge would continue to flow until it became true. The Fermi level is not necessarily halfway in the HOMO-LUMO gap but could lie anywhere in between. This picture is oversimplified, assuming that mixing between a molecule and an electrode is relatively weak compared with the interatomic interactions that develop the molecular electronic structure. The thiol-gold Lewis acid-base interaction may still be weak and polar enough that the Fig. 1D image is correct for these systems, but this may not be so for molecular wires attached by strong covalent bonds to either silicon or carbon electrodes. The experimental signature for weak coupling is sharp peaks in the conductance-voltage curve (2, 8, 9).

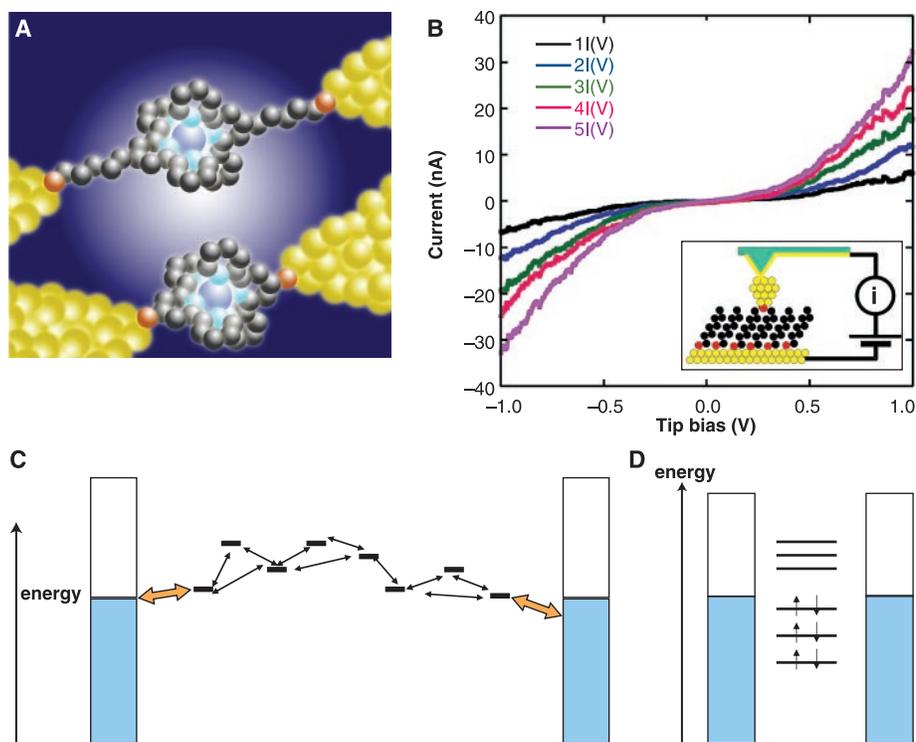
Different methods such as break junctions (8–11), metal dot electrodes atop monolayers (12, 13), metal wire crossings (14), and mercury drop contact junctions (15, 16) have been used to construct molecular transport junctions. More involved is the three-gate (molecular transistor) geometry, where the gate electrode provides an external potential that modifies the molecular electronic levels. The two simplest molecular transport junctions are wires made of either one single atom or a row of metal atoms. Quantized conductance was observed on disordered metallic wires in ionic solution (Fig. 2) (17) (that is, the conductance exhibited steps near 4, 3, 2, 1, or 0 quantum units). The quantum unit of conductance,  $g_0$ , is defined by

$$g_0 = 2e^2/h = (12.9\text{k}\Omega)^{-1} \quad (2)$$

where  $e$  and  $h$  are the electron charge and Planck's constant, respectively. This quantized conductance was predicted by Landauer (18), whose formulation of current in heterostructures forms the basis for much of the theory of molecular transport junctions.

The Landauer theory assumes that the electrons move smoothly from one electrode to the other, subject only to elastic scattering within the junction. In the presence of magnetic impurities or of ferromagnetic electrodes, spin-dependent transport (so-called "spin valve behavior") is expected. Spin-

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**Fig. 1.** (A) Schematic single molecule junction between two continuous electrodes [after (5)] (B) Schematic (inset) of an alkane thiol adlayer with gold dot current collector, measured using AFM. Actual data is also shown, corresponding to (suggested) transport through 1, 2, 3, 4, and 5 molecular strands [from (12)]. (C) Many site molecular wire, with striped arrows indicating coupling between molecular levels and electrode and black arrows indicating intersite interactions along the molecular chain. The filled and empty parts of the rectangles represent filled and empty levels of the electrode conduction bands. (D) Molecular orbital equivalent of  $1e$ , including the effects of electrode interaction, such that the electrode Fermi level lies in the HOMO-LUMO gap.

polarized electron emission has been seen from a chiral adlayer on gold illuminated by polarized light (19), and Kondo-effect measurements show maximal current at near-zero voltage (4, 5).

Several phenomena observed in molecular junctions have counterparts in mesoscopics (20). Molecules are essentially small, uniform quantum dots and their main qualitative difference from mesoscopic dots lies in the discreteness of the molecular electronic spectra. Peaks in the current-voltage curve of mesoscopic dots (21) are usually associated with coulomb repulsion within the junction. They appear most clearly in the “Coulomb blockade limit” where the dot-electrode tunneling barrier is large and dot capacitance is small. The current peaks when two charge (or redox) states of the dot become degenerate, enabling a change in the electronic population on the dot. As a function of the source-drain potential, the  $I$ - $V$  behavior in this regime has discrete steps, implying peaks in the conductance-voltage plot. The same phenomenon occurs in molecules (Fig. 3); however, the current-voltage response is influenced by the discrete electronic spectra of molecular bridges of the same charge state.

### Types of Transport Junction

Molecular conductors can also be subdivided into single-molecule junctions and molecular monolayer junctions. The molecules in the junctions can be divided into the hard, rigid, linear structures characterized by carbon nanotubes (22) and silicon nanowires and the soft, more typical, molecular organic materials such as 1,4-benzene dithiol (11, 14), copper phthalocyanine (3), or 4,4'-biphenyl dithiol (13, 14), on which we will focus.

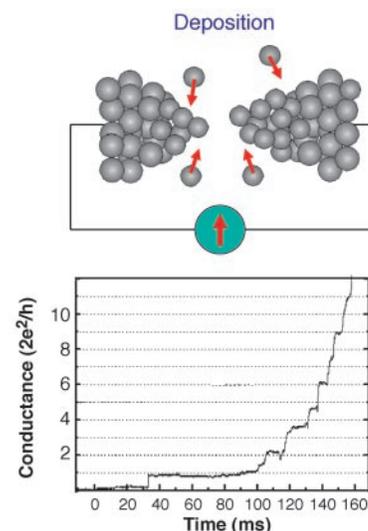
Several experiments on soft molecules may have indeed measured transport through single molecules, and statistical analysis can be used to isolate the properties of individual molecules even if the junction contains many molecules (12) (Fig. 1B). Experiments in  $\sim 1$  nm gaps in gold wires, with silicon backplate gating, have observed single-molecule conductance (4, 5) (Fig. 3). Studies in films are harder to interpret: even if the molecules do not communicate directly with one another, changes in the electrode properties due to the monolayer adsorption may completely change the current-voltage characteristics compared with what would have happened with a single molecule.

### Molecular Junction Properties

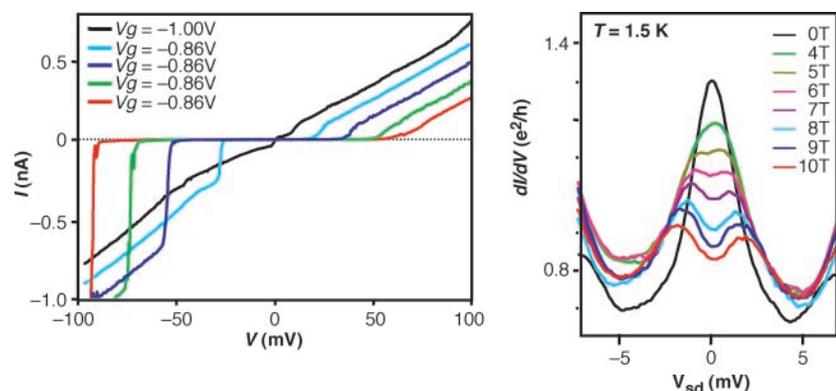
When a molecule is coupled to macroscopic electrodes, the discrete molecular levels mix with the metal electron states continuum. The high densities of metal states will then confer new properties on the molecular energy levels: these broaden and shift, and attain finite lifetimes because of the much higher state densities in the electrodes. These lifetimes are closely related both to the molecule-electrode coupling and to the bare electrode density of states. This realization underlies the theory of transport in molecular junctions that requires, in addition to standard quantum chemistry input, treatment of the interaction between the molecule and its environment in a nonequilibrium situation.

Conduction is an irreversible process and is only defined in the presence of some dissipating or dephasing bath. The molecular electronic system of primary importance in junction transport interacts with at least three different continuous bath environments. The most important are the electronic states within the metal already discussed. In the Landauer formulation (18), current occurs because electrons are elastically scattered between two electronic baths corresponding to the leads or electrodes. In this coherent limit, energy is dissipated in the lower potential lead; no energy dissipation occurs in the molecule itself.

Though this Landauer picture may be appropriate for small molecules or atomic wires, we know from electron transfer phenomena that electrons are coupled both to the vibrations of the molecule itself and to whatever solvents or ions may be present in the junction. The coupling of electronic and nuclear motions is the basis for electron transfer rates, and for its explanation in terms of the Marcus-Hush-Jortner formulation (23).



**Fig. 2.** Schematic of underwater metallic atomic wire and observed conductance results [after (17)].



**Fig. 3.** Single molecule transport measurements prepared using the structure of Fig. 1A. The characteristic on the left corresponds to the Coulomb blockade, whereas that on the right demonstrates Kondo resonance [after (5)].

As sketched in Fig. 1D, when contact is made between the molecules in a junction and the electrodes, the electronic structure is substantially modified. In the absence of applied fields, the Fermi levels of the two metals must be equal, and the effective Fermi level (between the HOMO and LUMO) of the molecule is established. This is often referred to as the band lineup problem (24), because it deals with lining up the potentials of the bands of the metal with the eigenstates of the isolated molecule.

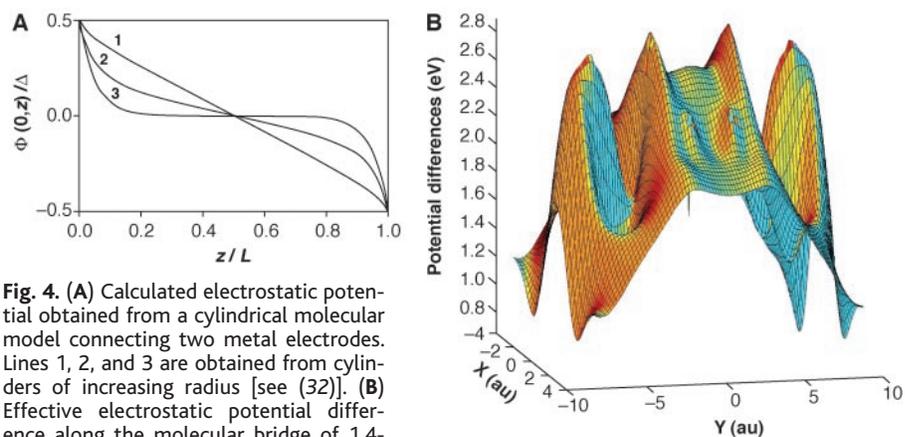
In the most straightforward approach to band lineup, one could simply calculate the eigenstates of an extended molecule, i.e., the molecule plus finite clusters of metal atoms on each side. The difficulty is that the overall spectral density arising from the metals matters. Though progress has been made utilizing these extended molecule schemes (24–26) that in itself is not enough: the extended molecule must be supplemented by the true spectral densities of the bulk metal. This is most easily done using scattering theory or, more generally, the nonequilibrium Green's function (NEGF) formulation of transport theory (20). Band lineup will be sensitive both to the electronic structure of the molecule and to the metals. It is therefore not meaningful to talk about the current-voltage characteristic of the molecule, but only of the molecular junction; changing the metal will change the Fermi levels, the band lineup, and the expected conductance spectrum.

The electrostatic potential  $\Phi$  across a molecular junction, in the absence of charge flow, must satisfy the Poisson equation relating charge density and  $\Phi$ . In the absence of the molecule,  $\Phi$  is a linear ramp. In the presence of the molecule, one must self-consistently determine  $\Phi$  from the Poisson equation and the density from the square of the wave function, the solution of the time independent Schrödinger equation.

Such calculations have been carried out using different approaches (24–32). Figure 4A shows (32) the calculated electrostatic

potential for a simple cylindrical model of a variable cross section wire. Figure 4B shows similar results for 1,4-benzene dithiol between gold electrodes obtained from a density functional–NEGF calculation (24). Although the potential has some characteristics of a screened ramp, with more effective screening for larger molecular cross section (Fig. 4A) it also has typical molecular lumps in the potential corresponding to atomic positions, and there is flattening toward the interface (Fig. 4B) (24).

Although Figure 4B come from a state-of-the-art calculation, the state of the art remains crude. One extra complexity arises from image effects. In classical electrostatics, the large polarizability of metals results in a disparity of dielectric constants. This can be described in terms of an image force that stabilizes charge near the electrode, even though this macroscopic picture is still inadequate for full understanding. One ongoing difficulty is understanding how the actual electrostatics reflect the applied potential, the electronic screening and redistribution, and the image effects arising from the disparity in dielectric response between metal and molecular matter.



**Fig. 4.** (A) Calculated electrostatic potential obtained from a cylindrical molecular model connecting two metal electrodes. Lines 1, 2, and 3 are obtained from cylinders of increasing radius [see (32)]. (B) Effective electrostatic potential difference along the molecular bridge of 1,4-benzene dithiol, calculated with DFT methods [after (24)].

## Formal Approaches to Conductance

The simplest discussion of transport in a molecular junction is to assume that incoming electrons are scattered both at the metal-molecule interfaces and along the molecular wire itself. The conductance will then depend on the net probability of scattering (31). A point first noticed by Landauer (18) is that such scattering does not have to be inelastic; even elastic scattering will prevent electrons making it through the junction. This coherent conductance (31) is expected to characterize most short molecular wires, particularly those in which transport occurs far from a resonance between the metal Fermi energy and the molecular eigenstates, and at low temperature for short wires. The conductance  $g(E, V)$  is then given by (19, 24, 29–31)

$$g(V) = 2e^2/h \sum_{ij} T_{ij}(E, V) \quad (3)$$

Here  $T_{ij}$  is the probability that a carrier coming from the left lead in transverse mode  $i$  will be transmitted to the right lead in transverse mode  $j$ . Molecular electronic structure theory combined with models for the interface and appropriate treatment (NEGF formulations, Lippman-Schwinger scattering approaches) of the mixing process lead to actual calculations of molecular transport.

This formal basis has been adapted in the extensive calculational work on molecular junctions. Despite this basic understanding, comparisons with experiment are still difficult because of the lack of availability and reproducibility of many of the experimental data and because of the complexity of formulating this problem properly.

## Inelastic and Thermal Effects in Molecular Conduction

In actual measurement, vibronic interactions between electrons and nuclear motion substantially modify the coherent picture. Inelastic scattering may occur in any situation in which the transport time becomes comparable to the time scale of any motions in the

environment surrounding the molecular electrons. For most molecular structures, these are the vibrations of order 10 to 1000 fs. Early break junction measurements (11) showed a temperature dependence (33) characteristic of thermal hopping; however, thermal rearrangement of the junction itself cannot be ruled out. In any case, inelastic contributions are not readily explicable in the Landauer picture. By contrast alkanethiol-gold junctions show pure tunneling transport (no temperature dependence, logarithmic decay of current with molecule length, deduced barrier height of 1.45 eV), as expected from a simple tunneling mechanism.

The effects of nuclear motion can be understood qualitatively in terms of a generalized Landauer-Buttiker traversal time or contact time for electron transmission through an N-site bridge. An estimate for this time (34) suggests that for long chains and small gaps, the travel time can become long enough to be comparable to molecular vibration periods. One then expects strong coupling between vibrations and electronic motion, resulting in trapping of the electrons and a transition from coherent to incoherent behavior (31). Such transitions have indeed been found in both long range electron transfer reactions (35) and in transport (36) (such hopping transport characterizes real ohmic wires).

Even when the electron does not trap and become polaron-like, inelastic behavior can facilitate transport by reducing energy barriers for injection. This point has been noted in several calculations (37, 38), showing that the effective tunneling barriers can be reduced by increasing vibronic coupling. Weak electronic-nuclear coupling may sometimes reduce the elastic transmission component and consequently may lead to an overall reduced transmission in certain voltage ranges (39).

### Molecular Conduction and Molecular Electron Transfer

Electron transfer (ET), the fundamental chemical process underlying all redox reactions, is closely related to transmission between two metallic electrodes through a conducting wire. On the basis of this similarity, one can show that (in the simple case of thermal, non-adiabatic electron transfer) there is a relation between the rate constant,  $k_{A \rightarrow D}$  and the conductance, because both processes depend on electron tunneling. This relation is approximately (40)

$$g \approx \frac{e^2}{\Gamma_D \Gamma_A F} k_{D \rightarrow A} \quad (4)$$

where the  $\Gamma$  factors are the inverse lifetimes of an electron on the donor and acceptor states when adsorbed on the metal electrodes, and  $F$  is the Marcus thermally averaged Franck-Condon factor depending on temperature and reorganization energy. This relation holds if the modi-

fication of the molecular electronic structure due to its interaction with the metal leads is small. A rough order of magnitude estimate for reasonable magnitudes of reorganization energies and molecule-electrode couplings leads to  $g(\Omega^{-1}) \approx 10^{-17} k_{D \rightarrow A} (s^{-1})$  (40). This result was originally obtained by comparing nonadiabatic ET with coherent tunneling, but has been extended to deal with hopping-type transport (41).

### Some Computational Results for Junction Conductance

A standard system in molecular junction studies has been a molecular junction consisting of benzene dithiol molecule (BDT) without the thiol hydrogen atoms, supported on one gold electrode and probed by a second electrode, which could be a scanning tip, another gold electrode, or gold nanodot acting as a current collector (Fig. 5).

To calculate the transport in these junctions, it is necessary to specify the geometry, a solution to the band lineup problem, how

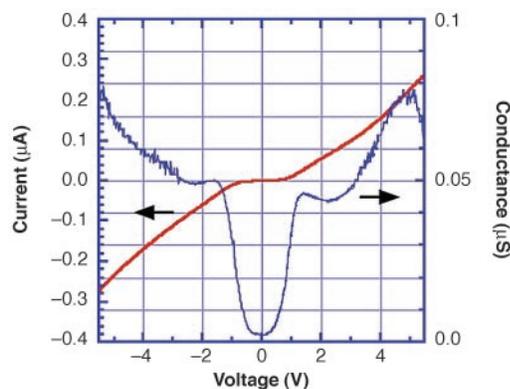


Fig. 5. Reported break junction measurement of 1,4-benzene dithiol between two gold electrodes at room temperature [from (11)].

the voltage on the junction will be treated, the model Hamiltonian and the methodology for conductance computation.

The issue of geometry is complicated. Though it is possible to calculate the optimal geometry at equilibrium, in the presence of constant current flow, simple variational principles are no longer available. Therefore, one cannot minimize energy by varying the geometry (42) and assumed geometries are used instead. Usually, the molecular geometry is optimized either for an isolated molecule or for an “extended molecule” using either first principles electronic structure theory or empirical force fields (43, 44).

The simplest calculations (45) of the  $I$ - $V$  characteristic of the BDT molecular junction assumed band lineup corresponding to the fermi energy at the mid-gap between HOMO and LUMO states (46) and symmetric division of the voltage drop between the two

molecule-electrodes interfaces. The extended Huckel tight binding model was used for the electronic structure calculation, and the current-voltage characteristic was obtained from the Landauer theory.

The assumptions concerning band lineup and effective voltage in the junction used in that calculation are reasonable but certainly not rigorous. More recent calculations use density functional theory within the molecule, evaluation of transport properties either by the NEGF picture (24–29) or by a Lippman-Schwinger approach (47) and describing the bulk electrode using either a jellium picture or a tight binding model. In the NEGF calculation, self-consistent solutions for the electronic structure of the extended molecule and the electrostatic potential distribution were obtained. They produce a consistent solution both to the band lineup problem and to the effects of voltage on the electronic structure of the molecule.

The results differ substantially from the simplest assumptions used in the extended Huckel calculation. Upon forming the chemisorptive bond between the two gold electrodes and the BDT molecule, substantial charge transfer from the electrode onto the molecule is indicated. The extent of this charge transfer is not clear. Results using a small basis set suggest that up to 1.0 electrons are transferred onto the extended molecule, but molecular cluster calculations using larger basis sets suggest far smaller transfers. In either case, the Fermi level of the equilibrated structure is closer to the HOMO than it is to the LUMO. Therefore, the assumption made in the Huckel calculations, that the voltage division factors are equal and the Fermi level lies at mid gap, is not consistent with these DFT calculations.

The scattering probability  $T(E)$  as a function of energy correlates closely with the density of states in the region between LUMO and HOMO. For higher or lower energies, there are new resonances corresponding to “metal-induced gap states,” that arise from hybridization of the metal and the interfacial sulfur.

Away from the small voltage linear regime, the molecular orbital energies change with applied voltage (Fig. 6). Calculations (24) also show small thermionic contributions at room temperature, and a symmetric current-voltage characteristic upon inversion of the voltage, as expected given the symmetric geometry of the junction.

These sophisticated calculations do not agree either with one another or with the experiments. Whereas Xue *et al.* (24) suggested transport through filled states, work

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using the jellium model for the metal implies (47) that transport occurs through the LUMO, not the HOMO (7). Wang (48) found the same results. All three calculations (24, 47, 48) agree with experiment that the first maximum in the conductance occurs at a voltage near 1.5 V, but their calculated conductances are about 500 times larger than measured (11). Others (49) have focused on the importance of the interface, because different geometries will give substantially different currents or (50) the possibility that multiple molecules contribute to the transport in such junctions.

Although many of the qualitative understandings of the current-voltage characteristics are accurate and well understood, quantifying the behavior remains difficult. Recently, Weber and colleagues (8), found that current-voltage characteristics were not necessarily symmetric across symmetric molecules. They suggested (as seems reasonable) that small changes in interface binding might give asymmetric response because of nonsymmetric binding, even when the electrodes are identical and the molecules are supposedly symmetric. This suggests, as do the experiments (12), calculations (51) and simple intuition concerning exponential decay of overlap, that the nature of the interface binding can dominate transport. Therefore, development of both experimental methods, perhaps involving scattering or spectroscopy, and computational methods utilizing direct force calculations are necessary to determine the correct geometric structure, before reliable calculations can be obtained.

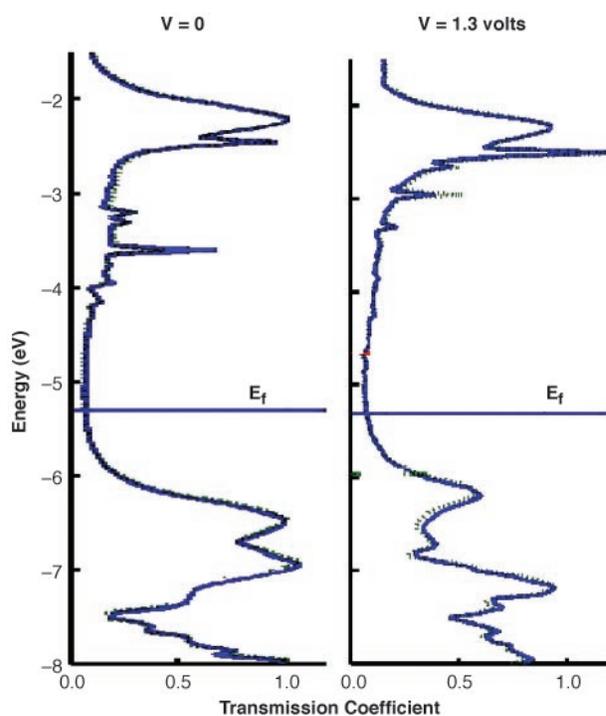
### Challenges and Prospects

Even once the simplest case of coherent single-molecule transport at fixed geometry is understood, major challenges still remain. Some of these (transport in single versus multiple molecule junctions, appropriate variational formulation to comprise geometry optimization as well as transport, and the role of interactions between electronic and vibrational degrees of freedom) are currently under investigation. The statistics of transport is also of interest; because of different geometric possibilities involved in binding and in transport, one expects to see behavior much more like that of single molecule spectroscopy than of ensemble average measurements (8, 9), although some averaging may take place on the

time scale of the measurement. There has been little work so far in the analysis of nanojunction statistics, although most of the early measurements on junction conductance reported in the literature indeed deal with statistical ensembles.

It is now clear from many measurements (3–5, 8–16, 51–53) that the observed transport is indeed mediated by the molecular bridge and depends on bridge properties. To arrive at true understanding and predictive capability in molecular transport junctions, even greater advances are required, including the following:

1) Characterization of the temperature dependence of conductance. This would help in understanding coherent and incoherent transport behavior as well as elucidating the contribution of different conformations. First experimental results along these lines are becoming available (8, 9).



**Fig. 6.** Computed transmission coefficient of the benzene dithiol junction, using density functional theory and NEGF formalism. Note that  $T(E)$  varies with applied voltage, because of changes in the electronic states [after (24)].

2) Characterization geometry and its evolution during transport.

3) Measurements with differing junction subunits (molecular conjugation, interface bonding “alligator clip” functional groups, electrodes). New work in several laboratories (54–57) using Si or C electrodes is showing striking new features, including selective bond cleavage and negative differential conductance.

4) More extensive work on gating of molecular junctions. The control and understanding of electrostatic potentials can then be placed on a firm footing, as it has been in

nanotubes (58) and is beginning to be in molecular junctions (59).

5) Elucidating the change in behavior from a single molecule conductance through junctions comprising a few molecules to molecular film conductors. This scaling behavior is important for its structure-function aspect as well as for understanding coherence and dephasing phenomena in such junctions.

6) Effects of changing chemistry and doping on the bridge: Can mechanisms be altered by chemical change, as in conducting polymers, and can we predict and control such behavior?

7) Characterizing transport junctions behavior in the presence of radiation. Can we address a junction optically, i.e., find how to couple radiation and transport in a controlled way? Does optical excitation enhance transport? Can we use vibrational or electronic spectroscopy to monitor (or even to control) junction properties? Can a transport junction act as an interferometer?

Aspects of molecular junctions in areas other than simple transport have been addressed only in preliminary ways. These include gating, switching, optical control, sensing, and transistor function of molecular wires, and involve actual device and/or chemical behaviors. Transient and AC transport phenomena have also not been investigated extensively, although it has been shown that theoretical steady state methods can be useful in analyzing such phenomena in simple junctions (31). Both theory and measurements (60–64) have shown that molecules can indeed use their ability to change conformation to act as gate switches, sensors and transistors. Understanding these functions on a reasonable theoretical basis requires analysis of both the transport itself and the relation between transport and other dynamical properties of the molecular species.

Finally, chemical reactions can occur in junction structures. This has been demonstrated in lovely experiments and calculations showing specific bond breaking and addition reactions in STM junctions (44, 52, 61).

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