Analytical Model for Molecular-Scale Charge Transport[†]

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We demonstrate a simple analytical model for elastic charge transport on the nanometer scale within a single molecule. It is based on the assumptions usually employed for quantum chemical calculations, except that of equilibrium between the currents flowing in opposite directions. It allows the possibility of a nonuniform potential distribution and imbalance between the population of states of opposite momentum. We analyze two implementable configurations and find the predictions to be consistent with recent experimental results.

Introduction

Since both the speed and the power consumption of an electronic device tend to improve as it is made smaller, it has been repeatedly proposed that functional electronic devices will ultimately consist of a single organic molecule.[1-4] Modern nanofabrication and atomic-scale sensing techniques have created the possibility of applying two or more electrodes to an individual molecule, allowing the establishment of a potential gradient and deviations from equilibrium. There have been recent reports of the observation of the conductance quantization,[5-7] which is a particularly simple prediction of the Landauer charge-transport formalism for the case of metallic nanowires.[8-10]

Active devices for electronic purposes cannot be constructed purely from metallic wires but must also contain moieties with semiconducting nonlinear behavior. Of particular interest are the asymmetric molecules of the D−σ−A type proposed by Aviram and Ratner (AR) as a useful molecular device.[11]

Within the Landauer formalism, the current is given by

$$I(V) = \frac{e}{h} \int_{-\infty}^{\infty} \tau(E,V) \Delta p(E,V) \, dE \qquad (1)$$

where $\Delta p(E,V)$ is the difference in the Fermi−Dirac occupation factors of the levels at energy E in the electrodes on the two sides and $\tau(E,V)$ is the corresponding transmission factor, usually expressed in quantum field-theoretical notation as[12-14]

$$\tau(E,V) = Tr[A_1 M A_2 M^{\dagger}] \qquad (2)$$

where M is an effective matrix element of the Green's function and A_1 and A_2 are the spectral functions of each electrode.

The basic assumptions of the Landauer formalism are essentially also those of the molecular orbital (MO) self-consistent field (SCF) methods most commonly used to analyze organic molecules. The detailed interactions between each electron and its neighboring electrons and nuclei are smeared out and replaced by an average field. Both are one-electron

methods, in which transition to the real world of many electrons is achieved via the Aufbau principle.

Inelastic processes are ignored. However, in good electronic materials these processes are only appreciable on length scales much greater than molecular. The dominant inelastic process for carriers in semiconductors is scattering from phonons (lattice vibrations). The mean free path is typically 100 nm,[15] significantly larger than the size of the average molecule. Even then, a single scattering event is largely elastic, retaining most of the carrier energy. Just as for elastic scattering from a charged impurity,[16] its major salient effect is momentum randomization rather than energy loss. After randomization, the electron is still hot but does not contribute to the overall current. Inelastic processes must subsequently occur to cool it toward thermodynamic equilibrium, but the rate of cooling is irrelevant to current flow and does not affect $I-V$ characteristics. Even in mesoscopic quantum-well devices, the current flow can be modeled quite adequately by elastic processes only.[17] Other inelastic processes, for example, the emission of light, are so rare that they can be treated as a small perturbation.

We do not claim that inelastic processes can always be ignored for charge transport in organic molecules. They are important for processes occurring in solution, for hopping transport, or in systems with pronounced polaronic effects. However such systems will not be suitable for high-performance molecular electronics.

In this paper, we demonstrate a model for the transmission factor $\tau(E,V)$ appropriate for an organic molecule and present approximate analyses of the cases in which one and two molecular orbitals, respectively, are significant in the conduction process. These two cases are adequate to describe recent experimental measurements on actual molecules. The work was inspired by a circuit analogy, which provides a concrete model for visualization, access to the considerable literature on circuit design, and useful results, special cases of which are in agreement with analyses by Hush and collaborators[12] and Datta and co-workers.[14]

Circuit Analogy

In usual MO SCF calculations, each electron in a molecule is associated with a discrete level spread out over the whole

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molecule. The theory leads to a set of simultaneous equations of the form

$$\sum_s (H_{rs} - ES_{rs})c_s = 0 \qquad (3)$$

where c_s is the coefficient of the atomic orbital φ_s. In a chemical context, the tight-binding Hamiltonian matrix with elements H_{rs} is often symbolized F and called the Fock matrix. S is the overlap matrix, with general element S_{rs} giving the overlap between orbitals r and s.

For a finite molecule, eq 3 has only countably many nontrivial solutions, each of which may be labeled with an integer i. The ith molecular orbital thus has energy E_i and atomic orbital coefficients c_{si}. To allow the possibility of current flow, the system must also contain effectively infinite electrodes, in which case nontrivial solutions exist for a continuum of values of the energy E.

While most of the atoms in the system belong to the two electrodes, greatest interest is attached to events happening in the finite organic molecule located between them. However, the probability that the electron in any given level is on the molecule is essentially zero. What is required is a way of dividing the system into interacting subassemblies. This is provided by a simple electrical analogue, noting the formal similarity between eq 3 and the equations for a source-free circuit network:

$$\sum_s Y_{rs}V_s = 0 \qquad (4)$$

where V_s is the voltage at the node s, and Y is the admittance matrix with general element Y_{rs} linking nodes r and s. The atomic orbital coefficients c_s can be considered to be "electron wave voltages". Atoms are "electron wave resonators". To allow a molecule to be represented in terms of inductors and capacitors, we must take the relativistic viewpoint that electrons have a rest frequency of 124 EHz, with all levels clustered within terahertz of this value (metric prefixes E and T stand for exa- and tera-, with values 10^{18} and 10^{12}, respectively). The nonlinear variation of admittance with frequency (proportional to energy) can then be linearized. The scaling factor for impedance is without physical significance.

Bonds are "electron wave inductors" with an admittance (the reciprocal of impedance) of iH_{rs}. Atoms are "parallel electron wave tuned circuits" formed by the parallel combination of an electron wave capacitor and an electron wave inductor. When the rth atom has been isolated by "shunting" all other resonators to ground, it resonates at H_{rr}. At other frequencies/energies E, the isolated atom has an "electron wave admittance" of $i(E - H_{rr})$. Without the shunts, the circuit does not resonate at these frequencies but instead at those of the molecular allowed states. Each level has a finite amplitude at any atom. The charge on an atom is the "electron wave energy" stored in it.

Figure 1 shows a simple conjugated molecule, butadiene, and its equivalent circuit at the level of Hückel theory. The value opposite each circuit element is its immittance (imaginary part of the admittance). It is readily apparent that the factor $\tau(E,V)$ of eqs 1 and 2 is equal to the power transmission factor of the analogue circuit. While this analogy does not add anything beyond eq 3 to the analysis of molecular charge transport behavior, it is easier to visualize. In molecular electronics the problem is one of design, and the analogy gives access to the wealth of literature on electrical wave filters, for example.[18]
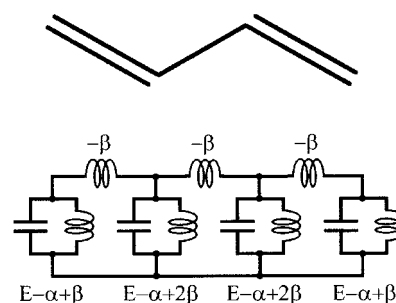

Figure 1. Simple conjugated molecule (1,3-butadiene) and its dynamic circuit analogue at the level of simple Hückel analysis, as described in the text.
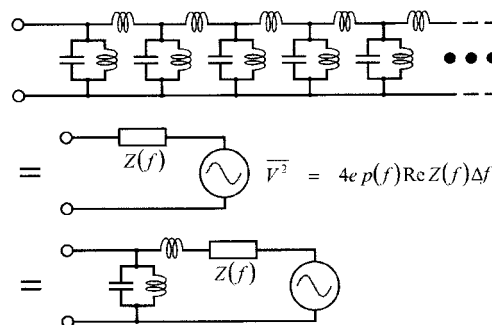

Figure 2. Dynamic circuit analogue of a semi-infinite polymer chain (a model for the electrodes).

Because of the conservation of charge, the analogue circuit for a finite molecule cannot have any "electron wave resistors", which would be a sink steadily dissipating charge. However, the lumped analogue circuit for a semi-infinite polymer chain can. It is well-known that a transmission line has a characteristic impedance Z, e.g., 50Ω coaxial cable. If the semi-infinite chain is replaced by the wave impedance Z, then the behavior of all other parts of the circuit is unchanged. The apparent nonconservation of charge corresponds to the transfer of charge from the part modeled in detail to the chain. As shown in Figure 2, random emergence of charge from the chain in accordance with the Fermi−Dirac fractional occupation spectrum $p(f)$ is represented by a random "electron wave voltage" source c in series with the wave impedance Z,[19] whose component in the frequency band from f to $f + \Delta f$ has variance

$$\overline{c^2} = 4ep(f) \operatorname{Re} Z(f) \, \Delta f \qquad (5)$$

Appendix A treats the case of a finite moiety weakly coupled to this semi-infinite chain. It is shown that when equilibrium is reached, the charge in the molecular level at f_0 is essentially equal to $ep(f_0)$. This result becomes exact in the limit of infinitely weak coupling. Despite the absence of anything corresponding to the Pauli exclusion principle in the one-electron model, this is the correct quantized occupation of the level. The infinite size of the system means that the levels are continuous, so that there is apparently no way of counting their number below a given energy as required by the Aufbau principle. However, it can be seen that this way of modeling infinite chains replaces the latter more usual procedure and additionally takes nonzero temperature effects into account. Moreover, since a finite molecule can be coupled to two or more semi-infinite polymer chains with different Fermi−Dirac distributions, it allows the possibility of departures from equilibrium and net current flow.

WKB Approximation

We are now ready to compute transmission factors $\tau(E,V)$. A problem essentially identical to this has long been studied in
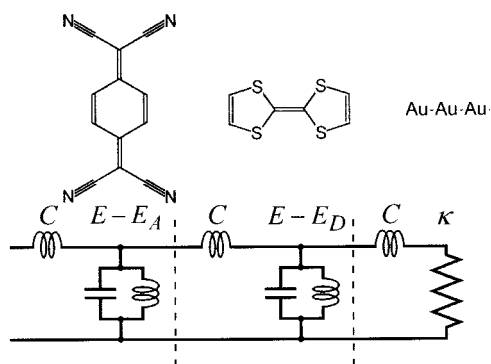
Figure 3. Sequence of aromatic moieties and tunneling gaps together with the circuit analogue for the calculation of the transmission factor in the WKB approximation as a product of transmission factors per stage.

the theory of passive electrical filters, and the resulting curve is known to depend sensitively on interactions between the parts. However, for present purposes, the detailed behavior of the transmission factor with energy is not required, as the only result with directly measurable physical significance is the integral of the transmission factor times the differential fractional occupation. Moreover, experimentally poorly controlled factors, such as molecular conformation and thickness of oxides/contaminants on electrodes, mean that approximations leading to errors of an order of magnitude are acceptable, as long as they provide an intuitive grasp of the intramolecular processes in play. The well-known WKB approximation[20−22] justifies setting the total attenuation for the whole molecule equal to the sum of attenuations of each moiety. Equivalently, the total transmission factor for the whole junction is approximated by the product of transmission factors for the individual moieties.

Consider the arrangement of Figure 3. Each stage is represented by a single electronic level of an aromatic moiety and the tunneling gap to the left. The tunneling gaps are just large physical separations between electroactive atoms, and in the circuit analogue they are represented by rather small admittances. In precise modeling, the moiety should be represented by a collection of interconnected resonators, and near the frequency of the electronic level, the voltages at input and output nodes may differ, resulting in a gearbox/transformer ratio term in the overall transmission factor for the gap-moiety stage. However, except in pathological cases, this ratio is within an order of magnitude of unity. It may be neglected at the present level of approximation, allowing the whole moiety to be represented by just a single resonator.

The transmission factor is defined as a ratio of electron currents, i.e., of "electron wave powers" in the circuit analogue. It is therefore the square of the voltage gain for the stage divided by the ratio of impedance levels. However, since the impedance levels in the two metallic electrodes on both sides can be taken to be the same, and the chain product of the impedance ratios is unity, the transmission factor for each "stage" (shown between the dotted lines) can be taken to be just the modulus squared of the voltage gain.

The stage with the donor moiety consists of a capacitance for the tunneling gap shunted to ground by a resonator and is representative for most of the stages. Its transmission factor is seen to be given to the required accuracy by a Lorentzian:[12]

$$\tau(E) = 1 / \left[1 + \frac{(E - E_D)^2}{C^2} \right] \tag{6}$$

This formula gives correctly the transmission factor for energies far from resonance, and the width of the band over which the transmission factor is near unity. The Lorentzian form is well-known for mesoscopic charge transport in, e.g., quantum-well structures.[23]

The rightmost stage does not have the same form. Like the other stages, the link element is the immittance of the tunneling gap, but in the place of the resonator it has the admittance κ of the single mode of the nanowire electrodes. The transmission factor is given by

$$\tau(E) = C^2 \kappa^2 \tag{7}$$

The WKB approximation with the transmission factors given in eqs 6 and 7 becomes exact in the case of a moiety with a single orbital located symmetrically between the electrodes.[12]

Current Flow Dominated by a Single Level

The simplest molecular junction consists of a single aromatic moiety between two metal electrodes and separated from them by tunneling gaps. We assume that only one level of the moiety lies between the Fermi levels of the electrodes at any given time and neglect effects of the field on its electron distribution.

At the required level of approximation, and with the two tunneling gaps chosen as equal for simplicity, the transmission factor for the succession of two stages is given by

$$\tau(E) = \frac{C^4 \kappa^2}{C^2 + (E - E_0)^2} \tag{8}$$

where E_0 is the energy of the single electronic level.

When the molecule is placed beween two electrodes, E_0 varies as the electrode potential does. At the first level of approximation, the charge on the moiety can be assumed to be independent of the applied voltage V, so that the potential on it can be determined by a simple lever rule. Taking the origin of potential at the left-hand electrode, the potential ϕ at a distance x from it is given by the "lever rule":

$$\phi(x) = Vx/d \tag{9}$$

Note that, even for the equilibrium case of zero applied potential V, the electrostatic potential of Maxwell's equations is far from constant in the region between the electrodes, going negative at the hard-core radius from electronegative nuclei such as oxygen, and reaching values near +100 V inside the radius of the inner shell electrons of each carbon nucleus. The smoothly varying value given by eq 9 can be considered to be either the local Fermi potential or the deviation from the potential distribution of the equilibrium case. The parameter E_0 of eq 8 is the position of the moiety level with respect to the Fermi levels of the electrodes in the equilibrium case.

If temperature effects are ignored, eq 1 gives a current proportional to the integral of this Lorentzian function between the two Fermi levels:

$$I = \frac{e^2 \kappa^2 C^3}{h} \left[\tan^{-1} \left(\frac{E_0 + epV}{C} \right) - \tan^{-1} \left(\frac{E_0 - eqV}{C} \right) \right] \tag{10}$$

where $0 \leq p \leq 1$ is the fractional position of the "center of gravity" of the moiety within the gap between the electrodes, and $p + q = 1$.

The resulting rounded-step-function current−voltage curve for an asymmetric case is shown in Figure 4. A similar characteristic has recently been generated by computer simula-
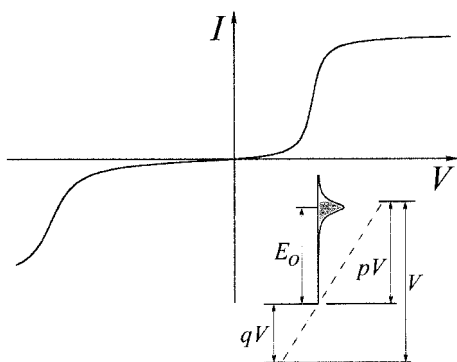
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Figure 4. Typical $I-V$ curve for a molecular junction with just one level near the Fermi level.

tion.[24] Hall et al.[12] give a particular case of this equation as an exact result for the case of a single atom placed symmetrically in the gap ($p = \frac{1}{2}$). Equation 10 gives a good fit to experimental $I-V$ data from noble metal−Langmuir−Blodgett (LB) mono-layer−noble metal cells.[25]

The essential aspects of this curve can be expressed simply. In the absence of bias the level is normally not at the Fermi level. Both directions of applied bias will ultimately bring it between the Fermi levels of the two electrodes. When this is the case, the passage of current between the electrodes is facilitated by resonant tunneling. The different voltage thresholds for conduction in the two directions reflect the asymmetry in the position of the moiety between the two electrodes.

A molecular junction can be said to be positively biased when the side on which an acceptor level lies is positive or if the side on which a donor level lies is negative. Considering the acceptor moiety to correspond formally to the P region of a PN junction, and the donor to the N region, positive bias corresponds to easy PN junction current flow, i.e., lowest voltage for a given current. This single-moiety case also gives easy current flow for positive bias.

Current Flow Influenced by Two Levels

The molecule proposed by Aviram and Ratner as a molecular rectifier[11] consists of donor and acceptor moieties, D and A, respectively, as shown in Figure 3. Each moiety is separated by tunneling gaps from the two electrodes and from each other.

As above, we assume that only one level of each moiety ever lies between the Fermi levels of the two electrodes. At the required level of approximation, and with the three tunneling gaps chosen as equal for simplicity, the total transmission factor for the succession of three stages is given by

$$\tau(E,V) = \frac{C^6 \kappa^2}{[C^2 + (E - E_A)^2][C^2 + (E - E_D)^2]} \quad (11)$$

E_A and E_D are the energies of the single electronic levels of A and D, respectively, both of which are functions of V. Novel behavior is only to be expected if both lie between the Fermi levels on both sides. Under this condition, $\Delta p = 1$ whenever $\tau(E,V)$ is appreciable, so that eq 1 for the total current simplifies to

$$I = \frac{e}{h} \int_{-\infty}^{\infty} \tau(E,V) \, dE \quad (12)$$

This has the form of a convolution of Lorentzians and is readily evaluated to be

$$I = \frac{e}{h} \frac{2\pi C^5 \kappa^2}{4C^2 + (E_A - E_D)^2} \quad (13)$$

On the assumption that the variation of E_A and E_D is described by the lever rule, the current−voltage relationship is bell-shaped, with a region of negative differential resistance (NDR) for voltages beyond that leading to alignment of E_A and E_D:

$$I = I_0 \left\{ 1 + \left(\frac{V - V_0}{\delta V} \right)^2 \right\} \quad (14)$$

where V_0 is the voltage at which the two levels are aligned, δV is the peak width, and I_0 is the peak current. The fact that the model predicts nonzero current at zero voltage is a consequence of the approximation made in eq 12.

Experimental results showing NDR have been reported by Chen et al.[26] and have already been explained with the help of a computer simulation.[27] In the latter paper, it is noted that high molecular conductivity is associated with a particular value of the molecular charge. However, the salient feature of the molecule leading to high conductivity is not so much this as the fact that the LUMO then extends over the whole molecule. In the present picture this is synonymous with alignment of local moiety levels.

There are two respects in which a naïve interpretation of eq 14 differs qualitatively from the results of Chen et al. First, the voltage at which the current peak occurred varied significantly with temperature. Within the present model, just as for the more sophisticated computer analysis,[27] this temperature dependence must be explained as the result of thermal expansion and changes of aggregation. These lead to changes in organic− organic and organic−metal orbital overlap and hence shifts of the exact positions of the organic levels with respect to the metal electrodes. Second, the $I-V$ peak of Chen et al. is not symmetrical but skewed to low voltages.

Like the single-level result of eq 10, easy current flow for the two-level case also occurs for positive bias. Note that, in the original paper by Aviram and Ratner,[11] an inelastic process was considered to occur in addition to the elastic mechanisms considered here. The direction of easy current flow for this mechanism was negative.

Refinement of Variations of Potential

An expression showing the skewed behavior observed by Chen et al.[26] can be obtained by refining the lever rule for determining the potential. This rule is only valid if the changes of the moiety charges with V are negligible compared to those on the adjacent electrode surfaces. Clearly, when the doubly occupied donor state at E_D approaches the vacant acceptor level at E_A, a significant quantity of charge will be transferred, changing the electrostatic potentials of both donor and acceptor from the lever-rule values.

An order of magnitude calculation based on plausible values for the AR molecule and Poisson's equation:

$$\nabla^2 V = -\rho/\epsilon \quad (15)$$

shows that the transfer of one electron can under some circumstances lead to a voltage change of order 100 V. Before alignment of the energy levels is reached, the direction is such as to oppose alignment, while beyond this point, the donor and acceptor charges resume their original, quiescent values.

The present formalism provides information on changes in charge. As shown in Appendix A, the circuit analogue model
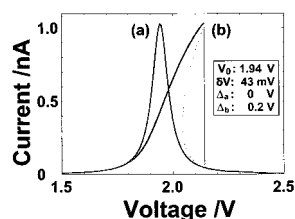
Figure 5. Typical $I-V$ curves for a D$-\sigma-$A molecular junction with (a) negligible change of charge state of the D and A moieties ("lever rule", $\Delta = 0$) or (b) appreciable change of moiety charge ($\Delta = 0.2$ V). The other parameters, chosen to give a fit to ref 26, are for both curves: $V_0 = 1.94$ V, $\delta V = 43$ mV, and $I_0 = 1.03$ nA.

gives the correct Aufbau charge distribution. Under most circumstances the charge on weakly coupled moieties is essentially quantized to integer multiples of e. However, since the Fermi$-$Dirac distribution is not completely abrupt but goes from fully occupied to fully unoccupied in a width of order kT/e, the transition from one charge state to the next occurs for a voltage change of this order of magnitude. Although the present SCF MO models do not handle the instantaneous Coulomb interaction, all include it as a time and space average, so that the resulting $I-V$ curve is expected to show the stepped behavior of the Coulomb blockade.

This may appear surprising in the light of the literature about the Coulomb blockade (e.g., ref 28), where the usual explanations involve the energy $Q^2/2C$ associated with a charge Q on a mesoscopic metal particle of capacitance C. The fact that each carrier on a metal island sees the same well-defined capacitance is due to the high polarizability of the metallic electrons. When the carrier is outside the metal, this polarizability gives rise to the classical image charge attraction, which must clearly be incorporated in the MO SCF potential. The smaller stabilization associated with smaller metal islands is completely equivalent to their lower image charge attraction. The case of an organic molecule is expected to be more complicated because of the reduced screening and less well-defined value of capacitance. However, Mujica et al.[29] have shown that MO SCF formalisms do predict stepped, Coulomb-blockade-type behavior in molecular $I-V$ characteristics.

Analysis shows that when a moiety interacts weakly with a number of electrodes at different potentials, the resultant charge is just the weighted mean of the charges that would pertain if the coupling were to only one electrode, with weights equal to the transmission factors to the different electrodes. For the D$-\sigma-$A case, the resultant characteristic can be derived from the curve of eq 14 by correcting the voltage V for the additional amount, proportional to $I/(2I_0 - I)$, required to compensate for the moiety charge:

$$V' = V + \Delta I/(2I_0 - I) \tag{16}$$

where, as before, I_0 is the peak current. The new sample parameter Δ is the maximum compensation voltage, occurring for $I = I_0$ when the two levels E_A and E_D are aligned.

Figure 5 shows $I-V$ curves for parameters relevant to the measurements presented in ref 26. Curve a shows the Lorentzian shape discussed above for the case when the coefficient Δ of the voltage offset is zero, i.e., when the moiety potential is determined essentially by the lever rule. Curve b shows the relationship when the charges on the moieties change appreciably on current flow, with $\Delta = 0.2$ V. The re-entrant dashed portion of the curve is unstable and cannot be obtained experimentally; instead, the vertical transition shown by a thin line is observed.

Conclusion

We have presented here two approximate quantum analyses of the current flow within an individual molecule, based on the Landauer formalism and molecular-orbital self-consistent-field methods. The analyses can be understood in an intuitive, pictorial way that avoids both multidimensional integrals and the requirement to solve large systems of simultaneous equations.

When a molecule interacts strongly with metal electrodes in its vicinity in such a way that coherent current flow becomes possible, it is challenged with electron energies other than those of the orbitals of the isolated molecule. To provide a concrete and more applicable picture of the dynamic electronic behavior of a molecule in this case, we have presented a circuit analogue. While firmly based on the Hartree$-$Fock formalism, this analogue allows the visualization of the individual character molecules or moieties retain even when strongly coupled, as well as intuition as to how this character blends to determine the behavior of the complete system. In addition, it makes available for molecular electronics design the wealth of intuition available in the literature of electric wave filters. We trust that chemists involved in molecular electronics are more interested than most in understanding how circuits operate. The analogy incorporates in an elegant way the correct local average distribution of electrons in both equilibrium and nonequilibrium situations.

In the two distinct cases considered, easy current flow occurs for positive bias with respect to the formal analogy to a PN junction diode. The opposite direction of easy current flow can only result from an inelastic mechanism. The present elastic transport theory agrees with experimental results reported for noble metal$-$electroactive Langmuir$-$Blodgett monolayer$-$noble metal structures[30] and for ultrathin multilayer structures.[31] It is qualitatively in agreement with measurements of nitro-amine-substituted molecules in a nanometer-size (30 nm) pore.[26] Moreover, the analytical derivation gives insights not available from the results of a computer program. It is rich enough to include stepped Coulomb-blockade characteristics related to the quantization of the number of electrons on the molecule.

The picture presented here should allow greater insight into the active electronic behavior of molecules.

Appendix A: Occupation of a Moiety

Within the circuit analogy, we derive here the occupation of a finite moiety linked weakly to an infinite chain in thermodynamic equilibrium.

First we must derive the expression for the energy stored in a set of pure reactive elements (inductors and capacitors) connected in an arbitrary pattern, limited initially to the case of excitation at a given frequency. Note that the impedance Z and admittance Y of a circuit are related by

$$Y = Z^{-1} \tag{A1}$$

The energy stored in a capacitor is given by

$$U = {}^1/_2 CV^2 \tag{A2}$$

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For a time-dependent voltage, this equation gives the average energy if V is taken to be the root-mean-square voltage.

Since the admittance of a capacitor is given by

$$Y = 2\pi i f C \qquad (A3)$$

then the energy may be re-expressed:

$$U = \frac{1}{4\pi}\left(\text{Im}\frac{dY}{df}\right)V^2 \qquad (A4)$$

Transforming from the purely imaginary Y to Z by use of eq A1 and noting that $V = ZI$, this equation is equivalent to

$$U = \frac{1}{4\pi}\left(\text{Im}\frac{dZ}{df}\right)I^2 \qquad (A5)$$

which is also appropriate for the energy stored in an inductor, normally expressed as

$$U = {}^{1}/{}_{2}LI^2 \qquad (A6)$$

If two circuits both obey eq A4, then clearly it is also valid for their combination in parallel, since both circuits then share the same voltage and the admittance of the combination is the sum of the individual values. If two circuits both obey eq A5, then clearly it is also valid for their combination in series, since both circuits then share the same current, and the impedance of the combination is the sum of the individual values. By induction, these equivalent equations are valid for all combinations of purely reactive elements.

For excitation with an arbitrary waveform, the different frequency components can be separated by Fourier transformation, and the average energy stored is the sum of the average energies over all frequencies.

We now apply these results to the case of a moiety with a finite number of resonances weakly linked to an infinite polymer chain with a noise source described by eq 5. First note that the impedance $Z(f)$ of a network of inductors and capacitors as a function of frequency is given by a rational function. All its zeroes and poles are distinct and lie on the real frequency axis. $Z(f)$ takes on only purely imaginary values there. As a result, it may be represented in the following form:[32]

$$Z(f) = \sum_r \frac{\alpha_r}{i(f - f_r)} \qquad (A7)$$

All the coefficients α_r are real and positive. The resonance frequencies f_r at which the impedance becomes infinite are the one-electron levels, within the framework of the MO SCF picture, of the finite moiety. The effect of the weak linkage is represented by a very small admittance C, which merely adds a term to this equation with $f_r = 0$.

Let us consider the moiety charge associated with each term of eq A7.

In the vicinity of f_r, the effect of the coupling capacitor, as well as that of all the other terms, is to add a pure imaginary amount iX to the impedance. iX varies smoothly in the vicinity of f_r and may be merged with the impedance of the semi-infinite polymer chain to give a new value Z_c. Since iX is pure imaginary, the amplitude of the noise voltage source is still given by $4ep\,\text{Re}\,Z_c\Delta f$. Transforming to a Norton equivalent circuit, the amplitude of the noise current source is $4epG\Delta f$, where $Y = 1/Z_c = G + iB$.

The contribution due to the to the average moiety charge in the frequency band from f to $f + \Delta f$ is given by

$$\Delta Q = \frac{4epG}{4\pi\alpha}\Big/\left\{G^2 + \left(\frac{f - f_r}{\alpha} + B\right)^2\right\}\Delta f \qquad (A8)$$

The only significant contribution to the charge is in the immediate vicinity of f_r so that the Fermi−Dirac fractional occupation p, G, and B can be taken to be constant. It is readily seen that the overall integral of this contribution is independent of G, B, and α and is equal to

$$\int \Delta Q = ep(f_r) \qquad (A9)$$

Hence the average charge on the moiety is automatically equal to the value expected from the Aufbau principle, taking into account partial occupation due to temperature effects.

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