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Unimolecular and Supramolecular Electronics II

Chemistry and Physics Meet at Metal-Molecule Interfaces

Volume Editor: Robert M. Metzger

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**Aims and Scope**

The series *Topics in Current Chemistry* presents critical reviews of the present and future trends in modern chemical research. The scope includes all areas of chemical science, including the interfaces with related disciplines such as biology, medicine, and materials science.

The objective of each thematic volume is to give the non-specialist reader, whether at the university or in industry, a comprehensive overview of an area where new insights of interest to a larger scientific audience are emerging.
Thus each review within the volume critically surveys one aspect of that topic and places it within the context of the volume as a whole. The most significant developments of the last 5–10 years are presented, using selected examples to illustrate the principles discussed. A description of the laboratory procedures involved is often useful to the reader. The coverage is not exhaustive in data, but rather conceptual, concentrating on the methodological thinking that will allow the non-specialist reader to understand the information presented.

Discussion of possible future research directions in the area is welcome.

Review articles for the individual volumes are invited by the volume editors.

In references *Topics in Current Chemistry* is abbreviated *Top Curr Chem* and is cited as a journal.

Impact Factor 2010: 2.067; Section “Chemistry, Multidisciplinary”: Rank 44 of 144
For these volumes in the Springer book review series *Topics in Current Chemistry*, it seemed natural to blend a mix of theory and experiment in chemistry, materials science, and physics. The content of this volume ranges from conducting polymers and charge-transfer conductors and superconductors, to single-molecule behavior and the more recent understanding in single-molecule electronic properties at the metal–molecule interface.

Molecule-based electronics evolved from several research areas:

1. A long Japanese tradition of studying the organic solid state (since the 1940s: school of Akamatsu).
2. Cyanocarbon syntheses by the E. I. Dupont de Nemours Co. (1950–1964), which yielded several interesting electrical semiconductors based on the electron acceptor 7,7,8,8-tetracyanoquinodimethan (TCNQ).
4. The erroneous yet over-publicized claim of “almost superconductivity” in the salt TTF TCNQ (Heeger, 1973).
5. The first organic superconductor (Bechgard and Jérôme, 1980) with a critical temperature $T_c = 0.9$ K; other organic superconductors later reached $T_c \approx 13$ K.
7. The interest in TTF and TCNQ begat a seminal theoretical proposal on one-molecule rectification (Aviram and Ratner, 1974) which started unimolecular, or molecular-scale electronics.
8. The discovery of scanning tunneling microscopy (Binnig and Rohrer, 1982).
9. The vast improvement of electron-beam lithography.
10. The discovery of buckminsterfullerene (Kroto, Smalley, and Curl, 1985).
12. The growth of various nanoparticles, nanotubes, and nanorods, and most recently graphene.
All these advances have helped illuminate, inspire, and develop the world of single-molecule electronic behavior, and its extension into supramolecular assemblies.

These volumes bring together many of the leading practitioners of the art (in each case I mention only the main author). Bässler sets in order the theoretical understanding of electron transport in disordered (semi)-conducting polymers. Saito summarizes in fantastic detail the progress in understanding charge-transfer crystals and organic superconductivity. Echegoyen reviews the chemistry and electrochemistry of fullerenes and their chemical derivatives. Thompson reviews the progress made in organic photovoltaics, both polymeric and charge-transfer based. Ratner updates the current status of electron transfer theory, as is applies to measurements of currents through single molecules. Metzger summarizes unimolecular rectification and interfacial issues. Kagan discusses field-effect transistors with molecular films as the active semiconductor layer. Allara reminds us that making a “sandwich” of an organic monolayer between two metal electrodes often involves creep of metal atoms into the monolayer. Rampi shows how mercury drops and other techniques from solution electrochemistry can be used to fabricate these sandwiches. Wandlowski discusses how electrochemical measurements in solution can help enhance our understanding of metal–molecule interfaces. Hipps reviews inelastic electron tunneling spectroscopy and orbital-mediated tunneling. Joachim addresses fundamental issues for future molecular devices, and proposes that, in the best of possible worlds, all active electronic and logical functions must be pre-designed into a single if vast molecular assembly. Szulczewski discusses the spin aspects of tunneling through molecules: this is the emerging area of molecular spintronics.

Many more areas could have been discussed and will undoubtedly evolve in the coming years. It is hoped that this volume will help foster new science and even new technology. I am grateful to all the coauthors for their diligence and Springer-Verlag for their hosting our efforts.

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Robert Melville Metzger
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Molecular Electronic Junction Transport: Some Pathways and Some Ideas

Gemma C. Solomon, Carmen Herrmann, and Mark A. Ratner

Abstract When a single molecule, or a collection of molecules, is placed between two electrodes and voltage is applied, one has a molecular transport junction. We discuss such junctions, their properties, their description, and some of their applications. The discussion is qualitative rather than quantitative, and focuses on mechanism, structure/function relations, regimes and mechanisms of transport, some molecular regularities, and some substantial challenges facing the field. Because there are many regimes and mechanisms in transport junctions, we will discuss time scales, geometries, and inelastic scattering methods for trying to determine the properties of molecules within these junctions. Finally, we discuss some device applications, some outstanding problems, and some future directions.

Keywords Conduction · Electron transfer · Electron transport · Molecular electronics

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1 Introduction

To a scientist, the fundamental properties of the real world break down into two broad categories, structure and dynamics. The two are often commingled – the baseball gives the home run, the planet gives its orbit, the muscle fiber gives contraction and expansion, and the donor/bridge/acceptor molecule gives phosphorescence, fluorescence, nonradiative decay, photovoltaic behavior, and electron transfer [1]. A molecular transport junction, which is the structure of most interest in this chapter, provides current flows as a function of voltage, temperature, geometrical arrangement, chemical composition, and density of environment.

Electron transfer in donor/bridge/acceptor molecules and currents in molecular transport junctions are closely related by the Born–Oppenheimer separation [2] that uses the mass difference between electrons and nuclei to permit isolated discussion of electron dynamics that almost always occur far faster than those of nuclei. The understanding that electron tunneling is a common feature between intramolecular electron transfer and transport in molecular junction structures was used by Nitzan to produce an approximate linear relation between the measurable quantities (rate constants for electron transfer, and conductances for molecular junctions) [3].

While chemists love structure (as a glance through any chemical journal will show), they are generally fascinated with mechanism. This short chapter is about some of the models, ideas, and understandings that have occurred in electron transport and molecular junctions [4–6]. The field is large, the problems are hard, the processes could be important both for our understanding and for many commercial applications, and finally the issues are fascinating for the chemical imagination.

The remainder of the chapter is structured as follows. Section 2 discusses the physical description of transport junctions, dealing with length scales, categorization, and the particular measurements that can be made. Section 3 is devoted to models – the general nature of models, and then the geometric, molecular, Hamiltonian, and transport models that are associated with molecular transport junctions and their interpretation.
Section 4 is entitled “Ideas” (for mechanisms and models). It deals with how we can interpret/calculate the behavior of molecular transport junctions utilizing particular model approaches and chemical mechanisms. It also discusses time parameters, and coherence/decoherence as well as pathways and structure/function relationships.

Section 5 is on one particular molecule, \( p \)-benzene dithiol. This is one of the most commonly studied molecules in molecular electronic transport junctions [7] (although it is also one of the most problematic). Section 6 discusses a separate measurement, inelastic electron tunneling spectroscopy \([8, 9]\) (IETS). This can be quite accurate because it can be done on single molecules at low temperatures. It occurs because of small perturbations on the coherent transport, but it can be very indicative of such issues as the geometrical arrangement in the molecular transport junction, and pathways for electron transport through the molecular structure.

Finally, some remarks on the different subfields of the larger topic of molecular electronics are found in Sect. 7.

2 Physical Description of Molecular Transport Junctions

By definition, a molecular transport junction consists of a molecule extended between two macroscopic electrodes. The nature of the molecule, the environment (whether it is solvated or not), the electrode’s shape and composition, the temperature, the binding of the molecule to the electrodes, and the applied field are all variables that are relevant to the measurement, which is usually one of differential conductance, defined as the derivative of the current with respect to voltage.

Figure 1 shows two things: a number of sketches of possible geometries for solid-state molecular transport junctions, and some electron microscopy images of actual functional transport junctions. There are two striking features to note: first, the
sketches are suggestive, but this is not evidence for their precision – in particular, we know essentially nothing about the coordination of molecules in transport junctions, nothing about the actual geometry (whether the molecule is standing, lying down, at a tilt angle). We do not know how many molecules are in the junction, and, if there is more than one, we certainly do not know their relative geometries.

On the other hand, the images show fairly definitively the structure of the metallic electrodes. We see that they are often regular at first sight (but often irregular at the atomic scale) and we know that when they are made of soft metals like gold or silver they can distort as the measurement is made. Therefore, our lack of understanding of length scales and geometries is one of the crucial aspects in molecular transport junctions that we will refer to time after time.

The structure of the molecular transport junction is reminiscent of the transport junctions used in a fascinating and important subarea of condensed matter physics: mesoscopic physics. In these (Fig. 2 shows an analogous chemical system), current, conductance, and higher derivatives are normally measured for systems containing a quantum dot or several quantum dots between two electrodes, usually in an environment in which gating can be applied. The two-dimensional electron gas is one of the standard systems in mesoscopic physics, one in which exquisite control can be achieved (Fig. 3). The striking difference between molecular and mesoscopic transport junctions is that the controls on geometry are very weak in the molecular situation – the fact that molecules are all the same as each other (one naphthalene is the same as every other naphthalene) does not help, because the length scale on which the system operates is so much larger.

Mesoscopic physics has defined many of the issues (Landauer limit transport [10, 11], Coulomb blockade regime [12], Kondo resonance regime [13–15]...) that will occur later in this chapter describing molecular transport junctions. These concepts are relevant, but must be reinterpreted to understand the molecular case.

Fig. 2 A quantum dot transport structure, consisting of a source, a drain, and a gate, with gold nanoparticles surrounded by DNA (the bright white dots). The transport through these structures can be fitted well to a simple Coulomb blockade limit description. From S.-W. Chung et al. “Top-Down Meets Bottom-Up: Dip-Pen Nanolithography and DNA-Directed Assembly of Nanoscale Electrical Circuits” Small (2005) 1, 64–69. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.
2.1 Categories, Break Junctions, and Structure

While many different molecular junction structures have been developed and utilized, they fall into three large categories. The first are measurements that by their nature observe ensembles of molecules. These include a range of systems comprising self-assembled monolayers (SAMs) measured in various ways, from molecular chemistry to the use of nanodot collectors to mesa-type structures supporting a small number of molecules [16]. Ensemble measurements are also made using conducting atomic force microscopy [17–19] with or without quantum dots as collectors. Other approaches that measure ensembles of molecules and their transport include the approach of using a liquid drop as one of the electrodes [20, 21] (Fig. 4). Finally, the nanopore structure [22] developed by Reed and his colleagues is a more elegant, and smaller, ensemble sort of measurement.

In sharp contrast to these are single molecule measurements, shown schematically in Fig. 5. These are normally done utilizing a break junction technique – a mechanical break junction [23–27] is one in which a thin region in a single metal is broken either by bending or stretching; the molecule is often trapped between the broken structures (Fig. 1). The electrochemical break junction [28] is one in which a metallic strand is stretched to breaking in a solution containing a molecule that can then bind to both broken ends of the strand. The difference is that the mechanical break junction is almost always used in vacuum, whereas the electrochemical break junction is almost always used in solution. Both can be gated, but the gating is very different – the mechanical break junction is gated by a third planar electrode reminiscent of a traditional semiconductor structure [15], while the electrochemical break junction is gated by a reference electrode, so that the measurements [29, 30] resemble single molecule electrochemistry.

A group in England has developed a very nice idea based on fluctuations [31]: here a molecule is chemisorbed on one end to a surface, and a conductive scanning tip is brought to within about a molecule length from the supporting metal. Thermal excitation then permits molecules to form instantaneous transport bridge structures between the planar support and the conductive electrode – one observes fluctuations
here, fluctuations that arise from the motion of the molecules between different bending geometries, as well as breaking the interaction with the tip altogether. The categories just described compromise the majority of the measurements on molecular transport junctions.

The lack of information about the molecular geometry within the junction raises a crucial issue. It is one that we will continue to return to, because it is the most vexatious issue – especially in contrast to vapor phase measurements, crystal structures, and even NMR structures, where one can place very tight metric constraints on bond lengths (certainly 0.01 Å accuracy can be obtained even by crude scattering methods). This is emphatically not true in these measurements – while techniques such as IETS and simultaneous measurement of conductance and Raman spectra [32] may give indirect information on molecular bonding in the junction, no instruments exist to measure the geometries of a transport junction directly, even in the absence of current flow, and it is even more difficult in the nonequilibrium situation when current is flowing.

It is possible to use electronic structure calculations combined with measurements in which the geometry is purposely varied to make some elegant deductions about the adsorption of molecules on the electrodes. A beautiful example is provided by work...
from the Columbia/Brookhaven group [33] employing electrochemical break junctions under extension, and using a combination of calculation and observation to suggest that the amine groups with which these molecules are capped select a single unsaturated gold atom to bind to – this is quite surprising in terms of the more standard sulfur terminations, and represents a real triumph of analysis. Similarly, beautiful measurements on gold wires [34] (not really a topic in molecular electronics, but one of great relevance, especially considering the role of the gold wires in electrochemical junctions) showed that there was a sharp correlation between the transport measurements and the electron microscopy measurements of geometric reorganization in the metal as current was passing through it.

In general, however, many relevant geometric parameters are unknown in molecular transport junctions, and therefore it is necessary to make assumptions, and calculations, to help in understanding the geometry. One interesting approach is
to ignore the actual conductance value for any specific molecule, and to use the same computational method (which is generally much simpler than the NEGF approach for conductance discussed in Sect. 4) to compare conductance values for a series of molecules. Lovely work of this kind has been published in the context of understanding transport in single-molecule electrochemical break junctions [35].

The discussion of calculations raises a significant point about the variational principle. Traditionally, the computational schemes by which quantum chemistry optimizes geometry are based on the static variational principle of Rayleigh and Ritz. This is easily derived from the Schrödinger equation, assuming that there is no external force acting on the system (that equilibrium can be defined, and that an energy minimum will exist at a particular geometry). These assumptions fail in a molecular transport junction, an open electronic system (the number of electrons on the molecule is not fixed but depends on the currents), in which the molecule is not at equilibrium (it sees different chemical potentials in the left and right electrode, if voltage is applied). This means that we have no simple static variational principle with which to optimize the geometry in a working transport junction. The usual approach taken here is to perform the minimization assuming that the junction is static, and then somehow to approach the problem of the difference between the static junction and the junction under bias, with current flowing. Since gold and silver are quite soft metals, and since we know it is very easy to modify the surface structures of them, the assumption that structure remains unchanged during a current/voltage experiment seems dubious. Therefore, there is no good theoretical method to calculate the molecular geometry – this is one of the major open challenges in molecular transport junctions.

2.2 Measurements

The quantities to be measured in transport junctions are current, voltage, conductance, inelastic electron tunneling spectroscopy (essentially the derivative of the conductance with respect to voltage), and the conductance as the molecular structure is distorted, generally by stretching [33, 36–38]. Additional measurements are sometimes made, including optical spectroscopy, vibrational spectroscopy (in particular Raman spectroscopy) [32, 39] and using particular applications such as the MOCSER entity [40, 41] (essentially a molecular transistor developed by the Weizmann group).

3 A Bit on Models

Science is largely about the world around us, about reality insofar as we can grasp it. But since the days of Euclid, and particularly since Lucretius, scientists have constructed models – that is, scientists have made simulacra, either conceptual or physical, in an
attempt to mimic aspects of what they perceive to be reality, but to do so in a more comprehensible or revelatory way. This tradition, now more than two millennia old, was reinvented by Newton, who modeled the universe in terms of particles with mass but no physical extension – Einstein followed with models for relativity, and modern physical science is probably most familiar with models used in dealing with the nature of quantum mechanics – that is, the nature of matter as we perceive it.

Several categories of models appear as the basis for the study of molecular electronics in general, and molecular transport junctions in particular. These are the geometrical (or molecular), Hamiltonian, and transport analysis models.

The geometrical models have been mentioned already, but must be referred to again. In building an understanding of transport junctions, we need to know the geometry at least at some level. The geometrical models are almost always simply atom placement, sometimes static and sometimes not. Since there is no legitimate way to compute the optimal geometry, it is simply assumed for some (possibly arbitrary) reason – this represents the geometric model, upon whose statics the dynamics of electron transport is pursued.

The molecular models are in a sense a subset of the geometrical ones – we assume that we know which molecules are present and we assume that we know their geometries (indeed sometimes we assume more than that, such as the usual assumption that thiol end groups lose their protons when forming their asymmetric bond with gold). In this we also necessarily assume that there are no other species, either on the electrode surface or in the surrounding media, that influence the current flow through the system.

Then, there are model Hamiltonians. Effectively a model Hamiltonian includes only some effects, in order to focus on those effects. It is generally simpler than the true full Coulomb Hamiltonian, but is made that way to focus on a particular aspect, be it magnetization, Coulomb interaction, diffusion, phase transitions, etc. A good example is the set of model Hamiltonians used to describe the IETS experiment and (more generally) vibronic and vibrational effects in transport junctions. Special models are also used to deal with chirality in molecular transport junctions [42, 43], as well as optical excitation, Raman excitation [44], spin dynamics, and other aspects that go well beyond the simple transport phenomena associated with these systems.

The Hamiltonian models are broadly variable. Even for an isolated molecule, it is necessary to make models for the Hamiltonian – the Hamiltonian is the operator whose solutions give both the static energy and the dynamical behavior of quantum mechanical systems. In the simplest form of quantum mechanics, the Hamiltonian is the sum of kinetic and potential energies, and, in the Cartesian coordinates that are used, the Hamiltonian form is written as

\[ H = \sum_i P_i^2 / 2m + V(\vec{X}). \]  

(1)

Here the electron mass is \( m \), \( P_i \) is the momentum of the given particle \( i \), and \( \vec{X} \) represents the vector of all displacements, both electronic and nuclear. We have assumed that, following the Born–Oppenheimer approximation, electronic and
nuclear motions are decoupled, and a purely electronic Hamiltonian can be defined as in (1) (with the nuclear coordinates entering only as parameters). For very simple systems like the hydrogen atom, quantum mechanics is solved in exactly this form by choosing the Coulomb potential for $V$ and then finding the eigenvalues and eigenfunctions analytically.

For anything bigger than the hydrogen atom, however, solving directly in terms of the coordinates and momenta becomes extremely difficult. Far more common is to express the wave function in terms of basis functions, introducing the idea of second quantization [45]. A simple way to think of second quantization is that it describes the quantum mechanics, from the beginning, in terms of a set of basis functions.

As a simple example, if we choose to work on the problem of the spectroscopy of the benzene molecule, we might make a model in which we ignore all repulsions among the electrons, we ignore the $\sigma$ electrons, and we take the $\pi$ electron wave function to be represented in terms of six sites each containing a single $p\pi$ orbital and centered at a carbon nucleus. We then restrict the electronic interactions to exist only between neighboring carbons. Still retaining the assumption that these $p\pi$ orbitals are orthogonal and form a complete basis set for our model, the model becomes the standard Huckel model, that can be written as

$$H_{\text{Huc}} = 1/2 \sum_i \sum_j \beta_{i,j} (a_i^+ a_j + a_j^+ a_i).$$

Here the operator $a_i^+$ creates (and the operator $a_i$ removes) an electron at site $i$; the $nn$ denotes near-neighbors only, and $\beta_{i,j} = \int dr \phi_i H \phi_j$ denotes a Coulomb integral if $i = j$ and a resonance integral otherwise. The second quantization form of this equation clearly requires a basis set. It is a model for the behavior of benzene – not a terribly accurate one, but one that helps us understand many things about its spectroscopy, its stability, its binding patterns, and other physical and chemical properties.

If the basis set is restricted to one $p\pi$ basis function on each $sp^2$ carbon, if the two-electron integrals ignore all three-center or four-center ones, and if we exclude exchange components, one has the Pariser–Parr–Pople model. If, further, all two-electron integrals are set to zero except for the repulsion between opposite spins on the same site and the one-electron tunneling terms are restricted to nearest neighbors, the result is the Hubbard Hamiltonian

$$H_{\text{Hub}} = H_{\text{Huc}} + U \sum_i n_{i,\uparrow} n_{i,\downarrow}$$

with $\beta$, $U$ the parameters of the model and $n_{i,\sigma} = a_{i,\sigma}^+ a_{i,\sigma}$ the number operator for an electron of spin $\sigma$ on site $i$.

In molecular transport junctions, the Hamiltonian models are usually based on Kohn–Sham density functional theory [46–48]. They use relatively small basis sets because the calculations are sufficiently complicated, they take a number of empirical steps for dealing with the basis sets and their potential integrals, and they
assume a static basis (that is, the ground and excited states are described in the same basis). The more complicated the model, the more complicated the calculation.

The tradition of model building only works when the right model is chosen for the right problem. For qualitative understanding of molecular charge transport, extended Hückel models can actually be useful [49] – to get quantitative information, one requires either a high level ab initio approach (going well beyond Hartree–Fock) or (much more commonly) a density functional theory with a fairly sophisticated functional, and with corrections to get the one-electron levels at roughly the right energy [50].

A great deal more could be said about models – to understand behavior like strong correlation, Coulomb blockade, and actual line shapes, it is necessary to use a number of empirical parameters, and a quite sophisticated form of density functional theory that deals with both static and dynamic correlation at a high level. Often this can be done only within a very simple representation of the electrons – something like the Hubbard model [51–53], which is very common in this situation.

General issues with models are discussed elsewhere. For our purposes here it is important to remember that model Hamiltonians are the only way in which any molecule larger than diatomic is ever described – in a sense, the science resides in using the right model for the right system, and solving it appropriately.

Models are also required for analysis of the transport. For calculations of current/voltage curves, current density, inelastic electron scattering, response to external electromagnetic fields, and control of transport by changes in geometry, one builds transport models. These are generally conceptual – more will be said below on the current density models and IETS models that are used to interpret those experiments within molecular transport junctions.

In mesoscopic physics, because the geometries can be controlled so well, and because the measurements are very accurate, current under different conditions can be appropriately measured and calculated. The models used for mesoscopic transport are the so-called Landauer/Imry/Buttiker elastic scattering model for current, correlated electronic structure schemes to deal with Coulomb blockade limit and Kondo regime transport, and charging algorithms to characterize the effects of electron populations on the quantum dots. These are often based on capacitance analyses (this is a matter of thinking style – most chemists do not consider capacitances when discussing molecular transport junctions).

Another set of models involves molecular mechanisms – how does current pass through molecules? We know that coherent transport (tunneling through the molecule) could occur in short molecules, and that the transition to hopping transport (electrons localized for long time scales compared to the scales on which they move between these localization sites) is common in electron transfer systems; by the Nitzan analogy we would expect the same to be seen in conductance junctions, and indeed this has been observed [54]. The mechanistic transition from tunneling to hopping is a fascinating one, with many areas still uncertain, particularly for ionic molecules like DNA.

The third set of models is for understanding the actual currents, and the pathways that the currents follow through molecular transport junctions. This is to some
extent a matter of visualization and categorization, but it is very helpful in understanding the mechanism of molecular transport.

Occasionally terms from models can be misused badly. For example, the standard, nonequilibrium Green’s function/density functional theory approach to transport (the most common one for general calculations on molecular junctions) [55–66] uses concepts like frontier orbitals [67] (homo/lumo) that come from a different part of chemistry. These are almost always used incorrectly – in frontier molecular orbital theory, the homo and lumo are well defined – one is the highest occupied molecular orbital, the other the lowest unoccupied molecular orbital. They are orbitals, they have shapes, and they have orbital energy levels. But they are one-electron constructs – for example, the lumo for naphthalene and for its cation, its anion, and its doubly charged dication are completely different. So that when, in a description of transport, we talk about electrons moving through the lumo, it is not the same lumo that is defined for the isolated molecule! The proper term would be “affinity level,” but that proper term is hardly used. This is important, because the changes in energy between the lumo of a closed-shell molecule and the lumo of its anion or cation can be very large (electron volts), so that the nomenclature is wrong, in a serious way.

The thicket of models is complicated, and with misunderstood notation (including homo/lumo), the careful user or reader of models has to be aware of exactly what is being done in any given analysis. While it is possible to decry the use of (in particular) the homo/lumo language, that language is universal. This can be avoided simply by thinking of them as affinity levels and detachment levels, as they really are.

Given the understanding that our description of molecular transport junctions is based on a description of the model that we build, we can proceed to some of the concepts that characterize the mechanistic behaviors.

4 Ideas and Concepts (from Mechanisms and Models)

Molecular transport junctions differ from traditional chemical kinetics in that they are fundamentally electronic rather than nuclear – in chemical kinetics one talks about nucleophilic substitution reactions, isomerization processes, catalytic insertions, crystal forming, lattice changes – nearly always these are describing nuclear motion (although the electronic behavior underlies it). In general the areas of both electron transfer and electron transport focus directly on the charge motion arising from electrons, and are therefore intrinsically quantum mechanical.

4.1 Coherence and Decoherence, Tunneling and Hopping

The simplest and most significant new idea in trying to understand molecular transport junctions comes from mesoscopic physics, and in particular from the
work of Landauer with Imry and Buttiker \[ 10, 11 \]. This in turn is based on a simple observation – in mesoscopic physics transport junctions, or in molecular transport junctions, there is a disparity of size scales: the molecule or quantum dot is very small compared with the electrodes. These macroscopic electrodes, then, set the chemical potentials, and once an electron enters one of them, it can be thought of as losing its phase immediately, and simply becoming part of the electronic sea in that metal. This is the fundamental Landauer idea: when voltage is placed across a transport junction, electrons travel from one electrode to the other. They travel through the molecule or quantum dot, on which they may reside for a long time or a short time. But once they enter the downstream electrode, that acts as a perfect sink – all phase coherence is immediately lost, and the electron has disappeared into the Fermi sea. This fundamental idea is crucially different from understanding a classical wire, and thinking of conduction in terms of Ohm’s law; in that situation there is no size separation, and the electrons are thought of as a current that generates heat and undergoes resistance as it moves—the description is initially classical, although it can easily be made quantal. In the Landauer/Imry/Buttiker approach, the transport is quite different – it is scattering (indeed it is elastic scattering in the simplest picture).

This approach to understanding transport leads to the Landauer/Imry/Buttiker formula for conductance which is

\[
g = g_0 \sum_i T_{ii} = \frac{2e^2}{h} \sum_i T_{ii}. \tag{4}\]

Here \( g \), \( g_0 \), \( T_{ii} \), \( e \), and \( h \) are respectively the conductance, the quantum of conductance equal to 77.48 microsiemens, the transmission through channel \( i \), the electronic charge, and Planck’s constant. The idea that conductance can be quantized is a remarkably new one compared with ohmic behavior – Fig. 6 shows experiments that directly demonstrate quantization of transport in atomic gold wires.

The sum in (4) runs over all the transverse channels of the system – that is, the channels that extend from the upstream to the downstream electrode. They normally are thought of (qualitatively) in terms of the molecular orbitals on the molecule, with appropriate modifications for mesoscopic systems.

While quantum chemistry cannot be used to work with the Landauer/Buttiker/Imry formula as it stands, a very different approach based on nonequilibrium Green’s functions yields a different formula (sometimes called the Caroli formula \[ 68 \], or the NEGF formula in the Landauer/Imry/Buttiker limit). It is, for the current \( I \):

\[
I = \frac{2e}{h} \int dETr \{ \Gamma(E, V)G^r(E, V)\Gamma^+(E, V)G^a(E, V) \} (f_L(E, V) - f_R(E, V)) \tag{5}\]

where \( G^r \) is the retarded Green’s function for electrons, \( \Gamma \) is the spectral density (twice the imaginary part of the self energy), and \( f \) is the Fermi distribution function. This equation can be rewritten, for clarity, as
$$I = 2e/h \int dET(E,V) \left( f_L(E,V) - f_R(E,V) \right),$$  \hspace{1cm} (6a)

$$T(E, V) = Tr\{ \Gamma(E, V)G^r(E, V)\Gamma^+(E, V)G^a(E, V) \}.$$ \hspace{1cm} (6b)

Here, the transmission, T, is expressed as (6b). The Landauer/Imry/Buttiker formula (almost always called the Landauer formula) then says that the left-to-right electronic current through a molecular transport junction is the integral of the transmission through the molecule, weighted by the statistical requirements that the electrons begin in an occupied level of one electrode and finish in an unoccupied level of the other electrode. This form is quite general, and it is the one on which almost all of the quantum calculations of simple transport are based. It does need to be generalized to deal with

Fig. 6 (a) Conductance steps in a Au wire as an STM tip was retracted. (b) Electron microscope images of gold bridges obtained simultaneously with the conductance measurements in (a). Left, bridge at step A; right, bridge at step B. (c) Intensity profiles of the left and right bridges shown in (b). The shaded area is the intensity from the bridge after subtraction of the background noise. (d) Models of the left and right bridges. The bridge at step A has two rows of atoms; the bridge at step B has only one row of atoms. The distance from P to Q (see b) is about 0.89 nm, wide enough to have two gold atoms in a bridge if the gold atoms have the nearest-neighbor spacing of the bulk crystal (0.288 nm) (Reprinted by permission from Macmillan Publishers Ltd: Nature (1998) Nature 395, 780–783, copyright (1998))
issues like electron correlation, photonic excitation, thermal processes, decoherence and dephasing, very strong correlation, magnetic effects, and other aspects of molecular transport junctions – but it is the basis from which most of that work is done.

One way to think about the Landauer formula is to say “conductance is scattering” [69]. In fact, conductance is elastic scattering, because in the original Landauer approach, all scattering is considered to be elastic – particles leave the electrode and are scattered elastically until they make it into the other electrode (or not). Inelastic events are not included, at least conceptually.

This language is a bit different from our ordinary understanding of conduction and resistance, but it is the right approach for systems that are by their nature quantal, and that have the length scale separation characteristic of transport junctions.

Mechanistically, it is a bit hard to swallow the idea that conduction through a molecule must go by elastic scattering. For example, suppose the molecule in question were really long – something like a DNA double helix with a hundred base pairs. Elastic scattering through such a structure would fall off exponentially with length, and therefore any transport that was seen could not be explained. The model that is used to derive the Landauer equation – that is, the model that assumes the space scale separation quoted above, and the elasticity of all collisions, can begin to fail. This brings in a series of chemical mechanisms that occur because of the nature of the molecules. These chemical mechanisms are well understood from problems like conductive polymers and electron transfer in molecular systems – they might be expected to occur in molecular transport junctions, and indeed they do.

One way to think about mechanistic change is in terms of time scales. This is familiar from classical kinetics where (for example) the steady state assumption assumes that the reactive intermediate is made and destroyed on exactly the same time scale, so that (after the induction period of the chemical reaction) the rate of the overall reaction could be found by assuming that the reactive intermediates exist at steady state. This leads to the idea of chemical mechanisms for dynamical processes, and to the question of time scales. The time scale problem in molecular transport junctions is complicated, but extremely important. One time scale that is unfamiliar to most chemists is the so-called Landauer/Buttiker time or contact time [70]. This is conceptualized as the time that the electron actually spends in contact with the molecule. This is not the same as the inverse of the rate, which describes how long it takes for an electron to go from one end to the other, but rather tells about how much time the electron is actually “on” the molecule – when it can contact other molecular degrees of freedom such as the vibrations through the electron/vibration interaction [71, 72]. A simple argument based on the uncertainty principle (that can be supported by scattering theory analysis) is that this Landauer/Buttiker contact time is given approximately by

$$\tau_{LB} = \frac{n\hbar}{\Delta E_g}.$$  

Here the variables are \(n\), which is the dimensionless length of the system in terms of subunits and \(\Delta E_g\), which is the gap energy between the Fermi level of the
electrode and the relevant molecular energy level. This formula looks like the uncertainty principle multiplied by a length, which seems reasonable. The uncertainty principle part is slightly counterintuitive: it says that the higher the injection barrier, the smaller the contact time. This is only unexpected because, if one were to talk about rates, the higher the barrier, the slower the rate, and therefore the longer the rate time. Conceptually, one gets around this by thinking of the Landauer/Buttiker contact time as describing how long the electron is under the barrier – in the original analysis this could be tested by looking at a spin flip within the barrier, as modulated by the presence of the tunneling electron.

Qualitatively, for a characteristic transport molecule like an alkane thiol or a small ring system, the gap is more than 1 V, the contact time is less than 1 fs, and there is simply not enough time for strong interaction between the electrons and the vibrations. But as resonance is approached, the time $\tau_{LB}$ can approach the period of molecular vibrations or motions, which can then enter into resonance. This mechanistic change is important – once the resonance regime is approached, the scattering is certainly not elastic, the behavior does not occur simply by tunneling, thermalization is possible, vibrational subpeaks should be seen in the transport, and the mode of transport is closer to the hopping mechanism seen in conductive polymers than to the tunneling mechanism also seen in conductive polymers [71].

Many other time parameters actually enter – if the molecule is conducting through a polaron type mechanism (that is, if the gap has become small enough that polarization changes in geometry actually occur as the electron is transmitted), then one worries about the time associated with polaron formation and polaron transport. Other times that could enter would include frequencies of excitation, if photo processes are being thought of, and various times associated with polaron theory. This is a poorly developed part of the area of molecular transport, but one that is conceptually important.

The Landauer formula assumes elastic processes. If the electrons move coherently (that is without any loss of energy or of phase) they will tunnel; if the energy gap through which they must tunnel becomes relatively small, they can tunnel a long way. Generally, the conduction in the tunneling regime is written as

$$g = k_0 e^{-\beta x}$$

where $k_0$ is a constant depending on the system, $x$ is the distance between the electrodes, and $\beta$ is the decay parameter corresponding to tunneling through a given molecular system.

### 4.2 Pathways and Analysis

The orbital description of electrons in molecules suggests that it should be possible to map the actual physical pathways by which electrons transfer through a molecule
between two electrodes, or at least identify the parts of a molecule responsible for mediating the electronic interaction between the two electrodes. Some of these pathways have been roughly described on the basis of inelastic electron tunneling spectroscopy – this is discussed in Sect. 6. However, a more general and useful analysis (this time based on theory rather than experiment) has been developed in terms of channels [73–80]. The most recent extension of the channels idea is based on continuity: if one imagines planes perpendicular to the line between the two electrode tips, then the current through all such planes must be identical at steady

**Fig. 7** Local transmission description of transport through an extended alkane (top left), a para linked di(thioethyne) benzene species (top right), and a meta-linked benzene species (lower figures and panels). In the two upper cases, transport goes through a single simple pathway in the alkane, and through two symmetrically disposed pathways in the para-benzene – this gives a relatively flat conductance or transmission spectrum as a function of voltage or energy. In the meta-benzene, different interference features occur (at roughly $-2.5, 0.2, \text{ and } 3.4 \text{ eV}$). The interference patterns shown near these features are characterized by ring-current reversal moving from one side of the interference feature to the other. Reproduced from [81]