QUANTUM TRANSPORT AND CURRENT-TRIGGERED DYNAMICS IN MOLECULAR TUNNEL JUNCTIONS

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The modelling of nanoelectronic systems has been the topic of ever increasing activity for nearly two decades. Yet, new questions, challenges and opportunities continue to emerge. In this article we review theoretical and numerical work on two new developments in the theory of molecular-scale electronics. First we review a density functional theory analysis within the Keldysh non-equilibrium Green function formalism to predict nonlinear charge transport properties of nanoelectronic devices. Next we review a recently developed quantum mechanical formalism of current-triggered nuclear dynamics. Finally we combine these theories to describe from first principles the inelastic current and the consequent molecular dynamics in molecular heterojunctions.

Keywords: Molecular electronics; resonance tunneling; nanoscience; inelastic conductance.

1. Introduction

The problem of molecular-scale electronics has been the source of fascination for theorists for almost two decades.1–62 Much of this research has been inspired by two historical papers; the 1959 address of Feynmann to the American Physical Society, entitled “There is Plenty of Room at the Bottom”63 and the 1974 letter of Aviram and Ratner on the possibility of molecular rectification.64 The rapidly growing activity in this area during the past few years is due in part to the development of experimental methods of producing and characterizing molecular-scale devices,65–115 in part to the anticipation for a variety of technological applications, and in part to the increasing power of modern computers.

A substantial component of the theoretical activity has been devoted to gaining qualitative insight into conductivity on the molecular level and exploring general properties of molecular wires.1–4,6–17,18,62 Simple models, such as the tight binding and extended Hückel Hamiltonians, have proven extremely useful to that end, providing a basis for understanding the role played by a variety of attributes. These include the nature of the molecule-electrode interface,4 and the length10 and chemical structure11 of the molecular moiety.

During the past eight years, considerable theoretical effort has been devoted also to the development, testing and application of ab initio methods of computing transport properties.30–60 Density Functional
Theory (DFT) has served as a basis for the majority of these studies, as discussed in detail in Sec. 2. The recent literature includes quantitative predictions of the transport properties of a variety of systems of fundamental and technological interest, including carbon-30,32,48,57 and metal-41,42,50,62 atom chains, carbon nanotubes,31,36,51 fullerences,46,49,52,58 and a variety of organic molecules.37–42,53,55,56 These developments have been well-timed with the rapid advance of experimental methods of measuring conductance through molecular devices.65–115

A third component of the theoretical activity has focused on the prediction of novel phenomena in the context of molecular-scale electronics. Part of this recent advance has considered opportunities of gaining new insights into, and control over, quantum conductance by means of laser fields. The weak field approach of Ref. 116 predicts that frequency tuning of a laser source illuminating a molecular heterojunction would furnish useful spectroscopic information about the system and, more interestingly, large conductance enhancement over a significant frequency range. The nonadiabatic approach of Ref. 117 illustrates the possibility of using molecular wires as coherent quantum ratchets, where the molecule serves to rectify a laser-induced current resulting in directional transport in the absence of voltage. Reference 118 explores new effects that arise from transport through several competing electronic configurations. Depending on the details of the electrode-molecule coupling, the predicted I-V curves exhibit current collapse and strong negative differential conductance due to the occurrence of a so-called “blocking” state.

In the present article we review recent work on both of the above emerging fronts: the development of ab initio methods for transport calculations and the prediction of novel phenomena in molecular-scale electronics. We first (Sec. 2) discuss the current state-of-the-art of ab initio description of elastic transport via molecular heterojunctions. The core of Sec. 2 is a non-equilibrium Green’s function approach, formulated within the Keldysh theory, which is of mathematical interest as well as practical utility.119 In Sec. 3 we review a recently developed theory of current-triggered dynamics in molecular-scale devices.120,121 Our theory is formulated within a time-dependent scattering approach and exposes, via an analytical limit, the mechanism by which tunnelling current at mild voltages can induce large amplitude motion in molecular devices. Within the same formalism we provide an expression for the inelastic conductance through molecular devices.121 In Sec. 4 we combine the theories of Secs. 2 and 3 in numerical simulations of the quantum transport and consequent molecular dynamics in molecular-scale devices of conceptual and chemical interest. We open Sec. 4 by illustrating that the machinery developed in Sec. 2 for calculation of elastic transport can be applied with minor additional numerical effort to realize numerically also the expression derived in Sec. 3 for the inelastic current. Having rationalized this result, we proceed to utilize it in several applications. In Sec. 5 we conclude with a discussion of avenues for future theoretical and numerical research.

Space considerations preclude us from reviewing all or even the major highlights of theoretical work in the area of molecular-scale electronics in the present article and hence our review is by no means comprehensive and inevitably biased. We refer the interested reader to several insightful and up-to-date review articles on related topics.61,62 and to a recent Special Issue on Transport in Molecular Wires,122 for a more complete overview of this increasingly multifaceted field.

2. DFT for Non-Equilibrium Transport

In this section we describe an ab initio approach for the calculation of elastic transport through molecular wires. In the next section we show that the machinery developed here can be extended to provide also the inelastic conductance through molecular devices.

The simplest model for a molecular device is schematically shown in Fig. 1, which consists of a molecular moiety connected to two semi-infinite metallic leads. The “molecular” moiety may be an organic system, a section of a carbon nanotube, a fullerene such as C60, a semiconductor quantum dot, etc. Conceptually and numerically it is convenient to partition space into three regions, as indicated by vertical bars in Fig. 1; a scattering region consisting of the molecule plus the portions of the electrodes where the molecular influence is significant, and two metal reservoirs, placed sufficiently deep into the electrodes for molecular effects to be screened. The electron scattering dynamics is confined to the central cell whereas the left and right cells serve to supply and accept the
Quantum Transport and Current-Triggered Dynamics in Molecular Tunnel Junctions

Fig. 1. Schematic illustration of an Au–C₆₀–Au molecular tunnel junction. The Au electrode consists of repeated unit cells extending to \( z = \pm \infty \), and its surface is oriented along the (100) direction. The bottom panel shows the calculated charge density at equilibrium, where perfect matching is obtained across the boundaries between the leads and the central scattering region.

Electrons. Previous work clearly demonstrated that many of the device characteristics of nano-electronic systems are directly related to specific atomic-scale degrees of freedom and to interactions of the scattering region with the device electrodes. Therefore, to make quantitative predictions of quantum charge transport through molecular-scale devices, a first principles formalism is essential.

A powerful technique, which has seen wide-spread application in condensed matter electronic theory, is the density functional theory (DFT). Several features specific to molecular-scale devices, however, complicate the analysis of quantum transport through molecular-scale devices under a finite bias potential with DFT. First, the system of Fig. 1 has open boundaries, provided by the infinitely-long electrodes. Recall that conventional DFT methods (e.g. the well-known plane wave methods discussed in Ref. 125 or real-space techniques such as that of Ref. 126) can treat two kinds of problems: (i) finite systems, as encountered in quantum chemistry, and (ii) periodic systems consisting of super-cells, as encountered in solid state physics. The open boundaries system of Fig. 1 falls in neither category; it requires the introduction of a new approach. Second, the device Hamiltonian \( \mathbf{H}[\rho(\mathbf{r})] \) needs to be computed within DFT using a charge distribution \( \rho(\mathbf{r}) \) that is constructed under a finite bias. Due to the external bias the electro-chemical potentials, \( \mu_i(f) + \Delta V_i(f) \), of the two electrodes are not equal and hence the device is out of equilibrium. Here \( \Delta V_i(f) \) is the bias voltage applied at the initial/final reservoir and \( \mu_i(f) \) is the corresponding chemical potential. The charge density therefore needs to be constructed under non-equilibrium conditions. Third, for open systems extending from \( z = -\infty \) to \( z = +\infty \), \( \rho(\mathbf{r}) \) includes the contribution of both scattering states, which connect the reservoirs at \( \pm \infty \), and bound states, which may reside in the scattering region. Finally, an efficient and transferable numerical procedure associated with the proper theoretical framework is needed in order to model systems of relevance, which often include hundreds of atoms.

Considerable progress has been made on these issues in recent years. The field has reached sufficient maturity during the past two years for two numerical packages for the prediction of non-equilibrium charge transport to be developed, McDCAL and Transiesta. In the following subsections we discuss the theory and implementation of non-equilibrium charge transport calculations at the molecular-scale within DFT.

Before proceeding with the details, it is important to note that all DFT-based techniques for transport calculations published to date, including the approaches detailed below, are based on a mean-field treatment of the electron interaction and correlation. These techniques are therefore suitable for analyzing molecular-scale conduction when electron-electron correlations are not strong. To properly describe transport problems involving strongly correlated electrons one may need to go beyond the mean-field approximation. The most commonly encountered devices are constructed such that the molecular region is strongly coupled to metallic leads. Here one does not expect strong correlation to play a major role and hence a mean-field analysis is expected to be adequate. The treatment of non-equilibrium transport involving strong correlation within an atomistic approach, is an interesting but difficult problem, which, to our knowledge, has not been addressed in a general fashion as yet.
2.1. The transmission coefficient

A most basic transport feature of nano-electronic devices, and one that is experimentally observable, is the current voltage (I-V) characteristics. In the limit of elastic transport the I-V curve can be calculated as,

\[ I = \frac{2e^2}{h} \int_{\Delta_1}^{\Delta_2} T(E, V_b)[f_i(E) - f_f(E)] \, dE \]  

(1)

where \( T(E, V_b) \) is the transmission coefficient at energy \( E \) and bias voltage \( V_b \), and \( f_i(f) \) is the Fermi distribution function in the initial (final) reservoir,

\[ f_{i(f)}(E, V_b) = 1/[1 + \exp[(E - E_F^{i(f)})/k_B T]] \].

(2)

It is important to emphasize that \( T(E, V_b) \) and the Fermi functions depend on the external bias voltage \( V_b \). In principle the integration range in Eq. (1) extends from \(-\infty\) to \(+\infty\) but the Fermi distribution functions limit it to a small (although temperature-dependent) range, \( \Delta_1 \rightarrow \Delta_2 \), with \( \Delta_1 \) smaller than \( \mu_{\text{min}} \) by a few \( k_B T \) and \( \Delta_2 \) greater than \( \mu_{\text{max}} \) by a few \( k_B T \), \( \mu_{\text{min}} \) (\( \mu_{\text{max}} \)) being the smaller (larger) of the two reservoirs’ chemical potentials, respectively. The transmission coefficient \( T(E, V_b) \) can be calculated within scattering matrix theory. An equivalent approach extracts \( T(E, V_b) \) directly from an appropriate Green function. Within the latter approach, and numerically more convenient approach extracts \( T(E, V_b) \) from the Green function.

\[ T(E, V_b) = \text{tr}[\Gamma_c G_c^R \Gamma_f G_c^A] \],

(3)

where \( G_c^{R(A)} \) is the retarded (advanced) Green function of the scattering region (see Fig. 1). The function \( \Gamma \) signifies the line-width arising from coupling of the scattering region to lead \( \lambda \), and is obtained from the corresponding self-energy \( \Sigma \) as,

\[ \Gamma_\lambda = i[\Sigma_\lambda - \Sigma_\lambda^{-1}], \quad (\lambda = i, f). \]

(4)

The retarded Green function of the scattering region, \( G_c^R \), is given as,

\[ G_c(E) = [E \mathbf{I} - \mathbf{H}_c - \Sigma]^{-1} \]

(5)

where \( \mathbf{H}_c \) is the Hamiltonian matrix of the scattering region of the device (see Fig. 1) and \( \Sigma = \Sigma_i + \Sigma_f \) is the total self-energy due to coupling of the scattering region to the initial and final continua. In terms of the interaction operators of the scattering region and the initial and final electrodes, \( \mathbf{H}_{i\ell} \) and \( \mathbf{H}_{f\ell} \), respectively, \( \Sigma_\ell \) is given as,

\[ \Sigma_\ell = \mathbf{H}_{i\ell} G_c \mathbf{H}_{f\ell} \]

(6)

with a similar expression holding for \( \Sigma_f \). In Eq. (6), \( G_c \) is the Green function for the semi-infinite initial lead, which can be calculated by established surface Green’s function techniques. Since only the atoms near the scattering region have significant contribution to the self-energy, the matrices in Eq. (5) are finite and hence can be inverted to obtain \( G_c \). Finally, the transmission coefficient is obtained from Eq. (3).

We remark that, although in principle any basis set could be used to represent the matrices in Eq. (5), in practice the choice of an economic basis is numerically essential, as the inversion problem is the costly stage of the calculation and scales poorly with the basis size. A plane-wave basis set is not suitable since it would render the matrix too large to be inverted, and in the present work a \( \{s, p, d\} \) LCAO basis set is used, as described below.

With Eqs. (1), (3), (5) and (6) established, the remaining problem is the calculation of the device Hamiltonian \( \mathbf{H}[\rho(r)] \). Several strategies have been developed to that end. In one approach only the central simulation box (the scattering region) is modelled, either as a finite cluster or as a super-cell. As larger portions of the electrodes are added to the scattering region, the Kohn–Sham (KS) potential near the molecule (see Fig. 1) resembles more closely the exact potential, which corresponds to infinitely long electrodes. The KS wave-functions obtained with this approach have incorrect boundary conditions for quantum scattering, in principle preventing their application to the calculation of electric current. This can be nevertheless remedied by carrying out an extra quantum scattering calculation after matching the super-cell or cluster potential to perfect electrode potential. An attractive feature of the cluster and super-cell approaches is that well-established techniques (plane-wave basis DFT in the case of a super-cell or quantum chemistry packages, such as Gaussian-98, in the case of a finite cluster) can be readily applied to the calculation of \( \mathbf{H} \). One drawback of the super-cell approach is that, because the effective device potential is derived for a problem with
periodic boundary conditions, it cannot describe devices where the two electrodes are not equivalent. More importantly, it is rather difficult for the supercell and cluster approaches to deal with systems under external bias. These approaches are thus best suited for calculating linear response transport coefficients, such as the equilibrium conductance.

A different, powerful DFT-based method is the Lippman–Schwinger (LS) scattering approach pioneered by Lang. Within this technique, the self-consistent KS equation is solved for open device structure and the charge density is constructed from the scattering states of the open device with a plane-wave basis set. Bound states can be introduced in an approximate fashion as discussed in Ref. 34. As such, this method correctly describes the boundary conditions of the device under external bias and, importantly, provides first principles I-V curves. A disadvantage of this approach, as implemented so far, is that the electrodes are described within a jellium approximation. While suitable for many applications, this representation is not appropriate to problems where the molecule-contact chemistry plays a role.

In what follows, we focus on an alternative ab initio formalism for calculating the device Hamiltonian, based on the combination of the non-equilibrium Green function (NEGF) method with DFT. The NEGF-DFT formalism is similar to the LS-DFT approach in that the Hamiltonian is determined self-consistently, accounting for the external bias and gate voltages and incorporating the proper open-system boundary conditions. The approach has several conceptual and computational advantages. It treats the atoms in the scattering region and in the leads on equal footing, such that realistic atomic leads (rather than jellium leads) are included, it treats the scattering and bound states of the device on equal footing, it allows for asymmetric devices, where the leads are not equivalent (e.g., composed of different materials) and finally, it is computationally efficient and hence capable of handling a large number of atoms. The last feature will prove particularly useful in the next section, where we will extend the approach to the inelastic case and to the description of current-induced dynamics.

### 2.2. The non-equilibrium Green’s function DFT approach

In this subsection we proceed to calculate the Hamiltonian \( \mathbf{H}[\rho(\mathbf{r})] \) within the NEGF-DFT approach. The atomic cores are defined by standard norm-conserving nonlocal pseudo-potentials and an LCAO \( \{ s, p, d \} \) orbital basis is used to expand the KS wave functions. The real space technique is appropriate to the open-system boundary conditions at hand. The use of a minimal basis set has been shown to result in an economic calculation with an acceptable accuracy for many problems. We note, however, that the approach lends itself to systematic improvement so as to give comparable accuracy to large basis set methods. To address the non-equilibrium nature of the problem, the NEGF-DFT constructs the charge density from the NEGF, rather than from the KS wavefunctions. Once the charge density is constructed, however, the rest of the self-consistent iteration procedure is identical to that of conventional iterative DFT approaches.

In what follows, we focus on the two major problems that arise in non-equilibrium transport calculations: the open-system boundary conditions (Sec. 2.2.1) and the construction of the charge distribution under external bias (Sec. 2.2.2).

#### 2.2.1. Open boundary condition for the Kohn–Sham potential

For the transport problem of Fig. 1, the effective KS potential \( V_{\text{eff}}[\rho(\mathbf{r})] \) requires in principle the charge distribution \( \rho(\mathbf{r}) \) corresponding to an infinitely large system because the electrodes extend to \( z \rightarrow \pm \infty \). A useful observation, however, is that \( V_{\text{eff}}[\rho(\mathbf{r})] \) deep inside a solid surface (the lead) is very close to the corresponding bulk KS potential. Therefore, the open boundary condition is satisfied within a “screening approximation”, i.e. we require,

\[
V_{\text{eff}}(\mathbf{r}) = \begin{cases} 
V_{i,\text{eff}}(\mathbf{r}) = V_{i,\text{bulk}}(\mathbf{r}) & Z < Z_i \\
V_{c,\text{eff}}(\mathbf{r}) & Z_i < Z < Z_f \\
V_{f,\text{eff}}(\mathbf{r}) = V_{f,\text{bulk}}(\mathbf{r}) & Z > Z_f ,
\end{cases}
\]

where the planes \( Z = Z_{i(f)} \) are the left (right) limits of the scattering region (indicated by the vertical lines in Fig. 1) that forms our calculation “box”. We remark that a sufficiently large portion of the leads should be
included in the calculation box in order for Eq. (7) to hold; this is verified through convergence tests. The potentials $V_{i(f),\text{bulk}}(r)$ describe periodic solid structures, and can be pre-calculated by standard supercell DFT methods. The real space potential matching of Eq. (7) allows us to deal with devices where the two electrodes are composed of different materials.

In numerical implementations, what is matched at the open boundary is not the full effective potential, $V_{\text{eff}}[\rho(r)]$, but rather the Hartree potential $V_H[\rho(r)]$. The reason is that once the Hartree potential is matched, $\rho(r)$ automatically matches across the boundary, and hence all other terms in the KS potential $V_{\text{eff}}[\rho(r)]$, which are simple functionals of $\rho(r)$, similarly match at the boundary. This ensures that Eq. (7) is satisfied within LDA. Thus, we solve the Poisson equation in the scattering region using an efficient multi-grid, real space numerical procedure with the Hartree potential of the bulk electrodes as boundary condition. With this procedure the external bias and gate potentials can be readily included as additional boundary conditions for the Poisson equation. One can then verify that $\rho_e(r)$ and $\rho_{i(f),\text{bulk}}(r)$ are equal at $Z_{i(f)}$ — provided that $Z_{i(f)}$ are chosen far enough inside the electrodes. The screening approximation effectively reduces the infinitely large problem to a finite problem, corresponding to the scattering region.

### 2.2.2. Density matrix for an open device system

We proceed to discuss the construction of the density matrix under external bias for an open system. This can be carried out either by direct summation over the eigenstates of the open device with the proper statistical weights, or indirectly, from the Keldysh NEGF. The two methods are formally equivalent but for two main reasons the NEGF is numerically more convenient. First, for open boundary problems, the bound states that reside in the scattering region (see Fig. 1) are rather difficult to calculate. The NEGF treats bound and scattering states on equal footing; both appear as poles of the Green function. Second, when the device is subject to voltage, the distribution function in the scattering region is not a Fermi distribution and needs to be calculated numerically. The non-equilibrium distribution is naturally taken into account within the NEGF approach.\(^{119}\)

The density matrix is calculated from the NEGF $G^<(E)$, as

$$\rho = -\frac{i}{2\pi} \int dE G^<(E)$$

where

$$G^< = G^R \Sigma^< [f_i, f_f] G^A.$$  \(^{(9)}\)

The above definition of $G^<$ is the Keldysh equation,\(^{119}\) where $G^R(A)$ is the retarded (advanced) Green function discussed above. The quantity $\Sigma^< [f_i, f_f]$ represents injection of charge from the electrodes. Within LDA this function is simple to calculate,

$$\Sigma^< [f_i, f_f] = -2i \text{Im} [f_i \Sigma^R_i - f_f \Sigma^R_f],$$  \(^{(10)}\)

where $\Sigma^R_{i(f)}$ is the retarded self-energy of the left (right) electrode. The distribution functions $f_{i(f)}$ of the electrodes are taken as Fermi distributions, $f_{\text{eq}}$, but with the chemical potential shifted by the applied bias voltage,

$$f_i(E, \mu_i + \Delta V_{b,i}) = f_{\text{eq}}(E, \mu_i + \Delta V_{b,i})$$  \(^{(11)}\)

$$f_f(E, \mu_f + \Delta V_{b,f}) = f_{\text{eq}}(E, \mu_f + \Delta V_{b,f}).$$  \(^{(12)}\)

Once the density matrix is constructed from Eqs. (8) and (9), the rest of the self-consistent DFT iteration is the same as in conventional DFT analysis. The use of the NEGF, as opposed to eigenstates of the open system, to construct charge density is the major new aspect of this \textit{ab initio} technique.

Numerically, an efficient procedure is needed for carrying out the energy integration in Eq. (8). The grid needs to be sufficiently dense to account for van Hove singularities at band edges of the DOS but not too dense to make the cost of the calculation prohibitive; we remark that the NEGF $G^<$ needs to be computed at each energy $E$. From the point of view of constructing the charge density, $\rho_e(r)$, the essential difference between $G^<$ and the retarded Green function $G^R$, is that $G^<$ contains information about the distribution function through the quantity $\Sigma^< [f_i, f_f]$. At equilibrium, i.e. when the chemical potentials of the electrodes are equal, $G^<$ reduces to a simple form,

$$\text{Im} G^< = -2f_{\text{eq}} \text{Im} [G^R].$$  \(^{(13)}\)

\(^{a}\)The reason for which bound states may reside in the scattering region is that the potential in the scattering region may be deeper than that of the leads.
Equation (13) also holds in situations where the electro-chemical potentials are different provided that \( f_i(E) = f_f(E) = 1 \). It follows that the integral in Eq. (8) can be partitioned into two terms: an “equilibrium” contribution, \( \rho_{eq} \), where the Fermi distribution functions are unity and a “non-equilibrium” contribution \( \rho_{neq} \) corresponding to the energy window between the two chemical potentials. Hence, the density matrix is given as \( \rho = \rho_{eq} + \rho_{neq} \), where

\[
\rho_{eq} = -\frac{1}{\pi} \text{Im} \left[ \int_{-\infty}^{\mu_{\text{min}}} dE G^R(E) \right], \tag{14}
\]

\[
\rho_{neq} = -\frac{i}{2\pi} \left[ \int_{\mu_{\text{min}}}^{\mu_{\text{max}}} dE G^<(E) \right], \tag{15}
\]

and \( \mu_{\text{min, max}} = \min(\max)(\mu_i + eV_{b,i}, \mu_f + eV_{b,f}) \). In Eqs. (14) and (15), the temperature is set to zero such that the distribution functions reduce to step functions. The extension to finite temperature is straightforward.

The equilibrium charge contribution \( \rho_{eq} \) can be calculated by a contour integral because the retarded Green function \( G^R \) has no poles in the upper half complex energy plane. A semi-circular contour is chosen, as illustrated in Fig. 2, where \( E_{\text{min}} \) is taken below all the eigenvalues of the Hamiltonian. The integration is accomplished using a Gaussian quadrature, ensuring rapid convergence with increasing number of quadrature points. Typically 30 quadrature points suffice to evaluate Eq. (14) (whereas direct integration of Eq. (8) requires in general a prohibitively large number of integration points to reach an acceptable accuracy). We note that such a complex contour automatically includes the charge contribution from all bound states below \( \mu_{\text{min}} \), which appear as poles of \( G^R \) along the real energy axis.

The non-equilibrium charge, Eq. (15), cannot be calculated by contour integration because for \( \mu_{\text{min}} < E < \mu_{\text{max}} \), Eq. (13) does not hold. Equation (15) is therefore evaluated directly along the real axis,

\[
\rho_{neq} = -\frac{i}{2\pi} \int_{\mu_{\text{min}}}^{\mu_{\text{max}}} dE G^R(E) \Sigma(f_i, f_f)G^A(E). \tag{16}
\]

Provided that there are no band edges between the chemical potentials of the reservoirs, the integrand is smooth along the real axis and a Gaussian quadrature converges with a small number of evaluations of \( G^< \).

Since the semi-infinite electrodes are taken into account through the self-energies [Eq. (5)], the density matrix needs to be explicitly calculated only in the scattering region (see Fig. 1). Changes in observables such as the band-structure energy or the number of electrons are evaluated in the scattering region by tracing over the indices of the density matrix corresponding to that region. Once the KS self-consistent potential \( V_{\text{eff}}(r) \) of the scattering region is iterated to convergence, the transport properties of the device are calculated via the Green function, as discussed in Sec. 2.1.

3. Inelastic Transport and Current-Triggered Molecular Dynamics

In this section we review a formalisim\textsuperscript{121} that extends transport to the inelastic regime and, in addition, accounts for dynamical processes in the molecular moiety that are induced by the inelastic current. As shown below, a key input to the theory is the electronic density of states of the voltage-biased device, whose numerical realization is detailed in the previous section.

For several reasons we focus on the case of resonant conductance. Resonances are ubiquitous in molecular heterojunctions because systems of relevance are typically conjugated molecules, these being good conductors.\textsuperscript{2,8} Furthermore, recent work\textsuperscript{120,134–137} has illustrated that resonant current is often inelastic, giving rise to interesting and largely controllable molecular dynamics. By contrast, under non-resonant conditions, at most minor motion of the nuclei is found, even when the device is subject to large (> 10\textsuperscript{7} Vcm\textsuperscript{-1}) electric fields.\textsuperscript{39,40}
The application of the theory to study STM-induced surface nanochemistry has been described in recent literature.\textsuperscript{121,120,134–136} In this scenario bound-free processes in the nuclear modes, such as desorption or dissociation, are of prime interest. In the present review we consider applications in a molecular junction environment, where bound-bound molecular processes (e.g., rotation, vibration and intermode energy flow) are of prime interest. In this section, however, we present the theory in all generality.

The complete Hamiltonian describing the coupled electronic-vibrational dynamics is written as,

\[ H = H_N + H_e + H_{e-N} \]  

where \( H_N \) is a system-specific nuclear Hamiltonian, \( H_e \) is the electronic Hamiltonian whose calculation is discussed in the previous section, and \( H_{e-N} \) is the non-adiabatic interaction coupling the electronic and vibrational motions.

The first term in Eq. (17) consists of the kinetic and potential energy operators underlying the nuclear motion and its form depends on the application in mind (see Sec. 4.2 for an example). The last two terms are expanded in the eigenstates of \( H_e \) as,

\[ H_e = \sum_{\nu} \epsilon_{\nu} c_{\nu}^\dagger c_{\nu} + \sum_{\mu} \epsilon_{\mu} c_{\mu}^\dagger c_{\mu}, \]  

and

\[ H_{e-N} = h_N(Q) \sum_{\mu,\nu} (\langle \mu|r\rangle \langle r|\nu\rangle c_{\nu}^\dagger c_{\mu} - \langle n_r\rangle). \]  

In Eqs. (18) and (19), \(|\nu\rangle\) and \(|\mu\rangle\) are stationary electronic states on the two electrodes, \(\epsilon_{\nu}\) and \(\epsilon_{\mu}\) are the corresponding energies, \(Q\) denotes collectively the nuclear coordinates, \(|r\rangle\) is the resonant orbital and \(\langle n_r\rangle\) denotes the equilibrium occupancy of \(|r\rangle\). We remark that Eq. (17) neglects dependence of the coupling between the discrete electronic state and the electronic continuum on nuclear coordinates. The range of validity of this approximation is commented on below.

Our objective is the rate of a resonance-mediated continuum-continuum transition in the electronic mode that is accompanied by a chemical reaction; a bound-bound or a bound-free transition in the nuclear modes. Formally this rate can be expressed non-perturbatively, within time-independent scattering theory, in terms of a transition matrix element in the complete electronic-vibrational space,

\[ w = \frac{2\pi}{\hbar} \sum_{\nu,\mu} \sum_{\nu} f_\nu(\epsilon_\nu)\left[1 - f_\mu(\epsilon_\mu)\right] \times |\langle v_\nu, \mu|T|v_\nu, \nu\rangle|^2 \delta(\epsilon_\nu - \epsilon - \epsilon_\mu). \]  

In Eq. (20), \( f_\nu(f_\mu)(E) \) is a Fermi-Dirac distribution function, Eq. (2), \( T \) is the transition operator, \(|v_\nu, \nu\rangle = |v_0\rangle|\nu\rangle\), \(|v_\nu, \mu\rangle = |v_\nu\rangle|\mu\rangle\), \(|v_0\rangle\) is the initial vibrational state, a bound eigenstate of the nuclear Hamiltonian, and \(|v_\nu\rangle\) is a final, bound or free eigenstate of the same Hamiltonian. We denote by \( \epsilon \) the energy transferred from electronic into vibrational, \( \epsilon = \epsilon_\nu - \epsilon_\mu \), and the subscript \( \epsilon \) to \( v_\epsilon \) serves as a reminder that the energy of the final state is restricted through energy conservation to \( \epsilon \) above the initial state energy. Here, \( v_0 \) denotes collectively the set of quantum indices required to fully specify the parent state. In the case of a bound-bound process in the nuclear mode (such as intermode energy flow, rotational or vibrational excitation or a surface exchange reaction), \( v_\epsilon \) has a similar significance. In the case of a bound-free reaction in the nuclear modes (such as a desorption or a dissociation), \( v_\epsilon \) denotes the scattering energy and the quantum indices specifying the internal state of the free product. In the latter case the \( v_\epsilon \) summation in Eq. (20) implies summation over the discrete indices and integration over the energy. The factor of 2 in the prefactor of Eq. (20) accounts for spin degeneracy. Within first-order perturbation theory, Eq. (20) is approximated as,

\[ w = \frac{2\pi}{\hbar} \sum_{\nu,\mu} \sum_{\nu} f_\nu(\epsilon_\nu)\left[1 - f_\mu(\epsilon_\mu)\right] \times |\langle v_\nu, \mu|H_{e-N}|v_0, \nu\rangle|^2 \delta(\epsilon_\nu - \epsilon - \epsilon_\mu), \]  

where \( H_{e-N} \) is given by Eq. (19).

We proceed to express Eq. (21) in a form that provides better insight into the coupled electronic-vibrational dynamics and is easier to handle numerically.\textsuperscript{121} To that end we first separate the vibronic matrix element in Eq. (21) into inter-dependent electronic and nuclear factors and introduce a complete set of eigenstates of the ground nuclear Hamiltonian,

\[ I = \sum_{\nu} |\nu\rangle\langle \nu| + \sum_n \int d\epsilon |\epsilon n^-\rangle\langle \epsilon n^-|, \]
where $|v\rangle$ are bound and $|en^\rightarrow\rangle$ are incoming-wave scattering states of $H_N$. We follow the standard convention of denoting by a “$-\,$” superscript scattering eigenstates satisfying incoming wave boundary conditions (i.e. eigenstates that correlate in the distant future with a state of well-defined set of quantum numbers). The collective index $v$ denotes the bound state vibrational indices and $n$ specifies the internal quantum numbers of the free state. With Eqs. (19) and (22), the transition matrix element in Eq. (21) assumes the form,

$$\langle v_e, \mu | H_{e-N} | v_0, \nu \rangle$$

$$= \langle \mu | r | \nu \rangle \langle v_e | \left\{ \sum_v |v\rangle \langle v| \right\} h_N(Q) | v_0 \rangle$$

$$+ \sum_n \int d|en^\rightarrow\rangle \langle en^\rightarrow| h_N(Q) | v_0 \rangle$$

$$= \langle \mu | r | \nu \rangle \langle v_e | \Psi \rangle \tag{23}$$

where we denote by $|\Psi\rangle$ a superposition of eigenstates of $H_N$,

$$|\Psi\rangle = \sum_v A_v |v\rangle + \sum_n \int d|en^\rightarrow\rangle \langle en^\rightarrow|,$$  

$$|\Psi\rangle = \sum_v A_v |v\rangle + \sum_n \int d|en^\rightarrow\rangle \langle en^\rightarrow|.$$  

with expansion coefficients $A_v = \langle v | h_N(Q) | v_0 \rangle$ and $A(en) = \langle en^- | h_N(Q) | v_0 \rangle$, determined by the resonant tunnelling process.

The physical picture described by Eqs. (23) and (24) is simple and general. The rapid electron (hole) scattering event produces a superposition of internally excited states of the ground electronic Hamiltonian $H_N$. The discrete state projection of this superposition, the first term on the right-hand side of Eq. (24), translates into bound state dynamics; vibration, rotation, intermode energy transfer or a surface exchange reaction. The scattering projection of $|\Psi\rangle$ translates into bound-free dynamics, such as desorption or dissociation.

In what follows we first (Sec. 3.1) specialize the discussion to the case of bound-free processes and next (Sec. 3.2) consider the case of bound-bound processes. In Sec. 3.3 we discuss the numerical implementation of the theory.

### 3.1. Bound-free dynamics

In this subsection we provide an explicit expression for the rate of bound-free processes, where one benefits from the simplification that the final state is a gas phase molecule and does not suffer vibrational relaxation due to interaction with the substrate. In order to relate the expansion coefficients in Eq. (24) to observable probabilities, we introduce a set of eigenstates of an asymptotic Hamiltonian, $|en\rangle$, related to the full scattering states of $H_N$, $|en^\rightarrow\rangle$, via the Lippmann–Schwinger equation

$$|en^-\rangle = |en\rangle + G_N V_N |en\rangle.$$  

In Eq. (25), $G_N$ is the Green operator corresponding to the Hamiltonian $H_N$ and $V_N$ is the potential energy operator in that Hamiltonian. In terms of the asymptotically observed states, Eq. (24) is written as,

$$|\Psi\rangle = \sum_v A_v |v\rangle + \sum_n \int d|en\rangle \langle en|,$$  

where $B(en) = \sum_{en'} \int d|en|d|en'\rangle A(en')$ is the amplitude to observe the state $|en\rangle$ at asymptotically long time. It is readily shown \cite{138} that the coefficients $B(en)$, containing the information of interest, are given in terms of the excitation coefficients $A(en)$ as $B = S_N A$, where $B$ and $A$ are column vectors with components $B(en)$ and $A(en)$, respectively, and $S_N$ is the scattering matrix corresponding to the nuclear Hamiltonian $H_N$.

Here we do not compute the energy-resolved $S$-matrix but rather use the established connection of the stationary and time-dependent scattering theories to solve for the nuclear dynamics in the time-domain. As shown elsewhere, \cite{138}

$$|\Psi(t)\rangle = \sum_v A_v(t) |v\rangle + \sum_n \int d|en\rangle \langle en|,$$  

with the initial condition $|\Psi(t = 0)\rangle = |\Psi\rangle$. The information of interest, $B(en) = \lim_{t \to \infty} e^{ieit/\hbar} B(en)$, is determined by propagating the wave packet subject to $H_N$ to a long time and projecting it onto the $|en\rangle$. The initial condition, $|\Psi\rangle$, is determined by the resonance scattering event, as discussed in Sec. 3.3, and contains the information about the brief evolution in the resonance state.
Substituting Eqs. (23) and (26) in Eq. (21), we express the bound-free reaction rate as,
\[ w(V_b, V_g; \tau) = \int d\epsilon P_{\text{reac}}(\epsilon; \tau) W_{\text{exc}}(\epsilon, V_b, V_g; \tau), \] (28)
where
\[ P_{\text{reac}}(\epsilon; \tau) = \sum_n |B(\epsilon n)|^2 = \sum_n \lim_{t \to \infty} \langle \epsilon n | \Psi(t) \rangle^2, \]
\[ W_{\text{exc}}(\epsilon, V_b, V_g; \tau) = \frac{2 \pi}{\hbar} \sum_{\mu, \nu} f_i(\epsilon_{\nu}) [1 - f_f(\epsilon_{\mu})] \]
\[ \times |\langle \mu | r \rangle \langle r | \nu \rangle|^2 \delta(\epsilon_{\nu} - \epsilon - \epsilon_{\mu}), \] (30)
and we indicated explicitly the dependence of the rate on the bias \((V_b)\) and gate \((V_g)\) voltages and its parametric dependence on the resonance lifetime \(\tau\). Equations (28)–(30) formulate the reaction rate in terms of the current that drives the reaction; \(W_{\text{exc}}(\epsilon, V_b, V_g; \tau)\) is seen to be the resonant component of the transmission rate through the molecular junction, related to the corresponding current as \(W_{\text{exc}} = j/e\), \(e\) being the electron charge. Thus, the electronic factor in Eq. (28), \(W_{\text{exc}}(\epsilon, V_b, V_g; \tau)\), describes the rate of excitation of the resonance while the nuclear factor, \(P_{\text{reac}}(\epsilon; \tau)\), is a normalized probability, describing the reaction probability per resonance excitation.

### 3.2. Bound-bound dynamics

We proceed to discuss the case of bound-bound dynamics in the nuclear modes, and first distinguish between reactive and non-reactive processes. Reactive processes are potentially of interest in the STM environment, where we envision resonance-mediated reactions serving as a route to nanochemistry. Here the product state is chemically distinct from the reactant. Such processes have not been described numerically as yet, to our knowledge, and their numerical study would be challenging, as it requires exploring a substantial portion of both potential energy surfaces involved. One of several motivations for numerical investment in such processes is their amenability to quantitative experimental characterization.\(^\text{139}\) The opportunity of inducing new surface reactions via a STM-triggered, resonance-mediated excitation is discussed elsewhere\(^\text{121}\) and not expanded on in the present article.

Non-reactive processes, where the final state is chemically identical to the parent state, are of potential interest in both tip-adsorbate-substrate and molecular device environments. In the former environment, current induced vibrational excitation is already being used in the context of vibrationally inelastic tunnelling spectroscopy, where it serves as a powerful probe of the structure and identity of adsorbates.\(^\text{140–144}\) In the latter environment we envision potential applications such as coherently driven molecular machines and manipulation of the conductivity of molecular wires.\(^\text{121}\)

The numerical study of bound-bound dynamics requires proper account of internal relaxation except in cases where the driving rate can be assumed fast as compared to the internal relaxation rate. In the latter case one proceeds along similar lines to those described in the previous subsection, namely, the (bound state) wave packet produced in the course of the excitation event is propagated subject to the Born–Oppenheimer potential \(V_N\), providing nuclear subspace attributes that need to be weighted by the rate of the charge transfer, \(W_{\text{exc}}\), that provides the energy required for reaction to take place. The nature of the attributes depends on the process envisioned. The simplest case scenario is that of vibrational excitation in effectively 1D systems, see Sec. 4. Here the collective index \(v\) in Eq. (24) reduces to a single quantum number and the rate of excitation of the corresponding state in the course of the resonance scattering event is given via the discretized version of Eq. (28),
\[ w_v(V_b, V_g; \tau) = P_v(\tau) W_{\text{exc}}(\epsilon_v, V_b, V_g; \tau). \] (31)

In Eq. (31), \(P_v(\tau) = A_v\) and \(W_{\text{exc}}(\epsilon_v, V_b, V_g; \tau)\) is given by Eq. (30). Time-resolved observables, such as the expectation value of a given coordinate in the case of vibrational or rotational excitation, or the expectation value of the energy in a given mode in the case of energy transfer, do not lead to observables but may provide useful insight, as discussed in Sec. 4.

### 3.3. Numerical implementation

Considering first the electronic dynamics, contained in the \(W_{\text{exc}}\) of Eqs. (28) and (31), we cast Eq. (30) in...
terms of projected densities of states as,
\[
W_{\text{exc}}(\epsilon, V_b; \tau) = \frac{2\pi}{\hbar} \int d\epsilon_f f_i(\epsilon_f) \left[ 1 - f_f(\epsilon_f - \epsilon) \right] \times \rho_i(\epsilon_f) \rho_f(\epsilon_f - \epsilon).
\]
In Eq. (32)
\[
\rho_i(E) = \sum \frac{\langle \nu | \tau \rangle^2 \delta(E - \epsilon) \rho_f(\epsilon_f - \epsilon)}{(33)}
\]
is the density of electronic states in the initial state, projected onto the resonance orbital, and an analogous expression holds for the projected density of states in the final state, \( \rho_f(E) \).

Equations (32) and (33) suggest an interesting result, namely that the inelastic conductance can be computed using the machinery that has already been developed for calculation of the Landauer elastic transport with minor additional numerical effort. Here we employ the density matrix derived in the previous section within the DFT-NEGF approach. The product \( \rho_i(E) \rho_f(E) \) is essentially the scattering density of states that connects the initial \( (i) \) and the final \( (f) \) electrodes across the scattering region; it contains all the information about the inelastic electronic dynamics through the Green function of Sec. 2.2.

With the excitation function constructed, we proceed to determine the function \( P_{\text{exc}}(\epsilon; \tau) \), Eq. (29), which contains the details of the nuclear dynamics. To that end we compute Born–Oppenheimer potential energy surfaces for the molecule–contacts system in the two states involved and solve the time-dependent Schrödinger equation subject to these potentials with a wave packet propagation technique.\( ^{120,134–137} \) The initial condition in Eq. (27) — the \( A_\nu \) and \( A(\epsilon, n) \) excitation coefficients — is determined by adaptation of the Menzel–Gomer–Readhead (MGR) model,\( ^{145} \) often employed to describe photon-stimulated desorption from metal surfaces.\( ^{146,147} \) This model approximates the resonant electron scattering event as an instantaneous transition of the initial bound eigenstate to the resonance state, propagation of the non-stationary state produced for a residence time \( \tau_R \) subject to the resonant state potential energy surface, followed by a second instantaneous transition of the evolved wave packet to the initial electronic state. The continuous nature of the relaxation process is taken into approximate account within the lifetime averaging model of Gadzuk.\( ^{148} \) In this approximation all observables extracted from the asymptotic wave packet are averaged over \( \tau_R \) with an exponential weight factor \( (1/\tau) \exp(-\tau_R/\tau) \), \( \tau = \hbar/|T| \) being the resonance lifetime. The reaction probability of Eq. (29), for instance, is computed as
\[
P_{\text{exc}}(\epsilon; \tau) = \frac{1}{\tau} \int_0^\infty d\tau_R \exp \left( -\frac{\tau_R}{\tau} \right) P_{\text{exc}}(\epsilon; \tau_R),
\]
where \( P_{\text{exc}}(\epsilon; \tau_R) \) is extracted from the asymptotic form of a wave packet that resided a time \( \tau_R \) in the resonance state. Similarly, the expectation value of a given coordinate or of the energy in a given mode is obtained as,
\[
\langle O(t; \tau) \rangle = \frac{1}{\tau} \int_0^\infty d\tau_R \exp \left( -\frac{\tau_R}{\tau} \right) \langle O(t; \tau_R) \rangle,
\]
\[
\langle O(t; \tau_R) \rangle = \langle \Psi(t; \tau_R) | O | \Psi(t; \tau_R) \rangle.
\]

Our calculation of the potential energy surfaces underlying the nuclear dynamics is inevitably approximate, the nature of the approximation depending on the application and on the observable sought. In the case of STM-triggered reactions, under conditions typical of resonance-mediated manipulation experiments,\( ^{135,149–152} \) the tip is remote from the substrate (by 7 Å in the experiment of Ref. 135 and by ca. 20 Å in that of Ref. 149, for instance) and the electric field and field gradient at the surface are negligible. In this situation the tip barely modifies the eigenstates of the substrate–adsorbate complex and a valid approximation is obtained by constructing potential energy surfaces for the substrate–adsorbate system free of external fields and simulating the (tip-induced) dynamics subject to these surfaces. The potential surfaces can be determined within standard DFT-based surface-slab techniques with periodic boundary conditions.\( ^{134,135} \) For non-metalic substrates a cluster approximation of the surface is often adequate.

To deal with the molecular device environment, we construct potential energy surfaces for the molecule–two contacts Hamiltonian by replacing the semi-infinite electrodes with a cluster model. Such calculations can be carried out at the DFT- or MP2-level at reasonable computational cost. Although a cluster model of the metal electrodes is not expected to provide a valid description of transport properties (see Sec. 2), it is adequate for calculation of the Born–Oppenheimer potential energy surfaces underlying the
current-induced molecular dynamics. The accuracy of such models nevertheless need to be examined for each system in mind. This is done by repeating the dynamical calculation using potential energy surfaces constructed with metal clusters of increasing size. We remark that calculation of the nuclear dynamics is typically much less costly than solution of the electronic structure problem.

In both tip-adsorbate-substrate and molecular wire environments, a useful simplification arises from the rapid nature of current-triggered dynamical events, which invites reduced-dimensionality models. Evolution in the resonant state competes with electronic relaxation and is thus of fs time-scale. Reaction in the neutral state competes with internal relaxation and is thus of sub- to few-ps time scale. On such short time scales, a small portion of the resonance state potential energy surface is explored and, subsequent to electronic relaxation, energy is distributed within a restricted subset of modes.

4. Application

In this section we apply the formalism of Secs. 2 and 3 to study the quantum transport and the consequent current-driven dynamics of a Au–C_{60}–Au molecular tunnel junction. Charge transport through C_{60} and other fullerene molecules have attracted considerable attention, although a Au–C_{60}–Au tunnel junction, and the problem of current-driven molecular dynamics have only been recently investigated. Our choice of system is motivated by intriguing experimental observations reported by Park et al. Our interest, however, is not in the specifics of the Au–C_{60}–Au junction or in the modelling of the experiment of Ref. 153. Rather, we use this system to illustrate several general features of charge transport at the molecular-scale and its reflection in current-triggered dynamical events. Our model is depicted in the upper panel of Fig. 1.

4.1. Charge transport

The transport properties are calculated using our NEGF-DFT electronic package McDCAL as discussed above. We fix the C_{60} at the middle of the Au–Au gap with an Au–C_{60} distance of 3.3 a.u. The semi-infinite atomic-scale Au electrode consists of repeated unit cells extending to $z = \pm \infty$. Each unit cell includes nine Au atoms and the electrode surface is oriented in the (100) direction. As discussed in Sec. 2.2, we model the atomic cores with the standard norm-conserving non-local pseudo-potentials of Ref. 132, and use $\{s, p, d\}$ atomic basis sets. The entire calculation is carried out on a Pentium-IV processor.

To verify the reliability of the screening approximation discussed in Sec. 2.2.1, the lower panel of Fig. 1 displays the charge density of the complete device at equilibrium. As can be clearly seen, the charge density matches perfectly across the boundary between the leads and the central scattering region. This indicates that the portion of leads included inside the central region is sufficiently long for the screening assumption to be satisfied.

Figure 3 shows the calculated transmission coefficient $T(E, V_b)$ through the device of Fig. 1 as a function of the electron energy $E$ for three different bias voltages $V_b$ at zero gate potential. Most notable is the sharp transmission peak that indicates resonance-mediated conductance. This resonance plays a crucial role in the current-induced molecular dynamics discussed below. At zero bias, the resonance lies just above the Fermi level of the device (the Fermi level is shifted to $E_F = 0$ in Fig. 3). As the bias voltage increases, the peak position shifts to higher energies. The magnitude of the shift depends on details of the

![Fig. 3. Transmission coefficient $T(E, V_b)$ versus electron energy $E$ for three bias voltages $V_b$. The sharp transmission peak, which results from a resonance of the fullerene+contacts Hamiltonian, dominates the conductance as well as the current-triggered dynamics. The inset shows the calculated I-V curve from which metallic behavior is evident. Reproduced with permission from Ref. 137.](image-url)
potential drop across the device. For symmetric systems we expect the bias voltage to drop equally at the two metal-molecule junctions but for asymmetric ones this is not necessarily the case. In the present system, although the electrodes are composed of the same material, the structure of the C$_{60}$ breaks the left-right symmetry, leading to an asymmetrical voltage drop at the contacts. Consequently the transmission peak position shifts by about $\sim 0.15$ eV when $V_b$ is increased by 0.2 V, i.e. by more than $V_b/2$. The inset of Fig. 3 shows the calculated current-voltage characteristics (I-V) of the Au–C$_{60}$–Au tunnel junction, where metallic behavior is evident. Similar metallic behavior has been reported before$^{46}$ for Al-contacted C$_{60}$ systems.

The transmission peak of Fig. 3 can also be shifted by applying a gate voltage $V_g$. Figure 4 shows the effect of a gate voltage on the transport properties at zero bias. As discussed in Sec. 2.2.1, $V_g$ is included in the self-consistent analysis through the electrostatic boundary condition for the Hartree potential. A finite $V_g$ is seen to shift the peak position through its effect on the device eigenvalues, while changing the shape of the $T(E,V_g)$ curve through its effect on the eigenfunctions. The tunability of the transmission peak is accentuated in Fig. 5 where the transmission coefficient at fixed energy and bias voltages is plotted as a function of the gate voltage. We find that the resonances of the molecule+contacts Hamiltonian, which dominate both the conductance and the current-induced dynamics, can be precisely controlled by the combination of external bias and gate voltages.

### 4.2. Current-triggered dynamics

In this subsection we describe inelastic transport and current-driven vibrational excitation in the device of Fig. 1 using the formalism of Sec. 3 and a wavepacket propagation technique.

Figure 6 shows the excitation function, $W_{\text{exc}}(\epsilon, V_b; \tau)$ of Eq. (32), versus the electronic-to-vibrational energy transfer, $\epsilon$, and the bias voltage, $V_b$. We find that the excitation function determined $\textit{ab-initio}$ for a voltage-biased molecular transistor follows nicely the form of the analytical approximation derived in Sec. 3,$^{121}$ namely, a sigmoidal function of voltage and energy.

The nuclear dynamics triggered by the inelastic transport of Fig. 6 is simple and general. The tunnelling event transiently places the nuclear system in a negative ion state of the Au–C$_{60}$–Au system. Due to the equilibrium mismatch between the neutral and ionic states, a nonstationary superposition of vibrational eigenstates is formed, which travels toward the ionic state equilibrium while continuously relaxing to the neutral state. Upon electronic relaxation the population has been redistributed between the vibrational

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Fig. 4. Transmission coefficient $T(E,V_g)$ versus electron energy $E$ for several gate voltages $V_g$. The transmission resonance is shifted by the gate potential. Reproduced with permission from Ref. 137.

Fig. 5. Transmission coefficient $T(E_F,V_b)$ at the Fermi level and zero bias voltage versus the gate voltage $V_g$. The transmission resonance is widely tunable by the gate potential.

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Fig. 6. The excitation function $W_{\text{exc}}$ of Eq. (32) versus the electronic-to-vibrational energy transfer, $\epsilon$, and the bias voltage, $V_b$ for a Au–C$_{60}$–Au device. The resonance feature manifested in the elastic transmission peak of Fig. 3 is associated also with a substantial inelastic component. This inelastic conductance drives the dynamics of Fig. 7. Reproduced with permission from Ref. 137.

levels of the neutral surface — the fullerene bounces between the gold contacts. If the driving rate is fast as compared to the internal relaxation rate, the motion is continuous. The evidence presented in Ref. 153 suggests that the energy transferred from electronic into vibrational in the course of the inelastic tunnelling event is deposited predominantly (or exclusively) in the center-of-mass vibration. Weak coupling between this mode and the internal modes of the C$_{60}$ thus leads to one-dimensional motion on the time-scales of relevance.

In the harmonic limit these dynamics are readily solved for analytically. We expand the non-stationary superposition evolving on the ionic surface as,

$$\psi(t, z) = e^{-i\omega t/2} \sum_v C_v u_v(z - \delta z_{\text{eq}}) e^{-i\nu \omega t},$$  \hspace{1cm} (36)$$

where $z$ denotes distance from the surface, measured with respect to the neutral state equilibrium configuration, $\delta z_{\text{eq}}$ is the equilibrium displacement of the ionic with respect to the neutral state, $\omega$ is the vibrational frequency, assumed equal in the two states, $u_v$ are harmonic oscillator functions and

$$C_v = \langle u_0(z) | u_v(z - \delta z_{\text{eq}}) \rangle = \frac{\zeta_{\text{eq}}^v \exp(-\zeta_{\text{eq}}^2/4)}{\sqrt{2\pi \nu}} , \quad \zeta_{\text{eq}} = \sqrt{\mu \omega \delta z_{\text{eq}}},$$  \hspace{1cm} (37)$$

$\mu$ being the mass. (The use of a coherent superposition, Eq. (36), to describe the complex dissipative dynamics in question is justified within the lifetime averaging approximation discussed in Sec. 3.3, where-in the continuous nature of the relaxation process is accounted for by averaging all observables over the resonance state residence time with an appropriate weight function. For detailed discussion of the validity of this approximation in a different context see Ref. 154.) Substituting Eq. (37) in (36) we have that the probability density in the resonance state oscillates without change of shape about the ionic state equilibrium configuration with amplitude $\delta z_{\text{eq}}$ and frequency $\omega$,

$$|\psi(t, z)|^2 = \sqrt{\frac{\mu \omega}{\pi}} e^{-(\zeta_{\text{eq}} - \zeta_{\text{eq}} \cos \omega t)^2} , \quad \zeta = \sqrt{\mu \omega \delta z_{\text{eq}}}. \hspace{1cm} (38)$$

In the harmonic limit the probability of excitation of the $v$th vibrational level of the neutral state upon electronic relaxation is

$$P_v(\tau_R) = \left| \sum_{v'} C_{v'} \langle u_0(z) | u_{v'}(z - \delta z_{\text{eq}}) \rangle e^{-i\nu \omega \tau_R} \right|^2 .$$  \hspace{1cm} (39)$$

In particular, the probability of capture into the ground vibrational level is

$$P_0(\tau_R) = \left| \sum_v \frac{\zeta_{\text{eq}}^2 \exp(-\zeta_{\text{eq}}^2/2)}{2\nu v!} e^{-i\nu \omega \tau_R} \right|^2$$

$$= e^{-\zeta_{\text{eq}}^2(1 - \cos(\omega \tau_R))} .$$  \hspace{1cm} (40)$$

As expected, vibrational excitation, $\sum_{v \neq 0} P_v$, vanishes and elastic conductance ensues in the limit of small equilibrium displacement; $P_0(\tau_R, \delta z_{\text{eq}} \to 0) \to 1$, and in the limit of short residence time in the ionic state; $P_0(\tau_R \to 0, \delta z_{\text{eq}}) \to 1$.

Considering next the vibrational dynamics of the Au–C$_{60}$–Au device, we adopt the potential energy surfaces given in Ref. 153 based on electronic structure calculation$^{155}$ of the C$_{60}$/Au(110) system. A relatively small equilibrium displacement, 4 pm, is predicted by the calculation of Ref. 155 and used in the dynamical simulations illustrated below. For generality, we comment also on the numerically observed effect of varying this parameter.
The inset of Fig. 7 shows the probability of capture into the lowest five vibrational levels as a function of $\tau_R$. The long $\tau_R$-behavior of the $P_v(\tau_R)$ is given for pedagogical completeness; only the small $\tau_R$ edge of the figure is of physical relevance since, for the lifetime of the resonance in question (Fig. 3), $\tau_R$ values beyond $\approx 450$ fs do not contribute to the lifetime averaged result of Eq. (34). $P_0(\tau_R)$ (solid curve) follows closely the structure predicted by Eq. (40) although, due to the anharmonicity of the potential, the periodicity of Eq. (40) is lost and the amplitude of subsequent recurrences decreases slowly with $\tau_R$. As $v$ increases, $P_v(\tau_R)$ broadens and shifts to larger values of $\tau_R$ (modulo $2\pi/\omega$), reflecting the spatial location and breadth of the vibrational eigenfunctions of the neutral state Hamiltonian. With increasing equilibrium displacement, $\delta z_{eq}$, the $P_v(\tau_R)$ become better localized in time, decaying exponentially to zero between recurrences, as predicted by Eq. (40).

The physical vibrational excitation probabilities, $P_v(\tau)$ of Eq. (31), are plotted versus $\tau$ in the main frame of Fig. 7 for $v = 0, \ldots, 4$. $P_0(\tau)$ decays to a nonzero asymptotic value that decreases with increasing $\delta z_{eq}$. The higher-$v$ probabilities increase monotonically from zero and saturate on a value that depends sensitively on $\delta z_{eq}$. As the equilibrium displacement increases, the vibrational excitation probabilities of progressively higher levels reach a maximum before decaying to the asymptotic plateau. This behavior follows from Eq. (34) and the $\tau_R$-dependence of the $P_v(\tau_R)$, which becomes smoother with increasing $v$ and with decreasing $\delta z_{eq}$.

The inset of Fig. 8 shows the expectation value of $z$ in the neutral state wavepacket as obtained through Eq. (35) with a lifetime of $\tau = 26$ fs, corresponding to the width of the resonance shown in Fig. 6 (i.e. $\Gamma = h/\tau \approx 0.025$ eV). We find that the $C_{60}$ center-of-mass oscillates between the contacts at the fundamental frequency of the neutral surface and an amplitude approximately equal to the distance travelled in the ionic state. Slow damping of the oscillations is due to the anharmonicity of the potential.

The main frame of Fig. 8 shows the vibrational excitation rate of the Au–C$_{60}$–Au system, $w_v(V_b)$ of Eq. (31), as a function of the applied voltage $V_b$ for $v = 1$. Our results correspond to the unmodified molecular junction, $V_g = 0$, and are given for $\delta z_{eq}$ values covering the physically relevant range; for smaller $\delta z_{eq}$ the vibrational excitation vanishes [see Eq. (40) and the discussion below]. For larger values we find a finite desorption probability. The bias-voltage-dependence of the $w_v$ follows the $V_b$-dependence of
the $W_{\text{exc}}$ in Eq. (31), see Fig. 6, and is well approximated by the analytical expression of Ref. 121, as a result of the nearly pure Breit–Wigner form of the resonance mediating the dynamics. The excitation rates of vibrational levels $v > 1$ take a similar shape but respond differently to the magnitude of the equilibrium displacement.

We find that the essential dynamics is contained in the combination of the equilibrium displacement and the resonance lifetime. The former parameter determines the outcome through the exponential dependence of $P_{\text{react}}$ on $\delta Z_{\text{eq}}$, see Eq. (40). The latter parameter determines the rate through the balance between the $\tau$-dependencies of the electronic and nuclear dynamics. Whereas $W_{\text{exc}}$ decreases sharply with increasing $\tau$, $P_{\text{react}}$ increases exponentially with this parameter [see Eq. (40)]. The ability to manipulate the conductance by varying the distance between the electrodes and the gate voltage thereby translates into control of the current-driven dynamics.

There is obvious interest in the case of large inter-electrode separation, where the resonance lifetime is substantially longer than that discussed here (the relaxation rate decays exponentially with the distance of the molecule from the electrode), leading to correspondingly longer vibrational amplitudes. In this regime we expect the transport properties to become time-dependent, oscillating on the time-scale of the vibrational period in Fig. 7 (inset). Although picosecond time-resolution is not attainable with current technology, such time-modulated transport is an interesting observable to explore numerically and one that may lead to useful applications.\textsuperscript{156}

Finally, we note that Figs. 7 and 8 focus on the current-driven molecular dynamics and do not provide a self-consistent description of the back-effect of these dynamics on the conductance. Such analysis has been described in Refs. 13 and 18 in the limit of a 1D harmonic oscillator coupled with a tight binding electronic Hamiltonian. Application of the theory of Secs. 2 and 3 to treat self-consistently the general case is the topic of ongoing research in our groups, which we hope to report in the near future.

5. Conclusions

Our goal in this review has been to present a first principles formalism for predicting current-triggered molecular dynamics, a general phenomenon that, depending on the system properties, may have a major effect on nano-electronic devices. As current flows through a molecular junction, electrons may inelastically scatter off the nuclei, thereby transferring energy to the vibrational modes and triggering molecular motion. Such an energy transfer can be substantial at resonance electron energies, where the electron dwell-time in the scattering region is often long. The nuclear motion, in turn, dynamically alters the charge current and influences the device characteristics.\textsuperscript{156}

The formalism reviewed in Sec. 3 casts the problem in a form that provides useful insight into the coupled electronic-vibrational motion while introducing a convenient numerical approach of modelling these dynamics, see Eq. (28). Here the rate is given as an integral over a product of an electronic function, describing the resonant inelastic scattering in the electronic subspace, by a nuclear function that contains the details of the dynamics in the vibrational subspace. To model the electronic dynamics, we developed a NEGF-DFT formalism that provides self-consistent electron transport properties from first principles. The nuclear motion is described within a wavepacket propagation technique.

As a first application of our scheme we considered the simplest consequence of inelastic current through a molecular device, namely center-of-mass motion of a fullerene between the two gold contacts of single-molecule Au–C$_{60}$–Au heterojunctions. Our choice of model was motivated by recent experimental studies\textsuperscript{153} of the conductance of Au–C$_{60}$–Au transistors. We found substantial probabilities for excitation of high vibrational levels of the neutral state Au–C$_{60}$–Au Hamiltonian, corresponding to oscillatory motion of the fullerene center-of-mass between the contacts. The vibrational excitation is mediated by a long-lived negative-ion resonance located ca. 0.15 eV above the Fermi level.

We feel that the possibility of current-triggered dynamics in molecular devices opens a variety of new opportunities in the field of single-molecule science. In ongoing work we use the concepts outlined above to devise coherently-driven molecular machines, including a single-molecule rotor and a nano-sized rattle. Another application of the formalism of Sec. 3 that is addressed in ongoing research is surface nanochemistry mediated by STM-triggered resonances. An important effect that can be accounted for within the
present theory, properly extended to allow for \(Q\)-dependence of \(H_0\), is the effect of current-driven dynamics on the charge transport. The NEGF approach also allows us to investigate hybrid devices involving ferromagnetic electrodes and superconducting electrodes. Current-triggered dynamics in these hybrid systems have not been investigated in any fashion and could provide new and very interesting device physics. Another avenue for future research is the inclusion of dissipative effects due to coupling of the molecular device to a thermodynamic environment.

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