

Current-Driven Oscillations and Time-Dependent Transport in Nanjunctions

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Resonance inelastic conduction in molecular-scale electronics can be used to channel energy into a given mode of the molecular component to generate a desired motion. Dependence of the conductance properties on the molecular configuration, in turn, leads to a time-modulated current whose temporal properties are subject to control. We use an *ab initio* nonequilibrium formalism and the example of Au-C₆₀-Au junctions to illustrate the strongly correlated phenomena of current-driven dynamics and time-dependent conductance in nanoelectronics, noting implications to, and potential applications in, several disciplines.

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Molecular-scale electronics is currently the topic of active experimental and theoretical research owing to both the fascinating physics associated with conductance on the molecular level and the range of anticipated applications [1]. Conceptually related, and likewise the topic of considerable fundamental interest and practical potential, are molecular machines. Supramolecule based machines, driven as an ensemble, e.g., by light, chemistry, or electrochemistry, have been the topic of intensive research for over two decades, leading to laboratory-made turnstiles, shuttles, switches, and rotors [2]. Recent reviews point out, however, the need for a new form of molecular machines, which could be addressed individually, thus eliminating the ensemble average that is inherent to the solution phase [3]. A potential route to individually driven, nanosized molecular machines is proposed in Ref. [4], which illustrates that resonance inelastic current through molecular junctions can be used to channel electronic energy into a preselected mode of the molecular component of the device and hence induce directed motion. Current-driven molecular machines possess potentially several desirable features. They are individually driven, they operate in the dry state in a site specific manner, and they do not suffer from the problem of intramolecular vibrational energy redistribution, which has prevented the long sought realization of mode selective excitation in the gas phase [5].

In the present work we propose a new and exciting opportunity that carries implications to both the field of molecular electron transport and that of individually driven nanomachines, namely, the possibility of dynamical junctions whose conduction properties oscillate in time in a controlled manner. Time-dependent transport, for long the source of fascination in mesoscopic physics [6,7], has been attracting increasing interest in the molecular-scale domain in recent years [8]. To our knowledge, however, research so far has focused on externally forced phenomena, where an ac source drives the electrons. Spontaneous dynamical nanjunctions offer new phenomena and new opportunities, as shown below.

The qualitative physics underlying current-driven dynamics and time-modulated transport in nanjunctions is

simple and general. Resonance tunneling, ubiquitous in molecular-scale electronics, is often inelastic. Provided that the initial and resonance states are displaced in equilibrium, the vibrational system evolves during the lifetime. Upon rapid electronic relaxation the system is internally excited and molecular dynamics ensues. The conditions under which equilibrium displacement is found are well understood [4,9] and it is possible to design the junction so as to encourage or inhibit current-driven dynamics (either may be desired, depending on the function of the device). The device reaches a steady state when the electronic driving is compensated by internal relaxation of the excited mode due to coupling with the electrodes [10]. Resonance current thus provides a mechanism for channeling of electronic energy into a selected mode of the vibrational system. The current-driven nuclear motion, in turn, modulates the electric current.

The Au-C₆₀-Au single molecule transistor [11,12] serves as a simple example of an effect that we believe to be general. Our choice of model has several motivations. First, molecular nanjunctions based on fullerenes as the molecular moiety have been fabricated and probed in several laboratories and are expected to be amenable to design [11,13,14]. Second, fullerene-based junctions invite study as candidates for nano-oscillators. As such, they may offer potential applications ranging from a single spin NMR, based on the ability of nano-oscillators to respond to very small forces [15], to a miniature mass spectrometry, based on their sensitivity to minute mass changes [16]. Further potential applications, proposed below, may be envisioned in case the vibrations lead to oscillating current. Third, while offering rich electronic dynamics (*vide infra*), the Au-C₆₀-Au junction is conceptually and numerically simple in vibrational dynamics [17].

Our results are based on a recently developed theory of quantum transport and current-driven dynamics in molecular heterojunctions that combines a nonequilibrium solution of the electronic dynamics within the Keldysh Green's function approach, with quantum mechanical solution of the nuclear dynamics within time-dependent scattering theory. For space considerations we omit an account of

the formalism and its numerical implementation, providing as endnotes the details necessary to reproduce our results [18,19].

Figure 1 illustrates our model nanojunction. Under typical experimental conditions [11,13], the interelectrode distance exceeds that allowing the fullerene to couple equally strongly to both electrodes and the junction is asymmetric, with the C_{60} attached through van der Waals interaction to one electrode, while its distance from the other is controlled by electromigration [11]. This latter distance determines the current flowing through the junction under a given bias; the shorter the distance the larger the current. For concreteness we assume that the rigid C_{60} is attached to the left electrode (Fig. 1), finding an equilibrium distance of the fullerene edge from the left electrode of $d_{eq} = 5.13$ a.u. Experimentally the interelectrode distance is ca. 1 ± 0.5 nm [11] (comparison of our calculations with the data suggests $L \sim 1.45$). Here we fix L at 1.4 nm in illustrations, noting the effects of varying L in the discussion.

Figure 2(a) shows the transmission spectrum under zero bias voltage. The transmission consists of three resonance peaks, as indicated by dots, which arise as the threefold degenerate, lowest unoccupied molecular orbital of the isolated C_{60} , and is split by coupling to the electrodes. Each resonance is a Lorentzian function of the electron energy whose full width at half maximum provides the resonance decay rate as $\Gamma = \hbar/\tau$, τ being the corresponding lifetime; here $\tau = 3.6, 40.4,$ and 71.5 fs. Symmetry considerations, along with the band structure of the Au electrode [20], indicate that the 3.6 and 71.5 fs resonances are responsible for transport of electrons from the $p_x, p_y, d_{xz},$ and d_{yz} (doubly degenerate) bands of the electrode, whereas the 40.4 fs resonance is associated with $d_{x^2-y^2}$ electrons.

Inelastic resonance conduction channels sufficient energy into the center-of-mass motion for the fullerene to

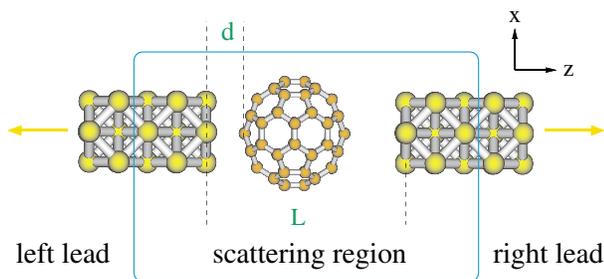


FIG. 1 (color online). Schematic illustration of the molecular junction, which consists of a C_{60} molecule in contact with two atomic scale Au electrodes extending to reservoirs. The electrodes are composed of unit cells with nine Au atoms oriented in the (100) direction repeated to $z = \pm\infty$. The simulation box making the scattering region [24] is enclosed by a rectangle. d is the distance of the C_{60} edge from the left electrode and L is the interelectrode distance.

oscillate between the electrodes in a unidirectional manner. The directionality is provided by the device asymmetry. The vibrational frequency is determined by the fullerene mass and the strength of the dispersion forces [21] between the electrodes and the molecule. The oscillation amplitude is controlled by the lifetime and the equilibrium displacement of the resonance with respect to the initial potential energy surface [4]. Both parameters, in particular, the latter, depend on the interelectrode distance L and are thus tunable to a certain extent. Here, the longest lived resonance, with $\tau = 71.5$ fs, is predominantly responsible for inducing center-of-mass motion, giving rise to oscillations of the C_{60} between $d = 5.05$ and 5.23 a.u. Figure 2(b) shows the transmission coefficient for different C_{60} locations; $d = 5.05$ (solid curve), 5.13 (dashed curve), and 5.23 a.u. (dot-dashed curve). As the fullerene approaches the center of the junction, the transmission is strongly

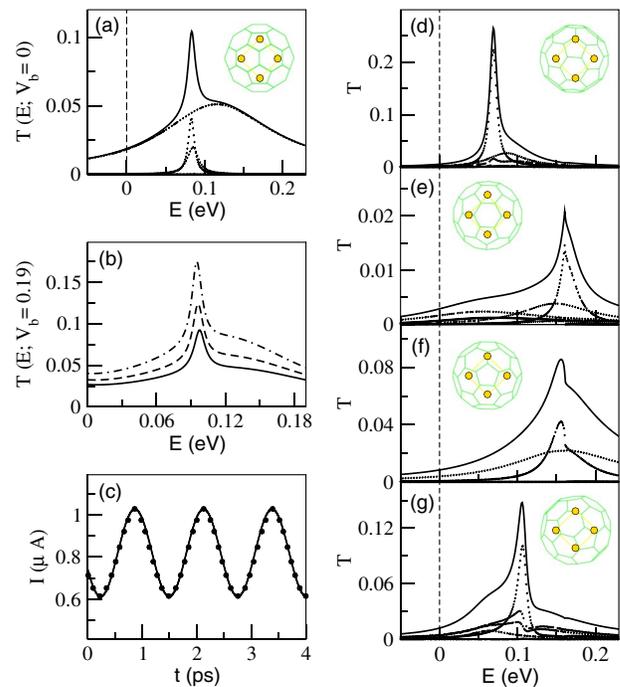


FIG. 2 (color online). Transmission spectra, $T(E; V_b)$, and time-dependent current, $I(t; V_b)$, for the device of Fig. 1. $L = 26.42$ a.u. and the Fermi level defines the zero energy. (a) $T(E; V_b = 0)$ at the equilibrium configuration, $d_{eq} = 5.13$ a.u., along with the three resonance peaks (dots) constituting the transport. (b) $T(E; V_b = 0.19$ V) for different C_{60} locations: $d = 5.05$ (solid curve), 5.13 (dashed curve), and 5.23 a.u. (dot-dashed curve). (c) Spontaneously oscillating current, $I(t; V_b = 0.19$ V), vs time. (d)–(g) $T(E; V_b = 0)$ along with its constituting resonance peaks (dots) for different C_{60} orientations. The electrode surface faces: (a)–(c) a 6-6 bond, (d) a 5-6 bond, (e) a hexagon, (f) a pentagon, (g) a mixed configuration. The insets show the molecular orientation as viewed along the z direction, where the solid circles mark the location of the gold atoms.

enhanced, owing to the strong dependence of the electron tunneling rate on the longer of the two C_{60} -electrode distances. The sharp dependence of $T(E, V_b)$ on the C_{60} location gives rise to time-dependent current.

This phenomenon is illustrated in Fig. 2(c), which shows the current through the junction vs time. $I(t, V_b)$ oscillates at the frequency of vibrations of the center of mass and a controllable amplitude. Here, the current oscillates at a frequency of 0.8 THz and an amplitude $0.21 \mu\text{A}$, with an average of $\bar{I} = 0.82 \mu\text{A}$, giving an ac/dc ratio of 0.26. Whereas the longest lived of the resonances of Fig. 2(a), with $\tau = 71.5$ fs, is predominantly responsible for inducing the center-of-mass vibrations, the broadest resonance, with $\tau = 3.6$ fs, is predominantly responsible for the large average conductivity, which allows the dynamical current to be readily monitored.

From the average current in Fig. 2(c) we roughly estimate the frequency of electron transport as $f \sim \bar{I}/e \sim 5$ THz, almost an order of magnitude larger than the nuclear vibrational frequency. Thus, ca. 6–7 electrons tunnel through the junction per cycle of the C_{60} oscillation, mostly mediated by the 3.6 fs resonance that serves solely to monitor the motion. Comparing the energy-integrated transmission peaks of the longest- and shortest-lived of the three resonances in Fig. 2(a), we estimate that an average of ca. one electron per two cycles of the C_{60} oscillation tunnels via the 71.5 fs resonance, sufficient to drive the oscillation, although not to probe it. Only a certain range of L values permits both a large ac/dc ratio and substantial average conductance. As L decreases, the coupling of the fullerene to the right electrode is enhanced, the resonances broaden, the average current grows, and the center-of-mass oscillation amplitude decreases. For $L = 25.42$ a.u., for instance, the lifetime of the resonance dominating the oscillation is 65.8 fs, leading to a C_{60} vibrational amplitude of 0.08 a.u. and a current oscillation amplitude of $0.23 \mu\text{A}$ with an average current of $\bar{I} = 3.15 \mu\text{A}$, corresponding to an ac/dc ratio of 0.07. For $L \leq 23.42$ a.u., the C_{60} is located at the center of the junction at equilibrium. For $L \geq 26.5$ a.u. the current drops below the limit that allows dynamical detection of the motion. It is important to stress that the potential energy surfaces underlying the center-of-mass dynamics are based on approximate data [11,21] and that the actual potential is likely to vary with details of the device. We found, however, that whereas the details of the transport and dynamics depend on the parameters of the potential energy surfaces, the phenomena of current-driven oscillations and consequent time-dependent current are robust. The message of Fig. 2(c) is thus qualitative, but general.

We note that a time-oscillating current is associated with a time-oscillating electromagnetic field. Our results suggest the intriguing possibility of devising a molecular-scale ac field generator, thus also a THz optoelectronic device [22], through current-driven dynamics in nanojunctions.

Whereas the C_{60} junction used as an example in the present study provides an infrared device, the choice of a heavier fullerene would slow down the motion and may lead to a microwave device [22]. A challenging problem in the context of current-driven dynamics in nanojunctions is the possibility of experimentally detecting the motion on the molecular scale. Here, the ac field associated with the motion provides opportunities for its direct, time-domain probing. Superconducting bolometers, for instance, have been shown to provide sensitive direct detectors for infrared and millimeter waves [23], and their design and optimization requirements appear compatible with those of nanojunctions.

Having illustrated the sharp dependence of the current on the location of the fullerene within the junction, it is interesting to briefly remark on its dependence on the orientation of the C_{60} with respect to the electrode surface. Several C_{60} orientations are considered in Figs. 2(d)–2(g), where the electrode surface faces a 5-6 bond, a hexagon, a pentagon, and a mixed configuration. By contrast to the case in Fig. 2(a), here the dominating resonances arise from the metal s , p_z , d_{z^2} band and are not eigenfunctions of the device Hamiltonian. The line shape and the dynamics in the 5-6 configuration (panel d) are dominated by the longest lived resonance, which is of near Lorentzian form with lifetime $\tau = 65.8$ fs. In the remaining configurations the dominating resonances are broadened and severely deformed from the Lorentzian shape.

The dramatic dependence of the transmission on the C_{60} orientation is counterintuitive at first sight, in view of the high symmetry of the fullerene. Inspection of the nodal pattern of the resonance wave functions in the xy plane attributes the sharp orientation dependence to an interplay between physical proximity of the carbon and gold atoms (see insets) and symmetry matches between the resonance orbital and metal bands. The better spatially localized the wave function in the contact, the sharper the resonance in the energy domain, giving rise to the lifetime difference between the resonances. Symmetry mismatch between the molecular and electrode wave functions in Figs. 2(e)–2(g) spoils the Lorentzian line shape characterizing the spectrum of Fig. 2(a). Space limitation requires that we defer details to a future publication. Thus, an optical or electronic method of inducing directed rotation of the C_{60} would likewise give rise to time-modulated current. (Thermal rotation, which would be nondirected, is not expected, as the 6-6 configuration is the more stable by at least 0.174 eV.)

In summary, we showed numerically that current-driven dynamics through molecular-scale junctions can be used to make devices whose conductance properties vary with time in a controllable manner. One of the intriguing consequences is a nanoscale generator of alternating current electromagnetic field in the THz regime. Our numerical results pertain to a single and rather simple example, namely, the

Au-C₆₀-Au junction, but our conclusions are expected to be more general. Elsewhere we show that inelastic resonance tunneling through certain biphenyl derivatives (appropriately attached to electrodes) leads to free torsion. In such systems the conductance changes by ca. one and a half orders of magnitude as the torsion angle varies between 0 and π , a very simple effect that results from the lost π conjugation at nonplanar configurations. In other systems of relevance we find inelastic current to lead to motion of the molecule into and out of alignment with the electrodes, which likewise dynamically modulates the conductivity. These observations suggest that intrinsically generated time-dependent current, with an associated time-dependent electromagnetic field, could be induced in a variety of molecular-scale junctions.

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