Classical Nuclear Motion in Quantum Transport

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(Received 21 December 2005; published 27 July 2006)

An *ab initio* quantum-classical mixed scheme for the time evolution of electrode-device-electrode systems is introduced to study nuclear dynamics in quantum transport. Two model systems are discussed to illustrate the method. Our results provide the first example of current-induced molecular desorption as obtained from a full time-dependent approach and suggest the use of ac biases as a way to tailor electromigration. They also show the importance of nonadiabatic effects for ultrafast phenomena in nanodevices.

DOI: 10.1103/PhysRevLett.97.046603 PACS numbers: 72.10.Bg, 63.20.Kr, 63.20.Ry, 73.63.−b

The study of electron-nuclei interaction (ENI) in solids has a long and important history, dating back to the early days of quantum mechanics. Since then, the ENI has become a pillar concept of our understanding in condensed matter [1]. Increase in computer power and the introduction of *ab initio* molecular dynamics [2] have made possible quantitative studies of ENI in many materials.

Recent advances in nanotechnology pose new questions about the ENI in out-of-equilibrium open systems at the nanoscale [3]. Among the techniques used to study the ENI in this context, quantum transport experiments stand out as a special case, since charge conduction is at the same time a way to characterize the nanodevice and a property to be exploited in its operating regime. A case in point is molecular junctions, where electron injection can stimulate local vibrations [4,5] and possibly electromigration [6]. More generally, describing ENI in time-dependent (TD) quantum transport is expected to become of great technological interest, since future nanodevices will operate under the influence of ever faster time varying external fields. Accordingly, those regarded at present as marginal transient effects will soon become center stage features. Assessing and engineering the ENI is then a key ingredient to increase the device efficiency [7,8]. To date, most theoretical studies have addressed the ENI in steady-state phenomena [9–15] and often perturbatively in the nuclear displacements [13–15]. Going beyond the harmonic approximation and including the ENI in a first-principles, TD framework is a difficult theoretical task which has received so far scarce attention [16–19].

In this work we propose a first-principles approach to TD quantum transport which treats the nuclear motion in the Ehrenfest dynamics (ED) and the electrons within time-dependent density functional theory (TDDFT) [20]. The ED has been extensively used in several contexts; in quantum transport, it was considered in [18]. The ED correctly displays many important features of ENI, but gives an incomplete account of the Joule heating of the nuclei by the electrons [19]. However, such effect is not the aim of this first work. Here we use ED which, while treating ENI at the mean field level, includes, as opposed to the Born-Oppenheimer approximation, electronic transitions. Our approach to transport permits the description of transient effects: it can be used to describe history dependent currents, hysteresis phenomena, etc. Another main advantage is that it can perform the TDDFT-ED of devices connected to infinitely long leads.

We illustrate the approach with two model devices, where the electrons interact only via the ENI: a Holstein wire (D1) and a diatomic molecule (D2). We choose these two rather different systems to show the versatility of our method in discussing transient phenomena and overcoming the limitations of adiabatic treatments. More in detail, our results show the following: (i) For weak electron-phonon (e-ph) couplings, D1 exhibits an almost periodic nuclear displacement (with period $= 1/\text{density}$), reminiscent of a Peierls distortion. On applying a dc bias, the nuclei oscillate (with decreasing amplitude) and the period changes to accommodate the current flow. On increasing the e-ph coupling, D1 changes from conducting to insulating. (ii) D2 is deformed by a small, suddenly switched on dc bias. Above a critical value of the bias, the molecule dissociates. This is the single most important result of this work. To our knowledge, it provides the first example of current-induced molecular desorption as emerging from the full TD dynamics of a nanodevice. (iii) The desorption cannot be described in any adiabatic formalism, since it is due to electronic excitations induced by the nuclear motion. (iv) The desorption can be tuned by the intensity and frequency of an ac bias, suggesting a way to control electromigration in molecular devices.

The method.—Following Refs. [21–23], in the initial ground state the central region (C) is in contact to semi-infinite left (L) and right (R) leads. With ENI, the Hamiltonian for C reads

$$\hat{H}_C[\mathbf{x}] = \sum_{i,j=1}^{M} V_{ij}(\mathbf{x}) c_i^\dagger c_j, \tag{1}$$

where M is the number of one-electron states of C and $\mathbf{x} = (x_1, \ldots, x_N)$ are the nuclear coordinates. Outside C, the nuclei are clamped. In the Kohn-Sham (KS) scheme of TDDFT [20], V_{ij} would be the (i, j) matrix element of the

KS Hamiltonian. The nuclear classical Hamiltonian is $H_{\rm cl} = \sum_{k=1}^{N} p_k^2/(2m_k) + U_{\rm cl}(\mathbf{x})$. The dynamics of the system is governed by

$$i\frac{d}{dt}|\Psi\rangle = \hat{H}_{\rm el}|\Psi\rangle, \tag{2}$$

$$m_k\frac{d^2x_k}{dt^2} = -\frac{\partial}{\partial x_k}(U_{\rm cl} + \langle\Psi|\hat{H}_C|\Psi\rangle), \tag{3}$$

where $|\Psi(t)\rangle$ is the many-electron state at time t, and $\hat{H}_{\rm el}[\mathbf{x}]$ is the electron Hamiltonian of the contacted system $L + C + R$. Given a configuration $\mathbf{x}$, $\hat{H}_{\rm el}[\mathbf{x}]$ is a free-particle Hamiltonian. The many-electron ground state $|\Psi_g[\mathbf{x}]\rangle$ consists of bound, resonant, fully reflected waves, plus left and right going scattering states. The parametric dependence of $\hat{H}_{\rm el}$ on $\mathbf{x}$ renders every eigenstate a function of $\mathbf{x}$. The ground-state value $\mathbf{x} = \mathbf{x}_g$ is computed using damped ground-state dynamics: starting from an initial $\mathbf{x}_0$, the coordinates are evolved according to $m_k\ddot{x}_k = -\gamma\dot{x}_k - \partial(U_{\rm cl} + \langle\Psi_g|\hat{H}_C|\Psi_g\rangle)/\partial x_k$, with γ the friction coefficient.

Having $\mathbf{x}_g$ and the corresponding $\{\psi\}$ one-electron orbitals, we apply an external bias and evolve the system. Assuming metallic electrodes and instantaneous screening, the size of C is chosen so that the potential drop at any time occurs entirely in C. Thus, the TD part of the electrode Hamiltonian is a spatially uniform shift $U_\eta(t)$, $\eta = L, R$. We use a novel mixed quantum-classical evolution algorithm, which combines a recently proposed generalization of the Crank-Nicholson method [23] for the $\{\psi\}$ with a Verlet-like integrator for the $\mathbf{x}$. Schematically, in terms of the discretized time $t_m = 2m\delta$,

$$\begin{aligned}
\{\psi^{(m+1)}\} &= \{\boldsymbol{S}[t_m, \mathbf{x}^{(m)}]\psi^{(m)}\},\\
p_k^{(m+1)} &= p_k^{(m)} + 2\delta F_k[\mathbf{x}^{(m)}, \{\psi^{(m+1)}\}],\\
x_k^{(m+2)} &= x_k^{(m)} + 4\delta p_k^{(m+1)}/m_k,\\
p_k^{(m+2)} &= p_k^{(m+1)} + 2\delta F_k[\mathbf{x}^{(m+2)}, \{\psi^{(m+1)}\}],\\
\{\psi^{(m+2)}\} &= \{\boldsymbol{S}[t_{m+1}, \mathbf{x}^{(m)}]\psi^{(m+1)}\},
\end{aligned} \tag{4}$$

with $\psi^{(m)} = \psi(t_m)$, $\mathbf{x}^{(m)} = \mathbf{x}(t_m)$, and $\mathbf{p}^{(m)} = \mathbf{p}(t_m)$. The unitary matrix $\boldsymbol{S}$ depends on time through $\mathbf{x}(t)$ and the TD bias $U_\eta(t)$, $\eta = L, R$. Full details of the electronic evolution can be found in Ref. [23]. The force $F[\mathbf{x}, \{\psi\}]$ is given by the right-hand side of Eq. (3).

To illustrate the method, we describe electrodes L and R in terms of one-dimensional tight-binding (TB) Hamiltonians with a hopping V between nearest neighbor sites (TB parametrization of Au wires suggest $|V|$ in the range 0.3–1.0 eV). Left and right going scattering states have energy ε within the band $(-2|V|, 2|V|)$ and can be obtained by solving the Schrödinger equation in C with appropriate boundary conditions. Bound state eigenenergies $\varepsilon_b < -2|V|$ satisfy $\det[\varepsilon_b\mathbf{1} - \boldsymbol{H}_C - \boldsymbol{\Sigma}(\varepsilon_b)] = 0$, and the associated wave function is given in C by the kernel of $[\varepsilon_b\mathbf{1} - \boldsymbol{H}_C - \boldsymbol{\Sigma}(\varepsilon_b)]$ [$\boldsymbol{H}_C$ is the projection of $\hat{H}_C$ onto the one-electron Hilbert space; $\boldsymbol{\Sigma}(\omega)$ is the embedding self-energy]. The topology of region C might also lead to states rigorously confined in C (see below). These are resonant eigenstates of the uncontacted $\boldsymbol{H}_C$ with zero amplitude at the interface with the two electrodes.

Model device D1.—The semiclassical Holstein model is a valuable tool to gain insight into e-ph interactions [24,25]. Here, we investigate TD transport through a Holstein wire described by

$$\hat{H}_C = V\sum_{i=-M}^{M-1}(c_i^\dagger c_{i+1} + \text{H.c.}) - g\sum_{i=-M}^{M} x_i\hat{n}_i, \tag{5}$$

where $\hat{n}_i = c_i^\dagger c_i$ is the local density operator and x_i are the phonon coordinates. The nuclear classical potential is $U_{\rm cl}(\mathbf{x}) = \frac{1}{2}\sum_{i=-M}^{M} m_i\omega_0^2 x_i^2$. The strength of the e-ph interaction is determined by the dimensionless parameter $\lambda = g^2/(2V\omega_0)$. In the original derivation by Holstein, x_i corresponds to an internal coordinate (bond length) at the ith site. We study D1 at half filling ($\varepsilon_F = 0$), in the adiabatic regime ($\alpha = \omega_0/V = 0.1$) at weak ($\lambda = 0.1$) and strong ($\lambda = 1$) coupling. A damped ground-state dynamics, as described above, was used to get the converged ground state x_i (Fig. 1, left panel) for a region C with $M = 7$. The energy spectrum between $-2|V|$ and ε_F was discretized and good convergence was achieved with $N_k = 500$ mesh points. For $\lambda = 0.1$, a Peierls-like distortion is seen: an even-odd behavior of x_i is manifest (in general, $P = 1/n$, and here $n = 0.5$), but exact periodicity is prevented by the finite size of C. The inset shows the local density of states

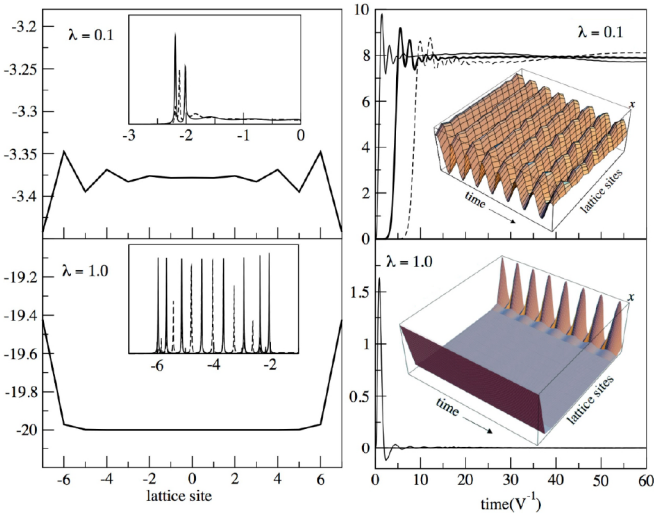

FIG. 1 (color online). Left panel: Ground-state displacement x_i, $i = -7, \ldots, 7$, at weak ($\lambda = 0.1$) and strong ($\lambda = 1.0$) coupling. The inset shows the LDOS (energy in units of $|V|$) on site -6 (dashed line) and site 0 (solid line). Right panel: current $I(t)$ (in units of $10^{-2}|V|$) at weak and strong coupling along the bond $(-7, -6)$ (solid thin line), (0, 1) (solid thick line) and (6, 7) (dashed line) after the sudden switching on of a bias $U_L = 0.5|V|$ in electrode L. The insets show a 3D plot of $\mathbf{x}(t)$ between $t = 0$ and $t = 480|V|^{-1}$ (in the top panel the range of $\mathbf{x}$ is between -3.2 and -4, while in the bottom panel the range is between -19.4 and -20).

(LDOS) close to the interface and in the center, respectively. At $\varepsilon < -2|V|$ we observe three peaks due to three bound states. The picture changes dramatically at $\lambda = 1$: The number of bound states equals the dimension of C and, almost uniformly, $x_i \simeq -20$. Only the x_i close to the interfaces are slightly above this value.

In Fig. 1 (right panel), we plot the current $I(t)$ in three different points of C after suddenly switching on a bias $U_L = 0.5|V|$ in the left electrode. All calculations use a time step $\delta = 0.01|V|^{-1}$. For both $\lambda = 0.1$ and 1.0, the current in the (short) transient is similar to the case with the x_i clamped (not shown), since electrons are much faster than nuclei. At $\lambda = 0.1$ the steady current shows superimposed oscillations of frequency ω_0. Instead, for $\lambda = 1$, all the $2M + 1 = 15$ bound states in C are occupied (including the Hartree potential would have led to a significant reduction of this excess density in C), no current fluctuations occur in the center and at the right interface, and only a very short transient is observed at the left interface. The insets display the TD Peierls distortion. For $\lambda = 0.1$ all the x's oscillate with an exponentially decreasing amplitude (within our simulation time $t = 480|V|^{-1}$). The overall shape of the x_i changes to accommodate the net electron flow. For $\lambda = 1$ no current flows and only the x_i close to the left interface oscillate. The decay of the amplitudes of the x_i is partially due to the inefficiency of ED in transferring energy from electrons to nuclei. We also considered the sudden removal of a bound electron, as obtainable, for example, by optical means: in this case, D1 provides a strong transient oscillating response (not shown). On speculative grounds, such behavior could be used for ENI-based photosensors.

Model device D2.—We consider a central region C with the simplest nontrivial topology, a four-atom ring. This is our model molecular device D2, with nuclear positions $\mathbf{r}_i \equiv (x_i, y_i)$, $i = 1, \ldots, 4$ (Fig. 2, top-left inset). In D2, only nuclei 2 and 3 (N2,3) are let to move in the xy plane. The origin of the xy plane is the midpoint of nuclei 1 and 4. For the hopping parameter we choose the form [26] $V_{i\neq j} = V_c \frac{e^{-r_{ij}}}{r_{ij}}$, $V_{i=j} = 0$, where $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$. The purely repulsive classical term is given by $U_{\rm cl} = \frac{1}{2}\sum_{i\neq j} A/r_{ij}^4$. We tune the parameters V_c, A, and r_{14} to ensure a reasonable domain of structural stability for D2. For $V_c = 4V$, $A = 0.75|V|$, and $r_{14} = 2$, D2 is stable against deformations up to $\sim$10% of the equilibrium distances. Also, we get the ground-state positions $\mathbf{r}_2 = (0, 0.8313)$ and $\mathbf{r}_3 = -\mathbf{r}_2$ (the 2–3 symmetry remains true in the presence of the bias). The LDOS has one peak below $-2|V|$, i.e., one bound state. There is also a resonant state $|\psi\rangle = \frac{1}{\sqrt{2}}(|2\rangle - |3\rangle)$ with energy $|V_{23}| > 0$ inside the band. The system is taken at half filling, and we switch on a bias U_L at $t = 0$. As for D1, $\delta = 0.01|V|^{-1}$, $N_k = 500$; for the masses of N2,3 we choose $100|V|^{-1}$.

In Fig. 2 we plot the TD currents I_L and I_R at the left and right interfaces, respectively. At small bias $U_L = 0.25|V|$, $I_{L,R}$ rapidly increase and after a short transient (with the nuclei essentially still) start to oscillate around a steady value. Inset (b) shows the corresponding nuclear dynamics. The equilibrium rhombic geometry changes and the molecule gets deformed in the biased system, with N2,3 having damped oscillations around two new positions (for the damping and ED, considerations similar to the case of D1 apply). We also notice from inset (a) that the charge density of N2,3 slightly increases.

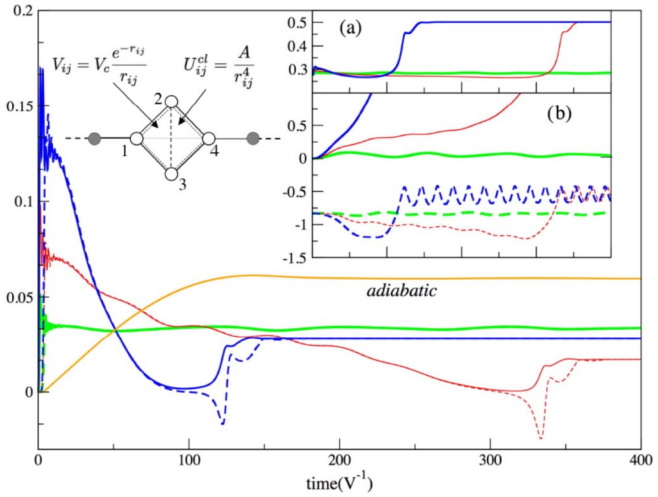

FIG. 2 (color online). $I_{L,R}(t)$ (in units of $|V|$) at the left (solid line) and right (dashed line) interface for a sudden switching $U_L = 0.25|V|$ [green (light gray) line], $0.5|V|$ [red (thin dark gray) line], and $1.0|V|$ [blue (thick black) line]. Inset (a): Time-dependent density n_3 of nucleus 3 (by symmetry $n_2 = n_3$ at any time). Inset (b): $x_3(t)$ (solid line) and $y_3(t)$ (dashed line) of nucleus 3 (by symmetry $x_2 = x_3$ and $y_2 = -y_3$ at any time). Time scale and color coding in insets (a) and (b) are the same as in the main figure. A schematic of the device D2 and the adiabatic result (labeled curve) are also shown.

Highly interesting is the strong bias case $U_L = 1.0|V|$. After a very short transient, $I_{L,R}$ sharply decrease (rather than oscillating around a steady value) and become zero at $t_0 \simeq 100|V|^{-1}$. After t_0, $I_{L,R}$ separate: I_L increases while I_R decreases, reaches a negative minimum, and then increases to eventually rejoin I_L at $t_1 \sim 160|V|^{-1}$. For $t > t_1$, $I_L \simeq I_R$ and their value equal the steady current (calculated from the Landauer formula) of the chain without N2,3. The behavior of $I_{L,R}$ can be understood looking at the nuclear dynamics [inset (b)]: the force exerted by the electron flow is strong enough for atomic migration to occur. N2,3 are pushed to the right by the current, overcome the confining potential, and get dissociated from region C. Thereafter, they form a diatomic molecule vibrating along y [see inset (b)] and traveling along x at uniform speed. The pronounced minimum of I_R shortly after t_0 is due to a sudden charge transfer from electrode R (via atom 4) to the diatomic molecule when N2,3 pass above nucleus 4. This is confirmed in inset (a) where the density suddenly increases in correspondence of the minimum in I_R. We also note that the total density of the dissociated molecule is about 1 (exact charge quantization would occur in the adiabatic

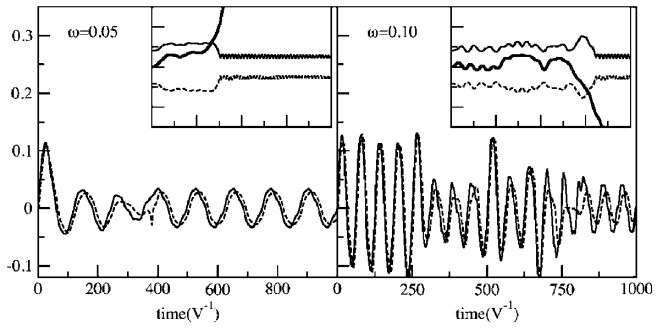

FIG. 3. Left panel: $I_{L,R}(t)$ (in units of $|V|$) at the left (solid line) and right (dashed line) interface for $U_L = 1.0|V|$, $\omega = 0.05|V|$. In the inset, $x_2(t) = x_3(t)$ (thick solid line) $y_2(t)$ (thin solid line), and $y_3(t)$ (dashed line). The time scale is the same as in the main panel. Right panel: same as left, but with $\omega = 0.10|V|$. Left and right insets have the same vertical scale.

approximation only). Here, including the Hartree potential would not lead to qualitative changes of the dissociation process. A more realistic model should also include the possibility for the molecule to chemisorb onto the electrode, to fragment, etc., but this is beyond the scope of the present Letter.

To address the dissociation mechanism, we study two different $U_L(t)$, with the same asymptotic value $0.5|V|$. For a sudden switching, one observes a behavior delayed but similar to the $1.0|V|$ case above. Instead, for an adiabatic switching [27] the dimer does not dissociate (in Fig. 2, the current is displayed in orange and labeled ''adiabatic''). We conclude that electronic excitations induced by the nuclear motion play a crucial role in the electromigration, a role that cannot be accounted for by any adiabatic formalism (without transients the nuclei experience no force). However, we observe that ED might overestimate the value of the critical bias for which dissociation occurs.

We next examined the response of D2 when subject to a high amplitude ac bias $U_L(t) = U_L \sin(\omega t)$, with $U_L = 1.0|V|$. At low ω (Fig. 3, left panel), the system qualitatively behaves as in the dc case, as clear from both current (main left) and coordinates (inset left) panels. The nuclei overtake the barrier before the change in $U_L(t)$ produces a force able to ''recall'' them back. After the desorption, $I_{L,R}$ oscillate as they would for a linear chain without N2,3. At larger ω (Fig. 3, right panel) the dissociation is delayed, since atoms 2 and 3 are recalled back a few times before leaving region C. Eventually, for high enough frequency ($>0.3|V|$, not shown) atoms 2 and 3 oscillate without leaving C (within our simulation time). These results point to a possible use of ac biases as a way to tailor molecular desorption in nanodevices.

In conclusion, we presented a mixed quantum-classical scheme to describe electron-nuclei interactions in quantum transport. The scheme is straightforwardly amenable to *ab initio* implementation. Our results show the necessity to go beyond adiabatic schemes and to use a full time-dependent, nuclear-dynamics approach for ultrafast transient phenomena which are expected to become important in future generation nanodevices.

We acknowledge useful discussions with G. J. Ackland, P. Bokes, and E. N. Economou. This work was supported by the European Community 6th framework Network of Excellence NANOQUANTA (No. NMP4-CT-2004-500198).

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[27] We take $U_L(t) = 0.5|V| \sin(\pi t/2t_0)$, $t \leq t_0 = 150|V|^{-1}$. To smoothen the switching as much as possible, we damp the nuclear motion using a friction $\gamma = 0.07$ up to $t < 200|V|^{-1}$ and let the system evolve without friction afterwards.