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To cite this version:

HAL Id: hal-02014483
https://hal.archives-ouvertes.fr/hal-02014483
Submitted on 11 Feb 2019

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Build-up of Vibron-Mediated Electron Correlations in Molecular Junctions

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(Dated: February 11, 2019)

We investigate on the same footing the time-dependent electronic transport properties and vibra-
tional dynamics of a molecular junction. We show that fluctuations of both the molecular vibron
placement and the electronic current across the junction undergo damped oscillations towards
the steady-state. We assign the former to the onset of electron tunneling events assisted by vibron-
emission. The time-dependent build-up of electron-hole correlations is revealed as a departure of the
charge-transfer statistics from the generalized-binomial one after a critical time tc. The phonon-back
action on the tunneling electrons is shown to amplify and accelerate this build-up mechanism.

PACS numbers: 72.10.-d, 72.10.Di, 85.65.+h, 72.70.+m

Introduction.—The scaling of electronic junctions down
to the molecule or single-atom size3–5 is known to suffer
from some limitations. To cite but a few of them: experi-
ments are poorly reproducible implying statistical av-
eraging on many samples6, transport characteristics are
highly dependent on geometry and chemical nature of
the tip or substrate7, and mechanical properties of
the junction are degraded by voltage-induced heating8, up
to reaching mechanical instability and final break-down9.

The previous limitations involve interaction between
electronic and vibrational degrees of freedom of the molecular
junction. It is thus of both fundamental and practical im-
portance for molecular electronics to better understand
the impact of electron-phonon (e-ph) excitations on elec-
tronic transport at the nanoscale.

Typical signatures of e-ph interactions are measured in
the conductance G(V) characteristics as peaks or dips10,
appearing each time the bias-voltage V crosses the in-
elastic threshold ℏω0/e, with ω0 the local-vibron fre-
quency, ℏ the reduced Planck constant and e the elec-
tronic charge. The analysis of the position and width of
these inelastic features11 contains information about the
e-ph matrix elements, the excited vibron frequencies and lifetimes12. More recently, signatures of electron-
vibron excitations were also reported on shot-noise S(V) characteristics13, revealing complementary information
about electronic correlations mediated by vibron excitation.

This extensive experimental activity has been sup-
ported by great theoretical efforts, the aim of which has
been to clarify the fundamental mechanism of electron-
tunneling assisted by vibron-emission and its impact on
quantum transport14–18. Despite all these efforts, the
understanding of electron-electron, electron-vibron in-
teractions and the role of electronic coherence at the
nanoscale remains mainly limited to the stationary (time-
independent) transport regime.

This topic has experienced a revival with the recent de-
velopment of single-electron sources19, which allow con-
trolled injection of well-defined single-electron excitations
in atomic point contacts. This has opened new avenues
for probing the short-time response of a nanojunction,
in the range 1–10 ns20. Further improvements in design-
ing broadband and low-noise detectors has been later re-
ported, with the first measurement of thermal decay of
current-fluctuations at ultrashort time scales 10–100 ps21.22
It is thus timely to develop new theoretical tools bridg-
ing the gap between molecular electronics and ultrafast
quantum electronics23,24. Such approaches should en-
able the computation of the mean current25–28, current-
current noise and higher-order cumulants of the current
fluctuations29–31, including the non-Markovian character
of electronic tunneling at low-temperature. For those
reasons, the understanding of interaction effects on time-
dependent transport is still a challenging issue.

In this Rapid Communication, we develop a compact
methodology based on nonequilibrium Green func-
tions (NEGF)29–31 for probing on the same footing time-
dependent electronic current-fluctuations and vibron dy-
namics of a molecular junction. We follow the junction
characteristics from short time-scales given by the inverse
electronic tunneling rate 1/Γ, to a longer time-window char-
acterized by the vibron-mode inverse damping rate 1/γd
and by electronic-current transient oscillations of period
2πℏ/(eV ± ℏω0). We show the departure of the charge-
transfer statistics from the non-interacting generalized-
binomial distribution32, at a critical time associated to
the build-up of vibron-mediated electron correlations.

Microscopic model.—Our approach is based on a micro-
scopic Hamiltonian for the molecular junction
\[ H(t) = H_M + H_R + H_T(t), \]
with
\[ H_M = ε_0 n_d + ℏω_0 a+ a† + \lambda (a + a†) \left( n_d - \frac{1}{2} \right), \]
\[ H_R = \sum_{r,k} \xi_{r,k} c^\dagger_{r,k} c_{r,k}, \]
\[ H_T(t) = \sum_{r,k} \left\{ t_{r,k}(t) c^\dagger_{r,k} d + t^\dagger_{r,k}(t) d^\dagger c_{r,k} \right\}. \]

Eq. (1) describes a single electronic level of energy ε0 and
a local vibration mode of frequency ω0, with d† (a†) the
creation operator of an electronic (vibrational) excitation on the molecule. Electron-phonon interactions couple the position operator of the phonon mode (in units of its zero-point motion) $x = a + a^\dagger$ to the charge operator of the molecule $n_d \equiv d^\dagger d$, with coupling strength $\lambda$. Eq. (2) models the metallic left (L) and right (R) leads, with $c^\dagger_{r,k}$ the creation operator of an electronic excitation in the $r = L, R$ reservoir with energy $\varepsilon_{r,k}$ and quasi-momentum $k$. The leads are supposed to be in thermal equilibrium at temperature $T$, and their respective chemical potentials to be maintained under a symmetric voltage-drop $\mu_{L,R} = \pm eV/2$. Finally, Eq. (3) describes the tunneling of electrons from lead $r$ to the molecular level, with the rate $\Gamma_r(\omega) = \pi/\hbar \sum_k |t_{r,k}|^2 \delta(\omega - \varepsilon_{r,k})$. Within the wide-band approximation, the rates are evaluated at the Fermi energy $\Gamma_r(\omega) \approx \Gamma_r(\varepsilon_F) \equiv \Gamma_r$, thus resulting in a total tunneling rate $\Gamma = \Gamma_L + \Gamma_R$. In order to probe the transient dynamics of charge-transfer across the junction, the tunneling hoppings $t_{r,k}(t) = t_{r,k}(0)$ are switched-on at the initial time $t = 0$, where $\theta(t)$ is the Heaviside step-function. Typical experimental parameters for molecular junctions are $\hbar \omega_0 \approx 10$ meV $- 100$ meV, $(\lambda/\Gamma)^2 \approx 1 - 5\%$ and $T \approx 4.2$ K. In the following, we adopt units such that $e = 1$, $\hbar = 1$ and the Boltzmann constant $k_B = 1$.

$\lambda$-coupling (\(\lambda/\Gamma\))^2 $\approx$ 20\% and phonon frequency $\omega_0/\Gamma \approx 0.5$ are taken a bit larger than in usual experiments in order to achieve fast-enough relaxation.

**FIG. 1.** Top panel: Time-dependent phonon population $n_{ph}(t)$ for two different initial conditions $n_{ph}(0) = 0$ (solid lines) and $n_{ph}(0) = n_{ph}^0$ (dashed lines). Lower panel: Vibrational displacement fluctuations $S_{\omega}(t)$ for the initial condition $n_{ph}(0) = 0$ (plain curves), compared to the relaxation of a classical harmonic oscillator (dashed-blue line) in the case $V = 0.5\omega_0$ and $n_{ph}(0) = n_{ph}^0 \approx 0$. Common to both panels: $\Gamma = 1$, $\Gamma_L = \Gamma_R$, $\varepsilon_0 = 0$, $\omega_0 = 0.5$, $\lambda = 0.45$, $T = 0$, $n_d(0) = 0$ and $V = 0.5, 1.5, 2.5, 3.5\omega_0$.

**NEGF approach.** We are interested in the full-counting statistics (FCS) of electron tunneling\textsuperscript{25–38}, which provides complete information about current-fluctuations. The central quantity in a FCS analysis is the quasi-probability distribution $P_q(t)$ that $q$ charges are transferred across the molecular junction between the initial and final measurement times 0 and $T$. The related moment generating function (MGF) $Z(\chi, t) = \sum_{q \in \mathbb{Z}} P_q(t)e^{i\chi q}$ and cumulant generating function (CGF) $\mathcal{F}(\chi, t) = \ln Z(\chi, t)$, generate upon $n$-successive derivations with respect to the counting-field $\chi$, the $n$th moment $M_n$ and cumulant $C_n$ of the distribution $P_q(t)$ respectively. The CGF is expressed as\textsuperscript{26,27}

$$\frac{\partial}{\partial \chi} \mathcal{F}(\chi, t) = -\text{tr} \left\{ \frac{\partial \Sigma_{T,\chi}}{\partial \chi} G_\chi \right\},$$

(4)

which recovers the stationary limit\textsuperscript{31,39}. Eq. (4) involves the time-dependent tunneling self-energy $\Sigma_{T,\chi}(t)$ of the molecular level $G_\chi(1, 2) = -i \langle T_{\phi} d(1) d^\dagger(2) \rangle$, and vibron mode $D_\chi(1, 2) = -i \langle T_{K} x(1) x(2) \rangle$. We adopt the shorthand notations for the time $t(\phi2) \equiv 1(2)$, and the time-ordering operator $T_K$, on the Keldysh contour $C_K$. We write in bold symbolic any matrix in the discretized contour. Notice that the dimension of the bold matrices increases linearly with time $t$. The NEGFs are evaluated with the counting-field $\chi(t)$ included into the hopping terms $t_{r,k}(t) \equiv t_{r,k}(\chi(t))\textsuperscript{29–31}$, with $\chi(t) = \pm s(t)/2$ for $t$ on the forward (backward) branch of $C_K$ and $s(t) = 1(-1)$ for $r = L(R)$.

We evaluate Eq. (4) within the Random Phase Approximation (RPA)\textsuperscript{24,42}, for which the molecular level and vibron NEGFs fulfill the following equations

$$G_\chi \approx G_{0\chi} + G_{0\chi} \Sigma_{ep,\chi} G_{0\chi},$$

(5)

$$D_\chi = \{d_0^{-1} - \Pi_\chi\}^{-1},$$

(6)

with $G_{0\chi} = \{g^{-1} - \Sigma_{T,\chi}\}^{-1}$ the NEGF of the molecular level coupled to the leads but not interacting with the vibron mode, $g$ the NEGF of the isolated level, and $d_0$ the bare vibron propagator. The electron self-energy $\Sigma_{ep,\chi}$ in Eq. (5) is the sum of an Hartree (H) term $\Sigma_{H,\chi}$, plus an exchange (XC) contribution $\Sigma_{XC,\chi}$, while $\Pi_\chi$ in Eq. (6) is the vibron self-energy, given by

$$\Sigma_{H,\chi}(1, 2) = \frac{1}{\hbar} \int_{C_K} dt \text{Im} \delta(1, 3) d(1, 3),$$

(7)

$$\Sigma_{XC,\chi}(1, 2) = i\lambda^2 G_{0\chi}(1, 2) D_\chi(1, 2),$$

(8)

$$\Pi_\chi(1, 2) = -i\lambda^2 G_{0\chi}(1, 2) G_{0\chi}(2, 1),$$

(9)

where $\delta(1, 2)$ is the delta-function defined on the Keldysh contour, and $n_{ph}(3)$ the counting-field dependent population of the molecular level. Consistently with the RPA, the electronic NEGF is truncated at second-order in the e-ph coupling strength $(\lambda/\Gamma)^2$\textsuperscript{34,45}, while the vibron propagator is obtained after resummat- ing a whole class of dominant ring-diagrams\textsuperscript{42}. Eq. (4) to (9) are the basis of our approach. We solve then
numerically, after discretizing the Keldysh contour. Within RPA, taking into account only $\Sigma_{X,C}$ in Eq. (5) ($\Sigma_{H,X}$ gives a smaller associated contribution to displacement currents), Eq. (4) can be integrated exactly and provides the following expression for the MGF:

$$Z(\chi, t) \approx \det \left\{ \tilde{G}_{x=0} \tilde{G}_{x=0}^{-1} \right\} \sqrt{\det \left\{ \tilde{D}_{x=0} \tilde{D}_{x=0}^{-1} \right\}}.$$

We have checked numerically that within RPA and for our range of parameters, the continuity equation for the electronic current is fulfilled.

Vibrion dynamics. – We focus first on the average phonon population $n_{ph}(t) \equiv \langle a^\dagger(t) a(t) \rangle$. We show in Fig. 1 (top panel) the time-evolution of $n_{ph}(t)$ for a symmetric junction $\Gamma_L = \Gamma_R$ with a resonant molecular level $\varepsilon_0 = 0$, corresponding to a perfectly transmitting junction. At the initial time, the molecular level is unoccupied, $n_{ph}(0) = 0$, while the vibron mode is in its ground state, i.e. $n_{ph}(0) = 0$ (plain-curves). Consistently with a rate equation description, we find that the vibron occupation slowly relaxes towards the steady-state value $n_{ph}^{st} = (V - \tilde{\omega}_0) \theta (V - \tilde{\omega}_0) / 4\tilde{\omega}_0$, with a dissipation rate $\gamma_\alpha = 2\lambda^2 \tilde{\omega}_0 / \pi \Gamma^2$ and renormalized (softened) phonon frequency $\tilde{\omega}_0 = \omega_0 - 2\lambda^2 / \pi \Gamma$. We estimate $\tilde{\omega}_0 \approx 76\% \omega_0$ and $\gamma_\alpha \approx 5.4\% \Gamma$, implying a relaxation time $1/\gamma_\alpha \approx 18/\Gamma$ which is consistent with the low-voltage numerical curves. For higher voltages ($V \geq 2.5\omega_0$), inelastic electron-tunneling events heat up the phonon mode, while the dissipation rate becomes voltage-dependent. As expected, the relaxation is faster for the initial condition $n_{ph}(0) = n_{ph}^{st}$ closer to the steady-state (dashed-curves).

The fluctuations of the vibron displacement $\delta_{xx}(t) \equiv \text{Re} \langle \delta \chi(t) \delta \chi(0) \rangle$ are shown for $n_{ph}(0) = 0$ in Fig. 1 (lower panel). In the case $V = 0.5\omega_0$ (blue curve), $\delta_{xx}(t)$ exhibits damped-oscillations with period $2\pi / \tilde{\omega}_0$, and decoherence time $1/\gamma_\alpha \approx 2/\gamma_d$, in good agreement with the relaxation of a classical harmonic oscillator (dashed-blue curve): $\delta_{xx}(t) \approx \left(1 + 2n_{ph}^{st}\right) e^{-\gamma_d t} \left(\cos (\tilde{\omega}_0 t) + \frac{2\alpha}{\gamma_d} \sin (\tilde{\omega}_0 t)\right)$. We notice a phase-shift between the plain and dashed curves due to the retardation of the vibron in responding to the tunneling electrons. The value of $\gamma_\alpha$ is found larger than half the dissipation rate as a result of additional dephasing induced by elastic tunneling of electrons.

Electronic transport. – We consider now the average symmetrized current across the junction $I(t) \equiv \frac{\delta I}{\delta t} C_1(t)$, and time-derivative of the related symmetrized charge-fluctuations $S(t) = \frac{\delta C}{\delta t} C_2(t)$. We define the excess current $\delta I(t) = I(t) - I_0(t)$ and excess current-fluctuations $\delta S(t) = S(t) - S_0(t)$ with respect to the current $I_0(t)$ and current-fluctuations $S_0(t)$ in the non-interacting case ($\lambda = 0$). We show in Fig. 2 the time-evolution of $\delta I(t)$, for the same parameters as in Fig. 1. We find that $\delta I(t)$ oscillates and relaxes toward the steady-state inelastic current: $\delta I^{st} \approx - (\lambda / \Gamma)^2 \left\{ 2n_{ph}^{st} V + (V - \tilde{\omega}_0) \theta (V - \tilde{\omega}_0) \right\} / 2\pi$. The transient oscillations with period $\approx 2\pi / (V + \tilde{\omega}_0)$, are associated to the maintained phase-coherence during vibron-assisted inelastic tunneling events. When approaching the steady-state, the gradual loss of coherence results in a power-law decay of the oscillation amplitude. We also probe the dependence with the junction transmission $\tau = 4\alpha / (1 + \alpha)^2$, by changing the ratio between the tunneling rates $\alpha = \Gamma_L / \Gamma_R$.

We show in Fig. 3 (top-panel) the excess conductance...
The discriminant $\Delta(t) = P_0^2(t) - 4P_1(t)P_{-1}(t)$ of the short-time approximation to the MGF $Z(z,t) = P_1(t)z + P_0(0) + P_{-1}(t)z^{-1}$, with $z = e^{i\chi}$. The lower panels show the position of the zeros of the MGF for $\alpha = 1$ (upper red row), $\alpha = 0.6$ (middle green row) and $\alpha = 0.2$ (lower blue row), with increasing times from left to right columns. Other parameters are the same as in Fig. 3.

FIG. 4. Top panel: Discriminant $\Delta(t) = P_0^2(t) - 4P_1(t)P_{-1}(t)$ of the short-time approximation to the MGF $Z(z,t) = P_1(t)z + P_0(0) + P_{-1}(t)z^{-1}$, with $z = e^{i\chi}$. The lower panels show the position of the zeros of the MGF for $\alpha = 1$ (upper red row), $\alpha = 0.6$ (middle green row) and $\alpha = 0.2$ (lower blue row), with increasing times from left to right columns. Other parameters are the same as in Fig. 3.

$\delta G(t) = \frac{d}{dt}\delta I(t)$ evaluated at $V \approx \omega_0$ (plain curves). As predicted by bare second-order perturbation theory, $\delta G(t)$ is negative for arbitrary values of $\alpha$ (with fixed $\varepsilon_0 = 0$). The difference between plain (RPA) and dashed (bare second-order) curves measures the impact of the vibron-heating mechanism. We find that the onset of a non-equilibrium vibron population in the junction tends to lower the stationary conductance while amplifying the transient oscillations of $\delta G(t)$. A similar conclusion is drawn in Fig. 3 (lower panel) for the voltage-derivative of the excess current-noise $\delta S'(t) = \frac{d}{dt}\delta S(t)$ at $V \approx \omega_0$. We remark an over-amplification of $\delta S'(t)$ at $\tau = 1$, due to phonon back-action. A quench of the transient oscillations and a change of sign of $\delta S'(t)$ is observed at $\tau = 1/2$ ($\alpha \approx 0.17$), as the dominant scattering channel changes from inelastic tunneling of electrons to elastic tunneling with emission-reabsorption of a vibron. We have checked that Fig. 3 is qualitatively unchanged for the initial condition $n_d(0) = 1$, except for small differences at very short times $t \leq 10/\Gamma$ where the transient dynamics is slowed-down by the suppressed charge-fluctuations of the occupied dot.

Zeros of the MGF. In order to characterize charge fluctuations beyond the first two cumulants, we investigate the analytical properties of the MGF $Z(z,t) = \sum_{n \in \mathbb{Z}} P_n(t)z^n \equiv \prod_j (z - z_j)/(1 - z_j)$ as a function of $z = e^{i\chi}$, extended to the full complex plane. The zeros $z_j$ of the MGF are either real or come in complex-conjugate pairs. For a non-interacting fermionic system, the MGF factorizes to $Z(z,t) = \prod_j (1 + p_j(z - 1))^{<0,51>$ with $p_j \in [0,1]$ being the probability of the binomial tunneling process, so that the zeros $z_j = 1 - 1/p_j$ lie on the negative real axis. Any departure of the zeros from the real axis is thus a direct signature of electron correlations $^{22,52,53}$. Similar studies were reported in the context of dynamical phase transitions, for the real-time evolution of bulk systems $^{54}$ or in relation to full-counting statistics $^{55}$, for which the zeros of the MGF were later determined experimentally. At short-times ($t < 15/\Gamma$), the MGF is dominated by single-electron tunneling events, i.e. $Z(z,t) \approx P_1(t)z + P_0(0) + P_{-1}(t)z^{-1}$, where $P_1(t)$ and $P_{-1}(t)$ are the respective probabilities of forward and backward tunneling. The sign of the discriminant $\Delta(t) = P_0^2(t) - 4P_1(t)P_{-1}(t)$ controls the location of the zeros of $Z(z,t)$ with respect to the real axis. We present in Fig. 4 the computed zeros of the full MGF as a function of time (lower-panel) and the corresponding behavior of the discriminant $\Delta(t)$ (upper-panel), for the same parameters as in Fig. 3. At short times ($t \lesssim 1/\Gamma$), the zeros lie on the negative real axis, for arbitrary $\alpha$, as expected for non-interacting systems $^{50,51}$. After some time ($t > 1/\Gamma$), the electrons have tunneled on the molecule and emitted a vibron. The onset of electron-hole interactions results into a merging of the zeros of the MGF at a critical time $t_c$, and their later splitting off the real axis for $t > t_c$. The time $t_c$ coincides with the change of sign of the discriminant $\Delta(t)$ from positive to negative, thus proving that the splitting of the zeros is due to a departure from the generalized binomial distribution of non-interacting electrons $^{52}$. We interpret this behavior as arising from correlations between single-electron inelastic tunneling events and inelastic back-scattering ones (single-hole transmission). For our available time-window and range of parameters, the phonon back-action mechanism leads to an amplification of the electron-hole correlations, and thus to a shorter $t_c$ compared to the case of bare second-order perturbation theory. At half transmission $\tau \approx 0.5$ ($\alpha \approx 0.2$), the zeros first split, then merge again at time $t \approx 6.2/\Gamma$, and finally stay on the negative real axis. This quench of electron-hole correlations happens as the dominant scattering process changes from vibron-mediated inelastic to elastic tunneling of electrons, thus resulting in a FCS closer to the one of a non-interacting junction.

Conclusion. In this Rapid Communication, we have investigated on the same footing the time-dependent transport properties and vibrational dynamics of a molecular junction. We have shown that the fluctuations of the vibron displacement exhibit damped oscillations toward the steady state similar to the relaxation of a classical harmonic oscillator. The short-time dynamics of current and current-fluctuations exhibit voltage-dependent oscillations, due to both the mean-field reorganization of molecular charges and to the onset of inelastic scattering. This short-time dynamics is mainly due the building-up of vibron-mediated electron-hole correlations, the signature of which is revealed...
as a splitting of the zeros of the MGF off the real axis, at a critical time $t_c$. The phonon back-action mechanism tends to amplify the electron-hole correlations, as well as the transient oscillations of electronic current-fluctuations. We believe that our work provides a first step to investigate the onset of many-body correlations in electronic transport, including the possibility to analyze vibron-mediated dynamical phase transitions, when reaching the stationary regime. Recent progress in the THz spectroscopy of photocurrents in molecular junctions and of photon-assisted shot-noise in graphene, constitute an alternative and promising route to investigate the subtle interplay between electrons and vibron dynamics at ultrashort time scales $\sim 1-10$ ps, along the lines proposed in this paper.

R.A. acknowledges support from Région de la Nouvelle Aquitaine, the Transnational Common Laboratory "QuantumChemPhys: Theoretical Chemistry and Physics at the Quantum Scale", and the Agence Nationale de la Recherche, project CERCa, ANR-18-CE30-0006. R.S.S., A.L.Y. and A.M.R. acknowledge financial support by Spanish MINECO (Grants No. FIS2014-55486-P and FIS2017-84860-R), and the Maria de Maeztu Program (Grant No. MDM-2014-0377).

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This expression is derived by neglecting the energy-dependence of the phonon self-energy in Eq. (12). This approximation at the pole is consistent with the rate-equation, and is valid when the broadening of the phonon spectrum $\gamma_x$ is very weak compared to the phonon frequency $\omega_0$. 


