Intermittent polaron dynamics: Born-Oppenheimer out of equilibrium

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We consider the non-equilibrium dynamics of a molecular level interacting with local phonon modes in the case of a strong polaronic shift which prevents a perturbative treatment of the problem. Instead, we find that in an adiabatic regime when the electronic states react faster than the phonon modes it is possible to provide a fully non-perturbative treatment of the phonon dynamics including random noise and dissipation. The result shows intermittent switching between bistable states of the oscillator with an effective random telegraph noise.

The adiabatic, or Born-Oppenheimer approximation is a key approximation in dealing with a variety of strong-coupling equilibrium problems in solid state, quantum chemistry and numerous other fields. It is based on dividing an interacting system into two coupled subsystems, one of which has a much lower characteristic frequency than the other, such as splitting the description of a molecule into nuclear and electronic degrees of freedom. As a result one argues that the inelastic processes are suppressed by the difference in energy scales and therefore the dynamics of the slower system is Hamiltonian, with an effective potential given by the faster system.

In non-equilibrium situations, such as molecular transistors or molecular junctions, a straightforward application of the Born-Oppenheimer approximation will, however, lead to incorrect or, at least, incomplete physical picture. While in many cases it is reasonable to assume that the mechanical motion of the molecule between the leads is slow compared to the dynamics of electrons hopping on and off the molecular orbitals, the energy of the electronic excitations (induced by the applied bias voltage) may be comparable with the energy scales of molecule’s mechanical motion. As a result, inelastic processes may occur, preventing a Hamiltonian description of molecule’s mechanical motion; instead, the effective molecular dynamics will include noise and damping.

A simple model, which incorporates the essential physics of the problem at hand can be described by the following Hamiltonian:

$$H_M = (\epsilon_0 + \lambda x) d^\dagger d + \frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{m\omega_\alpha^2 x^2}{2}. \quad (1)$$

Eq. (1) represents a mechanical oscillator coupled to the extra charge $d^\dagger d$ on a localized molecular orbital $\epsilon_0$. We consider a case of sufficiently big $\lambda$, so that the phonon deformation energy (or the polaronic shift) $\epsilon_p = \lambda^2/(2m\omega_\alpha^2) \geq \Gamma$, where $\Gamma$ is the resonant level width defined below. The large polaronic shift will prevent us from working perturbatively in $\lambda$. Instead, we will find below that it is possible to work fully non-perturbatively in the classical dynamics of the oscillator in an adiabatic limit where fluctuations about the classic trajectory can be treated perturbatively. This calculation may be viewed as a generalization of the Born-Oppenheimer approximation to this case far from equilibrium.

The coupling of the molecule to the leads is described by the Hamiltonian

$$H_T = \sum_{k,\alpha} \epsilon_{k\alpha} c_{k\alpha}^\dagger c_{k\alpha} + \sum_{k,\alpha} \Delta_{\alpha} \left( d_{k\alpha}^\dagger c_{k\alpha} + c_{k\alpha}^\dagger d_{k\alpha} \right), \quad (2)$$

where operators $c_{k\alpha}$ and $d_{k\alpha}$ describe spinless fermions in the left and right ($\alpha = L, R$) leads as in Fig. 1 and at the molecular orbital respectively. For simplicity the hybridization matrix elements $\Delta_{\alpha}$ between the leads and the molecule are assumed to be independent of the single particle states in the leads (labelled by index $k$ in Eq. (2)). It is convenient to define partial effective hybridization widths of the molecular orbital by $\Gamma_{\alpha} = \pi \nu_{\alpha} \Delta_{\alpha}^2$, where $\nu_{\alpha}$ are densities of states in the leads (the full hybridization width of the molecular orbital is $\Gamma = \Gamma_L + \Gamma_R$). The chemical potentials in the leads ($\mu_L$ and $\mu_R$) are assumed to be biased by an external voltage $eV = \mu_L - \mu_R$. The leads are assumed to be in zero temperature thermostats.

The full Hamiltonian, $H = H_M + H_T$, together with the boundary conditions fixed by the chemical potentials of the leads, provides a full description of the system. Here we are interested in the dynamics of the molecule as well as in the statistical characteristics of the current through the molecule under the strongly non-equilibrium conditions specified below. In particular we find that under the appropriate conditions the current through the system exhibits random telegraph noise. We also explicitly evaluate parameters of the noise in terms of the parameters of the problem stated above.

Before going into the detailed analysis of the problem we note that in the regime of strong electron-phonon coupling, e.g., $\epsilon_p \gg \Gamma$, the molecule is bistable, having metastable states with with either 0 and 1 charge occupancy of the molecular orbital. Indeed, for a negligibly small $\Gamma$, the energy states of the molecule with an empty electronic orbital are $E^0_M = \hbar \omega_0 (n + 1/2)$, $n = 0, 1, \ldots$, while for the occupied orbital the energies are $E^1_M = \epsilon_0 - \epsilon_p + \hbar \omega_0 (n + 1/2)$, e.g., Eq. (1). These two states are separated by an effective potential barrier of height $\sim \epsilon_p$ (for $\epsilon_p \approx \epsilon_0$).

There are two possible mechanisms for the transition of the molecule from one state to another, either the under-barrier tunnelling of the molecule and or the absorption of energy from the electronic subsystem. Transport of
a single electron through the system can be accompanied by the energy transfer to the vibrational degree of freedom of the molecule, i.e., the oscillator, by a value no greater than $V$. Therefore, for sufficiently low voltage $V \ll \omega_0$ the system is in equilibrium and the only available mechanism for its transition is through quantum tunneling.

A problem of this sort has been considered in the literature. It has been shown that the partition function of the system can be mapped onto that of interacting Coulomb gas in 1 dimension. The properties of the latter are well established based on the Renormalization Group (RG) arguments. The transition rate between the two metastable states of the molecule is proportional to the fugacity in the Coulomb gas model. For a symmetric case, $\epsilon_0 = \epsilon_p$, the rate is proportional to $\exp(-\epsilon_p/\omega)$, which is essentially the quasiclassical tunneling exponent. An additional logarithmic renormalization of the exponent comes from the orthogonality of electronic states corresponding to different positioning of the oscillator. It can be obtained from the RG equations. The case of finite, but small bias voltage ($V \ll \omega_0$), has recently been considered in Ref. [2].

In this paper we are primarily interested in the opposite case, $V \geq \omega_0$. This corresponds to a strongly out-of-equilibrium situation as the molecule can now efficiently absorb energy from electrons. If $V$ is small compared to $\epsilon_p$, i.e., the height of the potential barrier separating the two states, the system can depart from a given state only as result of a multi-quantum adsorption. A straightforward perturbation expansion in powers of $\lambda$ clearly can not be applicable in this limit, but the appropriate adiabatic expansion will be found below.

We wish to compute a propagator for the density matrix of the oscillator defined as

$$Z_{osc} = \text{Tr}_{el}[\rho_{el}\mathcal{T}_K S(-\infty, \infty) S(\infty, -\infty)] / \text{Tr} [\rho_{el}].$$

Here $S(-\infty, \infty)$ and $S(\infty, -\infty)$ are scattering operators for the full system, $S(\infty, -\infty) = \exp[-i \int_{-\infty}^{\infty} \mathcal{H} dt]$, $\mathcal{T}_K$ denotes the standard time ordering along the Keldysh contour [3]. The density matrix of the unperturbed electrons is the direct product of the uncoupled density matrices of electron reservoirs in the leads ($\rho_L$ and $\rho_R$) with an empty electron state in the resonant level ($\rho_D = dd^\dagger$), $\rho_{el} = \rho_L \otimes \rho_R \otimes \rho_D$. The trace in Eq. (3) is taken over the electronic degrees of freedom.

The oscillator effective action can be expressed in terms of a functional integral

$$Z_{osc} = \int D\lambda_x D\lambda_q e^{iS_0 + S^*} ,$$

where $S_0$ is a bare action of the oscillator, $S_0 = \int dt[\dot{\lambda}_x \dot{x}_q + m\omega_0^2 x_q]$, and $S^*$ results from the trace over the electrons. One important simplification that will enable us to work nonperturbatively in $x_q$ is that $S^*$ vanishes identically for $x_q = 0$, so that we can perturbatively expand $S^*$ in powers of $x_q$ for a given time-dependent $x_q(t)$. Using the cumulant expansion, the perturbative expansion of $S^*$ to a given order in $x_q$ can be expressed as a sum of connected diagrams, with Keldysh Green’s functions which are $2 \times 2$ matrices in the space of forward and return indices. The vertices are $x_q(t) \times \sigma_z$, where $\sigma_z = \text{diag}(1, -1)$ in Keldysh indices. The Green’s functions solve the Dyson equation $\hat{G}^{-1} = \hat{G}_0^{-1} + \lambda x_q(t) \times 1$.

The solution of this Dyson equation is a difficult problem. To make further progress, we exploit the smallness of the adiabatic parameter $\Omega/V$, where $\Omega$ is a characteristic frequency of the oscillator. For $V \neq 0$ the unperturbed Green’s function for the $d$ electron is oscillatory in time with period $\sim V^{-1}$. Therefore the difference in the time arguments of each $x_q(t)$ in a given term in $S^*$ should not significantly exceed $V^{-1}$; define $t_0$ to be the largest of these time arguments. Let us set $x_q(t) = x_q(t_0) + \dot{x}_q(t_0)(t - t_0) + \ldots$. Then, to compute a given term in $S^*$, we first compute the Green’s functions in the presence of a fixed $x_q(t) = x_q(t_0)$ and then perturbatively expand the Green’s functions in derivatives of $\dot{x}_q(t_0)$. One finds that a term with $n$ derivatives of $\dot{x}_q$ is the suppressed by $(\Omega/V)^n$.

The $x_q$ component of $\dot{x}(t)$ essentially defines deviations of the oscillator’s density matrix from the diagonal matrix. It can be easily checked that in an adiabatic approximation contribution of a bubble containing $n$ $x_q$-vertices scales as $(\lambda x_q/\Gamma)^n V/\Omega$ for $n \geq 1$. Therefore if we wish to integrate over $x_q$ in Eq. (1), we have to perform an integral of a sort $\int dx_q \exp[\{x_q + (V/\Omega)\eta(x_q)]$. In the spirit of the saddle point approximation, the factor $(V/\Omega)$ in front again suppresses higher powers of $x_q$ by powers of $(V/\Omega)$.

Thus, the same parameter $\Omega/V$ controls the higher derivatives of $x_q$ as well as the higher powers of $V$. Later, the validity of this expansion must be verified by a self-consistency check. We will find that in the region of interest, i.e., in case of two wells separated by a high barrier (see Fig. 1) $\Omega \ll \omega_0$ and therefore the expansion is well justified far from equilibrium with $\Omega << V$. Then, to leading order in $\Omega/V$ the effective action in Eq. (1) involves three diagrams: the diagram with a single $x_q$-vertex, the diagram with one $x_q$-vertex and one $\dot{x}_q(t_0)(t - t_0)$-vertex, and the diagram with two $x_q$-vertices. One has to evaluate the contribution of each of these three diagrams with the renormalized adiabatic Green’s function of the $d$ electron, defined by $\hat{G}^{-1} = \hat{G}_0^{-1} + \lambda x_q \times 1$. The off-diagonal components of $\hat{G}$, i.e., $-i(d_f(t)d_i^\dagger(t_0))$ and $-i(d_i(t)d_f^\dagger(t_0))$ can be explicitly expressed in terms of their Fourier transforms, $(1/2\pi i) \int d\omega \exp[-i\omega(t - t_0)]G_{ij}[\omega, x_q(t_0)], i, j = f, r$:}

$$G_{fr}[\omega, x_q] = 2i \frac{\Gamma_L \Theta(\mu_L - \omega) + \Gamma_R \Theta(\mu_R - \omega)}{(\omega - \epsilon_0 - x_q)^2 + \Gamma^2},$$

$$G_{rf}[\omega, x_q] = -2i \frac{\Gamma_L \Theta(\omega - \mu_L) + \Gamma_R \Theta(\omega - \mu_R)}{(\omega - \epsilon_0 - x_q)^2 + \Gamma^2}.$$
as $S_{x-c}^*$ =
\[ \int dt [iF(x_c)x_q + iA(x_c)x_c + (1/2)D(x_c)x_q^2], \]
where
\[ F(x_c) = \frac{\lambda}{2\pi} \int d\omega G_{fr}[\omega, x_c], \]
\[ A(x_c) = \frac{\lambda^2}{2\pi} \int d\omega G_{fr}[\omega, x_c] \frac{\partial}{\partial \omega}G_{rf}[\omega, x_c], \]
\[ D(x_c) = \frac{\lambda^2}{2\pi} \int d\omega G_{fr}[\omega, x_c]G_{rf}[\omega, x_c]. \]

The first term in Eq. (6) is a classical force exerted by electrons onto the oscillator. Therefore the effective potential for the oscillator is $U(x) = m\omega_0^2x^2/2 + \int^x dx' F(x')$. In the bistable regime, $\epsilon_p = (2m\omega_0^2) \geq \Gamma$, $0 < \epsilon_0 < \epsilon_p$, and not too high voltage, $\omega_0 < V < E_p$, $U(x)$ develops two minima separated by a barrier. The minima correspond to the states of the molecule with occupied and empty orbital. Though the approach developed in this paper allows to deal with a pretty arbitrary situation as long as $\Omega \ll V$, here we will concentrate on the study of the interesting bistable case. For mathematical simplicity let us assume that the hybridizations $\Gamma_L$ and $\Gamma_R$ with leads are equal. Then the two minima are located at $x_0 = \epsilon_0/\lambda$ and at $x_1 = (\epsilon_0 - 2\epsilon_p)/\lambda$, with energies $E_0 = -\epsilon_0^2/4\epsilon_p$ and $E_1 = -(\epsilon_0 - 2\epsilon_p)^2/4\epsilon_p$, see Fig. 1, while maximum is at $x = 0$. In the limit $E_p \gg \Gamma$ the wells are parabolic with frequencies of small oscillation equal to $\omega_0$.

FIG. 1: Symbolic representation of system’s energetics: the potential curve of the mechanical degree of freedom versus the electronic energy levels.

The last two terms in $S^*$ in Eq. (6) correspond to dissipation and fluctuation of the oscillator due to electrons. It is convenient to decouple the last term in Eq. (6) by introducing the Gaussian noise field $\xi(t)$ in the functional integral Eq. (11) by means of Hubbard-Stratanovich transformation and integrate out the $x_q$ field. As a result the partition function $Z_{osc}$ can be explicitly related to the distribution function for a classical particle, whose dynamics is governed by a Langevin equation:
\[ Z_{osc} = \int D\xi \int Dx_c \exp \left[ -\int dt \frac{\xi^2(t)}{2D(x_c)} \right] \delta_t \left[ m\dot{x}_c - F(x_c) + A(x_c)\dot{x}_c - \xi(t) \right], \]
where the Gaussian noise $\xi(t)$ is white, i.e., $\langle \xi(t)\xi(t') \rangle = D(x_0)\delta(t - t')$, and $\delta_t$ in Eq. (6) is a functional $\delta$-function. From now on we will drop the unnecessary $c$-subscript.

The damping of the oscillator defined by an effective friction coefficient $\gamma(x) = A(x)/m$, where $A$ is given by Eq. (6), is strongest in the vicinity of the barrier, $\gamma_{barrier} \sim \epsilon_p(\omega_0/T)$. Away from the barrier it decays as $\gamma(x) \sim x^{-4}$ and the system is underdamped everywhere except for a narrow region of width $\Gamma/\lambda$ at the barrier, where it approaches a separatrix and thus its period diverges. Therefore its natural to consider motion of the oscillator as a diffusion in energy space. The rate of change of the mean energy of the oscillator over a period depends on both dissipation and the fluctuation as $\langle dE/dt \rangle = -\langle A(x)x^2 \rangle_T + \langle \xi(t)x \rangle_T$. The friction-dependent term can be expressed in terms of the instantaneous energy of the oscillator as $-1/T \oint dt A(x)x^2$, where integral is taken over a period of motion $T$ of the oscillator. Since the motion of the oscillator during one period is nearly deterministic (for small fluctuation and dissipation), the noise introduced by the $\langle \xi(t)x \rangle_T$ term is also Gaussian. The first moment of this noise is given by $1/(2T) \oint dt A(x)x^2$, while the second moment is $1/T \oint dt A(x)x^2$. The Ito term offsets the damping term so that, due to fluctuations, the system tends to occupy states close to, but not exactly at, the bottom of the potential curve $U$. The Langevin equation for system’s energy can be cast in a form:
\[ \frac{dE}{dt} = -\gamma(E) + \xi_E(t), \]
\[ \langle \xi_E(t)\xi_E(t') \rangle = D(E)\delta(t - t'), \]
with the damping and the diffusion coefficients in the energy space:
\[ \gamma(E) = \frac{2}{T} \int dx \left[ A(x)\dot{x} - \frac{D(x)}{2}\dot{x}^2 \right], \]
\[ D(E) = \frac{2}{T} \int dx D(x)\dot{x}, \]
where $\dot{x} = \sqrt{2(E - U(x))/m}$, the period of motion $T = 2\int dx\sqrt{m/[2(E - U(x))]}$, and the integration runs between the turning points defined by $U(x) = E$.

Eq. (10) describes diffusion of the oscillator’s energy in the nonlinear potential $U$. The Fokker-Planck equation which corresponds to dynamics in Eq. (10) reads:
\[ \frac{\partial P}{\partial t} = \frac{\partial}{\partial E} \left[ \gamma(E)P \right] + \frac{1}{2} \frac{\partial^2}{\partial E^2} \left[ D(E)P \right]. \]
In case of the two-well potential there are three connected regions: two in each well and one above the barrier. Solutions of the Fokker-Plank equation in each region are related through a boundary conditions \( P_0(E = 0) + P_1(E = 0) = P_{\text{above}}(E = 0) \), and \( P_0(E = 0) = P_1(E = 0) \), which state that when the system reaches the separatrix, it is equally likely to be in both wells. In equilibrium, i.e., in the absence of the net flux, the stationary distribution for the oscillator can be found from an equation \( \gamma P_{\text{st}} = -\frac{1}{2} \partial (D P_{\text{st}}) / \partial E \).

The current operator can be defined as \( I = (\dot{N}_L - \dot{N}_R)/2 \), where \( \dot{N}_\alpha = \sum_\alpha \epsilon_{\alpha \alpha} c_\alpha \dot{c}_\alpha \). In the adiabatic limit the current expectation value can be expressed in terms of the stationary distribution of the oscillator as \( \int dE \mathcal{P}_{\text{st}}(E) \langle I(E) \rangle \). Here \( \langle I(E) \rangle = 1/T \int dt \langle I(x) \rangle \), where \( \langle I(x) \rangle \) is the expectation value of the current evaluated for a fixed position \( x \) of the oscillator (brackets stand for averaging over the electronic degrees of freedom only). Evaluation of the above integrals is easy for \( \epsilon_p \gg \text{max}(V, \Gamma) \). Then the oscillator tends to be near the bottom of one of the two potential wells with negligible probability of being near the top of the barriers, leading to

\[
\langle I \rangle = I_1 n_F^\alpha (\epsilon_0) + I_2 [1 - n_F^\alpha (\epsilon_0)],
\]

\[
n_F^\alpha (\epsilon_0) = \frac{1}{1 + \exp[4(\epsilon_0 - \epsilon_p)/V]},
\]

where \( I_1 = \Gamma_2 V/[2\pi(\epsilon_0 - 2\epsilon_p)^2] \) and \( I_2 = \Gamma_2 V/[2\pi \epsilon_0^2] \) are the currents through the molecule for the oscillator positioned at the minima of each well. The coefficient \( n_F^\alpha \) has the same form as the Fermi distribution function with temperature \( V/4 \) and chemical potential \( \epsilon_p \).

In this case, we find that each well has the same effective temperature \( V/4 \), and thus the occupation probability of a given well in Eq. (12) is given by a Boltzmann weight. In general, each well may have a different effective temperature; in that case, the oscillator may be more likely to be found in the higher energy state if the effective temperature of that well is lower.

The current-current correlation function requires evaluating the expectation value, averaged over electronic states, of \( \langle I(E, t_1) I(E, t_2) \rangle \). In the adiabatic limit the connected part of this expectation value can be expressed in terms of the stationary distribution of the oscillator as \( \int dE \mathcal{P}_{\text{st}}(E) \langle I^2(E) \rangle_{\text{con}}, \) where \( I^2(E) = 1/T \int dt \langle I^2(x) \rangle \). This corresponds to the shot noise \( \sim 2e(I) \).

The disconnected part is

\[
\int dE_1 dE_2 P_{\text{tr}}(E_1, t_1; E_2, t_2) \langle I(E_1, t_1) I(E_2, t_2) \rangle, \tag{13}
\]

where \( P_{\text{tr}}(E_1, t_1; E_2, t_2) \) is the 2-point distribution function for the oscillator. This part contains a contribution due to the oscillations in each well, and due to the transitions between the wells. For a sufficiently high barrier \( (E_p \gg V) \), the transitions (jumps) are rare events (note that \( V \) is playing role of temperature in the wells), and therefore the oscillations and the jumps occur on different time scales. The contribution of oscillatory motion is peaked at \( \omega = \omega_0 \), with a width of the order of \( \gamma x_{\text{min}} \).

The mean first passage times are the probabilities for the oscillator to be found in each well, \( P_{\text{st}, i} = \int dE \mathcal{P}_{\text{st}}(E) \). The transition probabilities \( P_{ij} \) between the two wells are exponentially decaying on time-scales \( \tau_i \), where \( \tau_i \) are the mean first passage times for each well. In this two-state approximation the correlation function corresponds to that of a telegraph noise with spectrum

\[
S_{ij}(\omega) = S_0^{\text{eff}}(\omega)/(1 + \omega^2 \tau_i^{-2}),
\]

where \( S_0^{\text{eff}}(\omega) = 4\tau^{-1} - \tau^{-3}(I_1 - I_2)^2, \) and \( \tau^{-1} = \tau_1^{-1} + \tau_2^{-1} \).

The mean first passage time \( \tau_i \) can be evaluated from the Fokker-Plank Eq. (11) based on standard techniques, i.e., by solving an equation adjoint to Eq. (11). One finds

\[
\tau_i^{-1} = \left( \frac{\omega_0}{V} \right)^2 I_i \exp \left( -\frac{4E_i}{V} \right), \tag{14}
\]

where \( E_1 = \epsilon_0^2/4E_p \) and \( E_2 = \langle \epsilon_0 - 2\epsilon_p \rangle^2/4E_p \), e.g., Fig. 1. The telegraph switching is thus highly sensitive to the bias voltage and can be controlled by both the bias voltage and the gate voltage through the variation of the molecular orbital energy \( \langle \epsilon_0 \rangle \) relative to the conduction bands of electrons in the leads.

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