I. INTRODUCTION

The basic building block for molecular electronic devices is a single molecular junction - a molecule attached to two metal electrodes held at different electronic chemical potentials. One of the most distinct features of molecular junctions in comparison to other nanoscale electronic devices is the absence of the structural rigidity and, as a result, the strong interplay between electronic and nuclear dynamics [1, 2]. Electron-vibration interaction leads to a variety of interesting transport phenomena such as negative differential resistance [3–7], Frank-Condon blockade [8, 9], current induced chemical reactions [10–12], cooling of nuclear motion by electric current [3, 13, 14].

Recently, there have been a significant experimental and theoretical interest in studying electron molecular electron transport properties which go beyond average electric current. Investigation of noise, full counting statistics, and fluctuation relations have been recently reported [15–22]. Electrical current fluctuations in molecules is no longer just a theoretical concept, they have become the important experimental method to characterize the physical mechanisms of electron transport in molecular junctions [23–26].

Electron transport through a molecular junction is unavoidably stochastic due to quantum nature of the process. Electrons are transferred from source to drain electrode across the molecular bridge one by one at random but specific times. What are the delay times between these electron tunnelling events and what are the distributions of these times? How does coupling of electronic and nuclear motion manifest itself in this distribution? These are the questions which interest us in this paper. The sequential stochastic processes, in general, and quantum electron transport, in particular, can be naturally understood and characterised in terms of waiting time distribution (WTD) [27]. WTD is a conditional probability distribution that we observe the electron transfer in the detector electrode (it does not matter drain or source electrodes, in the steady state they measure the same statistics) at time $t + \tau$ given that an electron was detected in the same electrode at time $t$. WTD is the complementary and much more intuitive physical quantity in comparison with very popular full counting statistics in quantum transport. WTD has recently gained significant popularity in the study current fluctuations in nanoscale and mesoscale systems [28–38].

The paper is organised as follows. Section II contains the derivation of master equation for electron transport through a molecular junction described by Anderson-Holstein model. In section III, we derive the main equations for WTD and waiting time cumulant-generating function. Section IV describes the results of numerical calculation. Section IV summarises the main results of the paper.

We use natural units in equations throughout the paper: $\hbar = k_B = e = 1$.

II. MASTER EQUATION IN THE POLARONIC REGIME

The molecule is described by spinless Anderson-Holstein model in which a single electronic level is coupled to a localised vibrational mode. Electrons can tunnel between the molecule and source (S) and drain (D) electrodes. The corresponding Hamiltonian is

$$H = H_{\text{molecule}} + H_{\text{electrodes}} + H_T. \quad (1)$$

The molecule is described by the following Hamiltonian:

$$H_{\text{molecule}} = \epsilon_0 a^\dagger a + \lambda (b^\dagger + b) a^\dagger a + \omega b^\dagger b, \quad (2)$$

where $\epsilon_0$ molecular orbital energy, $\omega$ is molecular vibration energy, and $\lambda$ is the strength of the electron-vibration coupling. $a^\dagger(a)$ creates (annihilates) an electron on molecular orbital, and $b^\dagger(b)$ is bosonic creation
(annihilation) operator for the molecular vibration. The electronic spin does not play any physical role in the discussed processes and will not be included explicitly into the equations. Electrodes consist of noninteracting electrons:

\[ H_{\text{electrodes}} = \sum_{k,\alpha=S,D} \epsilon_{k\alpha} a_{k\alpha}^\dagger a_{k\alpha}, \]  

(3)

where \( a_{k\alpha}^\dagger \) creates an electron in the single-particle state \( k \) of the source(drain) electrode \( \alpha = S(D) \) and \( a_{k\alpha} \) is the corresponding electron annihilation operator. The bias voltage applied to the junction is imposed by shifting symmetrically the chemical potentials of the electrodes \( V_{sd} = \mu_S - \mu_D \). The electron tunnelling is described by

\[ H_T = \sum_{k,\alpha=S,D} t_{\alpha}(a_{k\alpha}^\dagger a + h.c), \]  

(4)

where \( t_{\alpha} \) is the tunnelling amplitudes.

To eliminate electron-vibration coupling from \( H_{\text{molecule}} \) we perform Lang-Firsov unitary rotation of molecular operators \[33]\n
\[ a = \tilde{a} e^{\gamma(\tilde{b}^\dagger - \tilde{b})}, \quad b = \tilde{b} + \nu\tilde{a}^\dagger \tilde{a}, \]  

(5)

where \( \tilde{a}^\dagger(\tilde{a}) \) and \( \tilde{b}^\dagger(\tilde{b}) \) are transformed creation (annihilation) operators for molecular electron and vibration. The Lang-Firsov transformation is unitary so that it preserves commutation or anticommutation relations between the operators. The molecular Hamiltonian in the transformed operator basis becomes

\[ H_{\text{molecule}} = \tilde{\epsilon}\tilde{a}^\dagger \tilde{a} + \omega \tilde{b}^\dagger \tilde{b}, \]  

(6)

Here renormalised molecular orbital energy \( \epsilon \) includes polaron shift \( \epsilon = \epsilon_0 - \lambda^2/\omega \). The Hamiltonian for the electrodes is not affected and the tunnelling interaction becomes

\[ H_T = \sum_{k\alpha} t_{\alpha}(e^{-\gamma(\tilde{b}^\dagger - \tilde{b})} a_{k\alpha}^\dagger \tilde{a} + h.c) \]  

(7)

After Lang-Firsov transformation the eigenvectors and eigenenergies of molecular Hamiltonian are easily computed and standard theoretical methods are applied to derive the master equation \[40]\n
\[ \dot{P}_{0q}(t) = \sum_{q'} \Gamma_{1q',0q} P_{1q'}(t) - \Gamma_{0q,1q'} P_{0q}(t), \]  

(8)

\[ \dot{P}_{1q}(t) = \sum_{q'} \Gamma_{0q',1q} P_{0q'}(t) - \Gamma_{1q,0q'} P_{1q}(t), \]  

(9)

where \( P_{nq}(t) \) is the probability that the molecule is occupied by \( n \) electrons and populated by \( q \) vibration at time \( t \). The rates for the transition from state occupied by one electron and \( q \) vibrations to the electronically unoccupied state with \( q' \) vibrations by the electron transfer from the molecule to \( \alpha = S, D \) electrode is \( \Gamma_{0q,1q'} \) and the rate for the transition when electron is transferred from \( \alpha \) electrode into the originally empty molecules simultaneously changing the vibrational state from \( q \) to \( q' \) is \( \Gamma_{1q,0q'} \). The total probability is normalised

\[ \sum_q P_{0q}(t) + P_{1q}(t) = 1. \]  

The transition rates rates are computed using the Fermi-golden rule \[40\]. They are

\[ \Gamma_{1q,0q'} = \gamma_{q,q'}(1 - f_{\alpha}[\epsilon - \omega(q' - q)]). \]  

(10)

and

\[ \Gamma_{0q,1q'} = \gamma_{q,q'} f_{\alpha}[\epsilon - \omega(q' - q)]. \]  

(11)

The rates depends on the the occupation of electrodes given by Fermi-Dirac numbers

\[ f_{\alpha}(E) = \frac{1}{1 + e^{(E - \mu_{\alpha})/T}}, \]  

(12)

where \( T \) is the temperature and \( \mu_{\alpha} \) is the chemical potential of the electrode \( \alpha \). The transition rates are proportional to

\[ \gamma_{q,q'} = 2\pi t_{\alpha}^2 |X_{q,q'}|^2 \rho_{\alpha}, \]  

(13)

where \( \rho_{\alpha} \) is density of states in the electrode \( \alpha \) taken at energy \( \epsilon \) and

\[ X_{q,q'} = \langle q | e^{-\lambda/\omega(b^\dagger b)} | q' \rangle. \]  

(14)

is the Frank-Condon factor.

We introduce vector of probabilities, which is ordered such that the electronic populations enter in pairs for each vibrational sub-bands:

\[ \mathbf{P}(t) = \begin{bmatrix} P_{00}(t) \\ P_{10}(t) \\ P_{01}(t) \\ P_{11}(t) \\ \vdots \\ P_{0N}(t) \\ P_{1N}(t) \end{bmatrix}, \]  

(15)

where \( N \) is the total number of vibrational sub-bands included into the calculations. We also define the identity vector of length \( 2N \):

\[ \mathbf{I} = \begin{bmatrix} 1 \\ 1 \\ 1 \\ 1 \end{bmatrix}. \]  

(16)

The normalisation of probability is given by the scalar product between \( \mathbf{I} \) and \( \mathbf{P}(t) \), which is defined in a standard mathematical way as

\[ (\mathbf{I}, \mathbf{P}(t)) = \sum_{q=0}^{N} P_{0q}(t) + P_{1q}(t) = 1. \]  

(17)
III. QUANTUM JUMPS OPERATORS FOR ELECTRON TUNNELLING AND WAITING TIME DISTRIBUTIONS

Let us re-write the master equation (18) in the matrix form

$$\dot{P}(t) = \mathcal{L}P(t),$$

(18)

where $\mathcal{L}$ is the the total Liouvillian operator, which can be explicitly identified using eqs. (19). We also define 4 different quantum jumps operators $J^S_\pm$, $J^D_\pm$, and $J^D_\pm$ for the transitions involving changes of molecular electronic population. The quantum jump operators are $2N \times 2N$ matrices which are defined through their actions on the probability vector:

$$(J^S_\pm P(t))_{mq} = \delta_{m1} \sum_{q'} \Gamma^S_{0q',q} P_{0q}(t),$$

(19)

$$(J^D_\pm P(t))_{mq} = \delta_{m0} \sum_{q'} \Gamma^D_{1q',0q} P_{1q}(t).$$

(20)

The jump operator $J^S_\pm$ transforms the system from the electronically empty state to the singly occupied state by tunnelling of an electron from the $\alpha$ electrode into the molecule. The jump operator $J^D_\pm$ describes the reverse process: it transforms the molecule from being occupied by one electron to being empty by transferring one electron from the molecule to the $\alpha$ electrode.

After these preliminary definitions and rearrangement of the rate equation, we are ready to derive the expression for WTD for each quantum jump operator. We assume that the system has evolved to the nonequilibrium steady state. That means it is described by the steady state density matrix, which is the null vector of the full Liouvillian

$$\mathcal{L} P = 0.$$ 

(21)

Let us begin to monitor time delays between sequential quantum tunnelling in the nonequilibrium steady state. First, we define WTD as the conditional probability distribution that we observe electron tunnelling $J^S_\pm$ at time $t+\tau$ given that the molecule undergoes the same quantum jump $J^S_\pm$ at earlier time $t$

$$w^S_\pm(\tau) = \langle I, J^S_\pm e^{(\mathcal{L}-J^S_\pm)\tau} J^S_\pm P \rangle.$$ 

(22)

WTD does not depend on the reference time $t$ in the steady state regime. Reading this equation from right to left elucidates its physical meaning. The system is prepared in state described by steady state probability vector $P$, it undergoes quantum jump $J^S_\pm$ at some arbitrary time, then the system evolves without experiencing any of the monitored quantum jumps for time $\tau$ (this dynamics is generated by nonunitary evolution operator $e^{(\mathcal{L}-J^S_\pm)\tau}$) and finally it undergoes the quantum jump $J^S_\pm$. In the end, by computing the scalar product with vector $I$, the resulting probability vector is summed over all electronic and vibrational states in order to give the total probability distribution for this event. Since we propagate the system with $e^{(\mathcal{L}-J^S_\pm)\tau}$, there were no other electron transfer events of the same type $J^S_\pm$ between time $t$ and $t+\tau$.

WTD (22) is not normalised yet. We assume that over all time $0 \leq \tau \leq +\infty$ the probability for a quantum jump to occur is unity. Integrating over the waiting time yields

$$\int_{0}^{\infty} d\tau w^S_\pm(\tau) = \langle I, J^S_\pm (J^S_\pm - \mathcal{L})^{-1} J^S_\pm P \rangle =$$

$$= (I, (J^S_\pm - \mathcal{L})^{-1} J^S_\pm P) = (I, J^S_\pm P).$$

We here take into account (easy to prove from the conservation of the probability) property of the Liouvillian that $(I, \mathcal{L}X) = 0$ for an arbitrary vector $X$. The normalized WTD becomes:

$$w^S_\pm(\tau) = \frac{(I, J^S_\pm e^{(\mathcal{L}-J^S_\pm)\tau} J^S_\pm P)}{(I, J^S_\pm P)}.$$ 

(23)

We have 4 different WTDs associated with each 4 quantum jump operators for electron tunnelling $J^S_\pm$, $J^D_\pm$, and $J^D_\pm$.

To compute higher-order expectation values and analyse the fluctuations, it is convenient to introduce the cumulant-generating function for the WTD as

$$K^a_\pm(x) = \int_{0}^{\infty} d\tau e^{x\tau} w^a_\pm(\tau).$$

(24)

This expression can be further simplified and brought to the form suitable for numerical calculations:

$$K^a_\pm(x) = \frac{(I, J^a_\pm \int_{0}^{\infty} d\tau e^{(\mathcal{L}-J^a_\pm+x)\tau} J^a_\pm P)}{(I, J^a_\pm P)} =$$

$$= -\frac{(I, J^a_\pm (\mathcal{L}-J^a_\pm+x)^{-1} J^a_\pm P)}{(I, J^a_\pm P)}.$$ 

(25)

We obtain all possible higher order cumulants simply by direct differentiation of $K^a_\pm(x)$ with respect to $x$.

IV. RESULTS

We first compute electric current as a function of the applied voltage bias $V_{sd} = \mu_S - \mu_D$. Fig.1 shows the current-voltage characteristics. It has been studied intensively in numerous works before and we show it here simply to serve as a reference - the characteristics steps in the current-voltage characteristic will be shortly connected to the behaviour of WTDs. The steps in the current is related to the resonant excitations of the vibration states by electric current which occur when the voltage passes through an integer multiple of the vibration energy. These steps are smoothed due to the temperature effects.
FIG. 1: Current $I$ as a function of applied voltage $V_{sd}$. Parameters used in calculations (all energy values are given in units of $\omega$): $\gamma_S = \gamma_D = 0.01$, $T = 0.05$, $\epsilon = 0$, $\lambda = 1$. Unit for electric current is $\omega$ (or if we put $\hbar$ and $e$ back, it is $e \omega$) and values of voltage bias $V_{sd}$ are given in $\omega$ (or $\hbar \omega/e$).

WTD between the detections of electrons transferred from the molecule to the drain electrode is shown in Fig. 2. We plot $w_{D}^-(\tau)$ as a function of $\tau$ for different values of the applied voltage. It is computed with the use of the parameter values: $\gamma_S = \gamma_D = 0.01$, $T = 0.05$, $\epsilon = 0$, $\lambda = 1$. Time $\tau$ is measured in $1/\omega$.

FIG. 3: Average waiting time, dispersion and mode time between the detection of an electron tunnelling from the molecule to the drain electrode. Parameters used in calculations (all energy values are given in units of $\omega$): $\gamma_S = \gamma_D = 0.01$, $T = 0.05$, $\epsilon = 0$, $\lambda = 1$. Time $\tau$ is measured in $1/\omega$ and values of voltage bias $V_{sd}$ are given in $\omega$.

The increase of electron-vibration interaction from moderate to strong coupling regime leads to some interesting changes in the waiting time behaviour. Fig. 4 shows the WTD for electron tunnelling from the molecule to the drain electrode $w_{D}^-(\tau)$ computed at $\lambda/\omega = 3$. The values of the probability distribution at the peak events that appears most often in the electron transport - it corresponds to the peak of the distribution, remains more or less constant.
is reduced and the distribution is more shifted towards the larger waiting times, indicating that it takes longer for electron to transverse the molecule when the electron is strongly coupled to the molecular vibration. As seen in Fig. 5 the mode of the distribution shows almost no voltage dependence and the average waiting time demonstrates step-wise decrease similar to the moderate electron-vibration interaction $\lambda/\omega = 1$ case. The main changes in WTD is the dramatic reduction of the dispersion of the waiting time for tunnelling electrons when we move away from the equilibrium by increasing the applied voltage bias.

Fig. 6 shows the WTD $w_D^+(\tau)$. It describes statistics of extreme events when electrons tunnel against the applied voltage bias from the drain electrode into the molecule. In equilibrium, when the voltage is zero, $w_D^+$ is exactly the same as the reverse tunnelling process $w_D^-$ - grand canonical ensemble equilibrium is maintained by balancing in and out particle jumps. As the voltage increases and the molecule departs from the equilibrium, the back-tunnelling events becomes rarer and rarer, the distribution decreased and becomes more and more skewed towards the long waiting time. At the large voltage the back-tunnelling events are completely suppressed and the average waiting time becomes infinitely large for this process.

V. CONCLUSIONS

We have studied WTD for electron transport through a molecular junction. The molecule is modelled by one molecular orbital coupled with a single localised vibration. We treat electron-vibration interaction exactly and the influence of molecular-electrode coupling is considered perturbatively within Born-Markov approximation. The obtained master equation is used to define 4 quantum jump operators associated with different electron tunnelling processes between the molecule and electrodes. We compute WTDs for these jumps operators and study these WTDs for different strengths of electron-vibration interaction and voltages.
We main observations are summarised below:

- The value of waiting time between electron transfer events that appears most often in the electron transport -mode of the WTD - shows little dependence on applied voltage bias and remains approximately the same as in the equilibrium.

- As the nonequilibrium develops (that means the increase of the voltage bias), the average value of the waiting times becomes smaller and moves closer to the mode time of the distribution. That means the skewness of the distribution is decreased with the growth of the electric current. The average waiting time shows stepwise dependence on the applied voltage. These steps are associated with the excitations of vibrational states by tunneling electrons.

- The dispersion of the WTD drops stepwise as a function of the increasing voltage bias. Likewise to the average time, these steps are associated with the excitations of vibrational quanta by electric current. In the strong electron-vibration coupling regime, the abrupt changes of the dispersion dominates the other variations in the WTD behaviour when the system departs away from the equilibrium.

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