# Quantum Charge Transport and Conformational Dynamics of Macromolecules 

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#### Abstract

We study the dynamics of quantum excitations inside macromolecules which can undergo conformational transitions. In the first part of the paper, we use the path integral formalism to rigorously derive a set of coupled equations of motion which simultaneously describe the molecular and quantum transport dynamics, and obey the fluctuation/dissipation relationship. We also introduce an algorithm which yields the most probable molecular and quantum transport pathways in rare, thermally-activated reactions. In the second part of the paper, we apply this formalism to simulate the propagation of a quantum charge during the collapse of a polymer from an initial stretched conformation to a final globular state. We find that the charge dynamics is quenched when the chain reaches a molten globule state. Using random matrix theory we show that this transition is due to an increase of quantum localization driven by dynamical disorder.


## I. INTRODUCTION

Understanding the mechanisms involved in the transport of charged and neutral quantum excitations inside macromolecules is a key step towards realizing nano-scale organic devices with functional (opto-)electronical properties, notably molecular wires and antennas. This perspective has motivated a huge activity devoted to investigating the conductance of inorganic ${ }^{[1+6}$, organic ${ }^{[7]}$ and biological ${ }^{8-11]}$ polymers.

Unlike quantum wires made of solid-state nano ribbons $\sqrt{12 / 15}$, flexible molecular wires in solution can undergo conformational transitions. This feature raises the problem of understanding the implications of the conformational dynamics on the quantum transport properties of the molecule. Recent experimental and theoretical studies have shown that even small thermal fluctuations of the DNA backbone can significantly alter its conductivity 911 . These effects should be greatly amplified in more flexible polymers, which can undergo cooperative transitions and major re-arrangements of the three-dimensional structure.

Investigating the quantum charge transport dynamics during a coil-globule transition of a flexible chain provides an ideal framework to probe the conformation/conductance relationship and assess the role of quenched and dynamical disorder. In particular, studying such a process involves the exploration of the crossover from a regime in which the quantum transport dynamics is effectively one-dimensional to one in which quantum excitations can diffuse in three dimensions. In addition, understanding under which conditions a molecular wire can display different conducting behavior in the swollen and collapsed phases may lead to designing nano-scale molecular switches, which can be activated by means of chemicallyor thermally- induced unfolding.

From a theoretical and microscopic standpoint, the study of quantum transport in molecular systems requires a formalism in which the electronic excitations are explicitly taken into account and the atomic nuclei are coupled to a solvent. In the existing approaches ${ }^{9016-18}$, the equations of motion which describe the time-evolution of the charge density and atomic coordinates are postulated phenomenologically. For example, in Ref. ${ }^{[1]}$ the DNA conductivity was computed by assuming that the atomic nuclei obey Newton's equation with a clas-
sical inter-atomic force field. In addition, charged groups in the DNA backbone and counter ions in the solvent were coupled electrostatically with the quantum charge. Such an approach neglects all non-Coulombic interactions between quantum and classical degrees of freedom. For example, the molecule may lower the total energy by assuming configurations in which the ionization energy of the quantum charges is increased. This interaction has in principle implications on the molecular dynamics.

In view of these considerations, it would be valuable if the equations describing the dynamics of electronic excitations and nuclear coordinates were rigorously derived starting from the general theoretical framework of open quantum systems ${ }^{19}$. On the one hand, this would guarantee that all the correlations between the quantum and classical degrees of freedom are consistently taken into account. On the other hand, it would ensure the fluctuation-dissipation relationship is respected, hence that the correct thermodynamics is recovered in the long-time limit.

In the first part of this paper, we use the Feynman-Vernon path integral formalism to provide such a derivation and develop a rigorous microscopic theory for the dynamics of quantum excitations in molecular systems in solution. The same path integral formalism is also used to derive an algorithm which efficiently yields the most probable molecular and quantum transport pathways in rare thermally-activated reactions.

In the second part of this paper, we use our quantum and stochastic equations of motion to investigate the propagation of a quantum charge inside a homo-polymer undergoing a coil-globule transition. We find that the charge dynamics is strongly suppressed due to a quantum localization driven by the dynamical disorder. Interestingly, this effect sets in only when the polymer reaches a compact conformation.

The paper is organized as follows. In section $\Pi$ we define define the quantum Hamiltonian for system. In section, III] we construct the path integral representation of the timedependent probability to simultaneously observe the molecule at a given conformation and the charge at a given molecular site. This path integral is then analyzed in section IV, in saddle-point approximation, and in section $\nabla$ we derive the set of equations of motion for the system and an algorithm
to predict the most probable pathways in thermally activated transitions. Section VI is devoted to the study of the collapse of the chain. Results, conclusions and outlooks are summarized in section VII

## II. A MICROSCOPIC MODEL FOR QUANTUM TRANSPORT IN MACROMOLECULES

Quantum transport processes in dynamical molecular systems depend on the time-dependent structure of the electronic ground-state and excited states. Clearly, an approach in which these wave-functions and the nuclear coordinates are selfconsistently calculated ab-initio would be extremely computationally expensive.

A commonly efficient strategy to reduce this computational complexity consists in coarse-graining of the electronic problem into an effective configuration-dependent tight-binding Hamiltonian. In particular, in the so-called Fragment Orbital approach ${ }^{\frac{16}{16}}$, one first identifies a set of molecular sites (so-called fragments) where the charge (i.e. a hole) can be found. For example, in DNA these sites can be identified with with individual Watson-Crick bases or with base-pairs. Then, the highest occupied molecular orbitals for each fragment herby denoted with $\phi_{i}\left(i=1, \ldots N_{s}\right)$ - are computed in density functional theory and Born-Oppenheimer approximation, neglecting the effect of the rest of the molecule.

The hopping of the charge between different molecular fragments is controlled by the standard tight-binding Hamiltonian:

$$
\begin{equation*}
\hat{H}_{M C}=\sum_{l, m=1}^{N_{s}} f_{l m} \hat{a}_{l}^{\dagger} \hat{a}_{m} \tag{1}
\end{equation*}
$$

where $f_{l m} \equiv T_{l m}-e_{l} \delta_{l m}$. The parameters $T_{l m}$ and $e_{l}$ are obtained from the fragment orbitals $\left|\phi_{l}\right\rangle$ and $\left|\phi_{m}\right\rangle$ :

$$
\begin{align*}
T_{l m} & \equiv\left\langle\phi_{l}\right| \hat{H}_{K S}\left|\phi_{m}\right\rangle  \tag{2}\\
e_{l} & \equiv\left\langle\phi_{l}\right| \hat{H}_{K S}\left|\phi_{l}\right\rangle \tag{3}
\end{align*}
$$

where $\hat{H}_{K S}$ is the Kohn-Shawn Hamiltonian. The hopping parameters $T_{l m}$ and the on-site energies $e_{l}$ can be taken to be real-valued.

In addition, if the molecule is connected to electrodes, the Hamiltonian $\hat{H}_{M C}$ must include also the coupling with the donor and the acceptor:

$$
\begin{align*}
\hat{H}_{M C} \rightarrow & \hat{H}_{M C}+\left(T_{D 1} \hat{a}_{1}^{\dagger} \hat{a}_{D}+\text { h.c. }\right)+\left(T_{N_{s} A} \hat{a}_{A}^{\dagger} a_{N_{s}}+\text { h.c }\right) \\
& -e_{D} \hat{a}_{D}^{\dagger} \hat{a}_{D}-e_{A} \hat{a}_{A}^{\dagger} \hat{a}_{A} \tag{4}
\end{align*}
$$

In the Born-Oppenheimer approximation, the fragment orbitals in Eq.s (2) and (3) depend parametrically on the coordinates of the atomic nuclei, which evolve in time under the effect of the inter-atomic forces, and of the interactions with quantum charge and with the solvent.

A consistent way to describe this dynamics is to consider the fully quantum Hamiltonian:

$$
\begin{equation*}
\hat{H}=\hat{H}_{M C}+\hat{H}_{M}+\hat{H}_{B}+\hat{H}_{M B} \tag{5}
\end{equation*}
$$

In this equation, $\hat{H}_{M C}$ is the tight-binding Hamiltonian defined in Eq. 1], while the Hamiltonian $\hat{H}_{M}$ controls the conformational dynamics of the molecule in the absence of quantum excitations,

$$
\begin{equation*}
\hat{H}_{M} \equiv \sum_{\alpha=1}^{N_{p}} \frac{\hat{p}_{\alpha}^{2}}{2 M}+\hat{V}(Q) \tag{6}
\end{equation*}
$$

where $Q=\left(q_{1}, \ldots, q_{N_{p}}\right)$ is the set of all $N_{p}$ atomic coordinates and $V(Q)$ is the molecular potential energy which includes the interaction between the different atoms and possibly a term to account for the electrostatic and hydro-phobic/philic interaction with the solvent.

The part of the Hamiltonian $\hat{H}_{B}+\hat{H}_{M B}$ describes the coupling of the molecule with a thermal heat-bath, modeled with an infinite set of harmonic-oscillators:

$$
\begin{align*}
\hat{H}_{B} & =\sum_{\alpha=1}^{N_{p}} \sum_{j=1}^{\infty}\left(\frac{\hat{\pi}_{j}^{2}}{2 \mu_{j}}+\frac{1}{2} \mu_{j} \omega_{j}^{2} \hat{x}_{j}^{2}\right)  \tag{7}\\
\hat{H}_{M B} & =\sum_{\alpha=1}^{N_{p}} \sum_{j=1}^{\infty}\left(-c_{j} \hat{x}_{j} \hat{q}_{\alpha}+\frac{c_{j}^{2}}{2 \mu_{j} \omega_{j}^{2}} \hat{q}_{\alpha}^{2}\right) \tag{8}
\end{align*}
$$

$X=\left(x_{1}, x_{2}, \ldots\right)$ and $\Pi=\left(\pi_{1}, \pi_{2}, \ldots\right)$ are the harmonic oscillator coordinates and momenta, $\mu_{j}$ and $\omega_{j}$ denote their masses and frequencies and $c_{j}$ are the couplings between atomic and heat-bath variables. The last term in Eq. (8) is a standard counter-term introduced to compensate the renormalization of the molecular potential energy which occurs when the heatbath variables are traced out (see e.g. discussion in Ref. ${ }^{[25}$ ).

The Hamiltonian (5) describes a close system at the fully quantum level. In the next sections, we shall use the path integral formalism to trace out the heat-bath variables and take the classical limit for the nuclear degrees of freedom.

## III. PATH INTEGRAL REPRESENTATION OF THE QUANTUM-DIFFUSIVE DYNAMICS OF THE SYSTEM

In this section we derive a the path integral representation of the time-evolution of the system described by the Hamiltonian (5).

Let us assume that the molecule is prepared in some configuration $Q_{0}$ and that a hole is initially created at some monomer site $k_{0}$. We are interested in computing the conditional probability $P_{t}\left(k_{f}, Q_{f} \mid k_{0}, Q_{0}\right)$ that after a time interval $t$ the molecule is found in conformation $Q_{f}$ and the charge at the site $k_{f}$. Such a probability is described by the following time-dependent reduced quantum density matrix:

$$
\begin{align*}
P_{t}\left(k_{f}, Q_{f}, \mid k_{0}, Q_{0}\right) & =\frac{\operatorname{Tr}\left[\left|k_{f}, Q_{f}\right\rangle\left\langle k_{f} Q_{f}\right| \hat{\rho}(t)\right]}{\operatorname{Tr} \hat{\rho}(t)} \\
& =\frac{\operatorname{Tr}\left[\left|k_{f}, Q_{f}\right\rangle\left\langle Q_{f}, k_{f}\right| e^{-\frac{i}{\hbar} \hat{H} t} \hat{\rho}(0) e^{\frac{i}{\hbar} \hat{H} t}\right]}{\operatorname{Tr} \hat{\rho}(0)} \tag{9}
\end{align*}
$$

where $\hat{\rho}(0)=\left|Q_{0} k_{0}\right\rangle\left\langle Q_{0} k_{0}\right| e^{-\frac{1}{K_{B} T} \hat{H}_{B}}$ is the initial density matrix, which assumes factorization with a thermal distribution for the heat-bath variables.

The goal of this section is to represent the conditional probability (9) as a path integral. This can be done relying on the so-called Feynman-Vernon formalism for open quantum systems, which has been extensively applied to study quantum brownian motion ${ }^{25]}$.

The path integral representation of the density matrix can be constructed in a way which is conceptually similar to that used to represent the standard Feynman propagator. The main difference is that it requires to perform the Trotter decomposition of two real-time evolution operators (forward and backwards in time) and an one imaginary time evolution (initial thermal distribution of the heat-bath variables).

It is convenient to adopt a field-theoretic language to represent the dynamics of the quantum charge, while using the position representation to describe the evolution of the atoms in the molecule and of the harmonic oscillators in the heat-bath. In practice, this corresponds to introducing the following resolution of the identity at each slide in the Trotter decomposition of the real- and imaginary- time evolution operators entering Eq. (9):

$$
\begin{equation*}
1=\int d Q \int d X \int\left(\prod_{k=1}^{N_{s}} \frac{d \phi_{k} d \phi_{k}^{*}}{2 \pi i}\right) e^{-\sum_{l=1}^{N_{s}} \phi_{l} \phi_{l}^{*}}|Q, X, \Phi\rangle \tag{10}
\end{equation*}
$$

where $\Phi=\left(\phi_{1}, \ldots \phi_{N_{s}}\right)$ are the eigenvalues of the bosonic coherent states constructed from creation and annihilation operators in Eq. (1).

An advantage of adopting a field-theoretic representation for the quantum charge dynamics is that the statistical weight of the coherent field configurations in the path integral can be written as the exponent of an action, i.e. $\int \mathcal{D} \phi \mathcal{D} \phi^{*} e^{\frac{i}{\hbar} S\left[\phi^{*}, \phi\right]}$. This property is very useful to develop the saddle-point approximation, and is not satisfied if the dynamics of a tightbinding Hamiltonian is represented using the discrete position eigenstates.

The conditional probability $\sqrt{97}$ in path integral form reads:

$$
\begin{align*}
& P_{t}\left(k_{f}, Q_{f} \mid k_{0}, Q_{0}\right)=\int d \bar{X} \int d X_{1} \int d X_{2} \int_{X_{1}}^{X_{2}} \mathcal{D} \tilde{X} e^{-S_{E}[\tilde{X}]} \\
& \int_{X_{1}}^{\bar{X}} \mathcal{D} X^{\prime} \int_{X_{2}}^{\bar{X}} \mathcal{D} X^{\prime \prime} \int_{Q_{0}}^{Q_{f}} \mathcal{D} Q^{\prime} \int \mathcal{D} \phi^{\prime} \mathcal{D} \phi^{\prime *} \phi_{k_{f}^{\prime}}^{\prime}(t) \phi_{k_{0}}^{\prime *}(0) \\
& e^{-\sum_{m} \phi_{m}^{\prime *}(0) \phi_{m}^{\prime}(0)} e^{\frac{i}{\hbar}\left(S_{M C}\left[Q^{\prime}, \phi^{\prime}, \phi^{\prime *}\right]+S_{M B}\left[Q^{\prime}, X^{\prime}\right]\right)} \\
& \int_{Q_{0}}^{Q_{f}} \mathcal{D} Q^{\prime \prime} \int \mathcal{D} \phi^{\prime \prime} \mathcal{D} \phi^{\prime \prime *} \phi_{k_{f}^{\prime \prime} *}(t) \phi_{k_{0}}^{\prime \prime}(0) \\
& e^{-\sum_{m} \phi_{m}^{\prime \prime *}(t) \phi_{m}^{\prime \prime}(t)} e^{-\frac{i}{\hbar}\left(S_{M C}\left[Q^{\prime \prime}, \phi^{\prime \prime}, \phi^{\prime \prime *}\right]+S_{M B}\left[Q^{\prime \prime}, X^{\prime \prime}\right]\right)} \tag{11}
\end{align*}
$$

In this equation $\phi_{l}^{\prime}(t), \phi_{l}^{\prime \prime}(t)$ are the complex bosonic fields associated to the charge coherent states propagating forward and backwards in time respectively and the action functionals ap-
pearing at the exponents read

$$
\begin{align*}
S_{M C}\left[Q, \phi, \phi^{*}\right] & =\int_{0}^{t} d t^{\prime}\left[\frac{M \dot{Q}\left(t^{\prime}\right)^{2}}{2}-V\left[Q\left(t^{\prime}\right)\right]\right. \\
& +\sum_{l, m} \phi_{l}^{*}\left(t^{\prime}\right)\left(i \hbar \frac{\partial}{\partial t^{\prime}} \delta_{l m}-f_{l m}\left[Q\left(t^{\prime}\right)\right]\right) \phi_{m}\left(t^{\prime}\right) . \\
S_{M B}[X, Q] & =\int_{0}^{t} d t^{\prime} \sum_{j}\left(\frac{\mu_{j} \dot{x}_{j}\left(t^{\prime}\right)^{2}}{2}-\frac{1}{2} \mu_{j} \omega_{j}^{2} x_{j}\left(t^{\prime}\right)^{2}\right)  \tag{12}\\
& \left.+\sum_{\alpha} \sum_{j}\left(c_{j} x_{j}\left(t^{\prime}\right) q_{\alpha}\left(t^{\prime}\right)-\frac{c_{j}^{2}}{2 \mu_{j} \omega_{j}^{2}} q_{\alpha}\left(t^{\prime}\right)^{2}\right]\right),  \tag{13}\\
S_{E}[X] & =\int_{0}^{\beta} d \tau\left[\sum_{j}\left(\frac{\mu_{j} \dot{x}_{j}(\tau)^{2}}{2}+\frac{1}{2} \mu_{j} \omega_{j}^{2} x_{j}^{2}(\tau)\right)\right] . \tag{14}
\end{align*}
$$

The path integrals over the harmonic oscillator variables are Gaussian and can be carried out analytically. One obtains

$$
\begin{align*}
& P_{t}\left(k_{f}, Q_{f} \mid k_{0}, Q_{0}\right)=\int_{Q_{0}}^{Q_{f}} \mathcal{D} Q^{\prime} \int \mathcal{D} \phi^{\prime} \mathcal{D} \phi^{\prime *} \phi_{k_{f}}^{\prime}(t) \phi_{k_{0}}^{\prime *}(0) \\
& e^{-\sum_{m} \phi_{m}^{\prime *}(0) \phi_{m}^{\prime}(0)+\frac{i}{\hbar} S\left[Q^{\prime}, \phi^{\prime}, \phi^{\prime *}\right]} \int_{Q_{0}}^{Q_{f}} \mathcal{D} Q^{\prime \prime} \int \mathcal{D} \phi^{\prime \prime} \mathcal{D} \phi^{\prime \prime *} \\
& \cdot \phi_{k_{f}^{\prime \prime *}}^{\prime \prime}(0) \phi_{k_{0}}^{\prime \prime}(t) \cdot e^{-\sum_{m} \phi_{m}^{\prime \prime *}(t) \phi_{m}^{\prime \prime}(t)-\frac{i}{\hbar} S_{M C}\left[Q^{\prime \prime}, \phi^{\prime \prime}, \phi^{\prime \prime *}\right]} e^{-\Phi_{F V}\left[Q^{\prime}, Q^{\prime \prime}\right]} \tag{15}
\end{align*}
$$

$\Phi_{F V}\left[Q^{\prime}, Q\right]$ is the so-called Feynman-Vernon influence functional ${ }^{25}$, which describes the fluctuation and dissipation induced by the coupling with the heat-bath and reads:

$$
\begin{align*}
& \Phi_{F V}\left[Q^{\prime}, Q^{\prime \prime}\right]=\frac{1}{\hbar} \int_{0}^{t} d t^{\prime} \int_{0}^{t^{\prime}} d t^{\prime \prime}\left[Q^{\prime}\left(t^{\prime}\right)-Q^{\prime \prime}\left(t^{\prime}\right)\right] \\
& {\left[L\left(t^{\prime}-t^{\prime \prime}\right) Q^{\prime}\left(t^{\prime \prime}\right)-L^{*}\left(t^{\prime}-t^{\prime \prime}\right) Q^{\prime \prime}\left(t^{\prime \prime}\right)\right]} \\
& +i \frac{\bar{\mu}}{2 \hbar} \int_{0}^{t} d t^{\prime}\left[Q^{\prime 2}\left(t^{\prime}\right)-Q^{\prime \prime 2}\left(t^{\prime}\right)\right], \quad\left(\bar{\mu}=\sum_{j} \frac{c_{j}^{2}}{m_{j} \omega_{j}^{2}}\right) . \tag{16}
\end{align*}
$$

$L(t)$ is a two-point correlation function which encodes the physics of the coupling of the molecular coordinates with the heat-bath and reads:

$$
\begin{equation*}
L(t)=\sum_{j} \frac{c_{j}^{2}}{\mu_{j} \omega_{j}}\left[\operatorname{coth}\left(\frac{\omega_{k} \hbar}{2 k_{B} T}\right) \cos \left(\omega_{j} t\right)-i \sin \left(\omega_{j} t\right)\right] . \tag{17}
\end{equation*}
$$

Note that the strength of the fluctuation and dissipation induced by the solvent and the time scales at which memory effects die out can be tuned by changing the parameters in the harmonic bath Hamiltonian (8). In particular, here we consider the so-called ohmic bath limit ( see e.g. Ref. ${ }^{[25}$ ), in which the $L(t)$ reduces to

$$
\begin{equation*}
L(t) \rightarrow L^{o h m}(t)=\frac{2 k_{B} T M \gamma}{\hbar} \delta(t)+\frac{i M \gamma}{2} \frac{d}{d t} \delta(t) \tag{18}
\end{equation*}
$$

and $\gamma$ is interpreted as the friction coefficient. In section $V$ we shall show that this choice leads to the natural generalization of the classical over-damped Langevin dynamics.

## IV. SADDLE-POINT APPROXIMATION OF THE PATH INTEGRAL

The path integral (15) provides an exact representation of the conditional probability given in Eq. (9) and cannot be solved without relying on some approximation. To this end, we observe that for any time $t$ there exists an obvious sum rule:

$$
\begin{equation*}
\sum_{k_{f}} \int d Q_{f} P_{t}\left(k_{f}, Q_{f} \mid k_{0}, Q_{0}\right)=1 \tag{19}
\end{equation*}
$$

The idea is then to use the path integral representation (15) to implement this condition, and analyze it in saddle-point approximation.

We begin by changing variables for the molecular coordinates:

$$
\begin{equation*}
y(t) \equiv Q^{\prime}(t)-Q^{\prime \prime}(t) \quad r(t)=\frac{1}{2}\left(Q^{\prime}(t)+Q^{\prime \prime}(t)\right) \tag{20}
\end{equation*}
$$

Next, we use the path integral 15 to re-write the sum-rule (19) as

$$
\begin{align*}
& 1=\sum_{k_{f}} \int_{Q_{0}} \mathcal{D} r \int_{0}^{0} d y \int \mathcal{D} \phi^{\prime} \mathcal{D} \phi^{\prime *} \phi_{k}^{\prime}(t) \phi_{k_{0}}^{\prime *}(0) \\
& e^{-\sum_{m} \phi_{m}^{\prime *}(0) \phi_{m}^{\prime}(0)+\frac{i}{\hbar} S_{M C}\left[r+y / 2, \phi^{\prime}, \phi^{\prime *}\right]} \int \mathcal{D} \phi^{\prime \prime} \mathcal{D} \phi^{\prime \prime *} \\
& \cdot \phi_{k_{f}^{\prime \prime}}^{\prime \prime *}(0) \phi_{k_{0}}^{\prime \prime}(t) \cdot e^{-\sum_{m} \phi_{m}^{\prime \prime *}(t) \phi_{m}^{\prime \prime}(t)-\frac{i}{\hbar} S_{M C}\left[r-y / 2, \phi^{\prime \prime}, \phi^{\prime \prime *}\right]} e^{-\Phi_{F V}^{\prime}[r, y]} \tag{21}
\end{align*}
$$

where the new expression for the Feynman-Vernon functional reads

$$
\begin{equation*}
\Phi_{F V}^{\prime}[r, y]=\int_{0}^{t} d t^{\prime}\left(\frac{M \gamma K_{B} T}{\hbar^{2}} y^{2}\left(t^{\prime}\right)+\frac{i M \gamma}{\hbar} \dot{r} \cdot y\right) . \tag{22}
\end{equation*}
$$

We now introduce a set of tensor fields $\rho_{l m}^{\prime}(t), \rho_{l m}^{\prime \prime}(t), \sigma_{l m}^{\prime}(t)$ and $\sigma_{l m}^{\prime \prime}(t)$ into the path integral by means the functional identities

$$
\begin{align*}
& 1=\int \mathcal{D} \sigma^{\prime} \mathcal{D} \rho^{\prime} e^{\frac{i}{\hbar} \sum_{l, m} \delta_{0}^{t} d t^{\prime} \sigma_{l m}^{\prime}\left(\rho_{l m}^{\prime}-\phi_{l}^{\prime} \phi_{m}^{\prime}\right)}, \\
& 1=\int \mathcal{D} \sigma^{\prime \prime} \mathcal{D} \rho^{\prime \prime} e^{-\frac{i}{\hbar} \sum_{l, m} \int_{0}^{t} d t^{\prime} \sigma_{l m}^{\prime \prime}\left(\rho_{l m}^{\prime \prime}-\phi_{l}^{\phi^{\prime \prime}} \phi_{m}^{\prime \prime}\right)} \tag{23}
\end{align*}
$$

The new expression for the sum-rule $\sqrt{19}$ is then

$$
\begin{aligned}
& 1=\int \mathcal{D} \rho^{\prime} \mathcal{D} \rho^{\prime \prime} \mathcal{D} \sigma^{\prime} \mathcal{D} \sigma^{\prime} e^{\frac{i}{\hbar} \int_{0}^{t} d t^{\prime} \sum_{l, m}\left(\sigma_{l m}^{\prime} \rho_{l m}^{\prime}-\sigma_{l m}^{\prime} \rho_{l m}^{\prime \prime}\right)} \\
& \int_{Q_{0}} \mathcal{D} r \int \mathcal{D} y e^{\frac{i}{\hbar} \mathcal{W}\left[r, y, \rho^{\prime}, \rho^{\prime \prime}\right]} e^{-\Phi_{F V}^{\prime}[r, y]}\left(\sum_{k_{f}} Q_{k_{f}}\left[\sigma^{\prime}\right] \mathcal{M}_{k_{f}}\left[\sigma^{\prime \prime}\right]\right)(24)
\end{aligned}
$$

where the functionals $Q_{k_{f}}$ and $M_{k_{f}}$ read

$$
\begin{align*}
Q_{k_{f}}\left[\sigma^{\prime}\right]= & \int \mathcal{D} \phi^{\prime} \mathcal{D} \phi^{\prime *} \phi_{k_{f}}^{\prime}(t) \phi_{k_{0}}^{\prime *}(0) e^{-\sum_{m} \phi_{m}^{\prime *}(0) \phi_{m}^{\prime}(0)} \\
& e^{\frac{i}{\hbar} S_{M F}\left[\phi^{\prime}, \phi^{\prime *}, \sigma^{\prime}\right]},  \tag{25}\\
\mathcal{M}_{k_{f}}\left[\sigma^{\prime \prime}\right]= & \int \mathcal{D} \phi^{\prime \prime} \mathcal{D} \phi^{\prime \prime *} \phi_{k_{f}}^{\prime \prime *}(0) \phi_{k_{0}}^{\prime \prime}(t) e^{-\sum_{m} \phi_{m}^{\prime \prime *}(t) \phi_{m}^{\prime \prime}(t)} \\
& e^{-\frac{i}{\hbar} S_{M F}\left[\phi^{\prime \prime}, \phi^{\prime \prime *}, \sigma^{\prime \prime}\right]} \tag{26}
\end{align*}
$$

while the functional $\mathcal{W}$ and $S_{C M}$ are defined as

$$
\begin{aligned}
\mathcal{W}\left[x, y, \rho^{\prime}, \rho^{\prime \prime}\right] & =\int_{0}^{t} d t^{\prime}\left\{M \dot{r} \dot{y}-V\left(r+\frac{y}{2}\right)+V\left(r-\frac{y}{2}\right)\right. \\
& \left.-\sum_{l, m}\left[f_{l m}\left(r+\frac{y}{2}\right) \rho_{l m}^{\prime}-f_{l m}\left(r-\frac{y}{2}\right) \rho_{l m}^{\prime \prime}\right]\right\}
\end{aligned}
$$

$$
\begin{equation*}
S_{M F}\left[\phi, \phi^{*}, \sigma\right]=\sum_{l, m} \int_{0}^{t} d t^{\prime} \phi_{l}^{*}\left(t^{\prime}\right)\left[i \hbar \frac{\partial}{\partial t^{\prime}} \delta_{l m}-\sigma_{l m}\left(t^{\prime}\right)\right] \phi_{m}\left(t^{\prime}\right) \tag{27}
\end{equation*}
$$

The path integral 24 is still and exact representation of the sum-rule. The saddle-point approximation is implemented by imposing the stationarity of the exponents with respect to the tensor fields $\sigma_{l m}^{\prime}, \sigma_{l m}^{\prime \prime}, \rho_{l m}^{\prime}$ and $\rho_{l m}^{\prime \prime}$ and with respect to the molecular paths $y$ and $r$. In particular:

- Imposing the stationarity with respect to the $r$ path leads to the equation

$$
\begin{align*}
M \ddot{y}= & 2 M \gamma \dot{y}-2 \frac{\partial}{\partial r}\left[V\left(r+\frac{y}{2}\right)-V\left(r-\frac{y}{2}\right)\right] \\
& -\sum_{l, m} \frac{\partial}{\partial r}\left[f_{l m}\left(r+\frac{y}{2}\right) \rho_{l m}^{\prime}-f_{l m}\left(r-\frac{y}{2}\right) \rho_{l m}^{\prime \prime}\right] . \tag{29}
\end{align*}
$$

- Imposing the stationarity with respect to the density tensor fields $\rho_{l m}^{\prime}$ and $\rho_{l m}^{\prime \prime}$ leads to the equations

$$
\begin{align*}
\sigma_{l m}^{\prime} & =f_{l m}\left[r+\frac{y}{2}\right]  \tag{30}\\
\sigma_{l m}^{\prime \prime} & =f_{l m}\left[r-\frac{y}{2}\right] \tag{31}
\end{align*}
$$

- Imposing the stationarity with respect to the conjugate fields $\sigma_{l m}^{\prime}\left(t^{\prime}\right)$ and $\sigma_{l m}^{\prime \prime}\left(t^{\prime}\right)$ leads to the equations

$$
\begin{aligned}
& \rho_{l m}^{\prime}\left(t^{\prime}\right)=\frac{1}{\sum_{k^{\prime}} M_{k^{\prime}}\left[\sigma^{\prime \prime}\right] Q_{k^{\prime}}\left[\sigma^{\prime}\right]} \sum_{k_{f}} M_{k_{f}}\left[\sigma^{\prime \prime}\right] \int \mathcal{D} \phi^{\prime} \mathcal{D} \phi^{\prime *} \\
& \phi_{k_{f}}^{\prime}(t) \phi_{l}^{*^{\prime}}\left(t^{\prime}\right) \phi_{m}^{\prime}\left(t^{\prime}\right) \phi_{k_{0}}^{\prime *}(0) e^{\frac{i}{\hbar} S_{C M}\left[\phi^{\prime}, \phi^{\prime *}, \sigma^{\prime}\right]}
\end{aligned}
$$

$$
\begin{equation*}
\rho_{l m}^{\prime \prime}\left(t^{\prime}\right)=\frac{1}{\sum_{k^{\prime}} M_{k^{\prime}}\left[\boldsymbol{\sigma}^{\prime \prime}\right] Q_{k^{\prime}}\left[\boldsymbol{\sigma}^{\prime}\right]} \sum_{k_{f}} Q_{k_{f}}\left[\boldsymbol{\sigma}^{\prime}\right] \int \mathcal{D} \phi^{\prime \prime} \mathcal{D} \phi^{\prime \prime *} \tag{32}
\end{equation*}
$$

$$
\begin{equation*}
\phi_{k_{f}}^{\prime \prime *}(t) \phi_{l}^{*^{\prime \prime}}\left(t^{\prime}\right) \phi_{m}^{\prime \prime}\left(t^{\prime}\right) \phi_{k_{0}}^{\prime \prime}(0) e^{-\frac{i}{\hbar} S_{C M}\left[\phi^{\prime \prime}, \phi^{\prime \prime *}, \sigma^{\prime \prime}\right]} \tag{33}
\end{equation*}
$$

The set of saddle-point equations of motion $\sqrt{297}-\sqrt{32}$ are simultaneously satisfied if, for any $t^{\prime} \in[0, t]$ one imposes

$$
\begin{align*}
y\left(t^{\prime}\right) & =0  \tag{34}\\
\sigma_{l m}^{\prime}\left(t^{\prime}\right) & =\sigma_{l m}^{\prime \prime}\left(t^{\prime}\right)=f_{l m}\left[r\left(t^{\prime}\right)\right],  \tag{35}\\
\rho_{l m}^{\prime}\left(t^{\prime}\right) & =\rho_{l m}^{\prime \prime}\left(t^{\prime}\right) \equiv \rho_{l m}\left(t^{\prime}\right) \tag{36}
\end{align*}
$$

Hence, backwards and forward evolution coincide, at the saddle-point level.

Using Eq. (32) we note that $\rho_{l m}$ can be re-written as:

$$
\begin{equation*}
\rho_{l m}\left(t^{\prime}\right)=\left\langle\Psi_{[\sigma]}\right| \hat{a}_{l}^{\dagger} \hat{a}_{m}\left|\Psi_{[\sigma]}\right\rangle \tag{37}
\end{equation*}
$$

where the quantum state $\left|\Psi_{[\sigma]}\right\rangle$ is defined as:

$$
\begin{equation*}
\left|\Psi_{[\sigma]}\right\rangle \equiv T e^{-\frac{i}{\hbar} \int_{0}^{t^{\prime}} d \tau \hat{H}_{e f f}[\sigma]}\left|k_{0}\right\rangle \tag{39}
\end{equation*}
$$

and the time-dependent Hamiltonian $\hat{H}_{e f f}[\sigma]$ is defined as

$$
\begin{equation*}
\hat{H}_{e f f}[\boldsymbol{\sigma}]=\sum_{l, m} \sigma_{l m}(t) \hat{a}_{l}^{\dagger} \hat{a}_{m} . \tag{40}
\end{equation*}
$$

Hence, the field $\rho_{l m}$ is identified with the (reduced) density matrix, evaluated on the state obtained by evolving for a time $t^{\prime}$ the initial quantum state $\left|k_{0}\right\rangle$, according to the timedependent Hamiltonian $\hat{H}_{e f f}[\sigma]$.

## V. QUANTUM AND STOCHASTIC EQUATIONS OF MOTION

In this section, we use the path integral representation of the conditional probability (9) and the saddle-point relationships (34)-(36) to derive a set of equations which describe the evolution of the quantum charge and the classical atomic nuclei, for a molecule in solution.

Our strategy consists in estimating the path integral over the charge density field $\rho$ and its conjugate $\sigma$ field in the lowestorder saddle-point approximation developed in the previous section. On the other hand, the integral over the molecular coordinates $y$ is evaluated at the one-loop level, i.e. including the effects of leading-order fluctuations around the saddlepoint solution $y(t)=0$. This guarantees that the dynamics of the molecular coordinates $r$ is stochastic, even at the classical level.

To implement this program, we impose that the density matrix field $\rho_{l m}^{\prime}=\rho_{l m}^{\prime \prime} \equiv \rho_{l m}$ and its conjugate field $\sigma_{l m}^{\prime}=\sigma_{l m}^{\prime \prime} \equiv$ $\sigma_{l m}$ obey the saddle-point relationship (35], (36) and we focus on the remaining part of the path integral, which concerns the molecular degrees of freedom, $\mathcal{D r}$ and $\mathcal{D} y$,

$$
\begin{equation*}
\mathcal{P}_{t}\left(Q_{f} \mid Q_{0} ;[\rho]\right) \equiv \int_{Q_{0}}^{Q_{f}} \mathcal{D} r \int \mathcal{D} y e^{\frac{i}{\hbar}\left(\mathcal{W}[r, y, \boldsymbol{\rho}]+i \hbar \Phi_{F V}^{\prime}[r, y]\right)}, \tag{41}
\end{equation*}
$$

where we have used Eq. 35 to eliminate $\sigma_{l m}$.

Retaining only the lowest orders in the expansion of the $y\left(t^{\prime}\right)$ path around the saddle-point solution $y(t)=0$ the functional at the exponent reads

$$
\begin{align*}
& \mathcal{W}[r, y, \rho]+i \hbar \Phi_{F V}^{\prime}[r, y]= \\
= & -\int_{0}^{t} d t^{\prime}\left[y ( t ^ { \prime } ) \cdot \left(M \ddot{r}\left(t^{\prime}\right)+M \gamma \dot{r}\left(t^{\prime}\right)\right.\right. \\
& \left.\left.+\frac{\partial}{\partial r} \mathcal{V}\left[r\left(t^{\prime}\right), \rho\left(t^{\prime}\right)\right]\right)+\frac{i k_{B} T M \gamma}{\hbar} y^{2}\left(t^{\prime}\right)\right], \tag{42}
\end{align*}
$$

where

$$
\begin{equation*}
\mathcal{V}[r, \rho]=V(r)+\sum_{l m} \rho_{l m} f_{l m}(r)=V(r)+\operatorname{Tr}[\hat{f}(r) \hat{\rho}] \tag{43}
\end{equation*}
$$

Since we have kept only terms which are at most quadratic in $y\left(t^{\prime}\right)$, the path integral over this variable can be evaluated analytically by completing the square. The resulting (unnormalized) expression for the path integral (41) is

$$
\begin{equation*}
\mathcal{P}_{t}\left(Q_{f} \mid Q_{0} ;[\rho]\right)=\int_{Q_{0}}^{Q_{f}} \mathcal{D} r e^{-\frac{\int_{0}^{t} d t^{\prime}\left\{M \bar{r}\left(t^{\prime}\right)+M \gamma^{\prime}\left(t^{\prime}\right)+\frac{\partial}{\partial r} \mathcal{V}[r, \overline{\mathrm{p}}]\right\}^{2}}{4 k_{B} T M \gamma}} \tag{44}
\end{equation*}
$$

We emphasize that the action in the exponent generalizes the well-known Onsager-Machlup functiona ${ }^{31}$ which appears in the path integral representation of the classical Langevin dynamics (a brief review is given in the appendix).

In macro-molecular systems in solution inertial effects are damped at a time scale $10^{-13} \mathrm{~s}$, which much smaller than the time scale associated to local conformational changes. If the acceleration term $M \ddot{r}$ at the exponent is neglected the path integral (44) becomes

$$
\begin{equation*}
\mathcal{P}_{t}\left(Q_{f} \mid Q_{0} ;[\rho]\right)=\int_{Q_{0}}^{Q_{f}} \mathcal{D} r e^{-\frac{M \gamma}{4 k_{B} T} \int_{0}^{t} d t^{\prime}\left\{\dot{r}\left(t^{\prime}\right)+\frac{1}{M \gamma} \frac{\partial}{\partial r} \mathcal{V}[r, \overline{\mathrm{\rho}}]\right\}^{2}} \tag{45}
\end{equation*}
$$

which is completely equivalent to the stochastic path integral defined in Eq. A11) for classical over-damped Langevin dynamics.

Hence, we conclude that the evolution of the system can be described by the following set of quantum and stochastic differential equations:

$$
\left\{\begin{array}{l}
\frac{d}{d t} r_{\alpha}=-\frac{1}{M \gamma} \frac{\partial}{\partial r^{\alpha}}(V(r)+\operatorname{Tr}[\hat{\rho} \hat{f}(r)])+\eta_{\alpha}(t)  \tag{46}\\
\frac{d}{d t} \hat{\rho}=-\frac{i}{\hbar}[\hat{f}(r), \hat{\rho}]
\end{array}\right.
$$

and we have condensed the Eq.s (37), (40), (35) and (36) into a single Van-Neumann Equation, where $[\hat{\rho}(t)]_{l m}=\rho_{l m}(t)$ and $[\hat{f}]_{l m}(r)=f_{l m}(r) . \quad \eta^{\alpha}(t)$ is the usual white delta-correlated Gaussian noise of the Langevin dynamics,

$$
\begin{equation*}
\left\langle\eta^{\alpha}(t) \cdot \eta^{\beta}(0)\right\rangle=6 \frac{k_{B} T}{M \gamma} \delta^{\alpha \beta} \delta(t) \tag{47}
\end{equation*}
$$

The set of equations (46) represents main result of this paper, as far as the formalism is concerned. Some comment on
these equations are in order. First of all, we emphasize that the Langevin equation for the molecular coordinates contains the force term

$$
\begin{equation*}
F_{\alpha}(Q) \equiv \operatorname{Tr}\left[\hat{\rho},-\frac{\partial}{\partial r^{\alpha}} \hat{f}(r)\right] \tag{48}
\end{equation*}
$$

This term is of fully quantum origin, as it follows directly from the the Hamiltonian (5). It expresses the influence of the charge distribution on the molecular motion: the atoms are driven towards configurations for which the energy of the charge is lower. This type of non-Coulombic charge-nuclei interaction is not included in the standard phenomenological approaches which have been used to simulate the dynamics of molecular wires ${ }^{11 / 17 / 26}$.

If the molecule contains charged atomic groups (e.g. like in DNA), one needs also to include their Coulombic interaction with the propagating quantum charge. This can be rigorously done by extending the potential energy function $\hat{V}(Q)$ in the original Hamiltonain (6) to:

$$
\begin{align*}
\hat{V}(Q) \rightarrow & \hat{V}\left(Q ;\left\{\hat{a}_{l}, \hat{a}_{l}^{\dagger}\right\}_{l=1, \ldots, N_{s}}\right) \\
& \equiv V(Q)+\frac{1}{2} \sum_{\alpha=1}^{N_{p}} \sum_{l=1}^{N_{s}} \frac{q_{\alpha} e}{\left|r_{l}-r_{\alpha}\right|} \hat{a}_{l}^{\dagger} \hat{a}_{l} \tag{49}
\end{align*}
$$

where $e$ is the charge of the hole and $q_{\alpha}$ is the (partial) charge of the $\alpha$-th atom. At the level of the Langevin equation (46), this coupling produces an additional Coulomb force term in the form:

$$
\begin{equation*}
F_{c}^{\alpha}\left(r, \rho_{l m}\right)=-\sum_{l} \int d r_{\alpha} \frac{e_{\alpha} e \rho_{l l}}{\left(r_{l}-r_{\alpha}\right)^{2}} \hat{u}_{l \alpha} \tag{50}
\end{equation*}
$$

where $\hat{u}_{l \alpha}=\left(r_{\alpha}-r_{l}\right) /\left|r_{\alpha}-r_{l}\right|$.
The equations of motion (46) can be integrated by simultaneously evolving the molecular positions and the initial quantum state, and then computing the corresponding density matrix field:

$$
\left\{\begin{align*}
r_{\alpha}(t+\Delta t) & =r_{\alpha}(t)-\frac{\Delta t}{M \gamma} \frac{\partial}{\partial r^{\alpha}}(V[r(t)]+\operatorname{Tr}[\hat{\rho} \hat{f}(r)])  \tag{51}\\
& +\sqrt{2 \frac{k_{B} T \Delta t}{M \gamma}} \xi_{\alpha}(t) \\
|\Psi(t+\Delta t)\rangle & =e^{-\frac{i \Delta t}{\hbar} \hat{H}_{e f f}[r(t)]}|\Psi(t)\rangle \\
\rho_{l m}(t+\Delta t) & =\langle\Psi(t+\Delta t) \mid l\rangle\langle m \mid \Psi(t+\Delta t)\rangle
\end{align*}\right.
$$

where $\xi_{a}(t)$ is a stochastic variable sampled from a Gaussian distribution with zero average and unitary variance.

The solution of the set of equations (46) through the algorithm (51) yields the real-time evolution of the atomic nuclei and of the charge density, starting from an initial condition. Like any approach based on the time integration of the equations of motion, this method is expected to be computationally inefficient to investigate rare thermally-activated reactions. The main difficulty arises from the fact that, on average, the first reactive event occurs on a time scale which scales exponentially with the height of barrier. Hence, very long trajectories have to be generated in order to investigate the dynamics of the reaction.

In order to overcome these difficulties, the Dominant Reaction Pathways (DRP) method was recently developed 0 20-24. This approach uses the path integral representation of the classical Langevin dynamics to derive a variational principle which yields the most probable reaction pathways connecting given initial and final configurations. To date, the DRP algorithm has been successfully applied to investigate a number of reactions which are extremely hard to simulate using standard MD algorithms, including conformational transitions of peptides from ab-initio simulations ${ }^{28}$, protein folding within realistic atomistic classical models ${ }^{[27]}$, as well as chemical reaction ${ }^{299}$ or particle-surface interactions ${ }^{30}$. Recently, the formalism has been extended to include quantum corrections to the motion of light nuclei ${ }^{30}$.

The Feynman-Vernon functional integral formulation of the dynamics developed in the previous sections offers the proper framework to extend the DRP method to the case in which the molecule contains quantum excitations. The starting observation is that the solutions of the saddle-point equations (34)(36) and the molecular path minimizing the effective action in the exponent of Eq. (44) yield the most probable coupled evolution of the charge density and of the molecular coordinates during transitions.

Assuming that the initial and final molecular configurations and the initial position of the charge are held fixed, the saddlepoint equations can be solved self-consistently by means of the following iterative algorithm:

1. A reaction pathway $r(t)$ connecting the initial configuration $Q_{0}$ and the final configuration $Q_{f}$ is computed by minimizing the Onsager-Machlup action at the exponent of Eq. (45), neglecting the coupling with the density matrix $\rho_{l m}\left(t^{\prime}\right)$. This can be efficiently done by using the algorithms described in Ref. $\mathbf{\Sigma}^{27128}$.
2. The deterministic evolution of the density field $\rho_{l m}\left(t^{\prime}\right)$ is computed from Eq.s (39) and (40), where the tightbinding coefficients in $H_{e f f}$ are evaluated along the path $r(t)$ obtained in the previous step.
3. The density matrix obtained in the previous step is plugged in Eq. (45), and an improved estimate of the molecular reaction path $r(t)$ is obtained by numerical relaxation of the generalized Onsager-Machlup action (45).

The process is iterated until convergence.

## VI. CHARGE LOCALIZATION IN A COLLAPSING CHAIN

Having developed the appropriate formalism, we are now ready to analyze the quantum transport dynamics during the collapse of a homo-polymeric chain.

According to the standard scaling theory ${ }^{34}$, the existence of an Anderson metal-insulator transition (MIT) in the thermodynamic limit and at zero temperature critically depends on the number of spatial dimensions. In particular, in the onedimensional Anderson model, an arbitrarily small amount of
disorder is sufficient to stop electric conduction. In threedimensions, a mobility edge is developed and the system remains in the metallic regime for sufficiently small disorder. If such idealized conditions were good approximations for realistic molecular wires in solution, then one might argue that the collapse into a molten globule of a polymer may lead to an increase of the conductance.

On the other hand, physical molecular wires in solution are complex mesoscopic systems subject to dynamical disorder and finite temperature effects. As a consequence, their conductance depends on a number of specific physical conditions, such as e.g. the chain length, heat-bath temperature, noise memory function, and so on.

Nevertheless, this systems may still display different conducting properties, depending if the polymer is in a coil configuration (where the transport dynamics is effectively onedimensional) or in a compact phase ( where the charge can diffuse in three-dimensions).

This discussion raises two main questions: does the dynamical disorder driven by the conformational fluctuations of the chain induce a strong charge localization already in the coil state? Is such a localization enhanced or reduced when the system reaches a compact configuration?

To address these questions, we use the framework developed in the previous sections to simulate the charge migration in a simple coarse-grained model for a polymeric collapse.

## A. Definition of the Model

We consider a chain composed by $N_{p}=36$ beads, each one representative of an individual monomer. These particles are linked by harmonic springs and can interact at distance through Van-der-Waals potential, which simulates the effective hydrophobic attraction and the steric repulsion:

$$
\begin{align*}
& V(Q)=\frac{1}{2} \sum_{\alpha} k_{s}\left(\left|r_{\alpha+1}-r_{\alpha}\right|-a\right)^{2} \\
& +\frac{1}{2} \sum_{\alpha \neq \beta} 4 \varepsilon\left[\left(\frac{\sigma}{\left|r_{\alpha}-r_{\beta}\right|}\right)^{12}-\left(\frac{\sigma}{\left|r_{\alpha}-r_{\beta}\right|}\right)^{6}\right] \tag{52}
\end{align*}
$$

The hole can propagate by hopping across $N_{s}$ sites, which are identified with the chain's monomers, hence $N_{s}=N_{p}$. The chain is not coupled to electrodes.

In the present illustrative toy model, the couplings in the effective configuration-dependent tight-binding Hamiltonian (1) are not evaluated microscopically from electronic structure calculations. Instead, their dependence on the monomer coordinatesis is defined phenomenologically as follows:

$$
\begin{equation*}
T_{i j}(Q)=T_{0} e^{-\frac{\left|r_{i}-r_{j}\right|^{2}}{2 a_{t}^{2}}}, \quad e_{i}(Q)=\varepsilon_{0} \tag{53}
\end{equation*}
$$

Note that the charge can hop between monomers which are specially close, even if they are far in the chain sequence.

The numerical value of the constants entering Eq.s (52) and (53) are listed in table We consider a heat bath of temperature $T=300 \mathrm{~K}$ and, while the mass and the friction coefficient

TABLE I: Parameter of the Hamiltonian for the toy-model molecular wire

| $k_{s}$ <br> $\left[\mathrm{~kJ} \mathrm{~mol}^{-1} \mathrm{~nm}^{-2}\right]$ | $a$ <br> $[\mathrm{~nm}]$ | $\varepsilon$ <br> $\left[\mathrm{kJ} \mathrm{mol}^{-1}\right]$ | $\sigma$ <br> $[\mathrm{nm}]$ |
| :---: | :---: | :---: | :---: |
| 1000 | 0.38 | 4 | 0.4 |
| $T_{0}$ <br> $\left[\mathrm{~kJ} \mathrm{~mol}^{-1}\right]$ | $\varepsilon_{0}$ <br> $\left[\mathrm{~kJ} \mathrm{~mol}^{-1}\right]$ | $a_{T}$ <br> $[\mathrm{~nm}]$ |  |
| 2 | -200 | 0.3 |  |

are chosen in such a way that $M \gamma=2000 \mathrm{amu} \mathrm{ps}^{-1}$. This set of parameters was chosen to ensure that the end-to-end propagation of the quantum charge across the wire and the collapse of the molecule occur at comparable time scales.

## B. Quantum Transport and Conformational Dynamics

The potential energy function of this model is characterized by a low degree of frustration. As a result, the collapse of the chain from an initial stretched coil configuration to a compact globular state occurs in just few ns. Such a time interval can be simulated directly by integrating the equation of motion (46).

Let us consider a polymer which is initially prepared in the fully stretched configuration shown in Fig. 1, with a quantum charge localized at the first monomer $|\Psi(t=0)\rangle=|1\rangle$. Then, the evolution of the system is predicted by means of the algorithm (51).

The elementary time-step in the integration of the Langevin equation for this simple coarse-grained model can be chosen to be $\Delta t_{M D}=10 \mathrm{fs}$, while the time-step in the quantum evolution of the charge wave-function has to be chosen much smaller, e.g. $\Delta t_{Q}=1 / 10 \Delta t_{M D}$. With such a choice of parameters, simulating few ns of dynamics takes only a few minutes on a standard laptop computer and the normalization of the charge wave-function remains constant within $1 \%$ accuracy over the entire simulated time interval.

Let us begin by discussing the charge migration dynamics in a static wire, i.e. assuming that the molecule remains 'frozen' in the initial fully stretched configuration. This configuration corresponds to a complete absence of disorder. In Fig. 11 we report the calculated evolution of the charge density in few ns of dynamics. We note that the propagation of the charge occurs through an attenuating traveling density wave, which reaches the end of the wire in about 3 ns . The secondary peaks are due to the fact that, at any instant, the charge has finite probability not to perform the transition. In the long time limit, the primary peak looses intensity, which signals that the charge is delocalized, with a consequent increase of the entropy.

Fig. 2 shows that the quantum transport dynamics is radically changed if the polymer is allowed to move under the effect of the internal forces and of the fluctuations induced by the solvent, which introduce dynamical disorder in the tightbinding Hamiltonian. We can clearly see that the migration of the charge is strongly hindered and that the initial density peak


FIG. 1: Time evolution of the charge density distribution in a frozen fully stretched polymer. The pictures in the upper-right corner represent the polymer conformation, the color of the backbone is proportional to the charge density.


FIG. 2: Time evolution of the charge density distribution in collapsing polymer. The pictures in the upper-right corner represent the polymer conformation, the color of the backbone is proportional to the charge density.
is completely dispersed after about one ns and hardly propagates into the second half of the chain. Hence, the charge transmission properties of the system are strongly affected by the configurational dynamics.

These results raise the question if the disorder-driven charge localization takes place already in the coil state, or only when the chain reaches the compact state. This question can be addressed in the context of random matrix theory ${ }^{35 / 36}$. This theory predicts that the level spacing distribution of a real orthogonal Hamiltonian with delocalized eigenstates should
obey the so-called Wigner-Dyson distribution ${ }^{1}$,

$$
\begin{equation*}
P_{W D}(s)=\frac{\pi s}{2} e^{-\frac{\pi s^{2}}{4}} \tag{54}
\end{equation*}
$$

In particular, we note that $P_{W D}(s)$ vanishes for $s \rightarrow 0$. This feature is called level repulsion and is a characteristic signature of delocalized eigenstates (i.e. of the metallic regime).

By contrast, the localization of the wave-functions reduces the overlap between adjacent modes, hence suppressing the level repulsion. In particular, in the extreme case in which there is no overlap between neighboring eigenvectors, the level-spacing distribution follows a Poisson distribution:

$$
\begin{equation*}
P_{P}(s)=e^{-s} \tag{55}
\end{equation*}
$$

We have computed the level spacing distribution by simulating 48 independent 3 ns -long evolutions starting from the same stretched coil configuration, with the charge initially localized at the left terminus of the chain. The level spacing distribution at different instants during the transition was then obtained by explicitally diagonalizing the quantum Hamiltonian (1).

The results are summarized in Fig. 3 In the early time of the collapse the spectrum is well explained by a WignerDyson statistics, hence the system displays good conducting properties even in the presence of disorder. On the other hand, after about 1 ns , revel repellence has completely disappeared and the spectrum is well described by a Poisson distribution, hence the system behaves like an insulator.

Note that the observed behavior contrasts with what would be expected from scaling arguments, implying that the mesoscopic character of this system and thermal effects play an important role.

The recent developments in single-molecule and ensemble manipulation techniques may allow to look for this effect. For example, using a conducting atomic force microscopy it is in principle possible to simultaneously measure the conductivity ${ }^{38139}$ and the end-point distance ${ }^{40141}$ of single polymers. Alternatively, by simultaneously applying laserinduced temperature jumps ${ }^{\sqrt[42]]{ }}$ and electron pulse radiolysis ${ }^{43}$ on an ensemble of neutral collapsed polymers it is possible to drive them into non-equilibrium swollen and electrically charged states. Then, the evolution of the conductivity in these systems during the subsequent thermal relaxation process may be monitored using time-resolved microwave conductivity techniques ${ }^{4}$.

## VII. CONCLUSIONS

In this paper, we have presented a formalism to quantitatively investigate the dynamics of quantum excitations inside macromolecules which move under the effect of the intramolecular forces and of the collisions with the solvent

[^0]

FIG. 3: Level spacing distribution for the tight-binding Hamiltonian, evaluated after after 0.1 ns (upper panel) and after 1 ns (lower panel)..
molecules. The resulting set of coupled stochastic and quantum equations of motion (46) contains a non-Coulombic force term which is not present in the approaches where equations of motion are postulated phenomenologically. Such a term has a quantum origin and explicitly couples the density matrix of the quantum particle to the molecular coordinates. The numerical simulations performed in a simple coarse-grained model have shown that this force can give significant contribution, of the same order of standard (i.e. Van-der-Waals) non-bonded interactions.

We have also used the path integral formalism for open quantum systems to derive an algorithm which yields the most probable pathways in the evolution of this system, from a given initial to a given final molecular conformation. This formalism may provide a computationally efficient method to investigate the non-equilibrium quantum transport dynamics during rare thermally-activated conformational transitions.

We have applied this formalism to study the migration of a quantum charge, during the coil-globule transition of a polymer. These calculations have shown that the dynamics of the quantum charge is strongly quenched during the collapse. By analyzing the statics of the eigenvalues spectrum, we have concluded that the disorder-driven increase of localization sets in only when the system reaches a compact conformation.

The formalism developed in this work does not only con-
cern molecular quantum wires, but can be applied to all molecular systems in solution which can support the propagation of quantum excitations. In particular, in the future it would be interesting to use it to investigate the transfer of neutral atomic excitations between amino-acids in peptide chains. This would provide a solid theoretical ground to bridge the gap between molecular simulations and experimentally observable circular dichroism and Förster Resonance Energy Transfer spectra in protein folding.

## Appendix A: Path Integral representation of the classical dynamics of a molecule in a thermal bath

The main goal of this work is to derive a path-integral based framework to study the evolution of quantum excitations in conformationally evolving molecular systems.

For comparison purposes, it is instructive to review the corresponding path integral formulation of the classical Langevin dynamics which is often used to study the conformational dynamics in the absence of quantum excitations. The so-called over-damped Langevin equation reads ${ }^{44}$ :

$$
\begin{equation*}
\dot{q}_{\alpha}=-\frac{1}{M \gamma} \frac{\partial}{\partial q_{\alpha}} V(Q)+\eta(t), \quad\left(\alpha=1, \ldots, N_{p}\right) \tag{A1}
\end{equation*}
$$

where $\gamma$ is the friction coefficient, $V(Q)$ is the potential energy function entering in Eq. (6) and $\eta(t)$ is delta-correlated Gaussian noise, satisfying the fluctuation-dissipation relationship:
$\left\langle\eta^{\alpha}\left(t^{\prime}\right) \cdot \eta^{\beta}(t)\right\rangle=\frac{6 k_{B} T}{M \gamma} \delta^{\alpha \beta} \delta\left(t-t^{\prime}\right) \quad\left(\alpha, \beta=1, \ldots, N_{p} \oslash \mathrm{~A} 2\right)$
Note that in the original Langevin Eq. there is a mass term $M \ddot{q}$. However, for macro-molecular systems this term is damped at a time scale $10^{-13} \mathrm{~s}$, which much smaller than the time scale associated to local conformational changes.

The stochastic differential Eq. (A1) generates a timedependent probability distribution $P(Q, t)$ which obeys the well-known Smoluchowski Eq.:

$$
\begin{equation*}
\frac{\partial}{\partial t} P(Q, t)=\frac{k_{B} T}{M \gamma} \nabla\left[\nabla P(Q, t)+\frac{1}{k_{B} T} \nabla V(Q) P(Q, t)\right] . \tag{A3}
\end{equation*}
$$

By performing the formal substitution

$$
\begin{equation*}
P(Q, t)=e^{-\frac{1}{2 k_{B} T} V(Q)} \Psi(Q, t), \tag{A4}
\end{equation*}
$$

the Smoluchowski Eq. (A3) can be recast in the form of an imaginary time Schrödinger Eq.:

$$
\begin{equation*}
-\frac{\partial}{\partial t} \Psi(Q, t)=\hat{H}_{e f f} \Psi(Q, t) \tag{A5}
\end{equation*}
$$

where

$$
\begin{equation*}
\hat{H}_{e f f}=-\frac{k_{B} T}{M \gamma} \hat{\nabla}^{2}+\hat{V}_{e f f}(Q) \tag{A6}
\end{equation*}
$$

is an effective Hamiltonian operator and

$$
\begin{equation*}
V_{e f f}(Q)=\frac{1}{4 k_{B} T M \gamma}\left((\nabla V(Q))^{2}-2 k_{B} T \nabla^{2} V(Q)\right) \tag{A7}
\end{equation*}
$$

The conditional probability $P\left(Q_{f}, t \mid Q_{0}\right)$ to find the system at the configuration $Q_{f}$ at time $t$, provided it was prepared in the configuration $Q_{0}$ at time $t=0$ is the Green's function of the Smoluchowski Eq., and can be related to the imaginary time propagator of the effective "quantum" Hamiltonian (A6):

$$
\begin{equation*}
P_{t}\left(Q_{f} \mid Q_{0}\right)=e^{-\frac{1}{2 k_{B} T}\left(V(Q)-V\left(Q_{0}\right)\right)}\left\langle Q_{f}\right| e^{-t H_{e f f}}\left|Q_{0}\right\rangle \tag{A8}
\end{equation*}
$$

Using such a connection, it is immediate to obtain an expression of the conditional probability $(\overline{A 8})$ in the form of a Feynman path integral

$$
\begin{equation*}
P_{t}\left(Q_{f} \mid Q_{0}\right)=e^{-\frac{V\left(Q_{f}\right)-V\left(Q_{0}\right)}{2 k_{B} T}} \int_{Q_{0}}^{Q_{f}} \mathcal{D r} e^{-S_{e f f}[r]} \tag{A9}
\end{equation*}
$$

where

$$
\begin{equation*}
S_{e f f}[r]=\int_{0}^{t} d t^{\prime}\left(M \gamma \frac{\dot{r}^{2}}{4 k_{B} T}+V_{e f f}[r]\right) \tag{A10}
\end{equation*}
$$

is called the effective action.
The conditional probability $P_{t}\left(Q_{f} \mid Q_{0}\right)$ is sometimes written also in the following equivalent form:

$$
\begin{equation*}
P_{t}\left(Q_{f} \mid Q_{0}\right)=\int_{Q_{0}}^{Q_{f}} \operatorname{Dr} e^{-S_{O M}[r]} \tag{A11}
\end{equation*}
$$

where $S_{O M}[r]$ is the so-called the Onsager-Machlup functional,

$$
\begin{equation*}
S_{O M}[r]=\int_{0}^{t} d t^{\prime} \frac{M \gamma}{4 k_{B} T}\left(\dot{r}+\frac{1}{M \gamma} \nabla V(r)\right)^{2} \tag{A12}
\end{equation*}
$$

Proving the equivalence between the expressions (A9) and (A11) is not straightforward, since it involves elements of stochastic calculus ${ }^{45 / 46}$.

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1 J.M. Tarascon, G.W. Hull and F.J. Di Salvo, Mater. Res. Bull. 19 (1984), 915.
${ }^{2}$ D. Vrbanic et al., Nanotechnology 15 (2004), 635.
${ }^{3}$ D. Mihailovic, Progr. in Material Science 54 (2009), 309.
${ }^{4}$ P. Prins, F. Grozema, F. Galbrecht, U. Scherf and L. D. A. Siebbeles, J. Phys. Chem. C 111 (2007), 11104.
5 X. Xiao, B. Xu and N.J. Tao, Nano Letters 4 (2004), 267.
${ }^{6}$ P. Prins, F. Grozema, F. Galbrecht, U. Scherf and L. D. A. Siebbeles, J. Phys. Chem. C 111 (2007), 11104.
${ }^{7}$ D.K. James and J.M. Tour, Top Curr. Chem. 257 (2005), 33.
${ }^{8}$ G. E. Lopez et al. J. Phys. Chem. A115 (2011), 5423.
${ }^{9}$ T. Chakraborty "Charge Migration in DNA". Springer-Verlag. Berlin Heidelberg, 2007.
${ }^{10}$ S. S. Mallajossyula and S. K. Pati, J. Phys. Chem. Lett. 1 (2010), 1881.
${ }_{11}^{11}$ P.B. Woiczikowski et al., J. Chem. Phys. 130 (2009), 215105.
12 D. S. Novikov, Phys. Rev. Lett. 99 (2007), 016802.
${ }^{13}$ P.G. Silvestrov and K.B. Efetov, Phys. Rev. Lett. 98 (2007), 016802.

14 J. Milton Pereira, Jr., F. M. Peeters and P. Vasilopoulos, Phys. Rev. B75 (2007), 125433.
15 M. Bazzanella, P. Faccioli and E. Lipparini, Phys. Rev. B82 (2010), 1. P. Faccioli and E. Lipparini, Phys. Rev. B80 (2009), 1.

16 T. Kubar, P.B. Woiczikowski, G. Cuninberti and M. Elnser, J. Phys. Chem. B112 (2008), 7937.
${ }^{17}$ D. S. Wallace, A. M. Stoneham, W. Heysef, A. J. Fisher and A. H. Harker, J.Phys.: Condens. Matter 3 (1991) 3879.

18 A. R. Leach, "Molecular Modeling: Principles and Applications" ( 2nd ed.). Pearson Education Limited. Harlow, 2001)

19 H.-P. Breuer and F. Petruccione, "The Theory of Open Quantum Systems". Oxford University Press Inc., New York, 2002.
${ }^{20}$ R. Elber and D.. Shalloway, J. Chem. Phys. 112 (2000), 5539.
${ }^{21}$ P. Faccioli, M. Sega, F. Pederiva, and H. Orland, Phys. Rev. Lett. 97 (2006), 1.
22 M. Sega, P. Faccioli, F. Pederiva, G. Garberoglio, and H. Orland, Phys. Rev. Lett. 99(2007), 1.
${ }^{23}$ E. Autieri, P. Faccioli, M. Sega, F. Pederiva and H. Orland, J. Chem. Phys. 130 (2009) 064106.
${ }^{24}$ G. Mazzola, S. a Beccara, P. Faccioli, and H. Orland, J. Chem. Phys. 134 (2011), 164109.
${ }^{25}$ H. Grabert, P. Schramm, G.-L. Ingold, Phys. Rep. 168 (1988), 115.
${ }^{26}$ M.M.D. Ramos and H.M.G. Correia, Soft Matter 7 (2011), 10091.
27 S. a Beccara, T. Skrbic, R. Covino and P. Faccioli, Proc. Natl. Acad. Sci. USA, Published ahead of prints on January 26, 2012. doi:10.1073/pnas.1111796109.
28 S. a Beccara et al., J. Chem Phys. 134 (2011), 024501.
${ }^{29}$ S. a Beccara, G. Garberoglio, P.Faccioli and F. Pederiva, 132 (2010), 111102.
${ }^{30}$ S. a Beccara, G. Garberoglio, and P. Faccioli, J. Chem. Phys. 135 (2011), 034103.
${ }^{31}$ L. Onsager and S. Machlup, Phys. Rev. 91 (1953), 1505.
32 P. Faccioli, J. Phys. Chem. B 122 (2008), 13756.
${ }^{33}$ P. Faccioli, A. Lonardi and H. Orland, J. Chem. Phys. 133, 045104 (2010).
34 B. Kramer and A. MacKinnon, Rep. Prog. Phys. 56 (1993), 1469.
${ }^{35}$ M.L. Mehta, "Random Matrices". Academic Press, Boston, 1991.
${ }^{36}$ A.D. Mirlin and F. Evers, Phys. Rev. B62 (2000), 7920.
37 T. Guhr, A. Müller-Groeling and H.A. Weidenmüller, Phys. Rep.,

299 (1998), 189.
${ }^{38}$ L. Cai, H. Tabata and T. Kawai, Nanotechnology 12 (2001) 211.
${ }^{39}$ D. Xu, G.D. Watt, J.N. Harb and R. C. Davis, Nano Lett., 5 (2005), 571.

40 J. Liphardt et al., Science 296 (2002), 1832.
${ }^{41}$ D. Collin et al., Nature 437 (2005), 231.
${ }^{42}$ B.Schuler and W.A. Eaton, Curr. Opin. in Struct. Biol. 18 (2008),
16.
${ }^{43}$ F. C. Grozema et al. J. Phys. Chem. A107 (2003), 5976.
${ }^{44}$ F. Schwabl, "Statistical Mechanics" (2nd Ed.). Springer-Verlag. Berlin-Heidelberg, 2006.
${ }^{45}$ A. Adib, J. Phys. Chem. B112 (2008), 5910.
${ }^{46}$ P. Faccioli, J. Chem. Phys. 133 (2010), 164106.


[^0]:    ${ }^{1}$ Note that, as usual, this distribution is normalized in such a way to enforce a unit average level spacing.

