Non-equilibrium Born-Oppenheimer potential energy surfaces for molecular wires

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We present a method for computing non-equilibrium, current-dependent Born-Oppenheimer potential energy surfaces for molecular wires. Calculations are performed for polyacetylene wire described by tight-binding model with electron-phonon interactions. We find that dimerization of the polyacetylene wire is amplified by electric current flow. We show that the boundary between transparent and opaque black states of the wire is blue-shifted by current.

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One of the major goals in modern nanotechnology is the construction of an electronic circuit in which molecular systems act as conducting element. Two critical issues should be thoroughly investigated to proceed with the design of real molecular devices: heating in a molecular junction and current induced conformational changes of a junction caused by electromigration. By the inelastic scattering of electrons the kinetic energy of current is transferred to the nuclear vibrations and then it is released as heat. The second process, electromigration, is the phenomenon of atom motion due to current induced forces and it is related to the transfer of electronic momentum to nuclei due to both elastic and inelastic scattering. The electromigration can lead to device breakdown at critical values of current and therefore current-induced forces may present a limitation for the development of molecular electronic devices. Very recently, controlled electromigration has been used constructively to make a single-molecular junction. Both issues, heating and electromigration, are ultimately related to understanding how Born-Oppenheimer (BO) potential energy surface of a molecular wire is responded to electronic current flow. If current-dependent BO potential energy surface of a molecular device is available, we can compute current-induced forces as the corresponding gradients as well as we perform the normal modes analysis to obtain the current-dependent vibrations.

Although the practical importance of a current-dependent BO surface can not be underestimated, some intricate theoretical questions connected to the difficulty in defining a generic variational energy functional for non-equilibrium steady state systems can be also puzzled out. Theoretical work to date has failed to define or even to prove the existence of the BO potential energy surface for molecular wires with current flow. The principle theoretical difficulty is the treatment of the transport problem as an electron transmission (Landauer approach) which is non-variational from the outset. A wire with current is by definition an open quantum system and as long as one works within a non-variational transport theory it is likely not possible to comprise a geometrical optimization of the nuclear degrees of freedom with electronic transport calculations within a single theoretical approach. There is the opinion that current induced forces can not be conservative although validity of this claim has been recently questioned. If a current induced force is not conservative then there does not exist a BO potential energy surface of which this force might be derivative. One of the goals of this Letter is to show that this is not true and that the Born-Oppenheimer potential energy surface can be properly defined and efficiently computed in the presence of current flow.

The Lagrange multiplier based transport theory takes its origin in the modern development of steady state non-equilibrium statistical mechanics. This theory is equivalent to a variational formulation where the constrained minimization of the expectation value of the Hamiltonian on the manifold of the desired current yields the transport properties. The “algorithm” of the Lagrange multiplier based transport theory to compute a current-dependent BO surface can be summarized as follows: (1) define the operator of the current via the continuity equation; (2) extend the Hamiltonian by adding the term $-\lambda J$ where $\lambda$ is a Lagrange multiplier; (3) compute the BO surface as the expectation value $0(\lambda)\langle H \vert 0(\lambda) \rangle$ where $0(\lambda)$ is the “ground state” of the extended Hamiltonian $H - \lambda J$.

In this Letter, using the Lagrange multiplier based transport theory we compute the current-dependent BO potential energy surfaces of conjugated polymer, polyacetylene, wire. Polyacetylene is a linear polymer, it consists of coupled chain of CH units forming a quasi-one-dimensional lattice. Each C has four valence electrons: two of them contribute to the $\sigma$-type bonds connecting neighboring carbons along the one-dimensional backbone, while the third forms a bond with the hydrogen. The remaining electron has the symmetry of a $2p_x$ orbital and contributes to $\pi$-bonds. In terms of the energy band description, the $\sigma$-bonds form low-lying completely filled band, while $\pi$-bond leads to half-filled energy band responsible for electron transport properties. The $\pi$-electrons can to a fair approximation be treated as a quasi-one dimensional electron gas within the tight-
Hamiltonian \( H \) is based upon the so-called Su-Schrieffer-Heeger (SSH) model for the band-structure of trans-(CH)\(_n\) lattices. The first term in \( H \) gives the energy for an electron with spin \( \sigma \) to hop between neighboring \( p_z \)-orbitals. The strength of this term is modulated by linear coupling to distortions \( x \) in the polymer lattice away from evenly spaced lattice positions. Finally, the last terms in \( H \) gives the harmonic interactions between lattice-sites arising from the \( \sigma \)-bonds between neighboring lattice atoms.

We begin the derivation by defining the operator of current via continuity equation. The number of electrons on the site \( n \) is given by the expectation value of the operator

\[
N_n = \sum_\sigma a_{n\sigma}^\dagger a_{n\sigma} .
\]  

By making use of the Heisenberg representation the continuity equation can be written as the Heisenberg equation-of-motion for the operator \( N_n \):

\[
\dot{N}_n = i [H_0, N_n] .
\]  

Given standard anti-commutation relations between the electron creation and annihilation operators, the r.h.s. commutator \( [H_0, N_n] \) can be readily computed. Comparing eq. (3) with the difference expression for continuity equation \( \dot{N}_n = -(j_n - j_{n-1}) \) we obtain the definition of the operator of current through site \( n \). By making the sum of on-site currents \( j_n \) along the wire we define the net, macroscopic current through the wire

\[
J = i \sum_{n\sigma} (t_o + (-1)^n \alpha x)(a_{n+1\sigma}^\dagger a_{n\sigma} - a_{n\sigma}^\dagger a_{n+1\sigma}) .
\]  

There are two distinct contributions to the net current. The term \( t_o(a_{n+1\sigma}^\dagger a_{n\sigma} - a_{n\sigma}^\dagger a_{n+1\sigma}) \) is the standard for molecular wires without electron-phonon coupling whereas the term \((-1)^n \alpha x(a_{n+1\sigma}^\dagger a_{n\sigma} - a_{n\sigma}^\dagger a_{n+1\sigma}) \) is the phonon-assisted current.

We assume now that there is a time-independent, constant current through the wire. A homogeneous current-carrying state is the same whether it is introduced by reservoirs or by a bulk driving driving field, the current enters the problem via a Lagrange multiplier \( \lambda \). To this end the Hamiltonian \( H \) is modified by adding the term which constrains the macroscopic current \( J \):

\[
H_J = H - \lambda J .
\]  

We have introduced here the phonon-unperturbed band energy

\[
\epsilon_k(\lambda) = 2t_o(\cos(k) + \lambda \sin(k)),
\]  

and the phonon-induced gap

\[
\Delta_k(\lambda, x) = -4\alpha x(\sin(k) - \lambda \cos(k)).
\]  

Both quantities, \( \epsilon_k(\lambda) \) and \( \Delta_k(\lambda, x) \) depend upon current via the Lagrange multiplier \( \lambda \) and if we let \( \lambda \) tend to zero we recover the usual zero-current results \( \Delta_0 \). Mixing \( c_{k\sigma} \) and \( c_{k+\pi\sigma} \) operators by the canonical Bogoliubov transformation

\[
\left( \begin{array}{c} \alpha_{k+\pi\sigma} \\ \alpha_{k\sigma} \end{array} \right) = \left( \begin{array}{cc} u_k & v_k \\ v_k & -u_k \end{array} \right) \left( \begin{array}{c} \epsilon_{k+\pi\sigma} \\ \epsilon_{k\sigma} \end{array} \right) ,
\]  

we obtain new quasiparticles \( \alpha_{k\sigma} \) and \( \alpha_{k+\pi\sigma} \). The coefficients of the Bogoliubov transformation is chosen in such a way that the extended Hamiltonian \( H_J \) should be diagonal. It leads to the following expressions for the coefficients

\[
u_k = \sqrt{\theta(\epsilon_k) \sin(\phi_k) + \sqrt{1 - \theta(\epsilon_k)^2}} ,
\]  

\[
u_k = \sqrt{\theta(\epsilon_k) \cos(\phi_k) + \sqrt{1 - \theta(\epsilon_k)^2}} 
\]  

where \( \theta(\epsilon) \) is the Heaviside step function and the mixing angle \( \phi_k \) is given by the formula \( \phi_k = 1/2 \arctan(\epsilon_k/\Delta_k) \). This canonical Bogoliubov transformation produces the non-interacting Hamiltonian for the quasiparticles \( \alpha_{k\sigma} \) and \( \alpha_{k+\pi\sigma} \):

\[
H_J = \sum_{0 \leq k < \pi} \sum_{\sigma} E_k(\alpha_{k+\pi\sigma}^\dagger \alpha_{k\sigma} - a_{k\sigma}^\dagger a_{k\sigma})
\]  

with the wave-vector \( k \) in the reduced Brillouin zone of the system. The band energy, \( E_k = \sqrt{\epsilon_k^2 + \Delta_k^2} \), and the mixing angle \( \phi_k \) in the canonical Bogoliubov transformation are functions of the phonon-unperturbed band energy, \( \epsilon_k(\lambda) \), and the phonon-induced energy gap, \( \Delta_k(\lambda, x) \).

It can be straightforwardly shown that this diagonalization of the Hamiltonian is equivalent to the variational
FIG. 1: Born-Oppenheimer potential energy surfaces for different values of the current: I=0.00 mA (lower panel), I=0.25 mA (middle panel) and I=0.50 mA (upper panel). The dimerization coordinate, \( x_o \), corresponds to the minimum on the BO surface and it is shown for each values of the current.

For any given lattice distortion \( x \) the nonlinear equation should be resolved for \( \lambda \). Then the band energy and the mixing angle \( \phi_k \) of the canonical Bogoliubov transformations are computed as functions of current.

We now discuss the main results obtained using the above model. The numerical calculations are performed for the half-occupied conductance band with the box length \( N = 1000 \). In all our calculations we use the following model parameters of the SSH model \( \alpha = 2.5 \text{ eV}, \alpha = 4.1 \text{ eV}, \text{ and } K = 21 \text{ eV/Å}^2 \). This parameterization of the ASH Hamiltonian is typically used to describe coherent electron transport in polyacetylene wire \( \text{[13]} \). In the first calculations, shown in Fig.1, we studied the changes of the BO surface as current flows through the wire. It is immediately evident from Fig.1 that the current substantially alters the Born-Oppenheimer potential energy surface of the polyacetylene wire. The minima on the BO surface correspond to the optimal non-equilibrium steady state geometries of the wire. The dimerization coordinate increases as current flows, i.e. the \( C = C \) double bonds are shortened and the \( C - C \) single bonds are elongated by the current induced forces. By increasing the current we also increase the barrier between the two-fold degenerate ground states, therefore the energy difference between evenly spaced polyacetylene and dimerized polyacetylene is increased as we increase the current. Since SSH Hamiltonian is very general and applicable in its present formulation to any long semiconductor wires we do expect that effect of current-amplified dimerization occurs in other quasi-one-dimensional wires as well. The results of our calculations are qualitatively consistent with the finding of Todorov, Hoekstra and Sutton \( \text{[14]} \) that current-induced forces generally form an alternating patterns in atomic wires. The critical value of the current at which the current-induced forces break the wire into pieces can be also determined. If we assume that the current-induced bond distortion larger than 0.2 Å will be sufficient to rupture the wire, the critical value of the current which the polyacetylene wire can sustain is 0.8 mA.

Finally, we turn our attention towards what physical quantities which are accessible experimentally can
FIG. 2: The current-dependent valence and conductance bands of polyacetylene wire, $E_k = \pm \sqrt{\epsilon_k + \Delta^2}$.

FIG. 3: The transparent-opaque boundary for polyacetylene wire as a function of current

be used to monitor the current-amplified polyacetylene dimerization. To this end we compute the response of the band structure of polyacetylene to current flow. The current-dependent band structure of the first Brillouin zone is plotted in Fig.2. Polyacetylene’s band is half occupied therefore the states with negative $E_k$ are completely occupied and the states with positive $E_k$ are empty. The current flow through the wire does not only produce the overall shift of the band energy within the reduced Brillouin zone but also changes the total bandwidth from 10 eV at zero current to 12.5 eV at $I = 0.5$ mA. The band gap between the valence and conductance bands is also modulated by current.

From the band structure calculations the band gap can be extracted as a function of the current. Then the band gap can be turned into the longest possible wavelength of absorbed radiation $\lambda_{\text{max}}$ and this is plotted in Fig.3 for different values of the net current density. Being a semiconductor wire, polyacetylene is transparent to the photons with wave length longer than $\lambda_{\text{max}}$ (i.e. with the energies within the band gap) but it is opaque to photons with wavelength shorter than $\lambda_{\text{max}}$ (within the bandwidth). It is clear from that the boundary between transparent and opaque black parts of the spectrum is blue-shifted by current flow in the polyacetylene wire. In other words, the color of the polyacetylene wire can be modified by electric current.

In this Letter, we have laid a theoretical ground-work for computing a Born-Oppenheimer potential energy surface for molecular wires with direct current. Within the Lagrange multiplier based transport theory we presented a computational tractable theoretical scheme to compute BO of molecular wire junctions. Based upon applications of the techniques to tight-binding model with electron-phonon interactions we predict that (1) the dimerization of the polyacetylene wire is amplified by current; (2) the transparent-opaque boundary is blue-shifted by current flow; (3) the generic mechanism of the semiconductor wire breakage is current increased dimerization.

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