Extending the Newns-Anderson model to allow nanotransport studies through molecules with floppy degrees of freedom

IOAN BÂLDEA(a)

Theoretische Chemie, Physikalisch-Chemisches Institut, Universität Heidelberg - Im Neuenheimer Feld 229, D-69120 Heidelberg, Germany, EU

E-mail: ioan@pci.uni-heidelberg.de; also at NILPR ISS POB MG-23 - RO 077125 Bucharest Romania, EU.

received 28 June 2012; accepted in final form 24 July 2012
published online 8 August 2012

PACS 73.63.Rt – Nanoscale contacts
PACS 81.07.Mb – Molecular nanostructures
PACS 85.65.+h – Molecular electronic devices

Abstract – The Newns-Anderson model is ubiquitous in studies of the molecular transport in the presence of solvent (outer) reorganization. The present work demonstrates that intramolecular reorganization can also be significant for the transport through molecules with floppy degrees of freedom, for which the Newns-Anderson model can be extended. The expressions of the model parameters deduced from electronic structure calculations for (4,4′)-bipyridine (44BPY) quantitatively differ from those characteristic for outer reorganization due to strong intramolecular anharmonicities. These expressions can be utilized as input in transport calculations for 44BPY-based molecular junctions of experimental interest (Xu B. and Tao N. J., Science, 301 (2003) 1221; Pobelov I. V. et al., J. Am. Chem. Soc., 130 (2008) 16045; Widawsky J. R. et al., Nano Lett., 12 (2012) 354).

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Introduction. – When an electron subjected to a source-drain bias $V$ is transferred from the negative electrode into (say) the empty LUMO of a neutral molecular system $M^0$ embedded in a molecular junction, a transient radical anion is created in a first process ($M^0 \rightarrow M^{-}$), which is subsequently transferred to the positive electrode ($M^{-} \rightarrow M^0$). If these charge transfer processes are fast (strong electrode-molecule coupling), they cannot be considered as separate events; electron transport proceeds by coherent tunneling. The nuclei are frozen at the optimum molecular geometry $Q_0$. This picture is ubiquitously adopted to describe vacuum molecular junctions within NEGF (nonequilibrium Green’s functions) approaches [1].

For molecular junctions immersed in electrolytes [2], this picture has a counterpart called adiabatic transport [3–5], which can be summarized as follows. At a given solvent configuration $Q$, the molecular device is traversed by a so-called partial electric current $j(V; Q)$ [3–5] which is the result of coherent tunneling. The slow solvent dynamics with respect to the electronic motion legitimizes the usage of a classical effective coordinate $Q$. Changes in $Q$ model solvent’s dipoles/charges that rearrange to stabilize the extra anion’s charge and induce significant variations of the Gibbs adiabatic free energy $\mathcal{G} = \mathcal{G}(Q; V)$ [3–5] at a time scale much shorter than the measurement times. Therefore, as schematically depicted in fig. 1, to compare with experiments one has to consider the so-called total current $I(V)$, which is obtained by ensemble-averaging the partial current with a weight function $\mathcal{P}(\mathcal{G}(Q); V)$ that depends on $\mathcal{G}(Q; V)$ (cf. eq. (10) below).

The Newns-Anderson model [6,7] is widely employed in these studies [3,5,8]. Since early studies on atoms absorbed on a metal surface [7], this model continues to be used to describe phenomena of recent interest for molecular electronics, e.g., transition voltage spectroscopy [9–12]. It models the molecule as a single level $\varepsilon_0$, which mediates the tunneling between the source and the drain. This level models the closest molecular orbital (LUMO for n-type conduction) to the metal’s Fermi energy $\varepsilon_F$. For a molecule immersed in electrolytes, its energy $\varepsilon_0 = \varepsilon_0(Q)$ fluctuates due to solvent reorganization [3,5,8].

The aim of the present letter is fourfold: i) to extend the Newns-Anderson model to include intramolecular nuclear reorganization; to show that this extension ii) is relevant for molecules of current interest in molecular electronics but iii) the underlying functional dependences...
differ from those describing the solvent reorganization; iv) to deduce these dependences from electronic structure calculations. Thus, information will be provided that can be subsequently used as input for transport studies based on realistic parameters. Transport calculations and comparison with experiments [13–15] deserve a special analysis and will be the object of a separate publication.

**Specific details.** As a concrete molecule, (4, 4′)-bipyridine (44BPY) will be considered in the present study. In view of its special structure (cf. fig. 2), with two active nitrogen atoms in para positions, 44BPY is particularly suitable for simultaneous binding to two metallic electrodes. It has been utilized to demonstrate for the first time the possibility of repeated formation of molecular junctions [13]. Compounds based on 44BPY, commonly known as “viologens”, attracted considerable attention for many decades. 44BPY molecules have been incorporated in redox active tunneling junctions to demonstrate the LUMO electrolyte gating [2]. Several theoretical studies devoted to electron transport in 44BPY [15–18] considered the coherent tunneling at fixed geometry but did not examine the impact of intramolecular reorganization.

The quantum chemical calculations for the present study have been done with the Gaussian 09 package [19] at the density functional theory (DFT) level by using the B3LYP functional. Basis sets of double-zeta quality augmented with diffuse functions (Dunning aug-cc-pVDZ) for the light atoms and with relativistic core potential (cc-pVDZ-PP from ref. [20]) for gold have been employed.

**The spinless Newns-Anderson model.** The central assumption of the transport approaches based on the Newns-Anderson model is that electric conduction is dominated by a single molecular level. As shown below, this should certainly be the case for molecular junctions based on 44BPY [13,15,21]. From ∆-DFT calculations [22], we deduced a HOMO-LUMO gap ∆ = E_C + E_A − 2E_N = 8.5 eV. This quantity, expressed in terms of the energies (E) of the cation and anion radicals, and neutral species (subscripts C, A, and N, respectively) is the counterpart of the so-called charge gap used in solid-state or mesoscopic physics (see ref. [23] and citations therein). Screening effects narrow down this gap [24], but it certainly exceeds the Kohn-Sham HOMO-LUMO gap (∆_KS = 4.97 eV [16]), which is known to drastically underestimate ∆. If the electrodes’ Fermi level were located midway between HOMO and LUMO (a situation wherein the Newns-Anderson model would inherently fail, since both HOMO and LUMO should contribute significantly), the transmission (Gamow formula)

$$T \approx \exp(-2d/\sqrt{2m/\hbar^2})$$

through an underestimated energy barrier of height ∆/2 = ∆_KS/2 = 2.49 eV and spatial extension d = 2d_{N+Au} + l_{44BPY} ≃ 2 × 2.4 + 7.11 Å ≃ 11.9 Å would yield a conductance $G/G_0 \approx 10^{-3}$, which is completely at odds with the experimental values ($G/G_0 \approx 10^{-6}$–$10^{-3}$ [13,15]). Here, $G_0 = 2e^2/h = 77.48 \mu S$ is the conductance quantum. To conclude, the assumption of a dominant MO appears to be reasonable for 44BPY. Whether the LUMO (electron/n-type conduction) or the HOMO (hole/p-type conduction) is the dominant MO cannot be determined from transport measurements in two-terminal setups alone. This issue can be addressed, e.g., in electrolyte gating [2] or thermopower studies [15]. Because they revealed an n-type conduction, we will restrict ourselves below to the case of a LUMO-mediated conduction.

Within the most general Newns-Anderson model [6,7], the single MO of energy $\epsilon_0$ it contains can be empty ($n_{\uparrow, \downarrow} = 0$), single ($n_{\uparrow} = n_{\downarrow} = 1$), or doubly ($n_{\uparrow} = n_{\downarrow} = 1$) occupied, corresponding to the neutral, radical anion, and dianion species, respectively. The second-quantized Hamiltonian has the expression

$$H = \sum_{\sigma=\uparrow, \downarrow} \epsilon_0 \left( n_\sigma + U n_{\uparrow} n_{\downarrow} + \epsilon_\text{ph} \langle Q \rangle \right),$$

where $n_\sigma = c^\dagger_\sigma c_\sigma$ denote electron number operators. A Hubbard-type interaction accounts for the Coulomb repulsion $U$ between the two spin directions. In an STM-setup, the molecule is coupled to two electrodes
(substrate $s$ and tip $t$). The average molecule-electrode couplings $\tau_{s,t}$ determine a nonvanishing level width characterized by the broadening functions $\Gamma_{s,t} \propto \tau_{s,t}^2$ [1].

The active MO is coupled to classical intramolecular (and, if the case, solvent) vibrational modes $Q$ that reorganize upon charge transfer. They modulate the MO energy $\varepsilon_0(Q)$ and store an energy $\varepsilon_{\phi h}(Q)$. This yields a $Q$-dependence of the total energy $E(Q) \equiv (H)$. For convenience, the energy at the neutral optimum $Q_0$ will be taken as energy zero, $E_N(Q_0) = 0$.

An important issue in molecular transport is whether the double occupancy of the active MO is significant or not. Albeit entirely correct only if a single-particle picture (on which the DFT description relies) is applicable, the analysis can be done by observing that eq. (1) can be described in terms of two single-electron states of energies $\varepsilon_1(Q) = \varepsilon_0(Q)$ and $\varepsilon_2(Q) = \varepsilon_0(Q) + U$ ($\varepsilon_1 < \varepsilon_2$, $U > 0$). The charge transfer efficiency is determined by the energy differences $\varepsilon_1,2 - \varepsilon_F$. Fluctuations in $\varepsilon_0(Q)$ induced by phonons are of the order of the reorganization energy $\lambda$, which typically amounts to a few tenths of electron volts [2]. So, a doubly occupied LUMO gives a significant contribution only if $U$ is at most of the order of $\lambda$; otherwise, the state of energy $\varepsilon_2$, too high above the Fermi level, is blocked, and only that of energy $\varepsilon_1$ is relevant.

The Coulomb blockade parameter $U$ cannot be directly determined from transport data in a simple manner [25–27]. Within DFT, $U \rightarrow U_{KS}$ obtained from energy splitting of the Kohn-Sham LUMO “orbitals” is $U_{KS} = 1.54, 1.52$, and $1.26\, eV$ for a 44BPY molecule in vacuum, in (aqueous) solution, and in solution with one gold atom attached at each of the two metal atoms, respectively. Similarly, to the case of the DFT HOMO-LUMO gap, $U_{KS}$ drastically underestimates $U$. A substantially higher value is obtained via the more accurate method of energy differences based on eq. (1), $U = E_N + E_D - 2E_A = 1.92\, eV$ (instead of $1.26\, eV$), for the last of the three aforementioned situations (substrate $D$ stands for diadion). Still, what is really important for the present purpose is that $U$ is much larger than the reorganization energies (see below). Transfer processes with a doubly occupied LUMO are energetically too costly and can be ignored in electronic transport through 44BPY. So, one can safely employ a spinless Newns-Anderson model Hamiltonian $(n = c^\dagger c)$,

$$H = \varepsilon_0(Q) n + \varepsilon_{\phi h}(Q),$$

as done in existing studies, e.g., refs. [3,5,8].

The total energies of the radical anion $E_A(Q)$ and neutral species $E_N(Q)$ can be used to microscopically compute the $Q$-dependence of the parameters entering eq. (2),

$$\varepsilon_{\phi h}(Q) = E_N(Q), \quad \varepsilon_0(Q) = E_A(Q) - E_N(Q).$$

Notice that the LUMO energy $\varepsilon_0(Q)$ expressed above is measured with respect to the vacuum. The reorganization energies of the radical anion ($\lambda_A$) and the neutral ($\lambda_N$) species are important quantities defined by

$$\lambda_N = E_N(Q_A) - E_N(Q_0); \quad \lambda_A = E_A(Q_0) - E_A(Q_A),$$

where $Q_A$ denotes the radical anion optimum geometry.

All the phenomenological approaches of molecular transport in electrolytes based on the spinless Newns-Anderson model of which we are aware (e.g., refs. [2,4,5,8,28]) assume harmonic $Q$-dependences of $E_N$ and $E_A$, and this yields ($Q \not= \{Q_\nu\}$; henceforth $Q_0 \equiv 0$)

$$\varepsilon_{\phi h}(Q) = \frac{1}{2} \sum_\nu \omega_\nu Q_\nu^2,$$

$$\delta\varepsilon_0(Q) \equiv \varepsilon_0(Q) - \varepsilon_0(Q = 0) = -\sum_\nu g_\nu Q_\nu.$$

In the cases where eqs. (5) and (6) apply, the above reorganization energies are equal,

$$\lambda_N = \lambda_A = \lambda \equiv \sum_\nu g_\nu^2 \frac{2}{\omega_\nu^2}.$$
vibrational modes. Composed of 20 atoms, the nonlinear 44BPY molecule has 54 normal vibrations. In the D$_2$ point group symmetry, they are distributed as 14A + 12B$_1$ + 14B$_2$ + 14B$_3$; 10A + 9B$_1$ + 9B$_2$ + 9B$_3$ are in-plane vibrations and 4A + 3B$_1$ + 5B$_2$ + 5B$_3$ are out-of-plane vibrations [31]. Our extensive calculations confirmed the expectation that significant contributions to the reorganization energy arise from the in-plane normal modes with A symmetry. Out of the ten in-plane modes of A symmetry we have identified two modes that dominate the inner reorganization. As expected, they are related to the main structural differences between 44BPY$^0$ and 44BPY$^{-}$.

One of these modes (normal coordinate $Q_{16}$) is related to the so-called quinoidal distortion [31] of the neutral molecule upon electron attachment (44BPY$^0$ + e$^-$ → 44BPY$^{-}$), with a shortening of the inter-ring C-C bond and of the C-C bond parallel to it, and a lengthening of the C-C bond between them as well as of the C-N bond. Adiabatic energy curves $E_{N,A}(Q_{46})$ reveal a virtually perfect harmonic behavior, which agree with eqs. (5) and (6) and yield equal partial reorganization energies $\lambda^2_{N} = \lambda^2_{A}$. Because its frequency ($\omega_{46} = 1642$ cm$^{-1}$ $\approx$ 0.2 eV) excellently agrees with the strong Raman band observed experimentally at 1645 cm$^{-1}$ [31]), this mode is too fast to significantly reorganize by the classical thermal activation considered in this study.

The inequality $\lambda_N \neq \lambda_A$ traces back to the most appealing feature of the molecular structure, namely the inter-ring twisting angle $\theta$. The mode directly related to the inter-ring torsional motion represents the floppy (label $f$) degree of freedom of 44BPY. Adiabatic energy curves $E_{N,A}(Q_f)$ along the normal coordinate $Q_f$ exhibit strong anharmonicities. Its (harmonic) frequency is very low ($\omega_f \approx 62$ cm$^{-1}$ in the isolated molecule, cf. table 1), but the impact on reorganization is important because large-amplitude oscillations are significant. The partial reorganization energy of the radical anion $\lambda^4_{N} \approx 0.16$ eV is almost two times larger than that of the neutral molecule ($\lambda^4_{N} \approx 0.09$ eV). From the adiabatic $E_{N,A}$-curves obtained by quantum chemical calculations, the functional dependences of the model parameters $\varepsilon_0(Q_f)$ and $\varepsilon_{ph}(Q_f)$ can be computed from eqs. (3). The results of these calculations are collected in fig. 3(a). They show significant deviations from the linear and quadratic $Q_f$-dependences of $\varepsilon_0(Q_f)$ and $\varepsilon_{ph}(Q_f)$, respectively. The latter approximations are represented as dashed lines in fig. 3(a).

Beyond the case of an isolated molecule. – The results discussed above refer to an isolated 44BPY molecule in vacuum. Cases of breakdown of the harmonic approximation for low-frequency vibrations in isolated molecules are well known in molecular physics [32]. However, we are not aware of studies pointing out the failure of the harmonic approximation for floppy molecules used to fabricate molecular junctions, like in the case discussed above. For molecular transport, it is also important to consider the case of a 44BPY molecule immersed in an electrolyte and linked to metallic electrodes [2,13,15].
In the present study on 44BPY in aqueous solution (label sol), the solvent has been considered within the polarized continuum model using the integral equation formalism (keyword SCRF=IEFPCM in Gaussian 09). The results (fig. 3(h) and table 1) indicate that the most important solvent effect is an almost constant shift in the LUMO energy. It is related to the strong interaction of the anion with the water molecules. The largest contribution to the vertical electron affinity in solution comes from the anion’s solvation free energy $\Delta G_A = E_A^{sol}(Q_A^{sol}) - E_A(Q_A) \simeq -2.01 \text{ eV}$. Here, $Q_A^{sol}$ denotes the optimized geometry of the radical anion in solution.

As a preliminary step in investigating the impact of electrodes, we have also considered the case of a 44BPY molecule with two gold atoms attached to the nitrogen atoms. The corresponding results (fig. 3(c)) reveal an effect qualitatively similar to that of the solvent.

So, apart from a nearly constant shift of the LUMO energy, for $Q_I$-values of interest (cf. fig. 3), the model parameters $\varepsilon_0(Q_I)$ and $\varepsilon_{ph}(Q_I)$ vary within ranges, which appear to be little sensitive to the presence of solvents or electrodes. The physics behind the similarity exhibited by the these numerical results is the following. The twisting angle $\theta$ of the 44BPY molecule is determined by the competition between the $\pi$-electronic interaction of the pyridyl fragments, which favors $\pi$-electrons delocalized between coplanar pyridyl rings ($\theta = 0$), and the steric repulsion between the ortho H atoms, which is diminished by a twisted conformation ($\theta \neq 0$) [33]. The latter prevails in the neutral species 44BPY$^0$ (empty/oxidized LUMO), which is nonplanar (fig. 2). By adding an extra electron (occupied/reduced LUMO), the energy gain resulting from $\pi$-electron delocalization between the two rings outweighs the steric repulsion, and the radical anion (44BPY$^{*-}$) becomes planar. Therefore, a structural transition from the twisted to the planar conformation can only be suppressed if a significant negative charge is transferred to the 44BPY unit. This cannot be achieved by immersing in solution, nor even by attaching gold atoms. In the latter case, the gold atoms acquire a small negative charge ($\sim -0.099 e$), which has a negligible impact on the torsion angle $\theta$.

Summary and outlook. – The present results emphasize the need to consider the inner relaxation in junctions based on molecules with floppy degrees of freedom; the reorganization energies deduced here ($\Lambda \sim 0.1$–0.2 eV) are comparable with those for outer (solvent) reorganization [2]. To avoid misunderstandings three comments are in order. i) The present analysis of the inner reorganization (conformational distortions) has implicitly assumed a given (e.g., atom, hollow, bridge) contact geometry; variations in the binding geometry may be larger (e.g., refs. [14,34]) but they are of a different nature. ii) The $Q_I$-dependence of the partial current and conductance discussed here refers to a given molecule (44BPY); this is qualitatively different, e.g., from the scaling $G \propto \cos^2 \theta$ discussed previously [14,34,35], which refers to various derivatives of a molecular family (e.g., biphens) wherein the torsion angle $\theta$ is varied, e.g., by a bridging (alkyl) chain. iii) $\theta$ cannot be specified in terms of the single normal coordinate $Q_I$ only. Thermal averaging over $\theta$ (as done for biphens) [14]) amounts to considering that, concomitant with the floppy mode $\omega_I$, other modes of much higher frequency are also thermally activated. Because such fluctuations are energetically costly in biphens, their effect is reduced [14].

While revealing that a spinless Newns-Anderson is justified for 44BPY, the present study has shown that $Q$-dependences of eqs. (5) and (6) assumed to work in electrolytes are inappropriate for the reorganization of low frequency intramolecular vibrations, which are characterized by a pronounced anharmonic behavior.

New formulas for $\varepsilon_0(Q_I)$ and $\varepsilon_{ph}(Q_I)$ have been deduced from microscopic calculations (cf. eqs. (9)), which replace the expressions of eqs. (5) and (6) used for solvent reorganization. The $Q_I$-dependence of the model parameters is important because the ensemble average needed to compute the experimentally relevant quantity, namely the total current $I(V)$, requires an integration over $Q_I$,

$$I(V) = \langle j(V; Q_I) \rangle = \int j(V; Q_I) P(Q_I; V) dQ_I. \quad (10)$$

The fact that 44BPY possesses a single low-frequency vibrational mode that significantly reorganizes represents an enormous simplification; otherwise, an ensemble average involving a $Q$-integration over all of the 54 internal degrees of freedom would be a formidable numerical challenge.

The thermal weight function $P(Q_I; V) \propto \exp[-G(Q_I; V)/(k_B T)]$ is determined by the Gibbs free energy $G(Q_I; V)$ of the (partial) oxidation state of the molecule (i.e., LUMO occupancy $0 < n(Q_I; V) < 1$) linked to biased electrodes. $G$ depends on $Q_I$, $V$, and (if applicable) on electrolyte’s overpotential [2–5]. The need to carry out an ensemble averaging is an essential
aspect, which renders purely \textit{ab initio} approaches (as used for rigid molecules in vacuum) inapplicable; therefore, feasible approaches to date have to resort to models.

The above results can (and will) be used in subsequent studies to deduce the current within the adiabatic transport approach, for which eq. (10) can serve as starting point. Expressions for the partial current \( j(V; \varepsilon_0(Q_f)) \) and the level (LUMO) occupancy \( n(\varepsilon_0(Q_f); V) \) are known [5,8,36,37]. Along with the expression of \( \varepsilon_{ph}(Q_f) \), the LUMO occupancy is required to express the \( Q_f \)- (and \( V \)-) dependent Gibbs adiabatic free energy \( G \). One should emphasize at this point that \( G(Q_f; V) \) is not simply related to the adiabatic energies \( E_{N,A}(Q_f) \); the former quantity characterizes a molecule linked to biased electrodes, while the latter quantities pertain to an isolated molecule.

Earlier studies demonstrated that even a single reorganizable harmonic mode, eq. (8), yields highly nontrivial adiabatic \( G \)-surfaces [5,8]. In view of the significant anharmonicities embodied in the expressions adequate for a floppy degree of freedom, one can expect more complex adiabatic surface topologies, with the need to distinguish between several important limiting cases. To simply motivate this, one should note that, unlike in electrolytes, reorganization effects in floppy molecules cannot be merely characterized with the aid of a single quantity \( (\lambda = \lambda_N = \lambda_A) \).

As shown recently [11,12], the impact of fluctuations on the MO energy offset \( \varepsilon_0 \equiv \varepsilon_0 - \varepsilon_F \) on the Ohmic conductance can be significant. Molecule-electrode interactions can be important sources of such fluctuations [11]. In view of the present study, in molecular junctions like those based on 44BPY fabricated experimentally [2,13,15], one can expect that, even in the absence of other effects, reorganization effects represent an important source for large \( \varepsilon_0 \)-fluctuations \( (\delta\varepsilon_0 \sim 0.2-0.4 \text{ eV}) \). As a straightforward application, one can employ eq. (10) to compute conductance histograms, which can be directly compared with those available from experimental studies [13,15].

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The author thanks HORST KÖPPEL for valuable discussions and the Deutsche Forschungsgemeinschaft (DFG) for financial support.

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