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Non-equilibrium Atomic Limit for Transport and Optical Response of Molecular Junctions

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ABSTRACT

Theoretical tools employed in *ab initio* simulations in the field of molecular electronics combine methods of quantum chemistry and mesoscopic physics. Traditionally these methods are formulated in the language of effective single-particle orbitals. We argue that in many cases of practical importance a formulation in the language of many-body states is preferable. We review methods of the non-equilibrium atomic limit and our contributions to their development and applications. In particular, model and *ab inito* simulations of quantum transport and optical response in molecular junctions illustrate convenience and importance of the methodology. Results of *ab initio* simulations are compared with experimental data.

KEYWORDS: molecular electronics, nanoplasmonics, inelastic transport, generalized quantum master equation, pseudo-particle non-equilibrium Green functions, Hubbard non-equilibrium Green functions.

INTRODUCTION

Since molecules were proposed as possible active elements of electronic devices in the founding paper by Aviram and Ratner,[1] and first measurements in single molecule junctions were reported,[2] molecular electronics experienced enormous progress due to fast development and refinement of nanoscale experimental techniques.[3,4] Along the way focus of the research has shifted from elastic current-voltage measurements in single-molecule junctions[5] to inelastic electron tunneling spectroscopy (IETS)[6] and atomic-scale molecular imaging,[7,8] to heat transport[9-12] and thermoelectric properties of molecular devices,[13-15] to noise measurements[16,17] and quantum interference effects in junction characteristics.[18-20] Recently molecular spintronics, where spin flux rather than charge current is monitored, has revealed itself as a branch of molecular electronics.[21-27] Finally, tremendous progress in laser technologies together with advances in fabrication techniques (in particular, the ability to produce nanometer scale gaps, creating areas of strong local electromagnetic field – "hot spots",[28-31] lead to the development of molecular optoelectronics,[32-34] where optical response of a current carrying junction reveals information on the vibrational structure,[35-37] heating,[38,39] and dynamics[40-43] of the open non-equilibrium molecular system.

Development of experimental capabilities to perform measurements in single-molecule junctions posed a challenge for adequate theoretical description. Such a theoretical method is expected to combine quantum chemistry methods for simulation of electronic (and vibrational) structure of a molecule with transport approaches to describe the response of an open non-equilibrium molecular system. Popularity of the density functional theory (DFT)[44,45] (or its time-dependent variant, TDDFT[46,47]) as a tool capable of large-scale electronic structure calculations together with the history of using non-equilibrium Green function technique (NEGF)[48,49] as a method for quantum transport in mesoscopic physics,[50,51] naturally led to combination of the two approaches into non-equilibrium Green functions – density functional theory (NEGF-DFT) technique.[52-54] The NEGF-DFT was successfully applied in *ab initio* simulation of both elastic[55-59] and inelastic[60-64] transport in molecular junctions where perturbation theory in intra-molecular interactions is applicable (either at off-resonant regime or when electron-vibration interaction is small).[65] Recently first principle simulations of noise in junctions were reported within the NEGF-DFT.[66] Note that while the technique has some methodological problems[67-70] (for example, Landauer-DFT may even lead to qualitative failure[71] in the prediction of transport characteristics), still recent developments of improved functionals,[72-74] state of the art combinations of DFT with many-body theory (in particular, GW),[75-77] and the development of the stochastic DFT approaches[78] assures popularity and usefulness of the methodology for many problems of practical importance in molecular electronics.

The close match between the NEGF and DFT stems from the common language of elementary excitations (*quasi-particles*) in description of the underlying system dynamics. Quasi-particles originated in the Landau theory of Fermi liquid[79] as an effective single-particle representation of elementary excitations on top of the ground state of a large many-body system. The language of quasi-particles found its application in many branches of condensed matter physics, and in particular in quantum transport in mesoscopic systems. In quantum chemistry this language is utilized when the electronic structure is represented as a set of atomic, molecular, or Kohn-Sham orbitals. As long as elementary-excitations are non- or weakly interacting, the corresponding description is extremely convenient since a complicated many-body problem is effectively reduced to a non (or weakly) interacting single-particle representation. This is usually the case in mesoscopic physics, where an object of interest (quantum dot) is a rather big system, so that adding or removing an electron does not lead to significant change in its electronic structure. Molecules utilized in electronic devices are usually much smaller objects, and thus are sensitive to oxidation/reduction/excitation. Still the quasi-particle description of transport is convenient as long as electron tunneling takes place far from molecular resonances or if intra-molecular interactions are weak. Note however that most interesting regime relevant for applications is resonant tunneling with relatively strong intra-molecular interactions. Indeed, a large response of the molecular structure to external perturbation (e.g. negative differential resistance,[80-86] current induced chemistry[87]) is a requirement for constructing an effective molecular device. In this regime one has to deal with strongly interacting quasi-particles, and thus a description in terms of many-body states of the isolated molecule – the non-equilibrium atomic limit - may become preferable (see Figure 1).

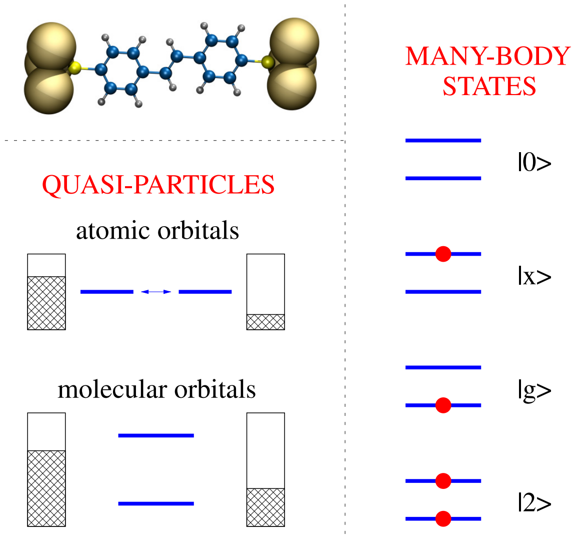


Figure 1. Two approaches to quantum transport in molecular junctions: quasi-particles vs. many-body states representation.

Many-body states are the basis of choice in many experimentally relevant situations when system degrees of freedom are mixed by interaction or when their quantization is non-trivial. For example, a breakdown of the Born-Oppenheimer approximation due to coupling between two quasi-degenerate electronic orbitals by molecular vibration was observed in molecular junctions.[88] In this situation, when mixing of electronic and vibration degrees of freedom leads to the physics of avoided crossing, a basis of vibronic states provides a more convenient representation for the transport problem. Similarly, when resonant IETS (RIETS) in Coulomb blockade regime shows vibrational features, which depend on charging state of a molecule,[89,90] quasi-particle representation is not the most convenient way to simulate those features. Another example in favor of many-body states representation comes from the field of molecular optoelectronics. Since single-molecule optical response is feasible only by amplification of the signal by surface plasmon-polariton excitations,[91,92] the process of radiationless energy transfer between molecule and contacts is important for any realistic theoretical description of optical response in molecular junctions.[93,94] For molecules chemisorbed on metallic surfaces molecular excitations are strongly mixed with plasmons in the contacts.[95-97] Moreover, in molecular junctions, where both charge and energy transfer happen simultaneously, rigorous description is complicated by the non-quadratic nature of the energy transfer matrix element, and corresponding theoretical considerations usually rely on approximations.[98,99] Similarly, such mixing is at the heart of the charge-transfer surface enhanced Raman spectroscopy (CT-SERS).[100] Clearly, representation of the Hamiltonian in terms of many-body states makes the treatment easier. Finally, a quasi-particle representation of an impurity spin degree of freedom (e.g. relevant for description of spin-flip IETS experiments in molecular junctions) is valid for excitations around a ground state only,[101] while a many-body formulation yields general and straightforward analysis of experimental findings.[102]

Below after an overview of the methods usually applied in the molecular electronics community to simulate quantum transport, when many-body states formulation is utilized, we review our implementations and generalizations of the methods. We then illustrate their applicability in models and *ab initio* simulations relevant for transport and optical response in molecular junctions. We summarize our findings and indicate future directions of research in the conclusions.

METHODS

Among the theoretical tools usually employed, when description in the language of many-body states $\{|S_i\rangle\}$ is required, wave function (WF) and density matrix (DM) based approaches are most common (see Fig.2). The former is often treated within single particle scattering theory framework,[103-108] and as long as elastic transport in a non-interacting system is in the focus, the approach is exact. In particular, the famous Landauer-Buttiker formalism[109] is the scattering theory consideration.[110,111] Note that quasi-particle representation works perfectly well for non-interacting systems. In the presence of inelastic processes single-particle scattering becomes invalid.[112,113] For example, it misses information on the blocking of scattering channels due to the Pauli principle, or distortion of the target due to intra-molecular interactions.

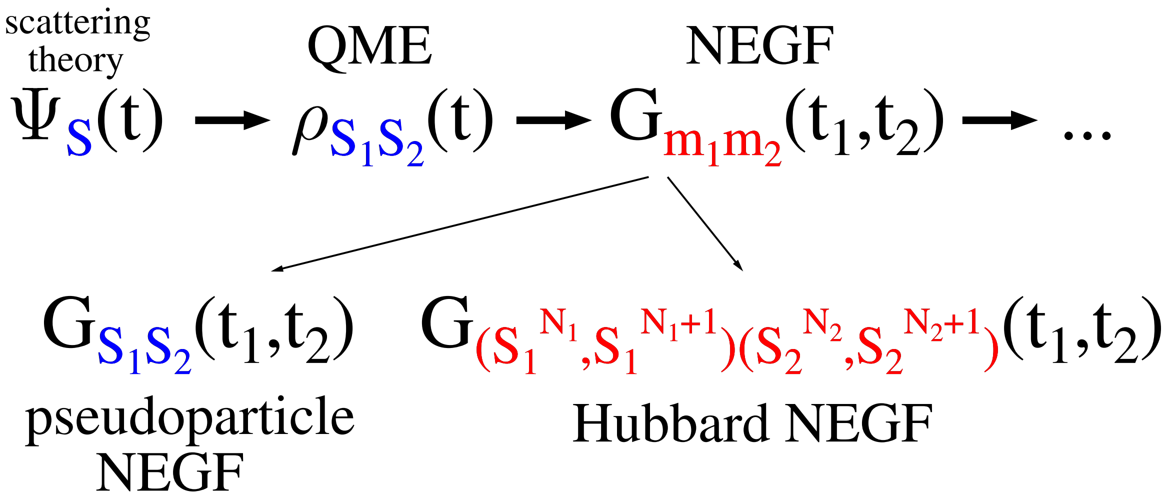


Figure 2. A scheme of many-body state formulations for quantum transport.

DM is a natural generalization in the case of reduced description where part of degrees of freedom (bath) is traced out. Here spatial correlation is taken into account, while the object is still time local. While formally an exact quantum master equation (QME) can be formulated,[114,115] in practice considerations based on perturbation theory in system-bath coupling are employed.[116-118] Second order perturbation theory leads to the Redfield QME; higher order (usually up to fourth) considerations are also available in the literature.[119-121] While Redfield QME has its own limitations,[122,123] the main problem in applying the methodology to describe transport in junctions is the fact that the formulation fails in the physically relevant low temperature regime, $T \ll \Gamma$ (T is temperature of the environment, Γ is electron escape rate).[120,124] With molecule chemisorbed on at least one of the junction contacts such restriction is unlikely to be satisfied: $T \sim 0.01 eV$ (at room temperature, $\Gamma \sim 0.01-0.1\, eV$ near metal surface.[125,126] Neglect of the molecule-contacts hybridization is not allowed in this case. The other deficiency arises in treating degeneracies in the system's many-body basis.[127]

To overcome the limitations and to explore a connection between DM and Green functions (GF, see below) approaches to quantum transport we pursued a non-perturbative approach in QME derivation. The starting point is writing exact equation-of-motion (EOM) for matrix element of the reduced density matrix $\sigma_{S_2S_1}(t) \equiv \langle S_2 | Tr_B[\hat{\rho}(t)] | S_1 \rangle = \langle \hat{X}_{S_1S_2}(t) \rangle$, where $\hat{\rho}(t)$ is full density operator, $Tr_B[\ldots]$ stands for trace over bath degrees of freedom, and $\hat{X}_{S_1S_2} \equiv |S_1\rangle\langle S_2|$ is the projection (Hubbard) operator onto many-body states of the system. The EOM expresses rate of change of the reduced DM in terms of the DM and two-time correlation functions of the Hubbard operators (lesser and greater projections of the Hubbard Green functions, see below).[128] As expected this expression is the first in an infinite chain of EOMs, which at each subsequent step involves more complicated multi-time correlations. The formulation is similar to hierarchical equation of motion approach,[129] except that our formulation involves many-body states of the system. To mimic a usual QME the chain should be truncated at the first step by expressing two-time correlation functions in terms of the reduced DM and an effective evolution. We formulated such truncations on the Keldysh contour[51]

$$\left\langle \hat{X}_{S_1S_2}(t_1)\hat{X}^{\dagger}_{S_3S_4}(t_2)\right\rangle \approx i\sum_{S_a,S_b}\left[U^{r}_{S_1S_2,S_aS_b}(t_1-t_2)\left\langle \hat{X}_{S_aS_3}(t_2)\right\rangle\delta_{S_b,S_4} - \left\langle \hat{X}_{S_1,S_a}(t_1)\right\rangle U^{a}_{S_aS_b,S_3S_4}(t_1-t_2)\delta_{S_2,S_b}\right] \quad (1)$$

and anti-contour[130]

$$\left\langle \hat{X}_{S_1S_2}(t_1)\hat{X}^{\dagger}_{S_3S_4}(t_2)\right\rangle \approx i\sum_{S_a,S_b}\left[\tilde{U}^{r}_{S_1S_2,S_aS_b}(t_1-t_2)\left\langle \hat{X}_{S_aS_3}(t_2)\right\rangle\delta_{S_b,S_4} - \left\langle \hat{X}_{S_1S_a}(t_1)\right\rangle \tilde{U}^{a}_{S_aS_b,S_3S_4}(t_1-t_2)\delta_{S_2,S_b}\right] \quad (2)$$

which yielded time-nonlocal[128] and time-local[131] versions of a generalized QME (GQME). The former is most suitable for the treatment of time-dependent and transient processes, while the latter is more convenient for the description of steady-state situations. Here $U^{r}_{S_1S_2,S_3S_4}(t) \equiv -i\theta(t) << \hat{X}_{S_2S_1} | e^{-iL_{eff}t} | \hat{X}_{S_4S_3} >>$ and $\tilde{U}^{r}_{S_1S_2,S_3S_4}(t) \equiv -i\theta(-t) << \hat{X}_{S_2S_1} | e^{-i\tilde{L}_{eff}t} | \hat{X}_{S_4S_3} >>$

are Liouville space retarded propagation operators on the contour and anti-contour, respectively, $U^{a}_{S_1S_2,S_3S_4}(t)=\left[U^{r}_{S_3S_4,S_1S_2}(-t)\right]^{*}$ and $\tilde{U}^{a}_{S_1S_2,S_3S_4}(t)=\left[\tilde{U}^{r}_{S_3S_4,S_1S_2}(-t)\right]^{*}$ are corresponding advanced operators, and L_{eff} ($\tilde{L}_{eff}$) is effective Liouvillian. In our studies[128,131] we employed the Redfieldian in place of the effective Liouvillian. This resolves limitations of low temperature and neglect of broadening in the QME. To overcome difficulties related to the presence of degeneracies in the system's many-body basis one needs to go beyond effective second order in the system-bath coupling. Substituting free system evolution in place of the effective Liouvillian reduces the GQME to the usual Redfield QME. Note that eq 1 is a generalization to Liouville space of an expression known in the standard non-equilibrium Green function (NEGF) methodology as the generalized Kadanoff-Baym ansatz (GKBA),[51] while eq 2 is its analog on the Keldysh anti-contour. Thus our formulation highlights a connection between DM and GF methodologies. Note also that alternative formulations deriving QMEs which display broadening are available in the literature[132-134] (see discussion in ref 128 on relation to our work), and that an essential systematic progress in this direction was reported recently.[135,136]

Time locality of the DM makes it mostly suitable for evaluation of time-local quantities. The GF is an object where correlation is preserved in both spatial and temporal variables. Non-equilibrium Green functions (NEGF) are the basis of the majority of *ab initio* simulations in molecular electronics. As discussed above, NEGF is formulated in the basis of elementary excitations, so that the spatial correlation is between quasi-particles, $\{m_i\}$, in the molecular (system) subspace of the problem (see Fig.2). Spectral decomposition of the quasi-particle creation operator, $\hat{c}_m^{\dagger}=\sum_{S_1,S_2}\langle S_1|\hat{c}_m^{\dagger}|S_2\rangle\hat{X}_{S_1,S_2}$, illustrates that one elementary excitation is a weighted mixture of all possible single electron transitions, $\hat{X}_{S_1,S_2}$, between many-body states of the molecule. Note the states $\left|S_1\right\rangle \equiv \left|S_1^{N+1}\right\rangle$ and $\left|S_2\right\rangle \equiv \left|S_2^{N}\right\rangle$ differ by single electron. Thus the closest many-body analog of the NEGF is a correlation function between Hubbard operators – the Hubbard NEGF. Alternatively, instead of working with the Hubbard (projection) operators one can consider second quantization in the space of many-body states (extended Hilbert space), $\hat{X}_{S_1,S_2} \equiv \left|S_1\right\rangle\left\langle S_2\right| \to \hat{p}_{S_1}^{\dagger}\hat{p}_{S_2}$. The physical subspace of this extended space is defined by the normalization condition (sum of probabilities to be in any of the available many-body states should be 1), $\sum_S \hat{p}_S^{\dagger}\hat{p}_S = 1$. Here $\hat{p}_S^{\dagger}$ ($\hat{p}_S$) are creation (destruction) operators of *pseudoparticles*. On-the-contour correlation functions of the pseudoparticles operators are called the pseudoparticle NEGF (PP-NEGF). Note that lesser and greater projections of both Hubbard and PP-NEGF taken at equal times, $t_1 = t_2 = t$, provide information on matrix elements of the reduced DM at time t.

The pseudoparticle (auxiliary operator) method originally was developed in condensed matter physics to describe strongly correlated systems. In the problem of a quantum dot with unpaired spin coupled to a bath, where three many-body states on the dot (empty and two singly-populated with different spin projections) are considered, the method is known as the slave-boson technique. Its non-equilibrium version was developed in refs 137-139. Recently interest to the methodology was renewed[140,141] due to development of the dynamical mean field theory (DMFT) approaches.[142,143] We proposed to apply the method to problems of quantum transport in molecular junctions, where description in the basis of many-body states of the molecule is preferred. In particular, we applied the methodology to describe quantum transport in resonant tunneling regime,[144-146] in problems of quantum nanoplasmonics,[147] and Raman spectroscopy of current-carrying junctions[148] (see corresponding sections below). In our opinion the PP-NEGF has several important advantages, which may make it a suitable alternative to NEGF for many problems of quantum transport in molecular junctions: 1. The method is capable of treating the quantum transport in the language of many-body states of an isolated molecule, thus taking into account all the intra-molecular interactions exactly; 2. The method is conceptually simple, developed well, its implementations are based on a set of controlled approximations (due to standard commutation relation of the pseudoparticles creation/annihilation operators all the luxury of the standard quantum field theory is at service of this many-body states based description); 3. Already in its simplest implementation (the non-crossing approximation, NCA) the method goes far beyond standard QME schemes, while retaining comparable level of numerical cost for simulations. Moreover, with systematic improvements (standard diagrammatic perturbation theory) are available, we judge the potential of the methodology to be higher than that of the generalized QME schemes. Note that similar to any approximate scheme the PP-NEGF has its own limitations (mostly in the low temperature regime).[137,149,150]

Contrary to pseudoparticles the Hubbard NEGF is formulated in the physical space (no necessity to restrict resulting expressions to a subspace of the problem). However formulation of the EOMs is less straightforward – commutation relations between the Hubbard operators do not allow utilization of the standard quantum field theory. Nevertheless, introducing auxiliary fields and employing technique of functional derivatives,[48] it is possible to write down exact EOMs for Hubbard GFs.[151-156] To make the EOMs practically suitable one has to use approximations to eliminate the auxiliary fields. For example, dropping the fields in the exact EOMs constitutes the first Hubbard approximation (HIA). This leads to[155]

$$\left[i\frac{\partial}{\partial\tau}-\omega-P\Sigma\right]G=P \tag{3}$$

where τ is the Keldysh contour variable, G is the Hubbard GF, ω is the free (system) evolution, Σ is the self-energy due to coupling to the contacts (baths), and P is the spectral weight. All these are matrices in both the space of single electron transitions between many-body states of the system and the contour variables. Formally, eq 3 differs from the standard NEGF EOM by presence of the spectral weight P, the latter is the consequence of non-canonical character of the Hubbard operators commutation relations. Although in the absence of degeneracies in the eigenbasis of the system the approach was shown to be exact,[157] and several simulations of transport in junctions were performed successfully by us[155,158] and others,[154,159] practical applicability of the scheme in general requires some care. In particular, straightforward application of the methodology in the presence of degeneracies in the system does not guarantee Hermiticity of the resulting reduced DM.[155] Moreover, pointing to the HIA as (in some sense) the lowest-order expansion in the Hubbard NEGF, ref 160 questioned the possibility in principle to build systematic theories based on the Hubbard GFs. Note that the problems with the HIA are not unique for the Hubbard NEGF. Symmetry breaking resulting from truncating an infinite EOMs chain was discussed in early works on equilibrium zero-temperature GFs.[161] Recently the issue attracted attention in connection to transport in junctions.[162,163] Note that sometimes a proper symmetrization can be identified explicitly.[164]

In general, truncation of EOMs chain induces an uncontrolled approximation, which can be justified only a posteriori. In the theory of equilibrium GFs, it was shown that use of projection operators (PO), which is popular in deriving DM QMEs, allows one to build an EOMs chain in such a way that its truncation becomes a well controlled approximation[165] (only higher order system-bath correlations are neglected). We generalized the methodology to problems of quantum transport in ref 166. Corresponding EOMs have the from of eq 3, although free evolution matrix ω and self-energy Σ differ from those of the HIA. What is more important, POs allowed us to introduce a set of canonical GFs, $\Im$, whose on-the-contour EOMs

$$\left[i\frac{\partial}{\partial\tau}-W-S\right]\Im=1 \tag{4}$$

have a form of the usual Dyson equation. Here W and S are canonical forms of free evolution and self-energy, respectively. This result has three important implications: 1. It resolves the problem of symmetry breaking in truncation of EOMs chain; 2. It shows explicitly the way to build a systematic expansion around the non-equilibrium atomic limit within the Hubbard NEGF; 3. Eq (4) is an expression defining a set of quasi-particles for the non-equilibrium atomic limit. These quasi-particles are not the usual (atomic, molecular, or Kohn-Sham) orbitals.

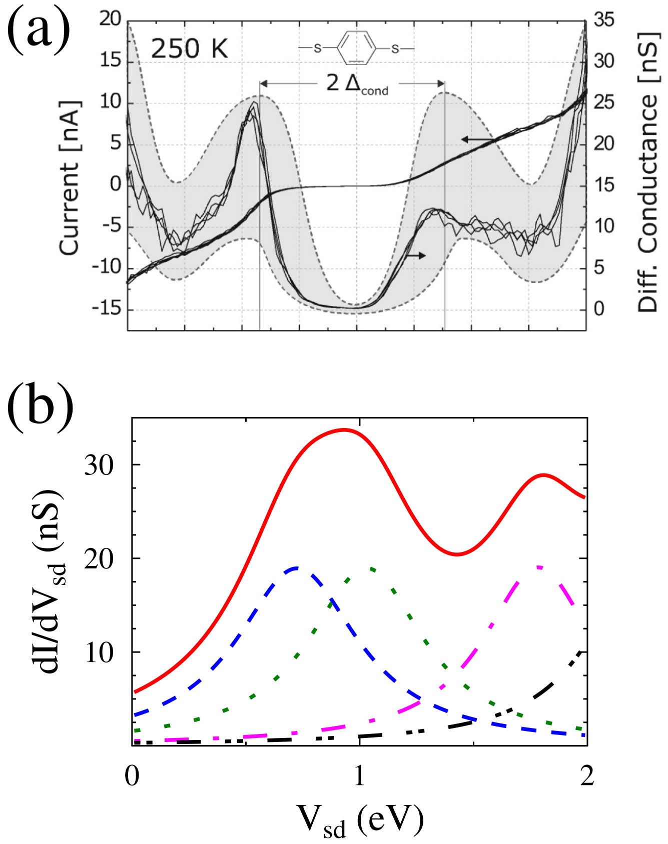
Finally, we note that while the non-equilibrium atomic limit treats all the on-the-molecule interaction exactly, correlations between molecule and contacts are accounted for only approximately. Schemes describing the latter (see e.g refs 167-176) are beyond the scope of this article. Note however, that such exact schemes are extremely heavy numerically, and thus hardly applicable in realistic *ab initio* simulations.

QUANTUM TRANSPORT IN MOLECULAR JUNCTIONS

Here we show model based and *ab initio* simulations of quantum transport in molecular junctions performed within the non-equilibrium atomic limit methods described in the previous section.

Elastic Transport

We start from elastic transport in benzene-1,4-dithiol molecular junction. This is the setup of the first single-molecule experiment,[2] reproduced with variations later in a number of measurements.[177,178] As the first experimental measurement in the field of molecular electronics, the problem attracted a lot of theoretical attention,[54,179-181] with calculations performed within the NEGF-DFT (or similar) methodology. Figure 3 demonstrates the application of a non-equilibrium atomic limit technique to simulate elastic transport in this junction.[1]



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[1] We note that in addition to elastic tunneling, higher order tunneling processes (such as inelastic cotunneling or pair tunneling) may contribute to the transport characteristics. Note however, that for model parameters relevant for the experiment of ref 178 (and utilized in our theoretical consideration in ref 158) these higher order processes can be safely ignored.

Figure 3. Elastic transport in the benzene-1,4-dithiol junction: (a) Experimental data. Reprinted with permission from E. Lortscher, H. B. Weber, and H. Riel, Phys. Rev. Lett. **98**, 176807 (2007). Copyright 2007 by the American Physical Society; (b) The Hubbard NEGF *ab initio* simulation of the total conductance (solid line, red) and contributions to it from individual transitions between many-body states of the molecule. Reprinted with permission from S. Yeganeh, M. A. Ratner, M. Galperin, and A. Nitzan, Nano Lett. **9**, 1770-1774 (2009). Copyright 2009 American Chemical Society.

Similar to quasi-particle based simulations we are able to reproduce conductance measurements within the Hubbard NEGF method. In addition to the total conductance (solid line) the non-equilibrium atomic limit technique allows us to identify also specific contributions ("electronic spectroscopy") due to individual transitions between many-body states of the system. In particular, the dashed line in Figure 3b corresponds to transition between neutral and anion ground states of the molecule, while the dotted, dash-dotted, and dash-double-dotted lines give contributions due to transitions between neutral ground and first, second, and third electronically excited states, respectively. Electronic structure simulations were performed within coupled cluster singles and doubles (CCSD), thus the result presented in Figure 3b is an illustration of a possibility to incorporate highly accurate quantum chemistry methods into quantum transport calculations, i.e. something which is not possible within the usual NEGF-DFT approaches.

Another example, where state-based methods may be preferable for elastic transport simulations, is non-linear conductance measurements (negative differential resistance, hysteresis, switching).[80-86] The observed behavior is often explained by the ability of a redox molecule to localize tunneling electrons, so that at each instant the redox state of the molecule defines transport characteristics of the junction due to Coulomb interaction between the redox site and the tunneling channels. Corresponding theoretical descriptions are based on models utilizing the Marcus theory for the redox center kinetics, with the Landauer approach employed for the quantum transport simulations.[182] In ref 145 we utilized the PP-NEGF methodology to judge about the applicability of the quasi-classical schemes in redox junction simulations. In particular, we showed that (as expected) at resonance the quasi-classical consideration breaks down. Also, we identified that depending on the ratio between characteristic intra-molecular (system) and contacts (bath) timescales different kinetic schemes should be employed in the off-resonant regime. Note that such timescale differences lead to measurable consequences.[183]

Inelastic Transport

One of the distinct features of molecules (as compared for instance to semiconductor quantum dots) is their configurational flexibility with a vibrational spectrum specific to a given molecular system. This implies that (a) inelastic effects in transport through molecular devices are a significant factor in their behavior, and (b) that the molecular vibrational spectrum can be employed as a basic diagnostic tool. Indeed, inelastic electron tunneling spectroscopy, noise measurements and, more recently, Raman scattering (see molecular optoelectronics section) are important characterization methods used to ascertain the presence of a molecule in the junction and to identify the active vibrational modes and their excitations (heating). As discussed above, quasi-particle based approaches are mostly adequate in the off-resonant regime. However, it is resonant inelastic transport, which is particularly relevant for technological applications. In addition, in this resonant transport regime, electronic and vibrational correlations have the strongest impact on transport, since the (effective) electron-vibration coupling is large, and the time spent by excess electron on the molecule is long. In particular, when actual charging (oxidation/reduction) or excitation of a molecule takes place, the resulting reorganization of molecular electronic and vibrational structure leads to state-dependent vibrational modes[87] and non-Born-Oppenheimer behavior[88] (see Figure 4a).

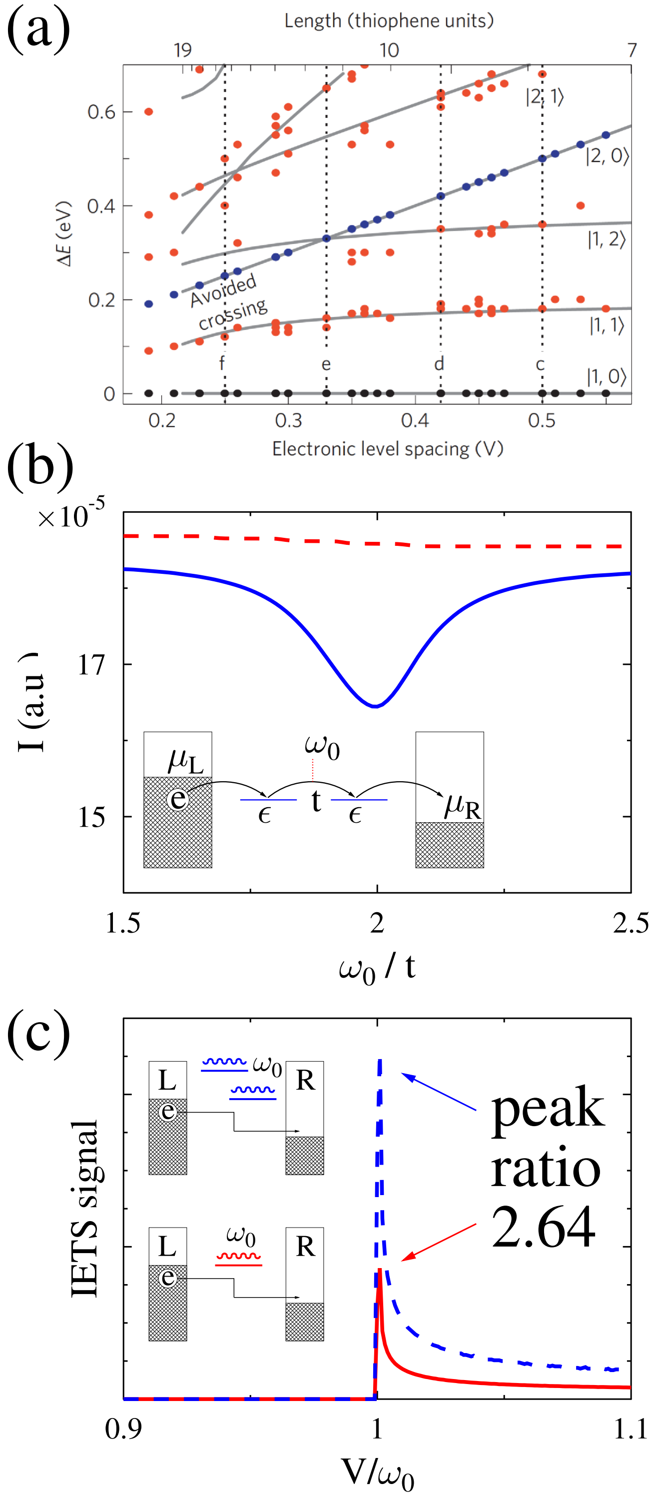

Figure 4. Inelastic transport: (a) Measurement of breakdown of the Born-Oppenheimer approximation (BOA) in oligothiophene molecular wires caused by vibrationally induced

electronic coherence. Reprinted by permission from Macmillan Publishers Ltd: J. Repp et al., Nat. Phys. 6, 975-979 (2010), Copyright 2010; (b) Model (see inset) simulation of breakdown of the BO approximation within the PP-NEGF (solid line, blue), the effect is missed by the standard NEGF (dashed line, red), A. J. White and M. Galperin, Phys. Chem. Chem. Phys. **14**, 13809-13819 (2012) – Reproduced by permission of the PCCP Owner Societies; (c) Model (see insets) simulation of vibrationally induced coherence in the IETS spectra. Reprinted with permission from M. Galperin and A. Nitzan, J. Phys. Chem. B **117**, 4449-4453 (2013). Copyright 2013 American Chemical Scoiety.

This regime is inaccessible within the standard NEGF formulations, which usually rely on the BOA and for strong interaction are mostly limited to linear electron-vibration coupling.[113] An approach capable of treating the electron-vibration interaction of any form and strength and without the BOA assumption is the "exact mapping" technique originally developed by Bonca and Trugman.[184-187] The essence of the "exact mapping" approach is representation of the many-body inelastic transport as a single electron scattering problem in a space of dressed states of the system. This is the main weakness of the technique when applied to transport in molecular junctions, and several *ad hoc* attempts to account for many-body character of the junction transport (presence of Fermi seas in the contacts) are available in the literature.[188,189] In ref 144 we pioneered the application of the PP-NEGF as a systematic non-equilibrium generalization of the "exact mapping" methodology. A model-based simulation of the breakdown of the BOA in junctions is presented in Figure 4b. The two timescales of the model (see inset in Fig. 4b) are defined by (a) the Rabi frequency, $\Omega_R = 2t$, due to elastic electron hopping between degenerate levels of the bridge; and (b) vibration frequency, ω_0, which defines inelastic electron tunneling between the levels of the bridge. At $\Omega_R = \omega_0$ the BOA does not hold, and (similar to experimental data presented in Fig. 4a) vibrationally induced coherence leads to interference in transport characteristics of the junction. The feature is accounted by the PP-NEGF (solid line), and is missed by the standard NEGF treatment (dashed line).

Note that usually inelastic processes are considered as a source of decoherence in the system. Coherence induced by electron-vibration coupling is less common, and Figs. 3a and b are experimental and theoretical manifestations of the effect. Another example where vibration induced coherence has an impact on measurable characteristics of a junction is shown in Fig. 3c. Here importance of a non-equilibrium atomic limit is demonstrated even for the off-resonant inelastic transport. Contrary to the usual interference between paths in space, in ref 190 we studied interference between paths in state space (coherence between dressed states of the multi-molecule junction), and the possibility of its experimental detection. Vibration induced coherence leads to a cooperative effect in multi-molecule junctions, which reveals itself in non-linear scaling of IETS signal with number of molecules. Note that describing the effect within a usual quasi-particle consideration is complicated even in the case of relatively weak electron-vibration coupling, where perturbation theory is applicable. The reason is the effective mean field character of low order considerations. For example, the popular self-consistent Born approximation (SCBA), an effective second order treatment of electron-vibration coupling, will not be able to account for the cooperative effect shown in Fig. 3c.

MOLECULAR OPTOELECTRONICS

The optical response of single molecules in junctions is detectable only in “hot spots” (areas of strong local field enhancement, usually caused by excitation of plamons in metal contacts). Correspondingly molecular optoelectronics roughly can be divided into two parts:

nanoplasmonics and optical response of molecular junctions. The former focuses on the formation of “hot spots” (plasmon excitations) and energy transfers in the system, while the latter deals with the formulation of techniques capable to describe optical response of open non-equilibirum molecular systems. Below we present examples of applications of methods of the non-equilibrium atomic limit to problems of the two branches of molecular optoelectronics.

Molecular Nanoplasmonics

Usually plasmon excitations are studied utilizing the laws of classical electrodynamics, while molecules in junctions are treated quantum mechanically.[94,191,192] Recently, quantum features in plasmon resonances of nanoparticles started to attract attention of researchers.[193-198] Molecular chemisorption on metallic surfaces results in strong hybridization between plasmon and molecular excitations[199,200] (see Figure 5a). Strictly speaking factorization into molecular and plasmon degrees of freedom is not safe in this case, and taking into account the inherently quantum character of molecular system, a quantum consideration of the whole system is required. The first attempt of a quantum consideration of a molecular Fano resonance near metallic nanoparticles was restricted to linear response regime.[201] Moreover, the quasi-particle language employed in the study made consideration of the strongly coupled regime relatively hard, so that a mean-field treatment of the molecule-plasmon coupling was employed in ref 201.

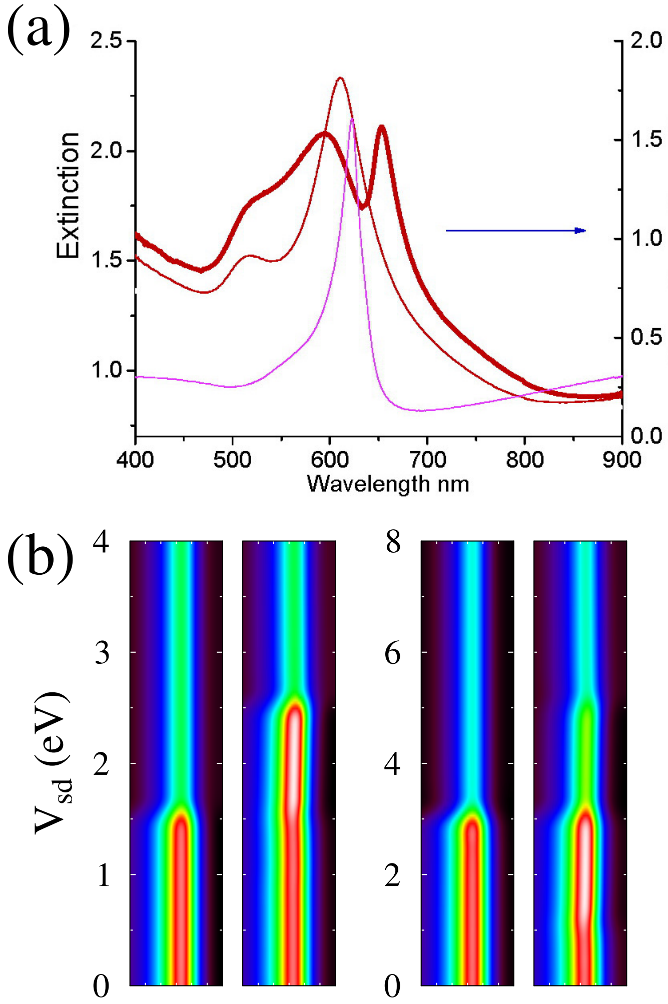

Figure 5. Molecular nanoplasmonics: (a) Extinction spectrum of the molecular J-aggregate on a gold nanorod in strongly coupled regime (thick line, red) together with an independent spectra of the J-aggregate (thin line, magenta) and gold film (thin line, red). Reprinted with permission from G. A. Wurtz et al. Nano Lett. **7**, 1297-1303 (2007). Copyright 2007 Amercian Chemical Society. (b) Molecular junction Fano resonance vs. applied bias for asymmetric (left) and symmetric (right) bias profile across the junction. The PP-NEGF simulations are performed with (right panel in each group) and without (left panel) electron-electron interaction. Reprinted with

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Simultaneous charge and energy transfer between the contacts and the molecules in junctions under bias is an additional complication to be taken into account in quantum description of plasmonic effects in the system. In ref 147 we argued that the language of many-body states of the system is most appropriate in treatment of junctions with strong hybridization between molecular and contacts degrees of freedom. In particular, we considered the molecular Fano resonance in a non-equilibrium open molecular system with strong coupling between molecular excitations and plasmons in contacts. Simulations within the PP-NEGF approach, which treated the strong molecule-plasmon coupling exactly, showed that the dependence of the resonance on applied bias is sensitive to junction parameters such as intra-molecular interactions and potential profile across the junction (see Figure 5b). We note that the non-equilibrium atomic limit methodology not only generalizes previous considerations bounded to zero-temperature equilibrium (linear response) conditions, but is technically much more convenient in considerations of molecule-plasmon interactions in junctions, where combined coherent electron/energy transfer mechanisms play an important role in the observed physics. Note that a similar but approximate description within the standard NEGF formalism would require a fourth-order perturbation theory to take the effects into account; even then it would not be completely appropriate since for rather strong molecule-plasmon interactions a perturbative treatment (or even separation into pure plasmonic and molecular degrees of freedom) is not possible. Our study opens a way to deal with strongly interacting plasmon-exciton systems in non-equilibrium molecular devices.

The non-equilibrium atomic limit is preferred in any case when combined coherent charge and energy transfer in the system plays an important role. In molecular junctions, effects of coherence were observed in charge transport.[18,19] Similarly, coherence in energy (excitation) transfer was observed in exciton transport in the Fenna-Mathews-Olson complex.[202,203] Coupling of molecular and plasmon excitations in junctions described above is an example where coherence in the both charge and energy transfer is important. Another known example in molecular optoelectronics is CT-SERS. In ref 146 we employed the PP-NEGF in search for other measurable effects in coherent charge and energy transfer in molecular junctions. In particular, inspired by the known charge and spin fluxes separation effect, we demonstrated that tuning parameters of external laser field (amplitude and/or frequency) leads to coherence induced spatial separation of charge and energy (electron excitation) fluxes in multi-terminal molecular junctions (see Figure 6). Note that this observation may be relevant also for a technically similar consideration of propagation of vibrational excitation in junctions, and hence to constructing low-heating molecular devices.

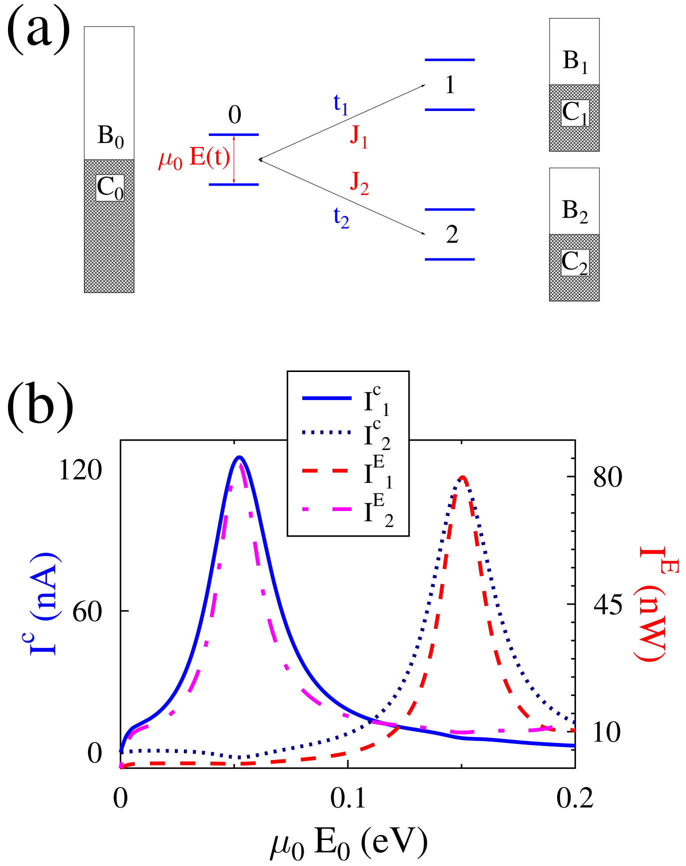

Figure 6. Coherence induced spatial separation of charge, I_i^c, and energy (electron excitation), I_i^E, fluxes in a multi-terminal molecular junction ($i = 1,2$). Shown are (a) model of the junction and (b) separation of the fluxes by tuning amplitude of external laser field. Reprinted with permission from A. J. White et al. Phys. Rev. B 88, 205424 (2013). Copyright 2013 by the American Physical Society.

Raman Spectroscopy in Molecular Junctions

Raman spectroscopy of current carrying molecular junctions attracted a lot of experimental attention recently.[30,34,38-40,42] Its popularity is due to a promise to become (in addition to IETS) a standard diagnostic tool capable of predicting both the presence of the molecule in the junction by its vibrational “fingerprint” and to provide information on vibrational and electronic heating of the device under applied bias. Theoretical formulation of Raman scattering in current carrying junctions is complicated due to the necessity to describe on the same footing two different processes: the Raman scattering and quantum transport. The former is a scattering event, i.e. the process with defined initial and final states. The latter is a process, where only initial state (usually in the infinite past) is defined (absence of a final state was the original reason to introduce the Keldysh contour[49]). To overcome this difficulty we separated the modes of the radiation field into the populated “incoming” and empty “outgoing” groups, and defined the Raman scattering as photon flux from the system into outgoing modes of the radiation field due to a coherent process, which treats interaction between the system and the “incoming” modes of the field within second order of perturbation theory.[204,205] Note that a similar route is taken also in the spectroscopy of isolated molecular systems at equilibrium.[206] Thus instead of formulating the Raman as a scattering event we write it as a flux. Expression for the flux of bosons (photons), $I_B^{ph}(t)$, between the system and a bath, B, can be derived in analogy with the Jauho, Meir, and Wingreen expression[207] for fermion flux (current) in junctions. The photon flux is[208]

$$\begin{aligned} I_B^{ph}(t) &\equiv -\frac{d}{dt}\sum_{\beta\in B}\left\langle \hat{b}_\beta^\dagger \hat{b}_\beta \right\rangle \\ &= -\mathrm{Re}\sum_{\alpha,\alpha'}\sum_{\beta\in B} U_{\alpha\beta}U_{\beta\alpha'}\int_{-\infty}^{t} dt'\left[\frac{\partial D_\beta^<(t-t')}{\partial t'}G_{\alpha,\alpha'}^>(t',t)-\frac{\partial D_\beta^>(t-t')}{\partial t'}G_{\alpha,\alpha'}^<(t',t)\right] \end{aligned} \qquad (5)$$

Here α,α' are molecular excitations, β indicates modes (photons) of the radiation field, $U_{\alpha\beta}$ is matrix element of interaction between molecular excitation α and mode β of the field, $D_\beta^{<(>)}$ is lesser (greater) projection of the GF describing free mode β in the bath B, and $G_{\alpha,\alpha'}^{<(>)}$ is lesser (greater) projection of the GF describing correlations of molecular excitations. Restricting the sum over β to the empty modes of the field, and keeping only the outgoing flux (second term in the right side of eq 5), yields the total outgoing photon flux from the system. If now we treat the molecular GF $G^{<}_{\alpha,\alpha'}$ in such a way that it contains information on (at least) second order in coupling to "incoming" modes of the radiation field, the resulting flux is the Raman scattering in molecular junctions.

Development of the theory described above was initiated by Prof. Abraham Nitzan. Applications to vibrational[204,205] and electronic heating,[209,210] CT-SERS,[211] and dynamical effects in Raman scattering in junctions[43,212,213] were considered within simple models employing quasi-particle formulations. To make the theory applicable to *ab initio* simulations and to present it in the form similar to the standard molecular spectroscopy, a many-body state formulation of Raman scattering is required. Recently, employing the PP-NEGF methodology and following the same line of argument, we derived an expression for Raman flux in terms of the many-body states of the molecule[154]

$$\begin{aligned} J(t) = 2\,\mathrm{Re} \sum_{\substack{g_i, x_1, x_2, g_f \\ \bar{g}_i, \bar{x}_1, \bar{x}_f, \bar{g}_f}} \varsigma_{g_i} \int_{-\infty}^{t} dt' \int_{-\infty}^{t} dt_1 \int_{-\infty}^{t'} dt_2 \Pi^{<}_{g_i x_1, \bar{g}_i \bar{x}_1}(t_1 - t_2) \Pi^{>}_{g_f x_2, \bar{g}_f \bar{x}_2}(t - t') \\ \times G^{>}_{\bar{x}_1 \bar{x}_2}(t_2, t') G^{>}_{\bar{g}_f g_f}(t', t) G^{>}_{x_2 x_1}(t, t_1) G^{<}_{g_i \bar{g}_i}(t_1, t_2) \end{aligned} \qquad (6)$$

Here $g_i(\bar{g}_i)$, $x_{1,2}(\bar{x}_{1,2})$, and $g_f(\bar{g}_f)$ are initial, intermediate, and final vibronic states of the Raman scattering, respectively. $\Pi^{<(>)}_{S_1S_2,S_3S_4}(t) \equiv 2\pi \sum_{\beta \in B} U_{S_1S_2,\beta} U_{\beta,S_3S_4} D^{<(>)}_{\beta}(t)$ is the lesser (greater) projection of the self-energy due to coupling of molecular excitations (S_1S_2 and S_3S_4) to the radiation field (note, lesser and greater projections choose, respectively, "incoming" and "outgoing" modes of the radiation field). $G^{<(>)}_{S_1S_2}(t_1, t_2)$ is the lesser (greater) projections of the pseudoparticle GF. Finally, $\varsigma_S = -1(+1)$ if S is a many-body state of Fermi (Bose) type. At steady-state, when Green functions depend on the difference in their time indices, transformation to the Fourier space in eq 6 becomes possible, and the resulting expression does not depend on t.

Expression for Raman flux in molecular junctions in terms of molecular many-body states makes connection to quantum chemistry calculations employed for isolated molecular systems straightforward. In ref 154 we utilized it for *ab initio* simulations of Raman scattering in a three-ring oligophenylene vinylene terminating in amine functional group (OPV3) junction (see Figure 7).

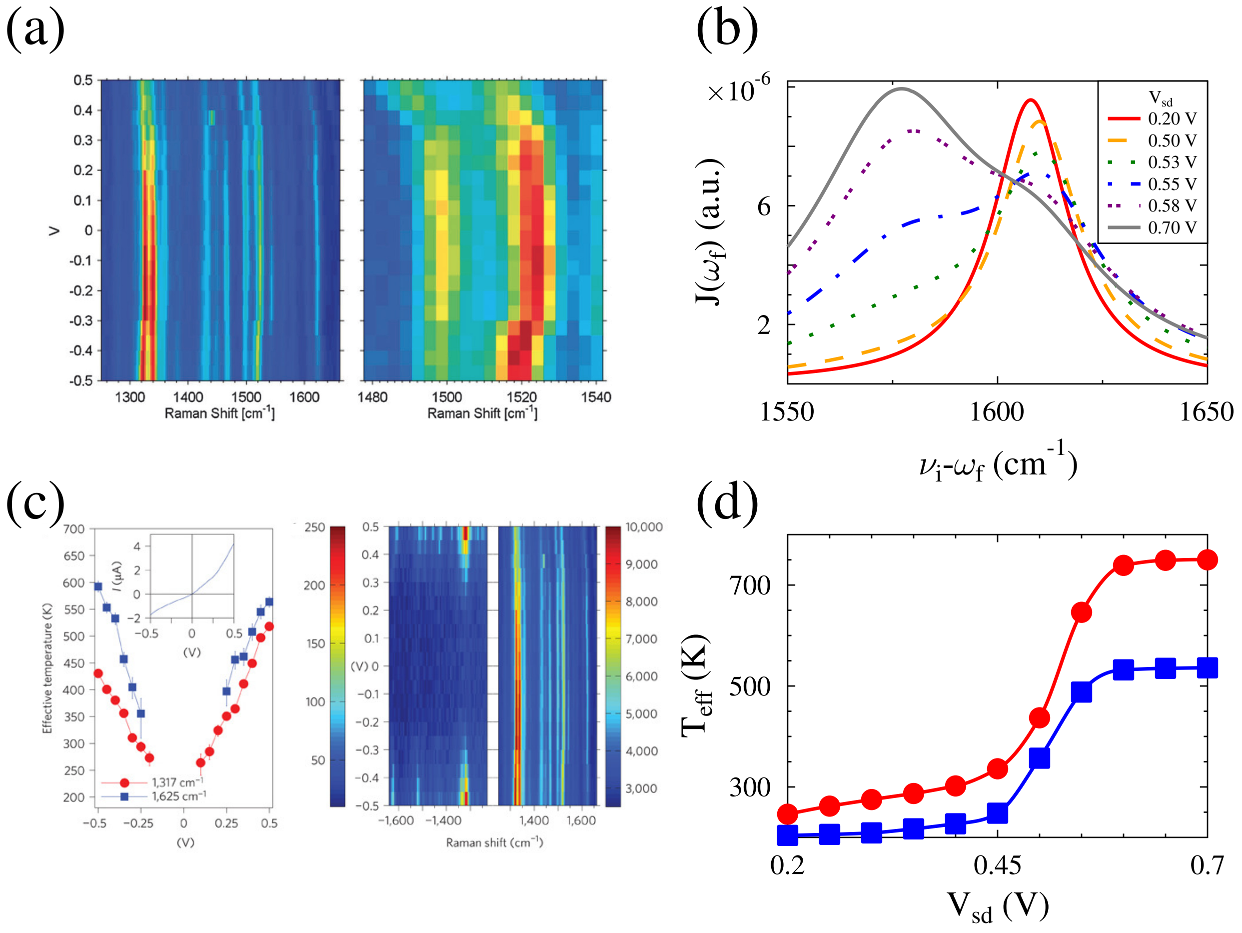

Figure 7. Raman spectroscopy of an OPV3 junction: (a) Experimental data on the Stokes line shift with bias; (b) First principles simulation of the Stokes scattering at a number of biases; (c) Experimental data on heating of vibrational modes of the OPV3 molecule; (d) Vibrational heating from the PP-NEGF simulations. Panels (a) and (c) are reprinted by permission from Macmillan Publishers Ltd: D. R. Ward et al., Nat. Nanotech. 6, 33-38 (2011), Copyright 2011. Panels (b) and (d) reprinted with permission from A. J. White et al. Nano Lett. **Accepted** (2014). Copyright 2014 Amercian Chemical Society.

We argue that participation of the OPV3 cation in Raman scattering under bias may be the reason for the Stokes line shift. Note that within the non-equilibrium atomic limit formulation, separation of the contributions to the overall process (similar to "electronic spectroscopy in the BDT junction conductance discussed above) is possible. Note also that results of calculations agree with available experimental data (compare Figures 7a and b). Similar to experimental estimate,[39] effective temperature of a normal mode can be deduced from the ratio of Stokes and anti-Stokes lines. Corresponding temperature estimate from the PP-NEGF simulation is also in agreement with the experimental measurements (compare Figures 7c and d).

CONCLUSIONS

Fast progress in the field of molecular electronics in the last decade has resulted from developments in laser and fabrication techniques at nanoscale. Theoretical tools for the description of a molecular junction's response to external stimuli combine electronic structure methods of quantum chemistry and quantum transport approaches of mesoscopic physics. Most often these techniques are formulated in the language of elementary excitations (quasi-partciles).

We argue that in many cases of practical interest the non-equilibrium atomic limit (formulation in the language of many-body states of an isolated molecule) may be preferable.

We review the theoretical tools of the approach, and our recent contributions to their development and application. In particular, we discuss generalized QME, PP-NEGF and Hubbard NEGF methodologies and their applications to quantum transport (elastic and inelastic) and optoelectronics (quantum nanoplasmonics and Raman scattering) in molecular junctions. We believe that the PP-NEGF is a preferable method for most *ab initio* simulations of junction responses, when a formulation in the language of many-body states is required. Although it has its own limitations, it definitely overpasses multiple generalized QME schemes available in the literature, at the same time being comparable to them in computational cost. At the same time, we think it is the Hubbard NEGF, which is potentially the most promising method of those discussed, due to its formulation in the physical space (contrary to the PP-NEGF) and time-nonlocality of the GFs (contrary to the GQME).

Future directions in research will include developments of methods of the non-equilibrium atomic limit and their applications. The former implies finding a path integral formulation for the Hubbard GFs, in order to establish a well-defined procedure of building conserving approximations in the Hubbard NEGF technique. Then extension of the methodology to multi-time multi-state correlations functions (relevant for molecular optoelectronics and statistical mechanics of open quantum systems) is required. In terms of applications, a first step is development of atomistic quantum *ab initio* modeling of the optical response of non-equilibrium electronic dynamics in molecular junctions. Such a formulation should combine quantum molecular nanoplasmonics and optical (Raman) response approaches discussed in the review.

Further developments may include the non-equilibrium atomic limit formulations of noise spectroscopy in junctions and of quantum thermodynamics in open molecular systems.

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Notes

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Maicol A. Ochoa obtained his BS in Chemistry and an MSc in Mathematics from the National University from Colombia in 2005 and 2010 respectively, and his PhD in Chemistry from Cornell University in 2012, where he investigated statistical methods for the analysis of single nanoparticle catalysis in Prof. Roger Loring's group. Currently, he is a postdoctoral scholar in the Department of Chemistry and Biochemistry in the University of California, San Diego, in Prof. Michael Galperin's group where he works in developing methodologies for description of quantum transport in terms of the Hubbard non-equilibrium Green's functions.

Michael Galperin graduated with MSc in Theoretical Physics from Ural State University, Russia, in 1991. He earned a PhD in Chemical Physics in 2003 at Tel Aviv University under the supervision of Prof. Abraham Nitzan. After postdoctoral positions at Duke University in 2002–2003, Northwestern University in 2003–2007, and Los Alamos National Laboratory in 2007–2008, he joined the faculty at University of California, San Diego where he is currently an assistant professor of Chemistry and Biochemistry. He is interested in quantum transport, excitation, dissipation and relaxation processes in open non-equilibrium molecular systems.

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ABBREVIATIONS

DM density matrix; QME quantum master equation; PO projection operator; EOM equation of motion; DFT density functional theory; TDDFT time-dependent DFT; SCBA selfconsistent Born approximation; GF Green function; NEGF non-equilibrium Green functions; PP-NEGF pseudoparticle NEGF; HIA first Hubbard approximation; IETS inelastic electron tunneling spectroscopy; RIETS resonant IETS; SERS surface enhanced Raman spectroscopy; CT-SERS charge transfer SERS.

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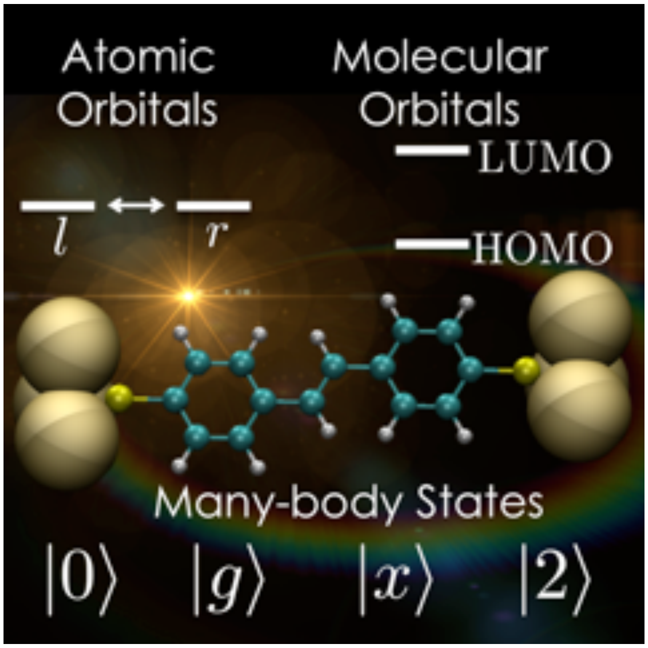
TOC IMAGE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