

Chapter 2

Quantum Transport Simulations Based on Time Dependent Density Functional Theory

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2.1 Introduction

Beginning with the landmark publication of Aviram and Ratner in the 1970s [1], interest in the basic question how current flows through individual molecules spawned a whole new research field termed molecular electronics. Several decades later, progress in the manipulation of materials at the nanoscale allowed to realize molecular junctions in a reliable and reproducible fashion even allowing for control of the current through suitable gate electrodes [2]. Classified by the molecule-contact interaction, different regimes of quantum transport could be identified, ranging from coherent ballistic transport for strong coupling to sequential tunneling and Coulomb blockade for weak coupling [3]. Even though the residence time of electrons on the molecule is extremely short, scattering may strongly modulate the transport characteristics of a device. This is seen in strongly correlated systems where the e-e interaction plays a dominant role or in tunneling spectra that are modified by inelastic electron-phonon scattering. These latter effects are theoretically often treated at the level of model Hamiltonians, which offer—through abstraction—an indispensable basic understanding of the physics involved.

Notwithstanding, atomistic first principles simulations of quantum transport have contributed significantly in the interpretation of experiments over the last years. These calculations provide not only detailed and unbiased information of the energetically most favorable binding configuration of molecular junctions, they are also used to quantify the current, especially for devices with strong molecule-lead coupling. In the majority of ab-initio studies the Landauer-Büttiker formalism is

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employed, in which the steady-state direct current through a contacted molecule is given by

$$I = \frac{2e}{h} \int_{-\infty}^{\infty} T(E, V)(f_L(E) - f_R(E)), \quad (2.1)$$

where $f_{L/R}$ denote the Fermi distribution functions of left (L) and right (R) leads [3]. The contacts are assumed to be in thermal equilibrium with chemical potentials that differ by the applied bias voltage V . The transmission function $T(E, V)$ describes the transparency of the junction at a given energy and peaks at the position of the molecular energy levels. With respect to the isolated case, the latter are shifted and broadened due to the interaction and hybridization with the lead atoms. Within non-equilibrium Green's function theory (termed NEGF in the following), the transmission may also be written as [3]

$$T = 4 \text{Tr}[\Gamma_L \mathbf{G}^r \Gamma_R \mathbf{G}^a]. \quad (2.2)$$

Here $\mathbf{G}^{r/a}$ denotes the retarded or advanced Green's function of the central region, while Γ depends on the surface density of states of the leads and the molecule-lead coupling. Both terms are directly amenable to a first principles evaluation using effective single-particle theories like Hartree-Fock or density functional theory (DFT). In this way the actual electronic structure of the device is accounted for, without the need to resort to few level models for the molecule or empirical wide band approximations for the leads.

From a principal point of view, steady state currents are quite naturally computed in the energy domain as exemplified by the Landauer-Büttiker formula (2.1) above. However, time domain approaches may offer a higher degree of flexibility: Arbitrary temporal shapes of the bias potential are easily incorporated in dynamical simulations, allowing for the description of alternating and transient currents or the study of switching processes in general. Moreover, one can also deal with time-dependent external fields that modulate the transport characteristics. This meets with current experimental efforts to investigate photo-induced and photo-assisted transport as well as molecular photoswitches [4–12]. Clearly, most of these applications can also be modeled using energy domain methods, especially for harmonic perturbations. An appealing property of dynamical simulations is however the possibility to treat systems far from linear response and at all orders of the driving frequency without additional computational effort.

In the first part of this work, a brief overview over several strategies to combine such time domain transport simulations with first principles electronic structure theory is given. For the latter, we restrict ourselves to a discussion of time dependent density functional theory (TDDFT) only. This method is by far the most employed many body approach in this field and provides an excellent ratio of accuracy over computational cost, allowing for the treatment of realistic molecular devices. This digest builds on the earlier excellent survey by Koentopp and co-workers on a similar topic [13]. Admittedly and inevitably, the choice of the covered material is biased by the authors interests and background.

2.2 Overview of Existing Methods and Recent Advances

2.2.1 Finite System Simulations

The very first application of *time dependent* density functional theory to molecular electronics was performed by Tomfohr and Sankey in 2001 [14]. The basic equations of motion solved in that work are the usual Kohn-Sham (KS) equations of TDDFT.

In atomic units ($\hbar = m_e = c = 1$) they read

$$i \frac{\partial}{\partial t} \psi_i(\mathbf{r}, t) = \left[-\frac{1}{2} \nabla^2 + v_{\text{KS}}[\rho](\mathbf{r}, t) \right] \psi_i(\mathbf{r}, t). \quad (2.3)$$

For a detailed derivation of Eq. (2.3) as well as a comprehensive introduction into time dependent DFT in general, we refer to the recent monograph by Ullrich on this topic [15]. Several reviews discussing different aspects of this already broad field are also available [16–18].

The local Kohn-Sham potential v_{KS} in Eq. (2.3) is chosen in such a way that the electron density $\rho(\mathbf{r}, t) = \sum_i^{\text{occ}} |\psi_i(\mathbf{r}, t)|^2$ obtained from the effective single particle orbitals ψ_i equals the true interacting many body density. According to

$$v_{\text{KS}}[\rho](\mathbf{r}, t) = v_{\text{ext}}(\mathbf{r}, t) + \int \frac{\rho(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{\text{xc}}[\rho](\mathbf{r}, t) \quad (2.4)$$

it consists of an external potential v_{ext} , the classical Hartree potential and the exchange-correlation (xc) potential v_{xc} . The external potential includes the attraction of the positively charged atomic cores and is also used to incorporate the external bias potential in some studies. Typical approximations for the unknown exchange-correlation functional $v_{\text{xc}}[\rho](\mathbf{r}, t)$ make use of standard ground state DFT functionals like the LDA and simply replace the stationary ground state density with the time dependent one at time t . This adiabatic approximation is widely used, but has also been made responsible for the overestimation of DC conductances seen not only in time dependent simulations, but also in (ground state) DFT treatments based on the Landauer-Büttiker formalism. In fact, it has been argued that even for steady state DC currents a time dependent treatment beyond the adiabatic approximation is strictly necessary [19–22].

Returning to the work of Tomfohr and Sankey, the metal-molecule-metal device model used in that study consisted of a benzenedithiol molecule coupled to two slabs of five monolayers of gold, finite in the transport direction but periodically replicated perpendicular to it. The authors assume a constant potential in the leads and a linear potential drop along the molecule. This is achieved by adjusting the external potential and keeping the density entering the Hamiltonian fixed at the ground state value without bias throughout the simulation. Propagation of the KS orbitals according to Eq. (2.3) then yields a time dependent density that allows one to quantify the number of electrons in the left and right lead by standard population analysis. It is found that electrons move to the high voltage lead and accumulate in

the finite reservoir until the resulting space charge fully screens the applied electric field. For some femtoseconds the current is however roughly constant and was found to agree with calculations in the Landauer formalism.

A similar approach was presented by Bushong and coworkers [23]. Here the initial conditions are such that the two metallic leads are oppositely charged. This is achieved by applying an energy shift to one of the electrodes. After the initial Kohn-Sham states are obtained from a conventional ground state DFT calculation, the energy shift is removed and the Kohn-Sham states are propagated fully self-consistently. For a 1-D linear chain of 20 to 60 gold atoms the current initially rises strongly, tends towards a nearly constant value with superimposed oscillations and then drops to zero. This drop-off time is related to the length of the atomic chain and can be increased by enlargement of the system. The authors point out that such transport simulations are in principal exact, since TDDFT is exact for finite systems, provided the exact non-adiabatic exchange-correlation functional was known. For systems with semi-infinite contacts the corresponding statement is not a priori valid and needs to be proven (see the second part of this chapter). Furthermore, the simulations show that the establishment of a steady state does not require dissipation in the form of electron-electron or electron-phonon scattering. Important is rather a large reservoir with a continuous density of states that allows for a “geometrical dilution” of the wave function [24].

In a series of publications also the group of Van Voorhis employs the finite cluster approach [25–27]. The bias potential is incorporated via a suitable external potential and switched on at the start of the time propagation. As shown in Ref. [25], the choice of the specific initial conditions does not seem to have a dramatic impact on the current dynamics. Like in Ref. [23], a self consistent determination of the initial density with shifted lead levels and subsequent removal of the shift leads to qualitatively similar results. As their TDDFT implementation is based on a standard software package for quantum chemistry, also hybrid xc functionals like B3LYP that contain a fraction of non-local Hartree-Fock (HF) exchange or even a pure Hartree-Fock Hamiltonian may be easily accessed. Results show that the zero bias conductance is significantly smaller for hybrid functionals compared to local or semilocal xc functionals. This agrees with similar findings in the Landauer-Büttiker formalism, where the conductance reduction is rationalized by the larger gap between the molecular frontier orbitals in HF based approaches. Interestingly, the current traces in Ref. [26] show significant oscillations even in the intermediate phase where a quasi steady state is reached. According to the authors, this feature is not related to too small reservoirs, but indicates a fundamental problem of the Landauer picture that relies on the formation of constant currents. It is claimed that the instantaneous charge accumulated in the device region suppresses transport and gives rise to the dynamic equivalent of the Coulomb blockade effect (for a recent discussion of this point see also [28]).

Mentioned should also be the recent work of Zhou and Chu [29] who formulate the time-dependent Kohn-Sham equations in reciprocal space:

$$i\frac{d}{dt}\psi_i(\mathbf{k}, t) = \int d\mathbf{k}' H(\mathbf{k}, \mathbf{k}', t)\psi_i(\mathbf{k}', t), \quad (2.5)$$

where $H(\mathbf{k}, \mathbf{k}', t) = (2\pi)^{-3} \int d\mathbf{r} H(\mathbf{r}, t) \exp[i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{r}]$. Discretization of a finite simulation box then transforms Eq. (2.5) into a matrix equation which may be solved by standard techniques. The main motivation for this reformulation is the fact that the current carrying states are extended in real space but confined in reciprocal space, exhibiting momenta only up to some maximum value that is governed by the applied bias. The authors compare results for some 1D models with real space implementations and seem to obtain good agreement at reduced computational cost.

One drawback of simulations with finite leads are the spurious back reflection of electrons reaching the contact boundary. This effect may be suppressed to arbitrary precision by increasing the size of the leads, which however also increases the computational cost. To overcome these problems, complex absorbing potentials (CAP) are used routinely in many branches of quantum dynamics [30] and this is also the approach taken by Baer and coworkers [31]. The authors investigate a six membered carbon chain embedded in jellium electrodes with constant electron density. At the edges of the contacts a spatially localized CAP is added to the Hamiltonian that involves a projection operator on the space spanned by the unoccupied Kohn-Sham states. In this way electrons are removed from the system before they reach the contact boundary without a strong perturbation of the lead density. This approach is used to compute the AC conductance properties of the device by subjecting it to a sudden turn-on of a small electric field. The Fourier transform of this signal is broad, which allows the complex admittance $Y(\omega) = I(\omega)/V(\omega)$ to be evaluated at frequencies up to the optical range. In the limit $\omega \rightarrow 0$, the conventional DC conductance G is recovered as a special case. In principle, the AC admittance is also amenable to static simulations in the framework of NEGF theory [32–37]. The advantage of TDDFT is that the full frequency information is available from a single time propagation. Moreover, as pointed out in Ref. [31], the screening of the applied field is fully accounted for in time dependent simulations as the Hamiltonian is constantly updated, reflecting changes in the device density through the Hartree and xc potentials. In this way the potential drop along the molecule is calculated rather than assumed.

In a recent contribution, Varga [38] presents an approach that is also based on absorbing potentials. In contrast to [31], the potential is kept constant at the equilibrium value in regions where the CAP is non-vanishing. Still electrons are removed from the simulation box, which finally leads to a decay of the current after several fs due to the depletion of charge carriers. In comparison to simulations without absorbing boundary conditions, it seems that the quasi steady state is maintained for a longer time, although calculations with exactly the same junction geometry would be required to address this point properly. Application of this approach to two representative molecular junctions shows that the TDDFT steady state current is significantly larger than the one obtained from the Landauer-Büttiker formula close to molecular resonances (a different point of view is presented in Ref. [39]).

In summary, simulations with finite reservoirs have the distinct advantage that TDDFT algorithms, propagation methods and computer codes are well established for isolated systems and can be used for transport calculations without major changes. Computational artifacts due to the finite reservoirs can and need to be kept under control by a systematic enlargement of the contact sizes.

2.2.2 Methods Based on Open Boundary Conditions

Given the problems with the finite size effects mentioned above, it seems natural to treat the full device using open boundary conditions with a finite central interaction region (C) and two semi-infinite contacts (L/R). In fact, this is the standard approach for calculations in the NEGF (Landauer-Büttiker) formalism and there is considerable experience in the technical treatment of such setups. The leads are usually modeled as periodically replicated units extending in the transport direction to infinity. Choosing these principal layers large enough so that there are only interactions between neighboring units, the surface density of states of the leads, as an example, may be easily obtained by recurrence relations without loss of generality [40].

Efforts to extend TDDFT in this direction were pioneered by several groups [41, 42]. In the approach of Kurth *et al.* the full KS Hamiltonian of the lead-molecule-lead system is partitioned in the following fashion:

$$\mathbf{H}_{\text{KS}} = \begin{pmatrix} \mathbf{H}_{LL} & \mathbf{H}_{LC} & \mathbf{0} \\ \mathbf{H}_{CL} & \mathbf{H}_{CC} & \mathbf{H}_{CR} \\ \mathbf{0} & \mathbf{H}_{RC} & \mathbf{H}_{RR} \end{pmatrix}. \quad (2.6)$$

Here $\mathbf{H}_{\alpha\alpha}$ ($\alpha = L, R, C$) denote the (still infinite) Hamiltonians of the left and right lead and the finite size Hamiltonian of the central device, respectively. The latter is chosen so large that direct interactions between the leads can be neglected. The partitioning in Eq. (2.6) may be realized by space discretization or by a representation of the Hamiltonian in a suitable localized basis. Inserting Eq. (2.6) into the time-dependent KS equations Eq. (2.3), leads to a reduced equation of motion for the wavefunction $|\psi_C\rangle$ in the central device region:

$$\begin{aligned} i\frac{d}{dt}|\psi_C(t)\rangle &= \mathbf{H}_{CC}(t)|\psi_C(t)\rangle + \int_0^t dt' \Sigma^R(t, t')|\psi_C(t')\rangle \\ &+ i \sum_{\alpha=L,R} \mathbf{H}_{C\alpha}(t) \mathbf{g}_{\alpha\alpha}^R(t, 0)|\psi_\alpha(0)\rangle. \end{aligned} \quad (2.7)$$

Here the retarded Green's function \mathbf{g}^R of lead α and the self energy Σ^R have been introduced:

$$\mathbf{g}_{\alpha\alpha}^R(t, t') = -i\Theta(t - t') \exp\left(-i \int_{t'}^t d\tau \mathbf{H}_{\alpha\alpha}(\tau)\right), \quad (2.8)$$

$$\Sigma_{\alpha\alpha}^R(t, t') = \sum_{\alpha=L,R} \mathbf{H}_{C\alpha}(t) \mathbf{g}_{\alpha\alpha}^R(t, t') \mathbf{H}_{\alpha C}(t'). \quad (2.9)$$

The latter term, $\Sigma^R(t, t')$, describes processes where an electron hops from the central device part into the leads at time t' and returns at time t . Its real part leads to a renormalization of the molecular energy levels due to the hybridization with the contact atoms, while the imaginary part broadens each discrete level into resonances [43]. In this way, the electronic structure of the semi-infinite leads is fully

accounted for by a matrix that has the dimension of the central part only. In addition, no spurious back reflection at the lead/molecule interface can occur if the self energy is computed exactly. In practice, however, the evaluation of the second term on the right-hand side in Eq. (2.7) is cumbersome, as the wavefunction at time t depends on the wavefunction at all prior times, which results in high memory needs for long simulations. Although computationally demanding, the mentioned term builds memory into the equation of motion and its exact treatment might be of significant importance if hysteresis effects become important [41]. Besides this memory integral, also the last term in Eq. (2.7) differs with respect to the KS equations for the isolated device. It describes the injection of electrons into the central part due to states that are initially localized on the leads.

The determination of the initial conditions for the equation of motion was realized in Ref. [41] by an algorithm that is essentially based on the diagonalization of the density of states projected on the central region ($-\text{Im}[\mathbf{G}_{CC}^R(E)]/\pi$). The correct normalization of the states $|\psi_C(t)\rangle$ may be found by matching the wavefunction at the interfaces, which is straightforward if the lead electronic structure is known analytically. The time propagation of the KS states is then performed by employing a norm conserving scheme reminiscent of the Cayley propagator [44] which finally allows for the computation of the current as the time derivative of the total number of particles in the leads [45]. This approach has been applied to a number of interesting transport problems, like the question whether or not a steady state may always be reached (a central assumption in the Landauer-Büttiker formalism) [46, 47], or the pumping of electrons through unbiased junctions due to appropriately timed gate voltages [45]. So far these simulations have been restricted to the independent particle level without the inclusion of electron-electron interactions.

2.2.3 Simulations Under Periodic Boundary Conditions

In the Landauer-Büttiker formalism one usually assumes that both leads are in thermal equilibrium at two chemical potentials that differ by the applied bias. Such a position dependent chemical potential was criticized by Kamenev and Kohn [48]. They suggested a physically more appealing setup with one single chemical potential for the entire system and a constant external electric field that drives the current. Proper inclusion of screening effects due to a self consistent determination of the electron density then also leads to constant bulk potentials in perfect metallic leads. In such a scenario, the voltage drop of the studied junction is the outcome of the calculation rather than the required input (see also [31]). Burke and co-workers [49] employ similar ideas and treat the lead-molecule-lead system under periodic boundary conditions, i.e., electrons leaving the simulation box at one side re-enter on the opposite side, avoiding the need for explicit reservoirs. In their simulations, a spatially uniform electric field is then applied¹ which leads to a continuous acceleration

¹In general, the treatment of finite electric fields under periodic boundary conditions requires special care, as the electronic ground state may become unbound (see for instance [50]).

of the electrons unless some form of dissipation enforces a steady state. To account for this, a master equation is derived in Ref. [49] that includes electron-phonon interactions as the dissipation channel. Simulations presented in Ref. [13] for an atomic gold chain in a relatively small unit cell show that a steady state develops indeed if a large dissipative coupling is present. This is in variance with the other approaches described so far where the treatment of the electronic degrees of freedom only is sufficient to achieve a steady state. In fact, Stefanucci *et al.* [21] state that the equilibration is due to destructive interference among the continuum of contact states and hence of purely electronic origin. As mentioned earlier, also Bushong and coworkers [23] argue in this direction. It is conceivable that the required dissipative coupling may be significantly reduced to realistic values for simulation boxes that are large compared to the electron-phonon mean free path. This is also the view expressed in Ref. [13] and it will be interesting to see whether electron-phonon interactions still represent a *conditio sine qua non* in this limit. In any case, the master equation approach incorporates additional physics into the transport description and—as a more technical point—is easily interfaced to existing plane wave DFT codes.

2.3 First-Principles Liouville-von Neumann Equation

In the remainder of this chapter, we now focus on one specific method not discussed so far, the Liouville-von Neumann approach in TDDFT. This scheme falls under point 2.2.2 from above as the contacts are treated as semi-infinite leads. In contrast to the approach by Kurth *et al.* [41], the basic variable is the Kohn-Sham one-particle density matrix rather than the Kohn-Sham orbitals. We begin with a discussion on the formal foundations of the method, before the relevant equations of motion are presented. Special emphasis is also laid on the exact treatment of the contacts in the *hierarchical equation of motion* approach.

2.3.1 Holographic Electron Density Theorem and Existence of First-Principles for Open Systems

The Hohenberg-Kohn (HK) theorem [51] states that the ground state electron density function determines all electronic properties of the system. Based on this theorem, a practical scheme was formulated by Kohn and Sham [52] in order to calculate the ground-state properties of electronic systems. As an extension of the HK theorem, the Runge-Gross theorem [53] states that the time-dependent electron density function determines uniquely all electronic properties of the corresponding time-dependent system. The Runge-Gross theorem provides the foundation for development of time-dependent density-functional theory (TDDFT) for calculating excited-state properties of electronic systems. Fournais *et al.* [54, 55] have proved in 2004 that electron density function of any time-independent real physical systems made

of atoms and molecules is real analytic except at nuclei. In 2010, Jecko has given a simpler proof for the real analyticity of electron density function [56]. This real analyticity of electron density provides a solid basis for the ground-state holographic electron density theorem (GS-HEDT) which states that any nonzero volume piece of the ground-state electron density determines the electron density of the entire system [57, 58]. In 2007, Chen and coworkers proved the time-dependent holographic electron density theorem (TD-HEDT). The theorem states that if the electron density function of a real finite physical system at t_0 , $\rho(\mathbf{r}, t_0)$, is real analytic in \mathbf{r} -space, the corresponding wave function is $\Phi(t_0)$, and a real analytic (in both t -space and \mathbf{r} -space) external potential field $v(\mathbf{r}, t)$ is applied to the system after t_0 , the time-dependent electron density function on any finite subspace D , $\rho_D(\mathbf{r}, t)$, has a one-to-one correspondence with $v(\mathbf{r}, t)$ (up to an additive merely time-dependent function), and determines all electronic properties of the entire time-dependent system uniquely. The TD-HEDT lays the foundation for the first-principles method for open electronic systems [59]. Just like the HK and Runge-Gross theorems, the HEDT asserts the existence of density-functional theory for open systems. The task is then to find the practical first-principles method for the open systems.

2.3.2 First-Principles Formalism: TDDFT-NEGF-EOM for Open System

Based on the TD-HEDT, Chen *et al.* have proposed and developed a practical first-principles formalism for open electronic systems and implemented it to simulate transient currents through electronic devices [42, 60]. The resulting first-principles formalism for open system starts from a closed equation of motion (EOM) for the Kohn-Sham (KS) reduced single-electron density matrix (RSDM) of the entire system, and reduces to the following Liouville-von Neumann equation by projecting out the electronic degrees of freedom of the electrodes:

$$i\dot{\sigma}_D = [\mathbf{H}_D, \sigma_D] - i \sum_{\alpha} \mathbf{Q}_{\alpha}, \quad (2.10)$$

where σ_D and \mathbf{H}_D are the RSDM and KS Fock matrix of the electronic device D , respectively, and \mathbf{Q}_{α} is the dissipative term between device D and electrode α . According to the TD-HEDT, \mathbf{Q}_{α} is in principle a functional of electron density in the sub-system D , $\rho_D(\mathbf{r}, t)$, and therefore Eq. (2.10) can be recast into a formally closed form

$$i\dot{\sigma}_D = [\mathbf{H}_D[t; \rho_D(\mathbf{r}, t)], \sigma_D] - i \sum_{\alpha} \mathbf{Q}_{\alpha}[t; \rho_D(\mathbf{r}, t)]. \quad (2.11)$$

The above equation is the resulting first-principles Liouville-von Neumann equation for open electronic devices. The transient electric current through the interface S_{α} can be evaluated through,

$$I_{\alpha}(t) = - \int_{\alpha} d\mathbf{r} \frac{\partial}{\partial t} \rho(\mathbf{r}, t) = -\text{tr}[\mathbf{Q}_{\alpha}(t)]. \quad (2.12)$$

Conventional adiabatic approximation for XC potential can be adopted to construct $\mathbf{H}_D[t; \rho_D(\mathbf{r}, t)]$. $\mathbf{Q}_\alpha[t; \rho_D(\mathbf{r}, t)]$ can be expressed exactly via the Keldysh formalism [61],

$$Q_{\alpha,\mu\nu}(t) = - \sum_{l \in D} \int_{-\infty}^{\infty} d\tau [G_{\mu l}^<(t, \tau) \Sigma_{\alpha, l\nu}^a(\tau, t) + G_{\mu l}^r(t, \tau) \Sigma_{\alpha, l\nu}^<(\tau, t)] + \text{H.c.}, \quad (2.13)$$

where $\mathbf{G}^<$ and \mathbf{G}^r are the lesser and retarded Green's functions, respectively, and $\Sigma^<$ and Σ^a are the lesser and advanced self-energies, respectively.

2.3.3 Hierarchical Equation of Motion for Reduced Single-Electron Density Matrix Based Liouville-von Neumann Equation

A hierarchical equation of motion (HEOM) [60, 61] is developed where for non-interacting systems, such as TDKS reference system in the present case, the hierarchy terminates exactly at the second-tier without any approximation [61]. Within the TDDFT-NEGF-HEOM formalism, the Liouville-von Neumann equation reads,

$$i\dot{\sigma}_D = [\mathbf{H}_D, \sigma_D] - \sum_{\alpha} [\varphi_{\alpha}(t) - \varphi_{\alpha}^{\dagger}(t)], \quad (2.14)$$

where φ_{α} is the first-tier auxiliary RSDM and is directly associated with the dissipation functional \mathbf{Q}_{α} as follows,

$$\mathbf{Q}_{\alpha}(t) = -i[\varphi_{\alpha}(t) - \varphi_{\alpha}^{\dagger}(t)] = -i \int d\varepsilon [\varphi_{\alpha}(\varepsilon, t) - \varphi_{\alpha}^{\dagger}(\varepsilon, t)]. \quad (2.15)$$

The corresponding HEOM for the KS RSDM and its auxiliary counterparts have been derived in Ref. [61] as follows (\mathbf{I} denotes the identity matrix):

$$\begin{aligned} i\dot{\varphi}_{\alpha}(\varepsilon, t) &= [\mathbf{H}_D(t) - (\varepsilon + \Delta_{\alpha}(t))\mathbf{I}]\varphi_{\alpha}(\varepsilon, t) + [f_{\alpha}(\varepsilon)\mathbf{I} - \sigma_D]\Lambda_{\alpha}(\varepsilon) \\ &+ \sum_{\alpha'} \int d\varepsilon' \varphi_{\alpha, \alpha'}(\varepsilon, \varepsilon', t), \end{aligned} \quad (2.16)$$

$$\begin{aligned} i\dot{\varphi}_{\alpha, \alpha'}(\varepsilon, \varepsilon', t) &= -[\varepsilon + \Delta_{\alpha}(t) - \varepsilon' - \Delta_{\alpha'}(t)]\varphi_{\alpha, \alpha'}(\varepsilon, \varepsilon', t) \\ &+ \Lambda_{\alpha'}(\varepsilon')\varphi_{\alpha}(\varepsilon, t) - \varphi_{\alpha'}^{\dagger}(\varepsilon', t)\Lambda_{\alpha}(\varepsilon), \end{aligned} \quad (2.17)$$

where $f_{\alpha}(\varepsilon)$ is the Fermi distribution function for electrode α ; $\Delta_{\alpha}(t)$ is the energy shift for all single-electron levels in electrode α due to the time-dependent applied voltage; and Λ_{α} is the linewidth matrix for electrode α . Here, the first- and second-tier auxiliary RSDM are defined as follows:

$$\varphi_{\alpha}(\varepsilon, t) = i \int_{-\infty}^t d\tau [G_D^<(t, \tau) \Sigma_{\alpha}^>(\tau, t; \varepsilon) - G_D^>(t, \tau) \Sigma_{\alpha}^<(\tau, t; \varepsilon)], \quad (2.18)$$

$$\begin{aligned}
\varphi_{\alpha,\alpha'}(\varepsilon, \varepsilon', t) = & i \int_{-\infty}^t dt_1 \int_{-\infty}^t dt_2 \{ [\Sigma_{\alpha'}^<(t, t_1; \varepsilon') \mathbf{G}_D^a(t_1, t_2) \\
& + \Sigma_{\alpha'}^r(t, t_1; \varepsilon') \mathbf{G}_D^<(t_1, t_2)] \Sigma_{\alpha}^>(t_2, t; \varepsilon) - [\Sigma_{\alpha'}^r(t, t_1; \varepsilon') \mathbf{G}_D^>(t_1, t_2) \\
& + \Sigma_{\alpha'}^>(t, t_1; \varepsilon') \mathbf{G}_D^a(t_1, t_2)] \Sigma_{\alpha}^<(t_2, t; \varepsilon) \}. \quad (2.19)
\end{aligned}$$

In practical calculations, it is difficult to evaluate the energy integral in the EOM of $\varphi_{\alpha}(\varepsilon, t)$. The following self-energy decomposition method is developed based on Cauchy's residue theorem [62]. The non-equilibrium self-energy, $\Sigma_{\alpha}^{\langle, \rangle}$, can be expressed in terms of the equilibrium self-energy, $\tilde{\Sigma}_{\alpha}^{\langle, \rangle}$. The energy integral of $\tilde{\Sigma}_{\alpha}^{\langle, \rangle}(\tau, t)$ (a.k.a. $\tilde{\Sigma}_{\alpha}^{\langle, \rangle}(\tau - t)$) can be written as the summation form by Cauchy's residue theorem [60],

$$\tilde{\Sigma}_{\alpha}^<(\tau - t) = \frac{i}{2\pi} \int_{-\infty}^{\infty} d\varepsilon f_{\alpha}(\varepsilon) \Lambda_{\alpha}(\varepsilon) e^{i\varepsilon(\tau-t)} = \sum_{k=1}^{N_k} \tilde{\Sigma}_{\alpha,k}^<(\tau - t), \quad (2.20)$$

$$\begin{aligned}
\tilde{\Sigma}_{\alpha}^>(\tau - t) &= \frac{-i}{2\pi} \int_{-\infty}^{\infty} d\varepsilon [1 - f_{\alpha}(\varepsilon)] \Lambda_{\alpha}(\varepsilon) e^{i\varepsilon(\tau-t)} \\
&= \sum_{k=1}^{N_k} \tilde{\Sigma}_{\alpha,k}^>(\tau - t), \quad (2.21)
\end{aligned}$$

and

$$\tilde{\Sigma}_{\alpha,k}^{\langle, \rangle}(\tau - t) = \mathbf{A}_{\alpha,k}^{\langle, \rangle \pm} \exp[\mp \gamma_{\alpha,k}^{\pm}(\tau - t)], \quad (2.22)$$

where $\tilde{\Sigma}_{\alpha,k}^{\langle, \rangle}$ is the k th decomposition expansion of the self-energy; and N_k is the number of poles counted in the integral contour. $\mathbf{A}_{\alpha,k}$ represents the coefficients for the integral results and $\gamma_{\alpha,k}$ is related to poles. Here, “+” and “-” symbols correspond to the upper and lower half plane for the integral contour, respectively. Similarly, $\Sigma_{\alpha}^{\langle, \rangle}(\tau, t)$ can be written as the summation form [60, 63]:

$$\Sigma_{\alpha}^{\langle, \rangle}(\tau, t) = \sum_{k=1}^{N_k} \Sigma_{\alpha,k}^{\langle, \rangle}(\tau, t), \quad (2.23)$$

with

$$\Sigma_{\alpha,k}^{\langle, \rangle}(\tau, t) = \exp\left[i \int_{\tau}^t \mathbf{A}_{\alpha}(\xi) d\xi \right] \tilde{\Sigma}_{\alpha,k}^{\langle, \rangle}(\tau - t). \quad (2.24)$$

And $\varphi_{\alpha}(\varepsilon, t)$ can also be rewritten in the same fashion,

$$\varphi_{\alpha}(t) = \int d\varepsilon \varphi_{\alpha}(\varepsilon, t) = \sum_{k=1}^{N_k} \varphi_{\alpha,k}(t). \quad (2.25)$$

By incorporating these two summations, Eq. (2.14) becomes

$$i\dot{\sigma}_D = [\mathbf{H}_D, \sigma_D] - \sum_{\alpha} \sum_{k=1}^{N_k} [\varphi_{\alpha,k}(t) - \varphi_{\alpha,k}^{\dagger}(t)]. \quad (2.26)$$

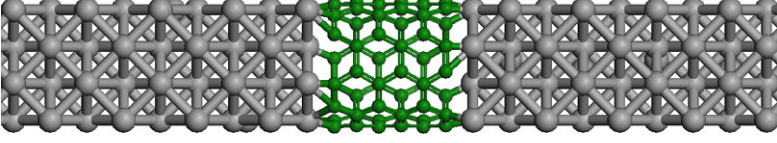


Fig. 2.1 A schematic diagram of a carbon nanotube based electronic device in the ball-and-stick representation

And the EOM for the first- and second-tier auxiliary RSDM now read

$$\begin{aligned} i\dot{\boldsymbol{\varphi}}_{\alpha,k}(t) = & \left[\mathbf{H}_D(t) - (i\gamma_{\alpha,k}^+ + \Delta_{\alpha}(t))\mathbf{I} \right] \boldsymbol{\varphi}_{\alpha,k}(t) - i \left[\boldsymbol{\sigma}_D(t) \mathbf{A}_{\alpha,k}^{>+} + \bar{\boldsymbol{\sigma}}_D(t) \mathbf{A}_{\alpha,k}^{<+} \right] \\ & + \sum_{\alpha'} \sum_{k'=1}^{N_k} \boldsymbol{\varphi}_{\alpha k, \alpha' k'}(t), \end{aligned} \quad (2.27)$$

$$\begin{aligned} i\dot{\boldsymbol{\varphi}}_{\alpha k, \alpha' k'}(t) = & - \left[i\gamma_{\alpha,k}^+ + \Delta_{\alpha}(t) - i\gamma_{\alpha',k'}^- - \Delta_{\alpha'}(t) \right] \boldsymbol{\varphi}_{\alpha k, \alpha' k'}(t) \\ & + i \left[\mathbf{A}_{\alpha',k'}^{>-} - \mathbf{A}_{\alpha',k'}^{<-} \right] \boldsymbol{\varphi}_{\alpha,k}(t) - i \boldsymbol{\varphi}_{\alpha',k'}^{\dagger}(t) \left[\mathbf{A}_{\alpha,k}^{>+} + \mathbf{A}_{\alpha,k}^{<+} \right], \end{aligned} \quad (2.28)$$

where $\bar{\boldsymbol{\sigma}}_D(t) = \mathbf{I} - \boldsymbol{\sigma}_D(t)$.

2.3.4 Adiabatic Wide-Band-Limit Approximation

To simplify the computation further, we consider an approximate scheme for $\mathbf{Q}_{\alpha}(t)$ based on the adiabatic wide-band-limit (AWBL) treatment for electrodes, as well as an adiabatic approximation for the memory effect. The scheme aims at simplifying the NEGF expression of $\mathbf{Q}_{\alpha}(t)$ [42],

$$\mathbf{Q}_{\alpha}(t)^{\text{AWBL}} = \{ \mathbf{A}_{\alpha}, \boldsymbol{\sigma}_D \} + \mathbf{P}_{\alpha}(t) + \mathbf{P}_{\alpha}^{\dagger}(t), \quad (2.29)$$

where $\mathbf{P}_{\alpha}(t)$ can be evaluated by

$$\begin{aligned} \mathbf{P}_{\alpha}(t) \approx & -\frac{i}{\pi} \left\{ \mathbf{U}_{\alpha}(t) \int_{-\infty}^{\infty} d\varepsilon f_{\alpha}(\varepsilon) e^{i\varepsilon t} \left[\frac{1}{\varepsilon \mathbf{I} - \mathbf{H}_D(0) + i\Lambda} \right. \right. \\ & \left. \left. - \frac{1}{[\varepsilon + \Delta_{\alpha}(t)]\mathbf{I} - \mathbf{H}_D(t) + i\Lambda} \right] + \int_{-\infty}^{\infty} \frac{d\varepsilon f_{\alpha}(\varepsilon)}{[\varepsilon + \Delta_{\alpha}(t)]\mathbf{I} - \mathbf{H}_D(t) + i\Lambda} \right\} \mathbf{A}_{\alpha}, \end{aligned} \quad (2.30)$$

with

$$\mathbf{U}_{\alpha}(t) = \exp \left[-i \int_0^t d\tau (\mathbf{H}_D(\tau) - i\Lambda - \Delta_{\alpha}(\tau)\mathbf{I}) \right], \quad (2.31)$$

where $\Lambda = \sum_{\alpha} \mathbf{A}_{\alpha}$ gives the device-electrode coupling matrix.

First-principles simulation has been carried out to simulate the transient current through a series of molecular and nanoscopic electronic devices, based on the AWBL approximation for \mathbf{Q}_{α} and LDA for exchange-correlation functional. Figure 2.1 depicts a carbon nanotube based electronic device. The device is a (5,5)

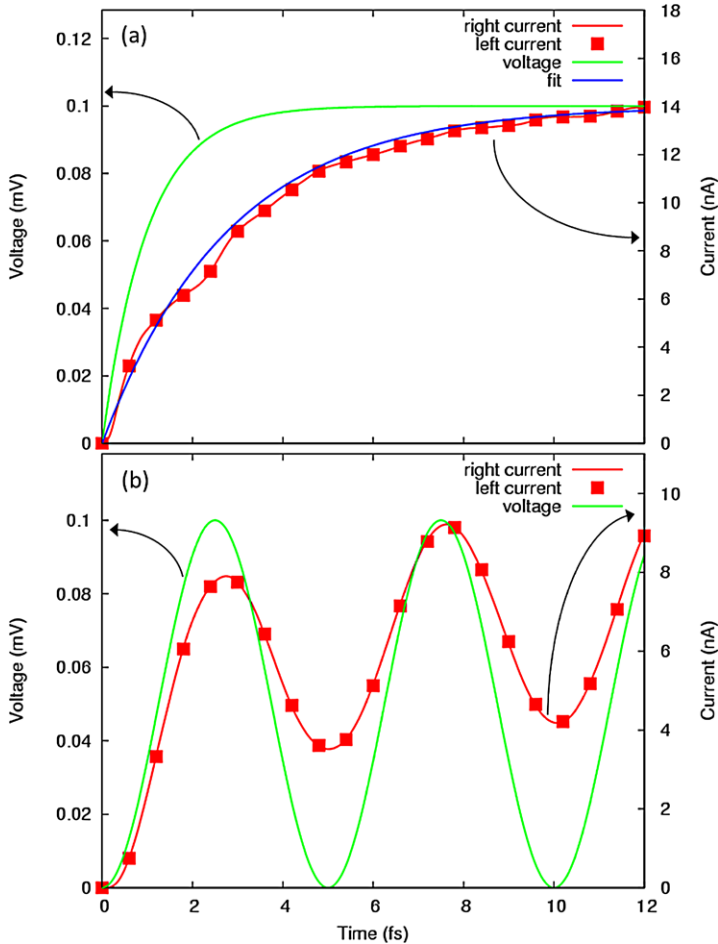


Fig. 2.2 (a) and (b) Transient current (*red line and squares*) and applied bias voltage (*green lines*) for the Al-CNT-Al system. (a) The bias voltage is turned on exponentially, $V_b = V_0(1 - e^{-t/a})$ with $V_0 = 0.1$ mV and the time constant $a = 1$ fs. The *blue line* in (a) is a fit to the transient current. (b) The bias voltage is sinusoidal with a period of 5 fs. The *red line* is for current from the right electrode, while *squares* are current from the left electrode. Reprinted from Ref. [64] with kind permission of © IOP Publishing (2008)

carbon nanotube, and the left and right electrodes are made of aluminum. Besides the carbon nanotube, the simulation box contains 48 aluminum atoms for each electrode. At time $t = 0$, a bias voltage is turned on, the transient current is simulated in real time. Figure 2.2 depicts the current versus time. Two types of bias voltage are applied, the exponential and the sinusoidal voltages as explained in the figure caption.

It is important to point out that there are 96 Aluminum atoms, 60 carbon atoms and a total of 1608 electrons in the calculation. This is an impressive achievement as

the conventional Liouville-von Neumann equation deals with model systems containing a few electrons. The first-principles formalism reviewed here is based on the Liouville-von Neumann equation for the reduced single-electron density matrix (rather than the conventional reduced many-electron density matrix), and is thus indeed much more efficient. Therefore, the first-principles Liouville-von Neumann equation for open systems combines the first-principles method and quantum dissipation theory.

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