Pride, Prejudice, and Penury of *ab initio* transport calculations for single molecules

F. Evers[1,2] and K. Burke[3]
[1] *Institut für Theorie der Kondensierten Materie,*
Universität Karlsruhe, 76128 Karlsruhe, Germany
[2] *Institut für Nanotechnologie, Forschungszentrum Karlsruhe, 76021 Karlsruhe, Germany and*
[3] *Department of Chemistry, University of California, Irvine, California 92697, USA*

(Dated: February 2, 2007)

Recent progress in measuring the transport properties of individual molecules has triggered a substantial demand for *ab initio* transport calculations. Even though program packages are commercially available and placed on custom tailored to address this task, reliable information often is difficult and very time consuming to attain in the vast majority of cases, namely when the molecular conductance is much smaller than e^2/h. The article recapitulates procedures for molecular transport calculations from the point of view of time-dependent density functional theory. Emphasis is describing the foundations of the "standard method". Pitfalls will be uncovered and the domain of applicability discussed.

I. INTRODUCTION

In an impressive sequence of experiments, it has recently been demonstrated that measuring the current voltage (I-V) characteristics of an individual molecule has become feasible. [1–8] Each molecule is an interesting species in itself exhibiting individual signatures in each IV-curve, such as step positions and heights [9] or inelastic excitation energies. [10, 11] For this reason, a clear demand for *ab initio* transport calculations of single molecules has emerged in recent years.

Such calculations are a difficult enterprise, because they must meet simultaneously two requirements. Powerful methods exist to deal with each one separately, but the combined problem still is one of the challenging adventures of theoretical physics and quantum chemistry.

Difficulty number one is that a molecule is a genuine many-body system, where the mutual interaction of the particles is important for understanding its properties. These include, in particular, the energy and shape of the (effective) molecular quasiparticle orbitals. Some of the salient aspects, such as the position of the molecule's atoms, the symmetry of molecular orbitals and their relative energies, are often described accurately by effective single-particle theories, such as density functional theory. For less basic questions, concerning for instance excitation energies or details of the electronic charge distribution, polarization, and charging effects, an advanced machinery equipped with methods and codes from quantum chemistry and electronic structure calculations is available.

Difficulty number two is related to the fact that a transport calculation investigates the effect of coupling the molecule to a macroscopic electrode, i.e. a reservoir with which particles (and energy) can be exchanged. It is the associated broadening of the molecular energy levels which is supposed to be understood quantitatively in transport calculations and therefore the coupling has to be modelled with great detail and care.

While the first difficulty can be resolved for sufficiently small molecular systems, the second one requires including many electrode atoms, i.e., a great number of degrees of freedom, in order to properly extrapolate to the macroscopic limit. These conditions are mutually exclusive (almost), and this is the particular challenge in molecular scale transport calculations with *ab initio* methods.

In reality, any *ab initio* transport calculation begins with a compromise accepting strong, often uncontrolled, approximations when dealing with one of the two mentioned difficulties. In the present "standard approach to molecular conductance" [12–14] a drastic simplification on the many-body side is being made. One is accepting the Kohn-Sham energies and orbitals that appear in structure calculations based on ground-state density functional theory (DFT) as the legitimate single particle states for a selfconsistent scattering theory of transport. The procedure has the tremendous advantage that including the reservoirs is then a very well defined process, if sufficient care is taken. For practical purposes, a formulation in terms of non-equilibrium Green's (or "Keldysh") functions is advantageous and therefore often used. [15] For non-interacting particles the theory is equivalent to a Landauer-Büttiker theory of transport[16, 17]. For KS-particles a slight generalization is introduced, in which the electronic charge distribution is calculated selfconsistently in the presence of the bias voltage.

Clearly, the use of DFT for the scattering states already includes many non-trivial interaction effects beyond the electrostatic Hartree interaction – Fermi liquid (FL) renormalizations in the language of condensed matter physics – even on the level of local or gradient corrected density approximations (LDA,GGA). [18] Still, ground and excited states of correlated electron systems are *not* single Slater determinants and therefore the validity of applying scattering theories designed for non-interacting particles to interacting systems is not straightforward to establish. Moreover, including correlation effects beyond FL renormalizations, which can be very important for transport characteristics like the Coulomb blockade or the Kondo resonance, is not inconceivable in a single determinant theory, but it certainly requires density functionals advanced far beyond LDA. In this respect it is tempting to use the advanced machinery of quantum chemistry to calculate a better approximation for correlated many-body states including more than one Slater determinant, however, this approach also has a serious drawback because it is limited to relatively small system sizes. The bare molecule appearing in typical transport experiments consists of typically 5-10 aromatic rings, which is a size already at the limits of what correlated methods could still reasonably deal with. Including in addition 10-200 metal atoms in order to accurately model the coupling to the leads in a controlled way appears to be out of reach at present. For this reason, only very few attempts limited to small molecules have been made in this direction. [19]

In this article, we describe three principle approaches to transport calculations based on time-dependent density functional theory (TDDFT). We shall first present a brief account of the basic principle strategies. Then, we explain in more detail one of them, the standard method of *ab initio* transport calculations. In Section II, we discuss an attempt to justify the procedure from the point of view of TDDFT [20–22], list loose ends and apparent conceptual difficulties.

Since the exchange-correlation potential $V_{\rm XC}(\mathbf{x})$ is not known exactly, in any practical calculation approximations like LDA have to be admitted. These are not controlled any more when one deals with realistic molecules. As a consequence, in addition to conceptual problems, appreciable artefacts related to approximate functionals can emerge, which have been well studied for standard DFT applications in quantum chemistry and electronic structure theory, and which carry over to transport calculations as well. [23] A brief list of deficencies most important for transport purposes has been included in Section III.

II. TDDFT AND TRANSPORT

Time dependent DFT is a well established generalization of (ground state) density functional theory and has been introduced by Runge and Gross [24] and expanded on by van Leeuwen [25].

RG-Theorem: For any interacting fermion system there is a unique dual system of *non*-interacting fermionic quasiparticles with the following property: the time dependent density of original and dual particles is identical for any driving field $V_{\rm ex}(t)$; the time evolution of dual ("Kohn Sham" or KS) fermions is governed by a Schrödinger-type equation decorated with a Hartree term and an exchange correlation potential $V_{\rm XC}[n]$, which can be expressed as a functional of the time dependent particle density and its history, $n(\mathbf{x},t)$. In the genereral case, $V_{\rm XC}[n]$ depends on the full many-body state at the initial time t=0.

Because the Runge-Gross-Theorem guarantees that the dual system delivers the exact time evolution of the interacting particle density, also longitundinal transport currents can be calculated by exploiting the continuity equation [50],

$$\dot{n}(\mathbf{x},t) + \nabla\cdot\mathbf{j}(\mathbf{x},t) = 0,$$

where a dot denotes a time-derivative. This observation underlies all applications of TDDFT to transport.

Quite generally, transport can be investigated in several different languages, which all are equivalent in the regime where their validity overlap. Even though we're ultimately interested in the standard method, the TDDFT version of the others will give valuable information, too. Therefore we shall briefly discuss them as well. We begin, however, by recalling the basic formalism of TDDFT.

A. TDDFT formalism

TDDFT is a machinery for propagating a density in time, not a many body wavefunction. Hence, as a prerequisite for applying the method an initial density (t=0) is required. It needs to be represented as a single Slater determinant $|0\rangle$ constructed from a (complete) set of effective single particle states ϕ_m . This is always possible, if at t<0 the system is in its ground state; then the KS-orbitals of ground state DFT are obvious candidates for ϕ_m. In this case, one has for the density matrix at $t = t' = 0$

$$n(\mathbf{x},\mathbf{x}') = \sum_m^{\rm occ.} \phi^*_m(\mathbf{x})\phi_m(\mathbf{x}'). \tag{1}$$

Time evolution of the state $|0\rangle$ together with its density matrix is mediated via $H_{\rm s}$:

$$H_{\rm s} = -\frac{1}{2m}\int d\mathbf{x}\ \psi^\dagger(\mathbf{x})\Delta\psi(\mathbf{x}) + V_{\rm H}[n(t)] + V_{\rm XC}[n(t)] + V_{\rm ex}(t) \tag{2}$$

with

$$V_{\rm H}[n(t)] = \frac{1}{2}\int d\mathbf{x}\ v_{\rm H}[n](\mathbf{x},t)\ \psi^\dagger(\mathbf{x})\psi(\mathbf{x}) \tag{3}$$

where $v_{\rm H}(\mathbf{x},t) = \int d\mathbf{x}'\ n(\mathbf{x}';t)/|\mathbf{x}-\mathbf{x}'|$ and

$$V_{\rm XC}[n(t)] = \int d\mathbf{x}\ d\mathbf{x}'\ v_{\rm xc}[n](\mathbf{x},t)\ \psi^\dagger(\mathbf{x})\psi(\mathbf{x}). \tag{4}$$

The nontrivial aspects originate from the fact that the orbitals $\phi_m(t)$ are not eigenstates of $H_{\rm s}$ at $t > 0$.

$H_{\rm s}$ can be explicitly time dependent in the probing potential, $V_{\rm ex}(t)$. An implicit dynamics exists via the Hartree and exchange-correlation terms, that depend on the time dependent particle density $n(\mathbf{x},t)$. A few remarks about the potential $v_{\rm xc}[n]$ debuting here are in place.

(a) The exchange correlation potential $v_{\rm xc}[n]$ is not just a density functional. Its precise definition requires specification of the initial many body state at $t=0$. But, for an initial non-degenerate ground state the dependence on the initial wavefunction is replaced by the initial density, thank to the Hohenberg-Kohn theorem.

(b) TDDFT strictly applies only to *finite* systems, and a generalization that uses the current as the basic variable is needed for infinite systems.

(c) In practice, it might be advantageous for the construction of useful approximations to allow for a more general, offdiagonal structure of $v_{\rm xc}[n](\mathbf{x},\mathbf{x}';t,t')$ that could also include (time dependent) gauge fields. Similarly, one can also consider $v_{\rm xc}[n]$ as a functional of the full density operator $n(\mathbf{x},\mathbf{x}';t,t')$, rather than only its diagonal elements, which is the particle density. Thus additional observables, like the current density, are introduced into the Hamiltonian. In statistical mechanics this is a standard recipe in order to eliminate a history dependence in kinetic equations[26], and here it serves exactly the same purpose [27].

Structure of XC potential if $V_{\rm ex}$ is weak

In this subsection, we analyze the non-equilibrium piece of the $v_{\rm xc}[n]$ potential. The idea is to exploit the fact, that it can be related to known correlation functions if the probing potential $V_{\rm ex}$ is weak.

We begin by recalling some basic facts of the theory of linear response for TDDFT. Since the density evolution of dual and original system, $n(\mathbf{x},t)$, coincide, they exhibit in particular the same susceptibility for the density, $\chi(\mathbf{x},\mathbf{x}',t-t')$, which describes the linear response to $V_{\rm ex}(t)$. What is usually measured is not the response to a probing but rather to the total electric field, which is the sum of external and induced (screening) fields. An important example is the linear conductance. It is the ratio of the current and the measured (total) electrostatic voltage drop at the resistor: $I/V_{\rm bias}$.

The corresponding response function is the Hartree-irreducible correlator:

$$\chi_{\rm irr}^{-1} \equiv \chi^{-1} + f_{\rm H}$$

($f_{\rm H}(\mathbf{x},\mathbf{x}')=1/|\mathbf{x}-\mathbf{x}'|$). In TDDFT the operator $\chi_{\rm irr}$ can be decomposed even further. Namely, the TDDFT Hamiltonian $H_{\rm s}$ has two pieces that react to density modifications. In addition to $V_{\rm H}$ incorporating the electrostatic screening, there is also an induced effect on $V_{\rm XC}$,

$$\chi_{\rm irr}^{-1} = \chi_{\rm KS}^{-1} - f_{\rm xc}, \qquad (5)$$

which can be split off in the same manner as $f_{\rm H}$. The truncated correlator $\chi_{\rm KS}$ describes the (bare) response of ground state DFT. The promised connection between the correlator $\chi_{\rm irr}$ and $v_{\rm xc}[n]$ is mediated via the XC kernel:

$$f_{\rm xc}(\mathbf{x},\mathbf{x}';t-t')=\delta v_{\rm xc}[n](\mathbf{x},t)/\delta n(\mathbf{x}',t'). \qquad (6)$$

Relations (5,6) are very useful, because due to a beautiful series of works by Kohn, Vignale and collaborators there is a simple approximation to the non-equilibrium contribution to $\chi_{\rm irr}$. [27, 28] In fact, these authors reveal the full hydrodynamic structure of $\chi_{\rm irr}^{-1}$ by exploiting the relation to the phenomenological theory of quantum liquids.

In their analysis, $f_{\rm xc}$ is the sum of two very different pieces:

$$f_{\rm xc} = f_{\rm xc}^{\rm adia} + f_{\rm xc}^{\rm non-eq} \qquad (7)$$

where $f_{\rm xc}^{\rm adia}=\delta v_{\rm xc}^{gs}[n]/\delta n$ and a gradient expansion of $f_{\rm xc}^{\rm non-eq}$ is given by $f_{\rm VK}$. The first term is fully analogous to $f_{\rm H}$ and it describes the exchange-correlation screening of the ground state DFT Hamiltonian to the probing field. Only in the second piece many body effects of a genuinely non-equilibrium nature appear: it incorporates the visco-elastic response of the electronic quantum liquid. Since the emerging term is local and dissipative, the corresponding forces are not conservative. This means, that $f_{\rm VK}$ cannot be incorporated as a pure density coupling – i.e. a potential term – in $H_{\rm s}$, but gives rise to a (time dependent) gauge field, instead, and is only described as a current-dependent kernel.

B. External driving field

In this section we return to the transport problem in TDDFT. To investigate transport currents generated by an external driving field, one needs to supplement $H_{\rm s}$ with an inhomogenous electric potential, $V_{\rm ext}(q,\omega)$, together with electrodes. [56] *Practical* applications with this approach in TDDFT suffer from the fact, that before one can perform the *dc*-limit ($\omega\to 0$), one first has to take the thermodynamic limit ($q\to 0$) of infinite system size. In realistic calculations this is usually a very cumbersome excercise.

From a *conceptual* point of view, thinking about currents as generated by weak external driving fields is rewarding, however, because one is led back to the Kubo formula and the theory of linear response. We thus can directly apply results from the preceeding section and in particular investigate the effect of visco-elasticity on the current flow.

1. Kubo formula

The Kubo formula provides an exact relation between the current density and the driving external and induced (effective) electric fields, that appear in the TDDFT calculation [29]:

$$j(\mathbf{x},\omega) = \int d\mathbf{x}' \ \sigma_{\rm KS}(\mathbf{x},\mathbf{x}',\omega)\left[E_{\rm ex}+E_{\rm H}+E_{\rm xc}\right](\mathbf{x}',\omega). \qquad (8)$$

where σ is the non-local conductivity tensor and where the electric fields derive from the potential terms given in Eq. (2). As always, susceptibilities for particle densities $\chi_{\rm KS}$ and currents $\sigma_{\rm KS}$ are related via the continuity equation:

$$\partial_t \chi_{\rm KS}(\mathbf{x},\mathbf{x}',t) = -\sum_{i,j=1}^{3} \nabla_i \nabla_j \sigma_{{\rm KS},ij}(\mathbf{x},\mathbf{x}',t). \qquad (9)$$

The structure analysis II A suggests to split the full current density into a bare response, j_0, and a remaining piece, $j_{\rm VK}$:

$$j = j_0 + j_{\rm VK}. \qquad (10)$$

We discuss the second term first. It is driven by a force field, $E_{\rm VK}$,

$$j_{\rm VK}(\mathbf{x},\omega) = \int d\mathbf{x}' \sigma_{\rm KS}(\mathbf{x},\mathbf{x}',\omega) E_{\rm VK}(\mathbf{x}',\omega). \qquad (11)$$

that is associated with $f_{\rm VK}$. In the hydrodynamic limit considered by Vignale et al. [28] it has an interpretation as visco-elastic force internal to the electron liquid, that can be described by the stress tensor, ς_{ij} (unperturbed density: $n_0(\mathbf{x})$):

$$E_{{\rm VK},i}(\mathbf{x},\omega) = n_0(\mathbf{x})^{-1} \sum_{k=1}^{3} \nabla_k \varsigma_{ik}(\mathbf{x},\omega). \qquad (12)$$

The relative magnitude of $j_{\rm VK}$ is small as compared to j_0, since the viscosity, η, of the electron liquid is quite small. Based on the homogenous value of η in two and three spatial dimensions a rough analytical consideration can give an estimate. [29] The ratio $j_{\rm VK}/j_0$ is expected to be typically of the order of 10% or less. In a numerical study the viscous corrections to the conductance of the benzene-dithiol molecule have been explicitly calculated. The effect is small, roughly 5%, as expected. [30]

Note, however that the previous conclusion is to be taken with a grain of salt. Strictly speaking, the explicit derivation of Eq. (12) assumes, that the inhomogeneities, which provide the "surface" for the viscous friction to appear, are very smooth: in the period ω^{-1} of the probing field, the electron should travel a distance not larger than the typical spatial scale ℓ on which the inhomogenuous background changes, $v_{\rm F}/\omega \ll \ell$. Applying this condition to molecules and assuming $k_{\rm F}\ell \sim 1$, one would get $v_{\rm F} k_{\rm F} \ll \ell\omega$, which is satisfied only at optical frequencies of the order of eV, but not in the *dc* limit. Nevertheless, the qualitative finding of the mentioned estimates – namely that viscocity effects tend to be small – should be indicative, because the (transverse) momentum exchange between electrons at low temperatures is a rare process due to phase space constraints. We believe that this basic principle pertains to electrons in a molecule as well. [57]

We thus propose that the dominating contribution in Eq. (10) is given by the response to the reactive forces,

$$j_0(\mathbf{x}) = \int d\mathbf{x}'\ \sigma_{\rm KS}(\mathbf{x},\mathbf{x}')\left[E_{\rm ex} + E_{\rm H} - \nabla_{\mathbf{x}'} v^{\rm gs}_{\rm xc}\right](\mathbf{x}'), \quad (13)$$

where our notation suppresses the ω-dependence.

2. *Bias voltage and Kohn-Sham voltage drop*

The expression (13) for the current density can be simplified, if we assume, that the dependence of the forces on the coordinate, $\mathbf{x}_\perp$, perpendicular to the current path, z, is negligibly weak. This assumption is not necessarily a good one for quantitative questions, but it allows us to discuss more clearly the difference between $\sigma_{\rm KS}$ and the conductivity, $\sigma_{\rm irr}$, measured in typical transport experiments:

$$j(\mathbf{x}) = \int d\mathbf{x}'\ \sigma_{\rm irr}(\mathbf{x},\mathbf{x}')\left[E_{\rm ex} + E_{\rm H}\right](\mathbf{x}'). \qquad (14)$$

If we make the proposed step and neglect the $\mathbf{x}_\perp$ dependence of the forces, we can integrate both sides of (14) over any cross section, and obtain

$$I = G\ V_{\rm bias} \qquad (15)$$

with a conductance

$$G = \int d\mathbf{x}_\perp d\mathbf{x}'_\perp \sigma_{\rm irr}(\mathbf{x}_\perp,\mathbf{x}'_\perp; z, z'). \qquad (16)$$

Due to particle number conservation, the cross-sectional integrals render the sum independent of z, z' in the *dc*-limit, $\omega \rightarrow 0$. As usual, the bias voltage is given by

$$V_{\rm bias} = \int_{\mathbf{x}_l}^{\mathbf{x}_r} d\mathbf{s}\ \left[E_{\rm ex} + E_{\rm H}[n]\right](\mathbf{s}). \qquad (17)$$

where $\mathbf{s}(t)$ is any path connecting the left with the right hand side of the molecule. $V_{\rm bias}$ should be picked up between points $\mathbf{x}_l$ and $\mathbf{x}_r$ sufficiently far away from the scattering region, in the near asymptotics, where the electrostatic potential energy surface has turned constant.

The same procedure can be repeated also for Eq. (13)

$$I = G_{\rm KS}\ V_{\rm KS} \qquad (18)$$

with an expression for $G_{\rm KS}$ completely analogous to (16). We have introduced the KS-voltage drop, $V_{\rm KS}$, given by the sum of *all* KS-forces, Eq. (13), along $\mathbf{s}(t)$,

$$V_{\rm KS} = V_{\rm bias} + V_{\rm xc}; \qquad V_{\rm xc} = -\int_{\mathbf{x}_l}^{\mathbf{x}_r} d\mathbf{s}\ E_{\rm xc}(\mathbf{s}). \qquad (19)$$

In the spirit of Eq. (10), we can decompose the deviation, $V_{\rm xc}$, of the measured bias and $V_{\rm KS}$ into two pieces

$$V_{\rm xc} = \int_{\mathbf{x}_l}^{\mathbf{x}_r} d\mathbf{s}\ \nabla_{\mathbf{s}} v^{\rm gs}_{\rm xc}[n](\mathbf{s}) - \int_{\mathbf{x}_l}^{\mathbf{x}_r} d\mathbf{s}\ E_{\rm VK}(\mathbf{s}). \qquad (20)$$

The first term can be integrated trivially: $v_{\rm xc}^{\rm gs}[n](\mathbf{x}_l) - v_{\rm xc}^{\rm gs}[n](\mathbf{x}_r)$. If the left and right hand side electrodes consist of the same material, then this difference can be nonvanishing only due to long range terms in $v_{\rm KS}^{\rm gs}$. In particular, local approximations like LDA or GGA cannot give a finite contribution in the XC part. The second term in Eq. (20) describes the genuine non-equilbrium forces, that result from the viscosity of the elctron liquid discussed above.

Eqs. (18) and (19) demonstrate, that a KS-particle behaves under bias very differently from a physical quasiparticle. The only long range forces, that the physical particle realizes upon applying $V_{\rm ex}$ are of the pure Coulomb type. For this reason, the bias voltage must be exactly equal to the difference in electro-chemical potentials:

$$V_{\rm bias} = \mu_{\mathcal{L}} - \mu_{\mathcal{R}}.$$

Interaction terms (beyond Hartree-level) do not occur. By contrast, the KS-particle experiences an effective voltage $V_{\rm KS}$, that can be quite different from $V_{\rm bias}$. This way of including interaction effects by adding the corrective term $V_{\rm xc}$ to the voltage drop is not very physical. A difficulty appears, that comes back on us in the next two subsections.

C. Initial value problem

The second access to transport investigates an initial value (so called “relaxation”) problem without any reference to a driving external field $V_{\rm ex}$. One considers a molecule and two reservoirs, left and right $(\mathcal{L}, \mathcal{R})$. At $t < 0$ the molecule is coupled to and in equilibrium with $\mathcal{L}$. At $t = 0$ a coupling to $\mathcal{R}$ is being switched on and the time evolution with $H_{\rm s}$ begins, as described in section II A. A current, I, starts to flow at $t > 0$, if $\mathcal{L}$ and $\mathcal{R}$ are not in equilibrium with one another. I is related to the time derivative of the number of particles in the electrodes, $N_{\mathcal{L},\mathcal{R}}$,

$$I(t) = -\dot{N}_{\mathcal{L}} = \dot{N}_{\mathcal{R}}. \tag{21}$$

As in the previous case, the current may be obtained via the continuity equation from an explicit TDDFT propagation of the electronic density. Since relaxation involves processes on all time scales, in principle the response function $\chi(\omega)$ can be extracted at all frequencies larger than the inverse observation time.

Also, the drawbacks of this approach are similar to the previous case: one has to include big reservoirs and to propagate many time steps if long time, low frequency properties, such as steady-state currents, are to be addressed. Due to this difficulty, the relaxation method with TDDFT has been applied mainly to obtain the high frequency response. In an incarnation where a step potential is switched on at t=0, it has also been used for transport studies in non-interacting model systems, but not for a full-fledged realistic TDDFT calculation, yet. [31] However, we mention that an application of the method for model studies of strongly correlated transport in interacting Hubbard chains has recently been very successful using the density renormalization group method. [32]

For our purpose, the formulation of transport in terms of an initial value problem is conceptually important, because it allows us to link time propagation of the density (TDDFT) with DFT-scattering theory.

Indeed, let us perform the following “Gedanken experiment” in which we allow ourselves to work with perfect reservoirs, and where we can do the time propagation of the density up to any time we wish. At the initial stages, $0 < t \ll t_{\rm trans}$, we shall encounter transient phenomena, which render the particle density near the contact region time dependent. Only at a much later stage, $t \gg t_{\rm trans}$ we arrive at the asymptotic non-equilibrium situation.

In order for the usual scattering formalism to be applicable, the asymptotic current carrying state of TDDFT, $|{\rm QS}\rangle$, should meet the following conditions:

c1: At zero temperature $|{\rm QS}\rangle$ is a single Slater determinant of left and right moving scattering states, $\psi_{l,r}$, which are eigenstates of the asymptotic TDDFT Hamiltonian $H_{\rm qs}$. The associated quasi-static KS-density matrix (definition see Eq. (22)) is invariant under time translations: $n_{\rm qs}(\mathbf{x}, \mathbf{x}'; t - t')$.

c2: The potential $v_{\rm xc}[n]$ takes an asymptotic form which is independent of the history.

c3: The KS-scattering states are occupied according to Fermi-Dirac distributions, $f_{\mathcal{L},\mathcal{R}}$, carrying the temperature and chemical potential of the reservoirs that they emanate from.

Discussion: Very little rigorous is known about the true nature of the non-equilibrium state of the interacting electron liquid. For this reason our discussion can be no other but very qualitative.

Condition **c1** puts a strong requirement on the physical relaxation process. Because the equal time density matrix $n_{\rm qs}(\mathbf{x}, \mathbf{x}'; 0)$ is time independent at $t \gg t_{\rm diss}$, particle and current densities must have become stationary:

R: After transient phenomena have died out, at $t \gg t_{\rm trans}$ a quasi-stationary non-equilibrium state is reached. “Quasi-stationarity” in this context is meant in the strong sense, in which the time evolution of the particle and current densities have come to a standstill.

It is plausible, that this requirement is always fullfilled in the linear regime of small voltages $\mu_{\mathcal{L}} - \mu_{\mathcal{R}}$. [58] For non-interacting particles, this is certainly true also in the non-linear case. [54] The situation is much less clear for interacting particles in the non-linear voltage range. In fact, due to the non-linear nature of the kinetic equations one suspects that phenomena like turbulence should occur. [33] This would imply densities and currents fluctuating in time even at $t \gg t_{\rm trans}$, so that $\mathbf{R}$ is not strictly satisfied. [55]

If indeed the quantum liquid goes turbulent, then part of the memory of the intial conditions never is lost. This is, because even small microscopic details in the initial values of the relevant kinetic fields (particle densities, currents etc.) will in general invoke a different dynamics at later times. For this reason, validity of **c2** is not guaranteed. However, usually there is no interest in a precise set of initial conditions. Possibly, a suitable averaging procedure (either over initial conditions or over a small time interval) could reestablish **c2** in an effective sense.

Returning to the case of small biases, let us emphasize that even if $|QS\rangle$ is a single Slater determinant, validity of **c3** is not automatically guaranteed. In order to see this, we imagine a surplus of particles in one reservoir (T=0), so that an electro-chemical potential difference maintains a particle flow to the other reservoir. If it is correct, that all current is carried by the scattering states in energy window situated between $\mu_{\mathcal{L}}$ and $\mu_{\mathcal{R}}$, then we find that the current linear in the voltage is necessarily given by $G_{\rm KS}(\mu_{\mathcal{L}}-\mu_{\mathcal{R}})$. The correction term $V_{\rm xc}$ is missing, so we arrive at a statement contradicting Eq. (18). This is the difficulty, already alluded to at the end of the last subsection. We will come back to it again in the following subsection.

D. Scattering approach

It is *the* advantage of scattering theory that all information is encoded in scattering states and no reference to time propagation is being made. The idea is to replace the initial value problem by an equivalent boundary problem. This is the philosophy adopted by the standard method of molecular transport calculations. Its persuasive, charming aspects are: (i) the method is stationary and (ii) the reservoirs are relatively easy to include.

The most important problematic aspect is that up to now a rigorous justification of the approach has not been given, and it is not obvious that it should exist. The validity of the scattering formalism has been rigorously established only for non-interacting particles. Whether the conditions **c1-c3** formulated in the preceeding section are really met, so that the treatment is legitimate also for KS-particles, is not fully clear at present. If they are taken for granted, the following selfconsistency procedure can be justified, which in essence is the standard method.

One starts with a guess for the equal time density operator $n_{\rm qs}(\mathbf{x},\mathbf{x}')$. Condition **c2** ensures, that nothing more is needed in order to construct a first approximation for the Hamiltonian $H_{\rm qs}$ – provided the functional $v_{\rm xc}[n]$ is given, of course.

In order to start the next iteration, one should know how to construct a better guess for the density operator from $H_{\rm qs}$. This is where **c3** and again **c1** kick in: according to **c1** scattering states can be found as the eigenstates of $H_{\rm qs}$, which then can be filled up successively in order to obtain $|QS\rangle$ and the improved density matrix. The procedure is completely analogous to the case of non-interacting particles:

$$\begin{aligned} n_{\rm qs}(\mathbf{x},\mathbf{x}') \ &= \sum_l f_{\mathcal{R}}(\epsilon_l)\ \psi_l^*(\mathbf{x})\psi_l(\mathbf{x}') \\ &\quad + \sum_r f_{\mathcal{L}}(\epsilon_r)\ \psi_r^*(\mathbf{x})\psi_r(\mathbf{x}'). \end{aligned} \tag{22}$$

At the end of the iteration cycle, selfconsistency is reached. This means that scattering states have been found in an effective potential that incorporates already the shifts in the charge distribution characteristic of the non-equilibrium situation which also generates the current.

The bottom line is that under the assumptions **c1-c3** there are only two minor differences between a ground state calculation and a standard *dc*-transport calculation:

1. A non-equilibrium density operator calculated from Eq. (22) replaces the ground state expression Eq. (1) (to be obtained with $f_{\mathcal{L}} = f_{\mathcal{R}}$).
2. In principle, a quasi-stationary functional should replace the ground state functional. In actuality, due to lack of any better choice, common ground state functionals are employed leading to additional artefacts, Section III.

E. Standard method and Kubo formula: discrepancies

The calculation of the *dc*-current can proceed directly from Eq. (22) which leads to a Landauer-Buttiker type description,

$$I = \int dE\ T(E,\mu_{\mathcal{L}},\mu_{\mathcal{R}})\,[f_{\mathcal{L}} - f_{\mathcal{R}}]\,, \tag{23}$$

where the transmission function, T, has been introduced. The kernel $T(E,\mu_{\mathcal{L}},\mu_{\mathcal{R}})$ can be expressed by the resolvent operator

$$G(E) = (E - H_{\rm qs} - \Sigma_{\mathcal{L}} - \Sigma_{\mathcal{R}})^{-1}$$

and self energies $\Sigma_{\mathcal{L},\mathcal{R}}$, which represent the boundary conditions at the surface of the electrodes. [34] One has

$$T(E,\mu_{\mathcal{L}},\mu_{\mathcal{R}}) = \mathrm{tr}\ \Gamma_{\mathcal{L}} G \Gamma_{\mathcal{R}} G^\dagger \tag{24}$$

where $\Gamma_{\mathcal{L},\mathcal{R}} = i(\Sigma - \Sigma^\dagger)_{\mathcal{L},\mathcal{R}}$. [20] For non-interacting particles, Eqs. (23,24) are equivalent to the Landauer formula and give the exact current. [12] The Landauer conductance, $G_{\rm qs}$=$T(\epsilon_{\rm F})e^2/h$, is the response of the current linear in the applied electro-chemical potential difference

$$I = G_{\rm qs}(\mu_{\mathcal{L}}-\mu_{\mathcal{R}}). \tag{25}$$

(We choose the nomenclature in the spirit of Sec. II B 2.) For non-interacting particles, rigorous results exist, which show that the Landauer conductance and the conductance obtained from the Kubo-conductivity, σ_{irr} coincide. [35] This is true, because in the absence of interactions

$$G = G_{\mathrm{KS}} = G_{\mathrm{qs}}. \tag{26}$$

However, the KS-particles are *not* truely non-interacting. This expresses itself in the fact that $G \neq G_{\mathrm{KS}}$, in general, because $V_{\mathrm{XC}} \neq 0$. In the present standard approach, one has $G_{\mathrm{qs}} = G_{\mathrm{KS}}$. Therefore, a term in the current proportional to V_{XC} is ignored. In order to include this term, one would have to manipulate the XC-functional used in H_{qs} such that the *bare dc*-current response becomes χ_{irr} rather than χ_{KS}. Note, that it is known that even within LDA the terms ignored can be important. Including them on the level of "adiabatic" LDA can shift resonances and therefore have a substantial impact on a transmission characteristics. [36]

III. GROUND STATE DFT: ARTEFACTS OF LOCAL DENSITY FUNCTIONALS

In this section, we discuss some well-known limitations of common density functional approximations, and their implications for transport calculations. [49]

By common density functional approximations, we will mean the original local density approximation of Kohn and Sham[40], the generalized gradient approximation, employing both the density and its gradient, eg PBE[41], and hybrids of GGA with exact exchange, such as PBE0[42] and B3LYP[43–45].

There are a variety of related deficiencies of all these approximations. The first is that they fail for one-electron systems, in which the exchange energy should exactly cancel the Hartree, while the correlation energy should vanish. The above density functionals generally fail this requirement, and are said to have a *self-interaction* error, meaning that the electron is incorrectly interacting with itself. [48]

A related difficulty is that the ground-state KS potential in such approximations is poorly behaved. For a neutral system, the exact KS potential decays as $-1/r$ for large distances. But with these approximations, the potential decays too rapidly, in fact exponentially with distance, due to the local dependence on the density. (Hybrid functionals do have a fraction of $-1/r$, but not the right amount.) This leads to potentials that are far too shallow overall, and HOMO's (highest occupied molecular orbitals) that are insufficiently deep.

The exact KS HOMO can be proven to be equal to the negative of the ionization potential, but this is not even roughly true for approximate KS potentials, for reasons given above. Thus the charge density in tail regions, i.e. where the density is low, is inaccurate. Furthermore, whenever a localized system is in weak contact with a reservoir, so that the average particle number on the system can be continuous, the exact KS potential jumps by a (spatially) constant amount whenever the particle number passes through an integer[46, 47]. This behavior is entirely missed by the above approximations, which smoothly interpolate between either side of this discontinuity.

These difficulties are either largely or totally overcome by the use of orbital-dependent functionals. The first popular one of these was SIC-LDA, the self-interaction corrected local density approximation, as introduced by Perdew and Zunger[48]. These days, many codes have been developed to handle orbital-dependent functionals and to find the corresponding KS potential, via the optimized potential method (OPM), a.k.a. optimized effective potential (OEP). Exact exchange potentials have the correct decay, their HOMO's are close to the negative of the ionization potential, and they jump discontinuously at integer particle number. [53]

How does all this affect transport calculations? There are two principal effects, one obvious, the other less so.

In the first, since transport is often a weak tunnelling process, the position of the molecular levels relative to the leads greatly affects the calculated current. If a molecule is weakly coupled to the leads, there is every reason to think that standard functional approximations will make huge errors in the calculation of currents. The levels will be misaligned not only in the equilibrium situation, but will respond completely wrongly to the transfer of charge into a localized molecular orbital. [51]

These deficiencies in common ground state functionals may be the reason why present DFT-calculations fail to correctly reproduce elementary ground state properties that manifest themselves in the transport characteristics. The most prominent example is the Coulomb blockade phenomenon, which usually is not reproduced quantitatively. [37] It is less well appreciated, that also the Kondo-effect belongs to this category of phenomena. Its manifestation is an extra resonance in the spectral function of the molecule at ϵ_{F}, the *Abrikosov-Suhl resonance*. In principle, this resonance is a ground state property. It affects the total charge on the molecule and for this reason it should be detectable with DFT, provided an appropriate (so far unknown) functional is used.

Furthermore, density functional approximations will artificially smear out a sharp resonance into a much weaker peak, spread out sometimes over several eV, between the LUMO of the uncharged molecule and the HOMO of the charged molecule. [29] This effect has already been demonstrated in calculations on simple models [51], and has recently been seen in a full OEP calculation. [52] Of course, for molecules that are chemically bonded to the leads, there is no region of very low density, and the potential should be reasonably accurate within the common approximations. So another question is: how big an effect is this in real experiments?

The second effect is more subtle, but could be more important in the chemically-bonded situation, perhaps.

The standard approximations, being local in nature, yield no XC correction to the potential drop across the molecule. In the language of the previous section, V_{KS} is identical to the real electrostatic potential drop, V_{bias}. But there is no reason that this should be true in reality, or in a more accurate calculation. Thus an exchange calculation should produce a finite effect. As mentioned above, a current-dependent approximation (VK) indeed produces a small, but finite, effect. Such calculations, performed self-consistently and at finite bias, need to account for this drop, and correct the Landauer formula to account for it. This means that the conductance is *not* just proportional to the transmission through the self-consistent KS potential. In one spatial dimension this means, that the current must be calculated using the total potential drop, including the XC contribution, and this must be divided by the electrostatic potential drop. In this case, it is hard to see how a simple single-particle effective potential could produce the exact conductance. [29]

Conclusion

The various issues that we have discussed – validity of a scattering approach, neglect of V_{XC}, deficiencies of commmon density functional approximations – raise serious doubts about the accuracy of the present standard method for transport calculations. How quantitatively significant these errors are is only poorly understood, at the moment. For such an estimate, time and orbital-dependent calculations are an important tool. [31] To gain further insight, it is important to go also beyond (TD)DFT. Work in this direction is in progress. Proposals include approaches based on a configuration interaction [19], the *GW*-method [38], and the LDA+U formalism [39]. All of the proposed directions have their virtues and drawbacks. It remains to be seen which one of them turns out to be most suitable to deliver conductances of real, large molecules which require a controlled handling of electrode effects.

Acknowledgements

FE expresses his gratitude to P. Schmitteckert, P. Wölfle and E. K. U. Gross for valuable discussions. Also, we thank V. Meded for useful comments on the manuscript as well as the Center for Functional Nanostructures of the Deutsche Forschungsgemeinschaft at Karlsruhe University and the DOE under grant DE-FG02-01ER45928 for their financial support for financial support (FE).

---

[1] D. Djukic, K. S. Thygesen, C. Untiedt, R. H. M. Smit, K. W. Jacobsen, and J. M. van Ruitenbeek, Phys. Rev. B **71**, 161402 (2005).
[2] S. Kubatkin, A. Danilov, M. Hjort, J. Cornil, J.-L. Brédas, N. Stuhr-Hansen, P. Hedegård, and T. Bjørnholm, Nature **425**, 698 (2003).
[3] Z. Li, B. Han, G. Meszaros, I. Pobelov, and T. Wandlowsky, Faraday discussions (2005).
[4] Latha Venkataraman, Jennifer E. Klare, Colin Nuckolls, Mark S. Hybertsen, Michael L. Steigerwald, Nature Letters **442**, 904 (2006).
[5] E. Loertscher, J. W. Ciszek, J. Tour, and H. Riel, Small **2**, 973 (2006).
[6] Z. K. Keane and D. Natelson, Nano Letters **6**, 1518 (2006).
[7] M.-H. Jo, J. E. Grose, K. Baheti, M. M. Deshmukh, J. J. Sokol, E. M. Rubmberger, D. N. Hendrickson, J. R. Long, H. Park, and D. C. Ralph, Nano Lett. **6**, 2014 (2006).
[8] J. Reichert, R. Ochs, D. Beckmann, H. Weber, M. Mayor, and H. von Löhneysen, Physical Review Letters **88**, 176804 (2002).
[9] M. Elbing, R. Ochs, M. Koentopp, M. Fischer, C. von Hänisch, F. Weigend, F. Evers, H. B. Weber, and M. Mayor, Proc. Natl. Acc. Sc. US **102**, 8815 (2005).
[10] H. B. Heersche, Z. de Groot, J. A. Folk, H. S. J. van der Zant, C. Romeike, M. R. Wegewijs, L. Zobbi, D. Barreca, E. Tondello, and A. Cornia, Physical Review Letters **96**, 206801 (2006).
[11] L. H. Yu, Z. K. Keane, J. W. Ciszek, L. Cheng, M. P. Stewart, J. M. Tour, and D. Natelson, Physical Review Letters **93**, 266802 (2004).
[12] M. Brandbyge, J.-L. Mozos, P. Ordejon, J. Taylor, and K. Stokbro, PRB **65**, 165401 (2002).
[13] Y. Xue, S. Datta, and M. Ratner, J. Chem. Phys **115** (2001).
[14] M. Paulsson, F. Zahid, and S. Datta, *Handbook of Nanoscience, Engineering and Technology* (CRC Press, 2002), cond-mat/0208183.
[15] L. P. Kadanoff and G. Baym, *Quantum Statistical Mechanics* (Addison-Wesley Publishing Comp. INc., 1962).
[16] R. Landauer, IBM J. Res. Dev. **1**, 233 (1957).
[17] M. Büttiker, PRL **57**, 1761 (1986).
[18] R. Dreizler and E. Gross, *Density Functional Theory* (Springer–Verlag, 1990).
[19] P. Delaney and J. C. Greer, Physical Review Letters **93**, 036805 (2004); G. Fagas, P. Delaney and J. C. Greer, Phys. Rev. B **73**, 241314 (2006).
[20] F. Evers, F. Weigend, and M. Koentopp, Phys. Rev. B **69**, 235411 (2004).
[21] G. Stefanucci and C.-O. Almbladh, Physical Review B **69**, 195318 (2004).
[22] G. Stefanucci and C.-O. Almbladh, Europhys. Lett. **67**, 14 (2004).
[23] J. R. Reimers, Z.-L. Cai, A. Biliċ, and N. S. Hush, Ann. N.Y. Acad. Sci. **1006**, 235 (2003).
[24] E. Runge and E. Gross, Phys. Rev. Lett. **52**, 997 (1984).
[25] R. van Leeuwen, Phys. Rev. Lett. **82**, 3863 (1999).
[26] W. Brenig, *Statistical theory of heat: Nonequilibrium Phenomena*, vol. II (Springer Verlag, 1989).
[27] G. Vignale and W. Kohn, Phys. Rev. Lett. **77**, 2037

(1996).

[28] G. Vignale, C. A. Ullrich, and S. Conti, Phys. Rev. Lett. **79**, 4878 (1997).

[29] M. Koentopp, K. Burke, and F. Evers, Physical Review B **73**, 121403 (2006).

[30] N. Sai, M. Zwolak, G. Vignale, and M. D. Ventra, Phys. Rev. Lett. **94**, 186810 (2005).

[31] S. Kurth, G. Stefanucci, C.-O. Almbladh, A. Rubio, and E. K. U. Gross, Phys. Rev. B **72**, 035308 (2005).

[32] D. Bohr, P. Schmitteckert, and P. Wölfle, Europhys. Lett. **73**, 246 (2005).

[33] R. D'Agosta and M. D. Ventra, cond-mat/0512326 (2005).

[34] F. Evers and A. Arnold, Proceedings of the *Summer-school on Nano-Electronics*, Bad Herrenalb Sept. 1-4, 2005, Springer 2006.

[35] H. U. Baranger and A. D. Stone, Phys. Rev. B **40**, 8169 (1989).

[36] X. Gonze and M. Scheffler, Phys. Rev. Lett. **82**, 4416 (1998).

[37] A. Arnold and F. Evers, unpublished (2006).

[38] K. S. Thygesen and A. Rubio, condmat/0609223v1 (2006).

[39] C. D. Pemmaraju, T. Archer, D. Sànchez-Portal, and S. Sanvito, condmat/0609325v1 (2006).

[40] W. Kohn and L.J. Sham, Phys. Rev. **140**, A 1133 (1965).

[41] J.P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996); **78**, 1396 (1997) (E).

[42] *Local and gradient-corrected density functionals*, John P. Perdew, K. Burke, and M. Ernzerhof, in *Chemical Applications of Density-Functional Theory* eds. B.B. Laird, R.B. Ross, and T. Ziegler, ACS Symposium Series 629 (ACS Books, Washington DC, 1996).

[43] A.D. Becke, Phys. Rev. A **38**, 3098 (1988).

[44] C. Lee, W. Yang, and R.G. Parr, Phys. Rev. B **37**, 785 (1988).

[45] A.D. Becke, J. Chem. Phys. **98**, 5648 (1993).

[46] J.P. Perdew, R.G. Parr, M. Levy, and J.L. Balduz, Jr., Phys. Rev. Lett. **49**, 1691 (1982).

[47] J. P. Perdew and M. Levy, Phys. Rev. Lett. **51**, 1884 (1983).

[48] J.P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[49] Connie Chang, Max Koentopp, Kieron Burke, and Roberto Car, in prep.

[50] M. Di Ventra, T.N. Todorov, J Phys Cond Matt **16**, 8025 (2004).

[51] C. Toher, A. Filippetti, S. Sanvito, and K. Burke, Phys. Rev. Lett. **95**, 146402 (2005).

[52] San-Huang Ke, Harald U. Baranger, and Weitao Yang, cond-mat/0609637v1.

[53] *Orbital-Dependent Functionals for the Exchange-Correlation Energy: A Third Generation of Density Functionals*, E. Engel, in *A Primer in Density Functional Theory.*

[54] G. Stefanucci, S. Kurth, A. Rubio, E. K. U. Gross, cond-mat/0701279; condmat/0607333.

[55] G. Stefanucci, condmat/0608401.

[56] Equivalently, a time dependent vector potential may also be introduced.

[57] An additional caveat should be mentioned, also: the viscosity η not only has a real (dissipative) but also an imaginary (reactive) piece. The effect of the latter has not been investigated so far and we have ignored it, here.

[58] For a thorough discussion of a related problem, see Chapt. 3 of Ref. 26.