DFT-based transport calculations, Friedel’s sum rule and the Kondo effect

Philipp Tröster¹, Peter Schmitteckert²,³, and Ferdinand Evers²,³,⁴

¹ Institut für BioMolekulare Optik, Ludwig-Maximilians-Universität München, D-80538 Munich, Germany
² Institute of Nanotechnology, Karlsruhe Institute of Technology, D-76021 Eggenstein-Leopoldshafen, Germany
³ Center of Functional Nanostructures, Karlsruhe Institute of Technology, D-76131 Karlsruhe, Germany
⁴ Institut für Theorie der Kondensierten Materie, Karlsruhe Institute of Technology, D-76128 Karlsruhe, Germany

(Dated: June 21, 2011)

Friedel’s sum rule provides an explicit expression for a conductance functional, \( G[n] \), valid for the single impurity Anderson model at zero temperature. The functional is special because it does not depend on the interaction strength \( U \). As a consequence, the Landauer conductance for the Kohn-Sham (KS) particles of density functional theory (DFT) coincides with the true conductance of the interacting system. The argument breaks down at temperatures above the Kondo scale, near integer filling, \( n_{\text{d}} \approx 1/2 \) for spins \( \sigma = \uparrow, \downarrow \). Here, the true conductance is strongly suppressed by the Coulomb blockade, while the KS-conductance still indicates resonant transport. Conclusions of our analysis are corroborated by DFT studies with numerically exact exchange-correlation functionals reconstructed from calculations employing the density matrix renormalization group.

The ground state density functional theory (DFT) owes its success to the fact that it proves enormously useful in the prediction of electronic properties of molecules, solids and surfaces. [1][2] Therefore, applications towards the electronic transport properties of single molecules and self assembled monolayers came together quite naturally with the corresponding experimental successes in the field. [3][4] Besides being useful for quantitative calculations, more fundamental properties of DFTs and the corresponding exact functionals have been an issue of intensive research. As an example we mention the question, what exactly is the nature of the approximations when using ground state DFT in combination with the Landauer formalism for transport calculations. [5][6]

The Landauer approach formulated in terms of non-equilibrium Green’s functions [7][8] and its validity for Kohn-Sham particles is also our topic in this work. It relates a single particle Hamiltonian, \( H_{\text{KS}} \), to the conductance via the transmission function, \( G = T_{\text{KS}}(\epsilon_F) e^2/h \). The definition is

\[
T_{\text{KS}}(E) = \text{Tr} \Gamma_{\text{KS}}(E) G(E) \Gamma_{\text{KS}}(E) G^\dagger(E)
\]

(1)

where \( \Gamma_{\text{KS}} = i(\Sigma_\alpha - \Sigma_\alpha^\dagger) \), \( G = (E - H_{\text{KS}} - \Sigma_\alpha - \Sigma_\alpha^\dagger)^{-1} \) and the trace is over the Hilbert space associated with \( H_{\text{KS}} \). The self energies \( \Sigma_\alpha \) describe the coupling of the KS-system to external reservoirs, \( \alpha = \mathcal{L}, \mathcal{R} \). They are given by a golden-rule expression, \( \Sigma_\alpha(E) = |V|^2 g_{\alpha}^{\text{KS}}(E) \), where \( V \) is the coupling matrix element and \( g_{\alpha}^{\text{KS}} \) is a Green’s function of the leads. [9]

Often quantum transport is dominated by a single orbital of the molecule or the quantum dot (QD), only. Therefore, in studies of correlated electron transport interacting level models are standard, e.g., the single impurity Anderson model (SIAM, see also [4])

\[
\hat{H}_{\text{QD}} = \epsilon_d \hat{n}_d + U \left( \hat{n}_{d\uparrow} - \frac{1}{2} \right) \left( \hat{n}_{d\downarrow} - \frac{1}{2} \right),
\]

(2)

where \( \hat{N}_d = \hat{n}_{d\uparrow} + \hat{n}_{d\downarrow} \) with \( \hat{n}_{d\sigma} = \hat{d}_{d\sigma}^\dagger \hat{d}_{d\sigma} \) and spin \( \sigma = \uparrow, \downarrow \). In such models an analogue version of (1) is valid featuring retarded and advanced Green’s functions of the interacting system, \( \Gamma_{\alpha,\sigma\sigma'} = \Gamma_{\alpha,\delta\delta'} \).

\[
T(E) = \frac{\Gamma_{\mathcal{L}} \Gamma_{\mathcal{R}}}{\Gamma_{\mathcal{L}} + \Gamma_{\mathcal{R}}} A_{\text{d}}(E)
\]

(3)

where we have introduced the spectral function of the interacting QD, \( A_{\text{d}}(E) = \text{Tr} \Gamma_\sigma (G^\dagger(E) - G(E)) \). [10]

By comparing Eq. (3) and (1), one might suspect, that in order to accurately reproduce the true value for the transmission, \( T(\epsilon_F) = T^{\text{KS}}(\epsilon_F) \), it is necessary for the KS-theory to also reproduce the true spectral function, \( A_{\text{d}}(E) \). It is easy to see, that the latter is not possible, however, unless \( U = 0 \). To this end we recall that \( A_{\text{d}}(E) \) carries the two Hubbard peaks at energies \( \epsilon_d \pm U/2 \). [11]

These peaks are not seen by the KS-system because the model (2) does not exhibit magnetism, so both spin channels, \( (\uparrow, \downarrow) \), are equivalent. Therefore, \( H_{\text{KS}} \) is diagonal, \( H_{\text{KS}} = \epsilon_d \mathbf{1} \delta_{\sigma\sigma'} \), and the KS-spectral function, \( A_{\text{KS}} = \text{Tr} \Gamma_\sigma (G^\dagger - G) \), supports a single peak centered about \( \epsilon_{\text{KS}}^{\text{d}} \), only. Despite of the absence of the Hubbard peaks in \( A_{\text{KS}} \) we argue that in addition to the ground state density also the KS-conductance coincides with the true value of the interacting system, \( T = T^{\text{KS}} \).

Moreover, we maintain that this statement is correct even though \( H_{\text{KS}} \) is not unique in the sense that the exchange-correlation on-site potential, \( \psi_d^{\text{KS}} = \psi_d^{\text{KS}} - \epsilon_d \), can be complemented by an XC-contribution to the couplings, \( V \to \psi_{\text{KS}}^{\text{d}} \), as well. Different combinations \( (\psi_d^{\text{KS}}, \psi_{\text{KS}}^{\text{d}}) \) produce an effective single particle Hamiltonian with the correct ground state density. In fact, as will be demonstrated below, the on-site exchange-correlation (XC) potential and the coupling to the leads can be drastically different. Correspondingly, the resonance position, \( \epsilon_{\text{KS}}^{\text{d}} \), and broadenings, \( \Gamma_{\mathcal{L},\mathcal{R}} \), that determine \( A_{\text{KS}} \) will be strongly XC-functional dependent. We will see that despite of this ambiguity in \( H_{\text{KS}} \) the KS-conductance is
an observable that takes a unique value coinciding with the true conductance.

We start with a general recollection about features of ground state DFT that follow directly from the first Hohenberg-Kohn theorem. [12] According to this theorem, we can reconstruct the external potential, \( v_{ex}(r) \) that an interacting gas of \( N \) electrons is exposed to, if the ground state density \( n(r) \) together with the Hamiltonian \( H_0 \) in the absence of any \( v_{ex}(r) \) is known. Thus we reproduce the full Hamiltonian \( \hat{H} = H_0 + V_{ex} \) from our knowledge of \( n(r) \) (up to a constant shift in energy).

Knowing \( \hat{H} \) we can calculate, in principle, all equilibrium response functions of the \( N \)-particle system, provided that the ground state is unique, once \( n(r) \) has been specified. Hence, we can consider such correlators to be a functional of the ground state density. [19] For example the dynamical density-density susceptibility, \( \chi[n](r, r', t - t') \), can be thought of being such functional of \( n(r) \). Correlators can also be calculated at finite temperature. Again, they can be thought of as a unique functional of the ground state density under the condition that the equilibrium state does not exhibit a broken symmetry which is not already encoded in \( n(r) \).

A correlation function of special interest to us is the current-current correlation function, i.e. the conductivity. Its longitudinal part describing the response to potential gradients is closely related to the density susceptibility:

\[
-\omega \chi[n](r, r', \omega) = \frac{\partial}{\partial r} \frac{\partial}{\partial r'} \sigma_{J}[n](r, r', \omega)
\]

The susceptibility, in turn, may be expressed as a conductance in transport experiments that operate with electrodes for which the Fermi-liquid description holds true. Hence, in such geometries also the conductance is a functional of the ground state density: \( G[n] \). Hence, this conductance can be calculated using the ground state DFT if the proper functional \( G[n] \) is being used.

The previous statement is as correct as it is useless for practical purposes unless a good approximation for \( G[n] \) can be given. Of course, even if such an approximation would be known, in practice calculations would still suffer from inaccuracies in approximate XC-functionals used to obtain \( n(r) \).

**Friedel’s sum rule for the SIAM.** The complete definition of the SIAM-Hamiltonian reads [13]

\[
\hat{H} = \hat{H}_{QD} + \sum_{\alpha = \mathcal{L}, \mathcal{R}} \hat{H}_{\alpha} + \hat{H}_T
\]

(5)

\[
\hat{H}_{\alpha} = -t \sum_{x=1,\sigma} \left( c_{x+1, \sigma, \alpha} \hat{c}_{x, \sigma, \alpha} + \text{h.c.} \right),
\]

(6)

\[
\hat{H}_T = -V \sum_{\sigma, \alpha} \left( \hat{c}_{1, \sigma, \alpha} \hat{d}_{\sigma} + \hat{d}_{\sigma} \hat{c}_{1, \sigma, \alpha} \right).
\]

(7)

The \( \hat{c}_{x, \sigma, \alpha} \) denote fermionic annihilation (creation) operators at site \( x \), lead \( \alpha = \mathcal{R}, \mathcal{L} \) The model is of interest to us because it affords the Friedel sum rule [13],

\[
A_{\alpha}(\varepsilon_F) = \frac{\sin^2 [\pi n_{d\alpha}(\varepsilon_F)]}{\Gamma/2}.
\]

(8)

where \( \Gamma = \Gamma_{\mathcal{L}} + \Gamma_{\mathcal{R}} \). By combination with [1] we relate the particle number on the quantum dot, \( N_d/2 = n_{d\uparrow} = n_{d\downarrow} \), to the conductance,

\[
G[n] = \frac{2e^2}{h} \frac{\Gamma_{\mathcal{L}}\Gamma_{\mathcal{R}}}{(\Gamma/2)^2} \sin^2 \left( \frac{\pi}{2} \frac{N_d}{2} \right),
\]

(9)

The identity constitutes an exact analytical expression for a conductance functional \( G[n] \). It is remarkable that in the case of symmetric coupling, \( \Gamma_{\mathcal{L}} = \Gamma_{\mathcal{R}} \), Eq. (9) relates the conductance associated with \( \hat{H} \) to a single system characteristics, only, which is the particle number on the QD, \( N_d \). This implies, that any change in the parameters of \( \hat{H} \) leaves the conductance invariant, provided that \( N_d \) is unchanged and that the conditions of applicability of [19] are still valid. One requirement for this is that both leads are (effectively) non-interacting and free of backscattering, so that the Fermi-liquid picture holds a zero temperature. The last condition is important because else \( \pi n_{d\alpha} \) would not properly account for the number of bound states (per spin) and the scattering phase.

Friedel’s sum rule and ground state DFT. The KS-Hamiltonian of ground state DFT reads

\[
\hat{H}^{\text{KS}} = \epsilon_{d}^{\text{KS}} \hat{N}_d + \sum_{\alpha} \left[ \hat{H}_{\alpha} + \sum_{x=1,\sigma} t_{x,\alpha}^{\text{KS}} \hat{N}_{x,\alpha} \right] + \hat{H}_T\]

(10)

where the onsite XC-potentials, \( \epsilon_{d}^{\text{KS}}[N] = \epsilon_d + v_{x,\alpha}^{\text{KS}}[N] \) and \( v_{x,\alpha}^{\text{KS}}[N] \), are functionals of the local particle density \( N_x \). At first sight, the KS-Hamiltonian, \( \hat{H}^{\text{KS}} \), does not meet the requirements for the validity of [9], since the XC-functional extends into the leads and thus might contribute to the scattering phase shift, \( \delta(\varepsilon_F) \). However, this impression is misleading as can be seen from the following argument. The Friedel sum rule in its general form relates the extra scattering phase shift, \( \delta(\varepsilon_F) \), induced by decreasing \( \epsilon_d \) (down from \( \infty \)) to the extra spectral weight, \( \Delta \mathcal{A}(E) \), thus generated:

\[
\frac{\delta(\varepsilon_F)}{\pi} = \int_{-\infty}^{\varepsilon_F} \frac{dE}{2\pi} \Delta \mathcal{A}_\sigma(E) = \Delta \mathcal{N}_\sigma
\]

(11)

The right hand side denotes the total change in the particle number per spin, \( \Delta \mathcal{N}_\sigma = \sum_x \Delta N_{x,\sigma} \), associated with the occupation of this extra weight. A special aspect of Eq. (8) is the implication that the sum rule is exhausted already by the density change on the QD, \( \Delta N_d = N_d/2 \), the net charge accumulated by bringing \( \varepsilon_d \) down is entirely concentrated in the QD. This latter statement must be correct also for the KS-theory, by definition. Since also KS-particles obey the relation [11] we conclude:
The good agreement between the results obtained with both methods illustrates the point emphasized above:...
Even though the KS-spectral function is not physical, the associated transmission is close to the precise value.

We briefly mention that this point can be highlighted further by constructing a version of KS-theory, in which not only the diagonal elements of the density matrix, i.e. $n_{\xi\sigma}$ but also off-diagonal elements are faithfully reproduced. This can be achieved by adding to the on-site potential also a modification of hopping matrix elements, i.e. $V \rightarrow V^{KS}$ such that the expectation value of the kinetic energy of the impurity coupled to the first lead site within the KS description matches the one obtained from DMRG; for the technical details see [15]. Responding to this change the width of the KS-spectral function of the modified theory is no longer close to the original one, $\Gamma^{KS} \rightarrow \Gamma^{KS'}$. Since the charge in the QD must remain unchanged, we expect a compensating shift in the on-site energy, $\varepsilon_d^{KS} \rightarrow \varepsilon_d^{KS'}$. As can be seen from Fig. 4 despite a substantial change, $V = 0.3$ is replaced by $\tilde{V} = 0.1\ldots$, the transmission when evaluated via (12) is not changed. In view of Eq. (12) this finding is easily understood: $T(\varepsilon_F)$ is determined by the same ratio, $\Gamma^{KS}/(\varepsilon_d^{KS} - \varepsilon_F)$, that also fixes the density. Since by construction in all KS-models the density is the same, we have $\Gamma^{KS}/(\varepsilon_d^{KS} - \varepsilon_F) = \Gamma^{KS'}/(\varepsilon_d^{KS'} - \varepsilon_F)$, so the transmission remains the same, also.

**Conclusions.** We briefly discuss two generalizations of the preceding analysis. First, our argument was assuming a single level, only, while a real QD, e.g. a molecule, exhibits in general several levels. One expects, however, that the main conclusion remains valid as long as all levels contribute independently to the transport current. In particular, the sum rule (9) should remain a useful approximation for the true density functional. Second, our analysis heavily relies on the Kondo effect restoring full transmission in the case of single occupation of the dot. Suppose, that the Kondo temperature is very low, and that the measurement is done at slightly higher temperatures. Then transport is dominated by the Coulomb blockade and the conductance is strongly suppressed, $T(\varepsilon_F) \sim (\Gamma/U)^2 \ll 1$. On the other hand the particle density is essentially still the ground state one, $n(r)$, i.e. it is largely insensitive to this change and in particular $n_{d\sigma} \approx 1/2$. We conclude that in this case the Friedel sum rule (9) does not hold and that KS-theory (without breaking spin rotational invariance) does not reflect this change, i.e. we still have: $T^{KS}(\varepsilon_F) \approx 1$.

We acknowledge support by the Center of Functional Nanostructures at KIT. We also thank Gianlucca Stefanucci and Peter Wölfle for discussions. After completing our work we have learned about an independent research by Bergfield, Liu, Burke and Stafford [17]. Where they overlap, their conclusions coincide with the ones presented in this and an earlier publication [18].

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19. The functionals are uniquely defined, once the kinetic part of $\hat{H}^{KS}$, i.e. the piece that remains invariant under changes in $v_{\text{ext}}(r)$ and $n(r)$, is fixed.