

Assessing the accuracy of Kohn-Sham conductances using the Friedel sum rule

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We use the Friedel sum rule (FSR) to discuss the accuracy of exact and approximated Kohn-Sham density-functional theory for the calculation of the electrical conductance. For a two-level molecular junction model we prove that if the Kohn-Sham Hamiltonian reproduces the density of the interacting system calculated in some approximation then it also reproduces the conductance at the same level of approximation. This result is argued to be general for single-channel molecular conductors and is confirmed by means of the exchange-only and GW approximations. The former is found to underestimate the GW conductance. Using the FSR we show how small errors in the description of the density can lead to relatively large errors in the conductance.

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I. INTRODUCTION

The theoretical design of molecular conductors with tailored transport properties requires a quantum many-body theory able to accurately predict the electronic structure and associated electrical conductance.

A standard approach to calculate theoretical estimates of electrical conductances in molecular conductors relies on combining static Kohn-Sham density-functional theory (KS-DFT) (Ref. 1) with the so-called nonequilibrium Green's-function (NEGF) method^{2,3} and calculating the current by means of the Meir-Wingreen formula.⁴

KS-DFT has been and is an extremely successful method for the calculation of ground-state properties: electron density, ionization potential, and total energy are all given exactly by KS-DFT for any many-electron system, provided that the exact KS exchange-correlation (XC) potential is used. Yet the use of KS-DFT (exact or approximated) for calculating conductances is often questioned since KS orbitals lack rigorous physical interpretation.⁵

KS-DFT conductances typically turn out to be larger than their experimental counterparts by a factor that depends both on the calculation *and* on the experiment. In earlier comparisons⁶ this factor was $\sim 10^2$ while in more recent comparisons order-of-magnitude agreement between theory and experiment has been claimed.⁷ There are various uncertainties affecting the experimental conductance values: parasitic resistances, uncontrolled molecule-electrode coupling, and polarization effects associated with nearby gates and electrodes can be important and vary from experiment to experiment.⁸⁻¹⁰

There are also uncertainties in the theoretical results. Sai *et al.*¹¹ and Di Ventra and Vignale¹² (see also Ref. 13) propose dynamical XC contributions to the electrical resistance within time-dependent current-density-functional theory, that are beyond any static functional (exact or approximate). According to Refs. 11 and 12 this dynamical XC effect might be the dominant contribution to the resistance in systems where there are large density gradients and the viscosity of the underlying electron liquid is also large. In contrast, Jung *et al.*¹⁴ argue that a more accurate evaluation of the correc-

tion proposed in Ref. 11 reduces its effect down to a few percent. Therefore the size of these corrections remains unknown.

Self-interaction errors present in common *approximations* to KS-DFT are known to unphysically alter the conductance by discharging the molecular central region for a given value of the gate potential, as clearly demonstrated by Toher *et al.*¹⁵ A self-interaction-free approach is thus essential to obtain the right alignment between single-particle levels and the chemical potential of the electrodes and therefore to improve the results of KS-DFT conductance estimates.

The accuracy of *exact* KS-DFT has been addressed in model systems by Schmitteckert and Evers,¹⁶ who compared conductances obtained numerically from a density-matrix renormalization-group (DMRG) calculation to those obtained from the “exact” KS-DFT potential that reproduces the DMRG electron density. The calculated DMRG and exact KS-DFT conductances are in very good agreement, suggesting that dynamical XC effects are small.

Intuition also gives rise to contradictory scenarios when it comes to the problem of the accuracy of the conductances calculated using KS-DFT. On the one hand we know that there are large differences between the interacting and KS spectral functions, which suggests the possibility of large discrepancies between the exact and KS conductances, even within exact KS-DFT. On the other hand, our idea of the strength of a scatterer is related to the magnitude of the disturbance it causes on the electron density, relative to the system without scatterer.¹⁷⁻¹⁹ This disturbance is described exactly in exact KS-DFT and therefore one could also expect the differences between the interacting and Kohn-Sham conductances to be small.

In this paper we address the accuracy of *exact* KS-DFT. We give theoretical arguments as to when and why we expect differences between interacting and KS conductances to be small. Based on the Friedel sum rule (FSR),¹⁷⁻¹⁹ we identify physical systems of interacting electrons where KS-DFT yields the exact conductance. As a toy model of a correlated molecular junction we consider a two-level model. We calculate the electron density and conductance of the two-level model in the spin-compensated GW approximation, which is known to give accurate gaps in semiconductors²⁰ and has

been implemented recently by several authors to study similar systems in and out of equilibrium.^{21–24} We build single-particle KS Hamiltonians optimized to reproduce the GW electronic density (GWKS), calculating also the exchange-only KS Hamiltonian (XXKS). By means of the Meir-Wingreen formula⁴ we calculate and compare the GW, GWKS, and XXKS conductances for various interaction-strength and molecule-lead coupling parameters. We find that the calculated GW and GWKS conductances are in excellent agreement while significantly different from the XXKS conductance. We show this to be a consequence of the FSR.

The rest of the paper is organized as follows: in Sec. II we briefly describe the two-level model, the method used for calculating the conductance and the various approaches used for the description of the electronic structure: GW, GWKS, and XXKS. In Sec. III we present our numerical results, which are discussed in Sec. IV in terms of the FSR and time-dependent DFT (TDDFT). Our conclusions are summarized in Sec. V. The implications of the FSR for the accuracy of KS-DFT in more general systems are discussed in the Appendix.

II. GW AND KS-DFT CONDUCTANCES OF A TWO-LEVEL MODEL

The two-level central region is described by the Hamiltonian²¹

$$H_c = \sum_{i,\sigma} \epsilon_i \hat{n}_{i,\sigma} + U \sum_i \hat{n}_{i,\uparrow} \hat{n}_{i,\downarrow} + U_{HL} \sum_{\sigma,\sigma'} \hat{n}_{H,\sigma} \hat{n}_{L,\sigma'}, \quad (1)$$

where i denotes highest occupied molecular orbital/lowest unoccupied molecular orbital (HOMO/LUMO) level indices ($i=H,L$), σ is a spin index ($\sigma=\uparrow,\downarrow$), and $\hat{n}_{i,\sigma}$ is the number operator for electrons with spin σ in level i . The intralevel electron-electron interaction explicitly excludes self-interactions and its strength is controlled by the parameter U , which we take to be the same for both levels. The strength of the spin-independent interaction between electrons in different levels is controlled by U_{HL} , which is taken to be $U_{HL}=U/2$. At the particle-hole-symmetric point, there are on average two electrons in the central region and the single-particle energies are given by $\epsilon_H=-\Delta/2-U$ and $\epsilon_L=\Delta+\epsilon_H$, where Δ is an optical gap parameter.²⁵

To compute the linear-response conductance of the model, we use the NEGF approach and the Meir-Wingreen formula.⁴ The coupling to the noninteracting leads is described by a wideband model self-energy Σ_c which is characterized by a coupling parameter Γ and which assumes that both levels couple symmetrically to left and right leads. The weak-coupling particle-hole-symmetric regime describes a Coulomb-blockade scenario. Electron-electron interactions are treated using a Hartree-XC (HXC) self-energy, Σ_{HXC} , which is evaluated using either the GW approximation, $\Sigma_{\text{HXC}} \approx \Sigma_H + \Sigma_{\text{GW}}$, or KS-DFT, $\Sigma_{\text{HXC}} \approx \Sigma_H + v_C$, where v_C is the correlation part of the XC potential. Due to the absence of self-interactions the XXKS HXC self-energy is just given by $\Sigma^{\text{XXKS}} = \Sigma_H$. We evaluate Σ^{GWKS} at the particle-hole-symmetric point by writing the central-region KS Hamiltonian²⁶ as

$$H_c^{\text{GWKS}} = \sum_{i,\sigma} (\epsilon_i + \Sigma_i^H + \Delta_i^C) \hat{n}_{i,\sigma}, \quad (2)$$

where $\Delta_H^C = -\Delta_L^C$, and varying Δ_{HL}^C until the GWKS and GW HOMO/LUMO occupancies, n_{HL} , agree within the desired tolerance.²⁷

The retarded many-body Green's function is given by

$$G^r(\omega) = [(\omega + i\eta)I - h - \Sigma_c^r - \Sigma_{\text{HXC}}^r(\omega)]^{-1}, \quad (3)$$

where the superscript r indicates retarded quantities and h is the noninteracting part of the Hamiltonian given in Eq. (1). We evaluate G^r self-consistently, ensuring that conservation laws are satisfied.^{21–23} We consider the linear-response regime where the lesser Green's function is obtained by means of the fluctuation-dissipation theorem.⁴ The linear-response conductance is then given by $G=G_0 T(\epsilon_F)$, where $G_0=2e^2/h$ and the Fermi energy of the leads is taken to be zero ($\epsilon_F=0$). For symmetric coupling to the leads, the transmission function, $T(\omega)$, is obtained directly from the equilibrium central-region spectral function, $A(\omega)=-\text{Im} G^r(\omega)/\pi$, as $T(\omega)=\Gamma \text{Tr}\{A(\omega)\}$.

III. NUMERICAL RESULTS

For the numerical implementation we follow the prescription of Thygesen and Rubio.²³ In our calculations we fixed $\Delta=4$ and studied the dependence on Γ and U of the conductance and electron density as given by the GW, GWKS, and XXKS approximations. Our numerical results are shown in Fig. 1.

In the left panel of Fig. 1, we show the percentual difference between the GW and KS conductances (top), and HOMO occupancies/densities (n_H , bottom) calculated as a function of the coupling strength at the particle-hole-symmetric point. The GW and GWKS conductances are in excellent agreement for all the values of U and Γ considered but are substantially larger than the XXKS conductance. Similarly, the GW and GWKS HOMO densities are identical by construction since the GWKS XC potential is optimized to give the same level occupancies as the GW approximation, and they are smaller than their XXKS counterpart. Importantly in the weak-coupling regime n_H^{XXKS} and n_H^{GW} are in close agreement with each other, yet the conductance difference increases steeply as a function of Γ in that regime. XXKS underestimates the conductance of the model and overestimates the HOMO contribution to the density.

There are limits where all three conductances are expected to agree with each other; the uncoupled ($\Gamma=0$, $G=0$, and $n_H=2$) and very strongly coupled ($\Gamma \rightarrow \infty$, $G \rightarrow 2G_0$, $n_H \rightarrow 1$) and the noninteracting limit ($U=0$). For $\Gamma \neq 0$ the tail from the HOMO (LUMO) resonance exits (enters) the Fermi sea and we have $n_H < 2$, $n_L = 2 - n_H$, and $0 < G < 2G_0$. In our model XXKS is exact to first order in U since it exhausts all first-order diagrams. Conductance deviations between GW and XXKS start to be significant only for $U > 2$. The maximum difference between GW and XXKS occupancies/conductances arises for intermediate values of Γ . The deviation between GW/GWKS and XXKS results illustrates the importance of electronic correlations for $U > 2$.

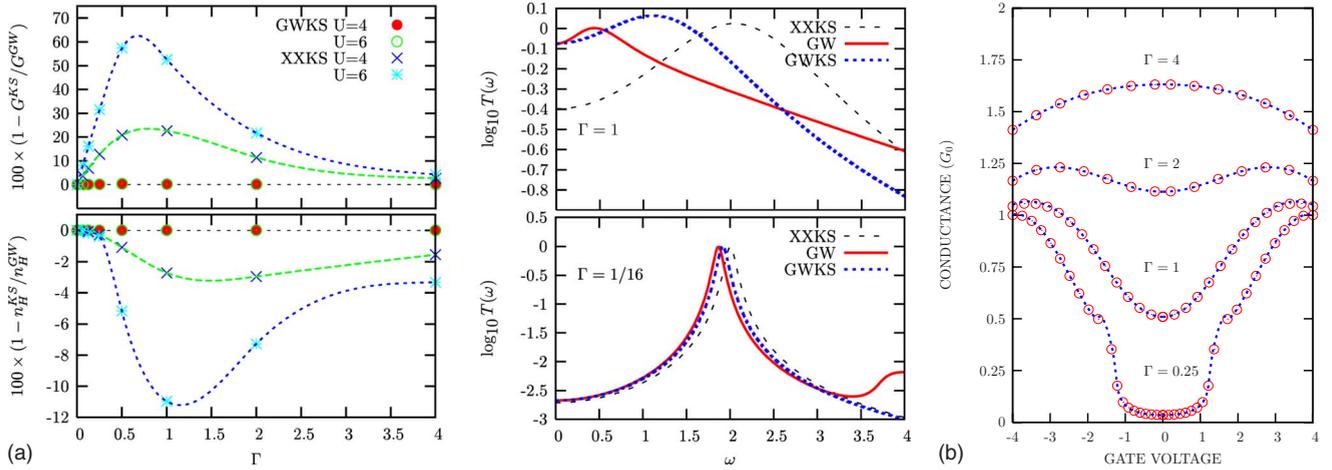


FIG. 1. (Color online) LEFT: Percentual difference between the GW and XXKS/GWKS conductances (top) and HOMO occupancies (bottom) as a function of the molecule-lead coupling strength for the values of U shown. CENTER: GW, GWKS, and XXKS transmission functions $T(\omega)=\Gamma \text{Tr}\{A(\omega)\}$ for $U=6$ in the weak ($\Gamma=1/16$; bottom) and intermediate ($\Gamma=1$; top) coupling regimes. RIGHT: Conductance as a function of the gate voltage calculated using the Meir-Wingreen formula (dots) and the Friedel sum rule $G=G_0 \sin^2(\pi n_H/2) + G_0 \sin^2(\pi n_L/2)$ (lines) for the values of Γ shown. The optical gap parameter was set to $\Delta=4$ in all the calculations. See the text for details.

In the central panel of Fig. 1, we show transmission functions calculated for $U=6$ and two values of Γ representing weak- (bottom) and intermediate- (top) coupling regimes. We again see that $T(\omega=\epsilon_F)$ is the same for the GW and GWKS methods, despite differences in the spectral function for energies other than Fermi energy. As a function of Γ , there are two many-body effects in the spectral function that are worth discussing. One is the reduction in the quasiparticle gap as a function of Γ , which has been addressed by Thygesen and Rubio.²¹ The other is the reduction in the GW quasiparticle width with respect to the KS width, seen by comparing top and bottom center panels in Fig. 1. Note that in the KS schemes the resonance width is equal to Γ since, for all frequencies, $\text{Im} \Sigma_{\text{HXC}}^{\text{KS}}=0$.

We now discuss these trends in terms of the FSR (Refs. 17–19) which in our model relates the level occupancies, $n_{H/L}$, with the scattering phase shifts, $\delta_{H/L}$, for electrons scattered by the central region. For such highly symmetric systems these phase shifts can in turn be related to the conductance. For the model considered the conductance at the particle-hole symmetric can be shown to be given by

$$G/G_0 = \sum_{i=H,L} \sin^2(\delta_i), \quad (4)$$

where the scattering phase shift associated with the HOMO/LUMO channel is

$$\delta_{H/L} = \frac{\pi n_{H/L}}{2}. \quad (5)$$

At the particle-hole-symmetric point $n_H=2-n_L$ and $\delta_H=\pi-\delta_L$. Thus the total conductance is just twice the HOMO contribution to the conductance,²⁸

$$G = 2G_0 \sin^2(\pi n_H/2). \quad (6)$$

Since the GWKS Hamiltonian is optimized to give n_H^{GW} it also gives the same *Meir-Wingreen conductance* as GW, de-

spite of their different spectral features. The same applies to the exact self-energy (as opposed to GW) and exact KS (as opposed to GWKS), provided that a Fermi-liquid picture applies and that the interaction does not change the number of scattering channels in the system.

In terms of the FSR we can understand the large deviation between XXKS and GW conductances originating from small deviations in n_H , seen in the left panel of Fig. 1, for small values of Γ . Consider a small error in the HOMO density, δn_H , due to the use of an approximate functional. The error in the conductance is $\delta G = 2\pi G_0 \sin(\pi n_H/2)\cos(\pi n_H/2)\delta n_H$ and the fractional error in the conductance is

$$\delta G/G = \frac{\pi \delta n_H}{\tan(\pi n_H/2)}. \quad (7)$$

Since $\tan(\pi n_H/2) \rightarrow \pm 0$ as $n_H \rightarrow 2$ small errors in the density lead to comparatively large errors in the conductance, as can be seen in the lower left panel of Fig. 1. Within our model functionals that overestimate (underestimate) n_H underestimate (overestimate) the conductance. For approximately charge-neutral molecular conductors, self-interaction errors underestimate n_H and thus, according to Eq. (7), should overestimate the conductance by a very large factor.

To qualitatively address the narrowing of the quasiparticle width with Γ , seen in the middle panel of Fig. 1, we consider the weak-coupling limit and equate KS-DFT and GW conductances using the GW and GWKS n_H in Eq. (6). This yields¹⁹ $\Gamma_{\text{GW}}/\Gamma = E_g^{\text{GW}}/E_g^{\text{KS}}$, where E_g and Γ are the HOMO-LUMO gap and resonance width, respectively. The GW width and gap are renormalized by the same amount with respect to their GWKS counterparts. The GW width and gap renormalization compensate each other to yield exactly the same Meir-Wingreen conductance as GWKS DFT.

Finally, we consider the validity of the Friedel sum rule, $G=G_0 \sin^2(\pi n_H/2) + G_0 \sin^2(\pi n_L/2)$, away from the

particle-hole-symmetric point, by varying the central-region electron number using a gate voltage and computing the conductance with both the FSR and the Meir-Wingreen formula. In the right panel of Fig. 1 we plot the GW conductance as a function of the gate voltage for $U=4$ and different values of Γ . The Meir-Wingreen and FSR conductances are also in good agreement away from the particle-hole-symmetric point. Accordingly, the GWKS and GW conductances are also close in these other regimes.

To summarize, we have shown an example of a system where (KS) Hamiltonians that reproduce the interacting density also reproduce the interacting conductance. Another such example, not shown here, is provided by the Anderson model. For a discussion of the implications of the FSR for the accuracy of the KS conductance in more general systems see the Appendix.

IV. DISCUSSION

Next we discuss the limitations of the present study, summarize the effects of approximations to KS-DFT, and explore the relationships between the results obtained here and previous results within TDDFT.

Using the generalization of the FSR due to Langer and Ambegaokar¹⁸ we show in the Appendix that, in systems with one scattering channel, interactions beyond KS-DFT do not introduce additional scattering at the Fermi energy and thus do not change the conductance. Therefore, in highly symmetric systems where a single-scattering channel dominates over all others, exact KS-DFT should provide a good description of the linear-response conductance.

We have illustrated this observation with a simple two-level model of a molecular junction. The model considered provides a simplified description of a molecular conductor with obvious limitations: a minimal Hilbert space where quasiparticle and single-particle orbitals coincide; Coulomb integrals are restricted to being only of the direct two-center kind; and a wideband model describing the coupling between central region and left and right leads. Within this model the FSR guarantees the accuracy of the *exact* KS-DFT Meir-Wingreen conductance. When $\Gamma \neq 0$ the central-region electronic levels are broadened and charge is transferred among them (Friedel's displaced charge¹⁷). This charge transfer governs the scattering phase shift for electrons scattered by the molecule and this phase shift can be related to the conductance, at least for highly symmetric systems such as the one considered here.¹⁹

The comparison between XXKS and GW allows us to study the effect of approximations to KS-DFT. In the weak-coupling regime XXKS provides a good description of the GW electronic density yet the error in the conductance quickly builds up as a function of Γ . Exchange-only approximations underestimate the charge transfer between molecular levels, overestimate the HOMO occupancy, and underestimate the conductance. The XXKS and GW conductances are, however, of the same order of magnitude for the values of U considered. We have checked that allowing for self-interactions in Σ_H at the particle-hole-symmetric point results in a severe overestimation of the conductance, in good

agreement with Toher *et al.*¹⁵ and with the above-given discussion.

In recent unpublished work²⁹ (see also Ref. 30 for related ideas), Bartlett, Fagas, and Greer arrive to similar conclusions: they show that, in correlated systems, methods based on the one-electron reduced density matrix yield the same current-voltage characteristics as NEGF approaches as long as both methods yield the same charge transfers. They also arrive to the same conclusions regarding approximate density functionals; functionals with self-interaction error overestimate the conductance by overestimating the charge transfer while exchange-only methods underestimate the charge transfer and thus the conductance.

Our results are also in line with previous studies based on TDDFT. According to Stefanucci and Almlahd³¹ the exact current can be expressed in terms of a Landauer-type formula in which the electrochemical potential of the leads is shifted by the voltage-induced variation in the XC potential. Thus exact static KS-DFT gives the exact linear-response Meir-Wingreen conductance *provided that the variation in the XC potential vanishes deep inside the leads*. The same conclusion can be drawn using the Kubo formalism within time-dependent current-density-functional theory.¹³ From this perspective, in models where the interaction is confined to the central region no static or dynamic XC contributions are to be expected. The FSR supports these results for single-channel molecular conductors (see the Appendix); more thought and calculations are needed to clarify this issue in general systems.

V. CONCLUSIONS

In conclusion, based on the Friedel sum rule we have argued that exact KS-DFT should provide a reasonable estimate of the conductance of a molecular junction since KS-DFT is able to reproduce the exact electron density of the perturbed system (Friedel oscillations and displaced charge).

We have illustrated these ideas by means of a two-level model, where the noninteracting Hamiltonian that reproduces the GW density yields also the GW conductance, despite differences in the spectral function away from the Fermi energy. There the Friedel sum rule relates the conductance and orbital charges. To reproduce the exact density KS-DFT needs to reproduce these orbital charges exactly and by doing so also reproduces the exact conductance.

We expect this result to apply approximately to effectively single-channel molecular conductors, where conduction is dominated by a single-scattering channel, such as the one discussed in Ref. 19.

Small errors in the orbital charges associated with the use of approximated functionals can result in comparatively large errors in the conductance. The XXKS and GW conductances are of the same order of magnitude; larger errors do arise when we allow for self-interactions in the calculations.

The results presented in this paper do not rule out the possibility of corrections in general systems (see the Appendix) but, together with the results of Schmitteckert and Evers in Ref. 16, support the idea that a self-interaction-free approximation to KS-DFT can provide the correct order of

magnitude for the conductance of a molecular junction.

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APPENDIX: FRIEDEL SUM RULE AND KOHN-SHAM CONDUCTANCE

In this appendix we address the consequences of the FSR for the accuracy of the KS conductance in general systems. Consider as unperturbed system a molecular conductor described within exact KS-DFT. Now in a certain finite region of the system we allow for electronic interactions described by means of many-body perturbation theory (MBPT). The perturbing potential will thus be $\Sigma_{XC}-v_{XC}$, where Σ_{XC} is the XC self-energy of MBPT and v_{XC} is the XC potential of KS-DFT. The perturbing potential is taken to be zero outside the specified (central) region. Since KS-DFT reproduces the electronic density of the system exactly such a perturbing potential does not displace any charge and thus one expects it to be a weak scatterer.

Langer and Ambegaokar¹⁸ use Luttinger’s theorem³² to prove a generalization of the FSR to systems of interacting electrons. This generalized FSR relates the displaced charge N to the scattering matrix $S(\epsilon_F)$ evaluated at the Fermi energy and reads

$$N = \frac{1}{\pi i} \ln \det S(\epsilon_F), \quad (\text{A1})$$

where spin degeneracy has been taken into account. This relation is satisfied for Fermi-liquid systems where the imaginary part of the exchange-correlation self-energy vanishes at the Fermi energy, i.e., $\text{Im} \Sigma_{XC}(\epsilon_F)=0$. To see what this means for the scattering phase shift associated with $\Sigma_{XC}-v_{XC}$ we introduce the total scattering phase shift, $\delta(\omega)$, in the usual way in scattering theory,

$$\det S(\omega) = \exp[2i\delta(\omega)] \quad (\text{A2})$$

and take into account that, for the exact v_{XC} , $\Sigma_{XC}-v_{XC}$ does not displace any charge and thus $N=0$. In this case Eq. (A1) becomes

$$\delta(\epsilon_F) = 0. \quad (\text{A3})$$

The condition that KS-DFT reproduces the exact density strongly restricts the scattering by $\Sigma_{XC}-v_{XC}$. The total phase shift contains contributions from different scattering channels, $\delta(\epsilon_F)=\sum_i \delta_i(\epsilon_F)$, and therefore Eq. (A3) does not imply $\delta_i(\epsilon_F)=0, \forall i$. Therefore in situations where many scattering channels are involved the FSR does not guarantee the accuracy of KS-DFT for the calculation of the conductance.

In high-symmetry systems, however, the total scattering phase shift may be dominated by a single-scattering channel and in such a case $\Sigma_{XC}-v_{XC}$ does not contribute to scattering processes *at the Fermi energy* and therefore KS-DFT calculations should yield highly accurate conductances, provided that an accurate XC potential is used in the calculation. The two-level model considered in the text provides one such example. Another example, not discussed here, is the Anderson model.

¹P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, *ibid.* **140**, A1133 (1965).

²C. Caroli, R. Combescot, P. Nozieres, and D. Saint-James, J. Phys. C **4**, 916 (1971); L. V. Keldysh, JETP **20**, 1018 (1965); L. P. Kadanoff and G. Baym, *Quantum Statistical Mechanics* (Benjamin, New York, 1962).

³J. Taylor, H. Guo, and J. Wang, Phys. Rev. B **63**, 121104(R) (2001); M. Brandbyge, J. L. Mozos, P. Ordejon, J. Taylor, and K. Stokbro, *ibid.* **65**, 165401 (2002).

⁴Y. Meir and N. S. Wingreen, Phys. Rev. Lett. **68**, 2512 (1992); H. Haug and A. P. Jauho, *Quantum Kinetics in Transport and Optics of Semiconductor Microstructures* (Springer-Verlag, Berlin, 1998).

⁵See, for instance, F. Evers, F. Weigend, and M. Koentopp, Phys. Rev. B **69**, 235411 (2004); A. Cehovin, H. Mera, J. H. Jensen, K. Stokbro, and T. B. Pedersen, *ibid.* **77**, 195432 (2008); M. J. Verstraete, P. Bokes, and R. W. Godby, J. Chem. Phys. **130**, 124715 (2009); A. Gagliardi, T. A. Niehaus, T. Frauenheim, A. Pecchia, and A. Di Carlo, J. Comput. Electron. **6**, 345 (2007); P. Darancet, A. Ferretti, D. Mayou, and V. Olevano, Phys. Rev. B **75**, 075102 (2005); A. Ferretti, A. Calzolari, R. Di Felice, F.

Manghi, M. J. Caldas, M. Buongiorno Nardelli, and E. Molinari, Phys. Rev. Lett. **94**, 116802 (2005).

⁶M. Di Ventura, S. T. Pantelides, and N. D. Lang, Phys. Rev. Lett. **84**, 979 (2000).

⁷S. M. Lindsay and M. A. Ratner, Adv. Mater. **19**, 23 (2007); M. Di Ventura, *ibid.* **21**, 1547 (2009); K. Varga and S. T. Pantelides, Phys. Rev. Lett. **98**, 076804 (2007).

⁸M. A. Reed, C. Zhou, C. J. Muller, T. P. Burgin, and J. M. Tour, Science **278**, 252 (1997).

⁹X. Xiao, B. Xu, and N. Tao, Nano Lett. **4**, 267 (2004).

¹⁰T. Dadosh, Y. Gordin, R. Krahne, I. Khivrich, D. Mahalu, V. Frydman, J. Sperling, A. Yacoby, and I. Bar-Joseph, Nature (London) **436**, 677 (2005).

¹¹N. Sai, M. Zwolak, G. Vignale, and M. Di Ventura, Phys. Rev. Lett. **94**, 186810 (2005).

¹²G. Vignale and M. Di Ventura, Phys. Rev. B **79**, 014201 (2009).

¹³M. Koentopp, K. Burke, and F. Evers, Phys. Rev. B **73**, 121403(R) (2006).

¹⁴J. Jung, P. Bokes, and R. W. Godby, Phys. Rev. Lett. **98**, 259701 (2007); P. Bokes, J. Jung, and R. W. Godby, Phys. Rev. B **76**, 125433 (2007).

- ¹⁵C. Toher, A. Filippetti, S. Sanvito, and K. Burke, *Phys. Rev. Lett.* **95**, 146402 (2005).
- ¹⁶P. Schmitteckert and F. Evers, *Phys. Rev. Lett.* **100**, 086401 (2008).
- ¹⁷J. Friedel, *Adv. Phys.* **50**, 539 (2001); *Nuovo Cimento, Suppl.* **7**, 287 (1958); D. C. Langreth, *Phys. Rev.* **150**, 516 (1966); A. Kawabata, *J. Phys. Soc. Jpn.* **60**, 3222 (1991); F. Stern, *Phys. Rev.* **158**, 697 (1967); M. Rontani, *Phys. Rev. Lett.* **97**, 076801 (2006).
- ¹⁸J. S. Langer and V. Ambegaokar, *Phys. Rev.* **121**, 1090 (1961).
- ¹⁹S. Datta and W. Tian, *Phys. Rev. B* **55**, R1914 (1997).
- ²⁰G. Onida, L. Reinig, and A. Rubio, *Rev. Mod. Phys.* **74**, 601 (2002).
- ²¹K. S. Thygesen, *Phys. Rev. Lett.* **100**, 166804 (2008); K. S. Thygesen and A. Rubio, *ibid.* **102**, 046802 (2009).
- ²²P. Myöhänen, A. Stan, G. Stefanucci, and R. van Leeuwen, *EPL* **84**, 67001 (2008); *Phys. Rev. B* **80**, 115107 (2009).
- ²³K. S. Thygesen and A. Rubio, *J. Chem. Phys.* **126**, 91101 (2007); *Phys. Rev. B* **77**, 115333 (2008).
- ²⁴X. Wang, C. D. Spataru, M. S. Hybertsen, and A. J. Millis, *Phys. Rev. B* **77**, 045119 (2008); C. D. Spataru, M. S. Hybertsen, S. G. Louie, and A. J. Millis, *ibid.* **79**, 155110 (2009).
- ²⁵We have checked that other parameter choices do not alter our conclusions.
- ²⁶Due to the abstract nature of the model considered it is not possible to distinguish between local and nonlocal potentials. The action of the Hamiltonian described by Eq. (2) may be the result of a local potential (for example, decreasing/increasing the confinement potential at constant charge increases/decreases the HOMO-LUMO gap) or a nonlocal one. In this sense the results of our model apply to both KS-DFT and generalized KS schemes, and in general to any noninteracting scheme able to reproduce the exact density.
- ²⁷We use indistinctively the terms “occupancies” and “densities” since $n(\mathbf{r}, \Gamma) = n_H(\Gamma) |\psi_H(\mathbf{r})|^2 + n_L(\Gamma) |\psi_L(\mathbf{r})|^2$.
- ²⁸The derivation follows closely that of the Anderson model, shown in Sec. 5.2 of Ref. 33.
- ²⁹R. J. Bartlett, G. Fagas, and J. C. Greer, arXiv:0710.5276 (unpublished).
- ³⁰G. Fagas, P. Delaney, and J. C. Greer, *Phys. Rev. B* **73**, 241314(R) (2006).
- ³¹G. Stefanucci and C. O. Almbladh, *Phys. Rev. B* **69**, 195318 (2004); *Europhys. Lett.* **67**, 14 (2004).
- ³²J. M. Luttinger, *Phys. Rev.* **119**, 1153 (1960); J. M. Luttinger and J. C. Ward, *ibid.* **118**, 1417 (1960).
- ³³A. C. Hewson, *The Kondo Problem to Heavy Fermions* (Cambridge University Press, Cambridge, UK, 1993).