

## Are Kohn-Sham Conductances Accurate?

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(Received 29 April 2010; published 19 November 2010)

We use Fermi-liquid relations to address the accuracy of conductances calculated from the single-particle states of exact Kohn-Sham (KS) density functional theory. We demonstrate a systematic failure of this procedure for the calculation of the conductance, and show how it originates from the lack of renormalization in the KS spectral function. In certain limits this failure can lead to a large overestimation of the true conductance. We also show, however, that the KS conductances can be accurate for single-channel molecular junctions and systems where direct Coulomb interactions are strongly dominant.

DOI: [10.1103/PhysRevLett.105.216408](https://doi.org/10.1103/PhysRevLett.105.216408)

PACS numbers: 71.10.-w, 71.45.Gm, 72.10.-d, 73.23.-b

The computer-aided design of nanoscale electronic components requires an electronic structure theory which is both computationally simple and able to accurately describe charge transport.

The standard approach to calculating theoretical estimates of electrical conductances in molecular conductors relies on combining static Kohn-Sham density functional theory (KS DFT) [1] with the so-called nonequilibrium Green's function (NEGF) method [2,3] and using the Meir-Wingreen formula [4]. This procedure amounts to calculating the transmission coefficient directly from KS states, which have no clear physical interpretation. Thus the KS conductances calculated in this way may be inaccurate [5], even if the exact KS exchange-correlation (XC) potential  $v_{XC}$  were used in the calculation.

Initial comparisons between KS and experimental molecular-junction conductances revealed discrepancies of several orders of magnitude [6]. Recent comparisons, however, show order-of-magnitude agreement between theory and experiment in many cases, with one significant trend: the KS conductance typically overestimates the experimental one [7]. Several factors may contribute to this trend: uncontrolled experimental conditions, approximations to  $v_{XC}$ , and the deficiencies intrinsic to the exact-KS conductance addressed here.

While the effect of approximations to  $v_{XC}$  on the KS conductance is well understood [8], the intrinsic deficiencies of the exact KS conductance have been addressed by various authors with somewhat contradictory results. Sai *et al.* [9] propose dynamical XC contributions to the conductance within time-dependent current-DFT (TDCDFT), which are not included in the KS conductance. The same effect was found Bokes *et al.* [10], using a TDDFT density response function in the Kubo formula. According to Ref. [9] these contributions reduce the conductance and may be dominant in molecular junctions. In contrast, Ref. [10] argues that these contributions could be small, even for low electronic concentrations where correlations are most important.

On the numerical front, we are aware of two works [11,12] that compare interacting and exact-KS conductances.

Schmitteckert and Evers [11] give examples where conductances obtained numerically from a density matrix renormalization group (DMRG) calculation are in good agreement with those obtained from the “exact” KS potential that reproduces the DMRG electron density, suggesting that dynamical XC effects are small. Recently, Mera *et al.* [12] have shown that the Friedel sum rule [13] guarantees the accuracy of the KS conductance in single-channel molecular junctions.

Therefore both the magnitude of these dynamical XC contributions and their dependence on device parameters remain to be determined. Furthermore, the problem has been attacked so far only from the perspective of TD(C) DFT. A clear understanding of dynamical XC corrections to the KS conductance from the perspective of many-body Green's function theory [14–16] (MBGFT) is still lacking, but would certainly help to firmly establish the accuracy of the exact-KS conductance. Such perspective may prove useful also for the development of correction functionals for the KS conductance.

This Letter aims to clarify limits of validity for the procedure of using the exact KS states to calculate the electrical conductance. We consider simplified molecular-junction models and use exact Fermi-liquid relations derived by Luttinger and Ward [15] and by Shiba [17] to show that the KS conductance generally fails to reproduce the exact conductance, except in certain limits which we identify. This failure originates from the lack of renormalization in the KS spectral function and is quantified in terms of Luttinger-type integrals discussed by Shiba [17]. The analysis given below provides a simple yet rigorous explanation of the results of Refs. [11,12]. In certain limits we arrive to the same conclusion as Refs. [9,10] (KS overestimates the conductance).

Let us begin by considering a molecule weakly and symmetrically coupled to left and right electrodes at zero temperature within KS. The coupling between the electrodes and the KS molecular orbitals (MOs) is described by a self-energy which is assumed to be diagonal in the KS MOs (weak coupling to featureless electrodes). The

bandwidth of the electrodes is assumed to be very large and hence the coupling self-energy is purely imaginary and energy independent. The  $i$ th diagonal element of the coupling self-energy  $i\gamma_i$  gives the inverse lifetime of the  $i$ th KS MO,  $\phi_i$  due to excursions in and out of the reservoirs. Under these conditions the KS conductance  $\mathcal{G}_{\text{KS}}$  is given in terms of the noninteracting retarded KS Green's function (GF),  $g_i^r(\omega) = [\omega - \epsilon_i - i\gamma_i]^{-1}$ , as [4]

$$\mathcal{G}_{\text{KS}} = -\frac{1}{\pi} \sum_i \gamma_i \text{Im} g_i^r(\mu), \quad (1)$$

where  $\mu$  is the chemical potential of the electrodes, the sum is over all KS MOs and the conductance is given in units of  $e^2/h$ . In Eq. (1),  $-\text{Im} g_i^r(\mu)/\pi$  is the noninteracting local density of states (i-LDOS) for electrons in the KS MO  $\phi_i$ , with energy  $\epsilon_i$ .

Electron-electron interactions are allowed only within the molecule and are formally accounted for using MBGFT, by means of the exact XC self-energy,  $\Sigma_{\text{XC}}(\omega)$  [15,16]. To simplify the analysis we assume that  $\Sigma_{\text{XC}}$  is diagonal in the basis set of KS MOs. This assumption is not too restrictive in terms of the kind of interesting physics known not to be captured by the KS system: for instance the Kondo effect is well described by the interacting Anderson model with just one MO and two spin orientations. The interacting conductance is then given in terms of the interacting retarded GF,  $G^r$ , as

$$\mathcal{G} = -\frac{1}{\pi} \sum_i \gamma_i \text{Im} G_i^r(\mu), \quad (2)$$

where  $-\text{Im} G_i^r(\mu)/\pi$  is the interacting i-LDOS.

Note that the electronic density in the molecule can be obtained by means of either  $g^r$  or  $G^r$ . In KS DFT the density reads  $n(\mathbf{r}) = \sum_i n_i^{\text{KS}} |\phi_i(\mathbf{r})|^2$ , where the fractional KS occupation numbers are given by  $n_i^{\text{KS}} = -\int_{-\infty}^{\mu} d\omega \text{Im} g_i^r(\omega)/\pi$ . Similarly the electronic density can be obtained from the interacting GF as  $n(\mathbf{r}) = \sum_i n_i |\phi_i(\mathbf{r})|^2$ , where the fractional interacting occupation numbers are given by  $n_i = -\int_{-\infty}^{\mu} d\omega \text{Im} G_i^r(\omega)/\pi$ . The interacting and KS electronic densities are the same provided that  $n_i^{\text{KS}} = n_i$ . This relation determines  $v_{\text{XC}}$  within our simplified KS scheme.

In what follows we show how in KS theory getting the density right generally means giving up the conductance. We begin by expressing the interacting conductance in terms of  $n_i$ . It follows from Refs. [15,17] (see also [18]) that  $n_i$  can be expressed as

$$n_i = \frac{1}{2} - \frac{1}{\pi} \arctan\left(\frac{\text{Re} G_i^r(\mu)}{\text{Im} G_i^r(\mu)}\right) - L_i, \quad (3)$$

where the Luttinger integral  $L_i$  is given by

$$L_i = \frac{1}{\pi} \text{Im} \int_{-\infty}^{\mu} d\omega G_i^r(\omega) \frac{\partial \Sigma_{\text{XC},i}^r(\omega)}{\partial \omega}. \quad (4)$$

Using  $G^r = [(g^r)^{-1} - (\Sigma_{\text{XC}}^r - v_{\text{XC}})]^{-1}$  and the Fermi-liquid condition  $\text{Im} \Sigma_{\text{XC},i}^r(\mu) = 0$  in Eq. (3), we write  $-\gamma_i \text{Im} G_i^r(\mu)/\pi = \sin^2[\pi(n_i + L_i)]$ , which directly gives the contribution to the interacting conductance from the MO  $\phi_i$ . Summing over all MO's, Eq. (2) becomes

$$\mathcal{G} = \sum_i \sin^2[\pi(n_i + L_i)]. \quad (5)$$

The same argument can be used for the KS system with one fundamental difference: the KS Luttinger integral  $L_i^{\text{KS}}$  satisfies  $L_i^{\text{KS}} = 0$  since in KS there are no frequency dependent terms such as  $\partial \Sigma_{\text{XC},i}^r(\omega)/\partial \omega$ . Therefore  $\mathcal{G}_{\text{KS}}$  is given by

$$\mathcal{G}_{\text{KS}} = \sum_i \sin^2(\pi n_i^{\text{KS}}). \quad (6)$$

In general,  $L_i \neq 0$  in interacting systems, while the noninteracting system with the same density satisfies  $L_i^{\text{KS}} = 0$  and therefore  $\mathcal{G}_{\text{KS}} \neq \mathcal{G}$ . For the KS system to have the exact conductance one indeed needs  $n_i^{\text{KS}} = n_i + L_i$  in Eq. (6). But this is incompatible with the ‘‘exact density condition,’’  $n_i^{\text{KS}} = n_i$  (unless the interacting system satisfies  $L_i = 0, \forall i$ ). In our simplified KS scheme ‘‘exact density’’ and ‘‘exact conductance’’ are not attainable simultaneously by solving an effective noninteracting problem. Hence there is a ‘‘KS conductance problem.’’

The comparison between Eqs. (5) and (6) gives insights into the origin of beyond-KS XC contributions to the conductance of a molecular junction. We see that the KS system captures the phase  $\pi n_i$ , which is Friedel's displaced charge [13], but misses additional phases ( $L_i$ 's). The appearance of  $\partial \Sigma/\partial \omega$  in Eq. (4) suggests that the  $L_i$ 's are a metric for renormalization: the KS i-LDOS consists of a single-particle resonance while the interacting i-LDOS quite generally shows quasiparticle and satellite resonances with renormalized intensities and widths. In general, the satellites in the i-LDOS can be above or below  $\mu$  regardless of whether  $\epsilon_i > \mu$  or  $\epsilon_i < \mu$ . Therefore interactions can displace spectral weight in the i-LDOS across the Fermi surface and redistribute charge among the orbitals. Fermi liquids satisfy Luttinger's theorem [15,17],  $\sum_i L_i = 0$ , which is a detailed-balance relation: a surplus of renormalized charge in some MOs is exactly compensated by a deficit in the rest. The  $L_i$ 's are a measure of the charge displaced from the KS MO  $\phi_i$  by the interactions and quantify the impact of renormalization on the conductance. Renormalization thus contributes to the scattering phase-shift in a given channel and then to the conductance. The KS system satisfies  $L_i^{\text{KS}} = 0$ , and therefore  $\mathcal{G}_{\text{KS}} \neq \mathcal{G}$ .

Next we address the accuracy of  $\mathcal{G}_{\text{KS}}$  by studying the behavior of the  $L_i$ 's in relevant physical scenarios. We first consider cases where the interacting system satisfies  $L_i = 0, \forall i$  and, according to Eqs. (5) and (6),  $\mathcal{G}_{\text{KS}} = \mathcal{G}$ :

(i) *For strictly single-channel molecular junctions,*  $\mathcal{G}_{\text{KS}} = \mathcal{G}$ .—As pointed out in Ref. [12] in the strict

single-channel case (one spin-degenerate KS MO; we drop the index  $i$ ), Luttinger theorem reads  $L = 0$ . Therefore, using Eqs. (5) and (6), the conductance is given by  $\mathcal{G} = \sin^2(\pi n) = \mathcal{G}_{\text{KS}}$ . Therefore we expect  $\mathcal{G} \sim \mathcal{G}_{\text{KS}}$  in those systems where conduction is dominated by a single scattering channel.

(ii) *In models with only direct Coulomb interactions between MO's,  $\mathcal{G}_{\text{KS}} = \mathcal{G}$ .*—It follows from the conservation rules that  $L_i = 0, \forall i$ , provided that the interactions conserve  $\phi_i$  [19]. Direct Coulomb interactions between KS MOs,  $\hat{U} = \sum_{ij} V_{ii,jj} \hat{n}_i \hat{n}_j$ , where  $V_{ii,jj} = \int d\mathbf{r} d\mathbf{r}' |\phi_i(\mathbf{r})|^2 |\mathbf{r} - \mathbf{r}'|^{-1} |\phi_j(\mathbf{r}')|^2$ , actually conserve the KS MO. Thus we expect  $\mathcal{G} \sim \mathcal{G}_{\text{KS}}$  in systems where direct Coulomb interactions are strongly dominant. Such systems can display interesting correlation effects (e.g., Kondo) for finite values of  $\gamma_i$ . But these interactions do not scatter one MO into another; direct interactions do not displace charge between the orbitals,  $L_i = 0$ , and hence there is no correction to  $\mathcal{G}_{\text{KS}}$ .

In the following we address the accuracy of  $\mathcal{G}_{\text{KS}}$  in molecular junctions at low temperatures as a function of gate voltage. The gate voltage controls the charge in the molecule and the low temperature conductance exhibits a sequence of conductance peaks and valleys as a function of gate voltage. Let us consider a molecular-junction model (Hubbard molecule), where the molecular Hamiltonian is written in a minimal basis set of local atomic orbitals as

$$\hat{H}_c = \epsilon_0 \sum_{\alpha,\sigma} \hat{n}_{\alpha,\sigma} + t \sum_{\sigma} (\hat{c}_{1,\sigma}^\dagger \hat{c}_{2,\sigma} + \hat{c}_{2,\sigma}^\dagger \hat{c}_{1,\sigma}) + U \sum_{\alpha} \hat{n}_{\alpha,\uparrow} \hat{n}_{\alpha,\downarrow} \quad (7)$$

where  $\hat{c}_{\alpha,\sigma}^\dagger$  ( $\hat{c}_{\alpha,\sigma}$ ) creates (destroys) an electron with spin  $\sigma$  in site  $\alpha = 1, 2$ ;  $\hat{n}_{\alpha,\sigma} = \hat{c}_{\alpha,\sigma}^\dagger \hat{c}_{\alpha,\sigma}$  is the number operator for electrons with spin  $\sigma$  in site  $\alpha$ ;  $t$  is the hopping amplitude;  $\epsilon_0$  can be interpreted directly as gate voltage; and  $U$  gives the on-site interaction between electrons with different spins. The coupling to the electrodes is symmetric and described by a diagonal wideband model. For practical reasons in the calculations we approximate MBGFT by the (conserving) self-consistent second-order many-body perturbation theory (MBPT). The conductance calculated using a conserving MBPT approximation satisfies both Eqs. (2) and (5); this is not the case in non-self-consistent MBPT where different ways of evaluating the conductance give different results [16]. By symmetry  $\Sigma_{\text{XC}}$  is diagonal in the basis set of KS MOs; the quasiparticle highest occupied and lowest unoccupied MOs (HOMO and LUMO) are symmetric ( $H$ ) and antisymmetric ( $L$ ) combinations of the two atomic orbitals. Writing the interaction terms in Eq. (7) in the product basis of KS MOs, one readily sees that it contains terms such as  $U c_{L,\uparrow}^\dagger c_{H,\uparrow} c_{H,\downarrow}^\dagger c_{L,\downarrow}$ , which scatter MO's into one another and hence the conditions for point (ii) are not satisfied. Therefore, despite the diagonality of  $\Sigma_{\text{XC}}$ , we expect corrections to  $\mathcal{G}_{\text{KS}}$ . The KS

Hamiltonian is built as outlined above, by finding the  $v_{\text{XC}}$  that satisfies  $n_i^{\text{KS}} = n_i$ .

The calculated  $\mathcal{G}$ —obtained from both Eqs. (2) and (5)—and  $\mathcal{G}_{\text{KS}}$  are compared as a function of gate voltage in Fig. 1(a): KS gives an excellent approximation to the conductance peaks, both for position and magnitude, but overestimates the conductance in the valley by a large factor. Figure 1(a) is in excellent agreement with the results obtained for other models in Ref. [11]. Here we explain this behavior in terms of Eqs. (5) and (6). As seen in Fig. 1(b)  $L_i$  is nonzero at the valley and vanishes as the molecule is discharged: corrections to the KS conductance are most important in the valley. Thus, based on Eqs. (5) and (6), as well as on our numerical calculations, we arrive to the following conclusions regarding the accuracy of  $\mathcal{G}_{\text{KS}}$  as a function of gate voltage:

(iii) *In the conductance peaks,  $\mathcal{G} \approx \mathcal{G}_{\text{KS}}$ .*—Around the conductance peak, conduction is expected to be dominated by a single KS MO, and thus, according to (i) above,  $\mathcal{G}_{\text{KS}} = \mathcal{G}$ . As an alternative argument, we note that around the conductance peak the occupancy of the relevant KS MO is  $n \sim 1/2$ , and thus, for  $L \ll n$  and to first order in  $L$ , Eqs. (5) and (6) give  $\mathcal{G} - \mathcal{G}_{\text{KS}} \sim \pi \sin(\pi n) \cos(\pi n) L + O(L^2) \sim O(L^2)$ . Thus, at the peak,  $\mathcal{G}_{\text{KS}}$  is exact to first order in  $L$ .

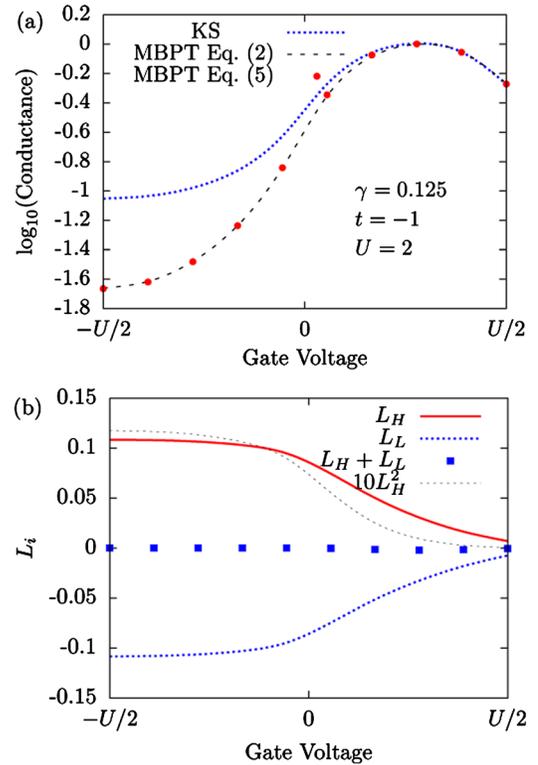


FIG. 1 (color online). (a) KS and interacting conductances as a function of gate voltage, calculated for the Hubbard molecule. (b) HOMO and LUMO Luttinger integrals, their sum  $L_H + L_L = 0$ , and  $10L_H^2$  calculated for the same model. At the conductance valley, KS overestimates the conductance. At the conductance peak  $\mathcal{G}_{\text{KS}}$  is exact to first order in  $L_H$ .

(iv) *In the conductance valleys we expect  $\mathcal{G} < \mathcal{G}_{\text{KS}}$ .*—In the low-conductance valleys we expect conduction to be dominated by the two frontier MOs and thus we approximate the transmission coefficient of the interacting system by a sum of two renormalized Lorentzians placed symmetrically about the Fermi energy, corresponding to the quasiparticle HOMO and LUMO states. Then the interacting conductance is  $\mathcal{G} \propto Z/E_g^2$ , where  $Z$  and  $E_g$  are the quasiparticle renormalization factor and gap [20]. Similarly for the KS system we obtain  $\mathcal{G}_{\text{KS}} \propto (E_g^{\text{KS}})^{-2}$ , where  $E_g^{\text{KS}}$  is the KS gap. Therefore we get  $\mathcal{G}/\mathcal{G}_{\text{KS}} = Z(E_g^{\text{KS}}/E_g)^2$ . Since  $E_g^{\text{KS}} < E_g$  and  $Z < 1$  [20], then  $\mathcal{G} < \mathcal{G}_{\text{KS}}$ : for example, using gap values for benzene in the gas phase, one gets  $\mathcal{G}/\mathcal{G}_{\text{KS}} \approx 0.24$  for  $Z = 1$  [21]; screening by gates and electrodes can make this ratio closer to one. The same expression for the ratio  $\mathcal{G}/\mathcal{G}_{\text{KS}}$  can be obtained perturbatively from Eq. (3). Similar relations between conductance and band-gap ratios have been discussed (for  $Z = 1$ ) by Cehovin *et al.* [5]. The ratio  $E_g^{\text{KS}}/E_g$  provides a measure of the degree of “unphysicality” of the KS system and is featured also in the theory of the so-called exchange-correlation electric field [22].

We compare our results listed in (i)–(iv) with previously published works. Points (i) and (ii) show that there are cases where KS works, and explain the results of Mera *et al.* [12] as a particular case of the present theory. Points (iii) and (iv) explain the numerical results of Schmitteckert and Evers [11]. Point (iv) is also in overall agreement with Refs. [9,10], showing that the conductance can be dominated by beyond-KS XC effects and that, typically,  $\mathcal{G} < \mathcal{G}_{\text{KS}}$ . We thus provide a comprehensive understanding of previous results regarding the accuracy of the exact KS conductance.

We would like to emphasize that the true DFT conductance is exact,  $\mathcal{G} = \mathcal{G}_{\text{DFT}}$ , since DFT is (formally) an exact theory of many-electron systems. The problem we address is intrinsic to the KS system. In this sense  $\mathcal{G}_{\text{KS}}$  may be regarded as a density functional approximation to  $\mathcal{G}$ . Thus one generally needs to add a corrective density functional  $\Delta$  to the KS conductance, so that  $\mathcal{G} = \mathcal{G}_{\text{KS}} + \Delta$ . In this work we effectively discussed the size of  $\Delta$  in terms of the  $L_i$ 's, for simple molecular-junction models.

In conclusion, we have shown how renormalization effects contribute to the conductance of molecular-junction models. The KS system does not capture this contribution and the KS conductance is not generally accurate. There are exceptions: the exact-KS conductance can be accurate in single-channel molecular conductors and systems dominated by direct Coulomb interactions.

This work was supported by the French National Research Agency (ANR), project Quantamonde.

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