

# Density functional description of Coulomb blockade: Adiabatic or dynamic exchange-correlation?

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Above the Kondo temperature, the Kohn-Sham zero-bias conductance of an Anderson junction has been shown to completely miss the Coulomb blockade. Within a standard model for the spectral function, we deduce a parameterization for both the onsite exchange-correlation potential and the bias drop as a function of the site occupation that applies for all correlation strengths. We use our results to sow doubt on the common interpretation of such corrections as arising from dynamical exchange-correlation contributions.

## I. INTRODUCTION

Electron transport [1] through molecular junctions is usually formulated using non-equilibrium Green's function (NEGF)[2] or an equivalent scattering formalism [3]. In atomistic simulations of electron transport [4, 5], density functional theory (DFT) [6, 7] is often used in combination with NEGF, producing the standard model[8] in which the interacting one-body Green's function and coupling matrices are replaced by their Kohn-Sham (KS) counterparts [4, 5]. Whether or not ground-state KS-DFT can in principle, under certain conditions, produce the exact conductance remains open[8], even at zero temperature and in the linear response regime. Thus there are two sources of error which can be difficult to disentangle: (i) replacing the interacting one-body Green's function with the KS Green's function, and (ii) replacing the exact KS Green's function by one from an approximate functional[9].

Model Hamiltonians provide excellent testbeds for this purpose, especially when highly accurate results are known and can serve as benchmarks for larger KS-DFT calculations. The Anderson impurity model [10] has attracted much attention recently[11–18]. Due to its generality, broad applicability, and exact solvability, studying transport through an Anderson junction is useful in understanding errors in atomistic calculations and in constructing accurate functionals for electron transport.

The KS system is defined as a junction with  $U = 0$  (see below), but whose onsite energy is chosen to make its site occupation match that of the interacting junction, which can be found exactly using the Bethe ansatz[19]. At zero temperature and in the linear response regime, the KS conductance, i.e., the conductance of non-interacting electrons in the KS potential, is exact[11, 12, 14], i.e., the first error is zero. This can be attributed to the Friedel-Langreth sum rule [20, 21], which implies the transmission is a simple function of occupation. By reverse engineering of the exact solution[12], one can study which features must be present in any approximation in order to generate an accurate transmission[13]. For example, the derivative discontinuity[22] is crucial as correlations

grow, and how rapidly it is approached as  $U$  grows is determined by the charge susceptibility of the system at particle-hole symmetry [13]. This derivative discontinuity has also been shown to be related to more general blockade phenomena [23, 24].

However, all this changes above the Kondo temperature[25], when the Kondo transmission peak is negligible, and the sum rule no longer applies. Accurate solutions are available [1], and the spectral function exhibits two Coulomb peaks in the strongly correlated regime. Between the two peaks, the linear-response conductance is very low due to Coulomb blockade. This temperature regime better mimics what happens in real molecular junctions than the zero-temperature limit where a Kondo plateau dominates. But the low-temperature KS conductance *always* satisfies the sum rule even when the physical conductance does not, and so is qualitatively incorrect between the two Coulomb peaks. Having spent years figuring out how to get the Kondo plateau into DFT, the difficulty is now to get rid of it at finite temperature [26].

It has long been argued[27–29] that time-dependent DFT produces *dynamic* corrections to the KS conductance, and that these are *necessary* to produce an accurate transmission. Making this identification, Ref. [15] shows that a simple model for the exchange-correlation (XC) kernel of time-dependent density functional theory (TDDFT) reproduces the right corrections, at least in the strongly correlated limit. This was further shown to depend, somewhat surprisingly, on the onsite occupation alone.

Here, we argue that the corrections that turn the KS conductance into the true conductance of an Anderson junction can plausibly be considered as a *non-local static* correction that in principle could be extracted from ground-state DFT. This possibility was suggested long ago [28] as the only alternative to dynamic TDDFT effects for altering a resonance in the transmission of such a junction. The origin of such an effect, within ground-state DFT, is the well-documented counteracting XC field that is significant for certain molecules and solids in response to a long-range electric field. The origin of

this field is the localization of orbitals on specific sites and the appearance of step-like features in the induced exchange-correlation potential that (correctly) reduce the polarization, relative to that of standard local, semilocal, and hybrid functionals[30]. These steps are reasonably accurately given by Hartree-Fock or optimized effective potential (OEP) calculations, because of their explicit orbital dependence[31]. They are in fact a field-induced derivative discontinuity.

To make this argument, we first accurately parametrize the onsite XC potential for temperatures that are low, but at which there is no Kondo plateau in the conductance, i.e., in the Coulomb blockade regime. Our parametrization is designed to work for all correlation strengths, not just for strong correlation. Next, we accurately parametrize the XC bias drop that ensures that a static KS calculation reproduces the physical conductance, again including both weak and strong correlation regimes. Finally, we explain how this can be interpreted in terms of the known counteracting XC fields.

## II. ANDERSON JUNCTION AT LOW TEMPERATURE LIMIT

To begin, the Hamiltonian for the Anderson junction[10] consists of an interacting impurity site coupled to identical featureless left and right leads:

$$\mathcal{H} = \varepsilon \hat{n} + U \hat{n}_\uparrow \hat{n}_\downarrow + \mathcal{H}_{\text{leads}} + \mathcal{H}_{\text{T}} \quad (1)$$

with  $\varepsilon$  the on-site energy and  $U$  the Coulomb repulsion when the site is doubly occupied,  $\hat{n} = \hat{n}_\uparrow + \hat{n}_\downarrow$ . Here  $\mathcal{H}_{\text{leads}}$  is the Hamiltonian of the two leads, and  $\mathcal{H}_{\text{T}}$  is their coupling to the site. In the wide band limit, the effect of tunneling is incorporated into an energy-independent constant  $\Gamma$  [32]. There are two dimensionless parameters:  $(\mu - \varepsilon)/U$ , with  $\mu$  the chemical potential of the leads, which moves the system on- and off-resonance, and  $u = U/\Gamma$ , which switches the system between weakly and strongly correlated. Below the Kondo temperature  $T_K$ , a characteristic temperature dependent on  $u$ , the exact spectral function has two Coulomb peaks and one Kondo peak whose width is related to  $T_K$ [33], and the sum rule applies. Above  $T_K$ , the Kondo peak disappears, the sum rule is violated, and the conductance comes from the two Coulomb peaks only [33].

Although no exact solution is available above  $T_K$ , the Green's function on the central impurity site can be accurately approximated as [1]

$$G(\omega) = \sum_{i=1,2} \frac{n_i}{\omega - \varepsilon_i + i\Gamma/2}, \quad (2)$$

where  $\varepsilon_1 = \varepsilon, \varepsilon_2 = \varepsilon + U, n_1 = 1 - n/2$ , and  $n_2 = n/2$ , with  $n \equiv \langle \hat{n}_c \rangle$  the occupation on the impurity site, and the coupling to the leads causes the broadening of  $\Gamma/2$ . Throughout this work, we use Eq. (2) as an *ansatz* for the exact solution, as it captures the right physics and

accurately mimics the numerical exact solution above  $T_K$ [1]. We also introduce a specific low temperature limit, namely  $\beta^{-1} \rightarrow 0$ , but  $\beta^{-1} \gg k_B T_K$ , where  $\beta$  is the inverse temperature and  $k_B$  the Boltzmann constant. Because  $T_K$  depends exponentially on the parameters, it is typically much smaller than any other temperature scale. We are in a regime above  $T_K$ , but at temperatures far smaller than any of the other energy scales of the problem. For example, Kurth and Stefanucci [15] discussed a case where  $U = 10, \Gamma = 1$ , and temperature  $\tau = 0.1$  ( $T_K = 0.06$ ). We have checked that by taking our low temperature limit, one obtains essentially the same numerical results as using  $\tau = 0.1$  in the Fermi function. In the rest of this work, we consider only this limit, which greatly simplifies the derivation and analytical forms are then available for the quantities of interest. We note that we use the same Eq. (2) as Ref. [15] for the benchmark solution above  $T_K$ , to facilitate comparison of our approach (static correction) and that in Ref. [15] (dynamic correction). Ref. [15] studied these effects for a range of temperatures but only for strong correlation; here we are interested in *all* correlation strengths, and find that low temperatures are well approximated by a specific low-temperature limit. In this limit, we find accurate analytic parametrizations with relative ease.

The spectral function  $A(\omega) = -2\text{Im}G(\omega)$  depends on the occupation  $n$  on the impurity site. Therefore  $n$  must be determined self-consistently:

$$n = \frac{1}{\pi} \int_{-\infty}^{\mu} d\omega A(\omega) = \frac{\pi - 2\theta_1}{\pi + \theta_2 - \theta_1}, \quad (3)$$

where  $\tan \theta_i = 2(\varepsilon_i - \mu)/\Gamma$  and, in the low temperature limit, levels are fully occupied up to  $\mu$ . Thanks to this limit, Eq. (3) is a closed-form for  $n$  in terms of the parameters. The linear-response transmission is then [15]:

$$T = -\frac{\Gamma}{2} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \frac{df}{d\omega} A(\omega) \xrightarrow{\beta^{-1} \rightarrow 0} \frac{\Gamma}{4\pi} A(\omega = \mu). \quad (4)$$

In Fig. 1,  $n$  and  $T$  are plotted as a function of  $\mu$ , for several values of  $u$ . For  $U \gg \Gamma$ , a plateau in  $n$  develops, i.e., a Coulomb blockade, which corresponds to the low conductance region between the two Coulomb peaks at  $\mu \approx \varepsilon$  and  $\mu \approx \varepsilon + U$ . This is very different from the Kondo regime, where there is always a Kondo plateau in conductance, as discussed in Ref. [12].

## III. KOHN-SHAM ANDERSON JUNCTION

We now construct a KS Anderson junction, i.e., one with  $U = 0$ , that generates the same occupation  $n$  as the interacting system by replacing  $\varepsilon$  with  $\varepsilon_s[n] = \varepsilon + v_{\text{HXC}}[n]$ , and analyze its conductance. Because the occupation on the impurity site is a number, the functional dependence is simply a function of  $n$ . The KS Green's function has only one pole:

$$G_s(\omega) = \frac{1}{\omega - \varepsilon_s[n] + i\Gamma/2}. \quad (5)$$

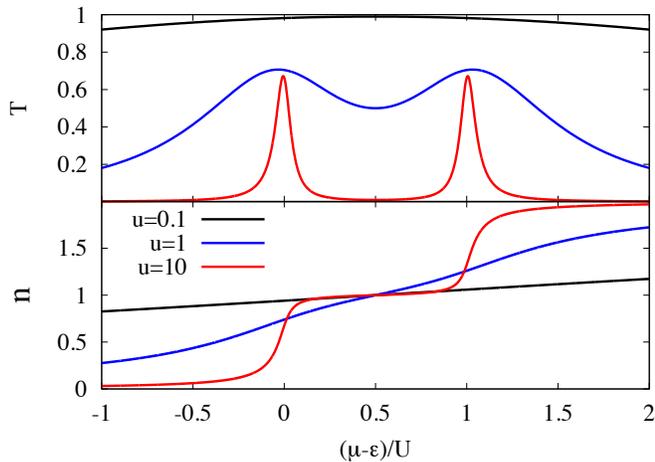


FIG. 1. Upper panel: Conductance  $T$  as a function of  $(\mu - \varepsilon)/U$ , plotted in unit of  $G_0 = 2e^2/h = 1/\pi$ , the conductance quantum. lower panel:  $n$  as a function of  $(\mu - \varepsilon)/U$ . Different  $u = U/\Gamma$  are used.

The Hartree-exchange-correlation (HXC) potential  $v_{\text{HXC}}[n]$  is defined such that:

$$n = \frac{1}{\pi} \int_{-\infty}^{\mu} d\omega A_S(\omega), \quad (6)$$

where  $A_S(\omega) = -2\text{Im}G_S(\omega)$  is the spectral function of the KS system. By definition[34], the KS occupation matches the physical one, i.e., the left hand sides of Eqs. (3) and (6) are identical, for a given set of  $\mu, \varepsilon, U$ , and  $\Gamma$ . Applying this condition yields:

$$v_{\text{HXC}} = \mu - \varepsilon - \frac{\Gamma}{2} \tan \left[ \frac{\pi}{2} (n - 1) \right]. \quad (7)$$

Note that this is *insufficient* to define  $v_{\text{HXC}}[n]$  because of the presence of  $\mu - \varepsilon$  [If Eq. (3) could be inverted to find  $\mu - \varepsilon$  as an explicit function of  $n$ , as is trivial numerically, this would suffice]. In Ref. [15], reverse engineering to find  $v_{\text{HXC}}[n]$  is done at three different temperatures above  $T_K$ , but for a fixed large  $u$  ( $=10$ ). Here the low temperature limit simplifies the algebra, and we study the  $u$ -dependence explicitly. Following the ideas of Ref. [13], we parametrize  $v_{\text{HXC}}[n]$  as

$$v_{\text{HXC}}^{\text{app}}[n] = \frac{U}{2} \left( 1 + \frac{2}{\pi} \tan^{-1}[\sigma(u)(n - 1)] \right), \quad (8)$$

where  $\sigma(u)$  is a parameter, determined by the exact condition of charge susceptibility at particle-hole symmetry[35]:

$$\chi = U \left. \frac{\partial n}{\partial \mu} \right|_{n=1} = \frac{4u}{(1 + u^2)(\pi + 2 \tan^{-1} u)}, \quad (9)$$

where Eq. (3) was used. The derivative is taken at the particle-hole symmetry point,  $n = 1$ , or equivalently

where  $\varepsilon = \mu - U/2$ . Imposing this condition fixes the parameter  $\sigma$  in Eq. (8) as  $\sigma(u) = \pi/\chi - \pi^2/(4u)$ . This procedure could be simply generalized to finite temperature, by using the finite-temperature susceptibility, but this is not the main concern of the present work. We briefly show and discuss finite-temperature effects in Section VI using the numerical solution, without analytically parametrizing the temperature-dependent functional.

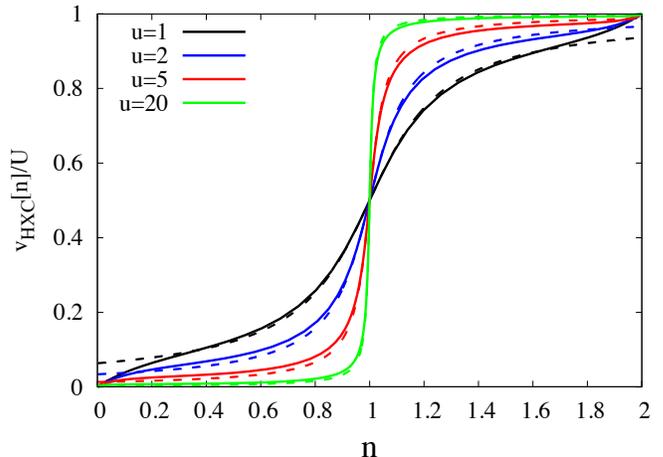


FIG. 2.  $v_{\text{HXC}}[n]$  as a function of  $n$  for various  $u = U/\Gamma$ . Solid lines are results from Eq. (7) with  $n$  calculated from Eq. (3), dashed lines are the approximation of Eq. (8).

In Fig. 2, both the  $v_{\text{HXC}}[n]$  that precisely reproduces the onsite occupation determined from Eq. (3) and the parametrization of Eq. (8) are plotted as a function of  $n$ , for different  $u$ . For  $U \gg \Gamma$ , a step in  $v_{\text{HXC}}$  develops, reflecting the onset of the derivative discontinuity as  $u \rightarrow \infty$ [34]. These kinds of features were discussed in Refs. [12, 13], at zero temperature. In the low temperature limit discussed in this work, these rules still apply. An important point is that, unlike Ref. [15], our parametrization applies for all values of  $U$  (both weak and strong correlation), and appears to fail only when the site is almost entirely empty or doubly-occupied. Our results match those of Ref. [15] when the temperature is low and the correlation is strong.

The KS conductance has the same form as in Eq. (4), but with  $A$  replaced by  $A_S$ . We compare the two quantities in Fig. 3. Here the KS conductance *always* satisfies the Friedel-Langreth sum rule, i.e.,  $T_s = \sin^2(\pi n/2)$  in the low temperature limit, and the plateau is always present, regardless of whether the physical system is in the Kondo regime (Ref. [12]) or not (this work). However the conductance from Eq. (4) has two peaks and is very small between the two peaks for  $U \gg \Gamma$  due to the ansatz of Eq. (2). For  $U \ll \Gamma$ , the KS conductance is quite accurate, but for larger  $U$ , it is wildly inaccurate. Whenever correlation is significant (or, equivalently in this model, the coupling to the leads is weak), the KS conductance is a large overestimate of the physical conductance. In par-

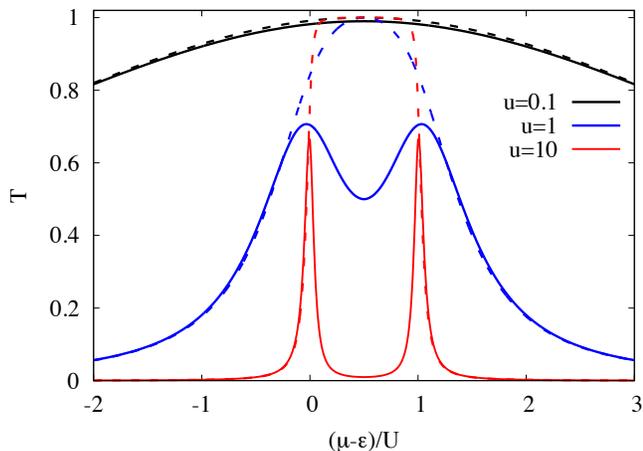


FIG. 3. Physical conductance (solid lines) from Eq. (4) and KS conductance (dashed lines) for various values of  $u = U/\Gamma$ , plotted in unit of  $G_0 = 2e^2/h = 1/\pi$ , the conductance quantum.

ticular, it misses entirely the Coulomb blockade effect, producing no drop at all between the Coulomb peaks. All this was beautifully shown in Ref. [15] for strong correlation for several temperatures. Although the Friedel-Langreth sum rule does not apply at finite temperatures, the discrepancy remains qualitatively the same.

#### IV. STATIC CORRECTION TO KOHN-SHAM CONDUCTANCE

It is no surprise that the KS conductance is not correct under such conditions, as it is extracted entirely from equilibrium DFT[36]. One can formally identify the corrections to the KS conductance[8], and capture them in terms of an XC correction to the applied bias:

$$\delta I = T \delta V = T_s \delta V_s, \quad (10)$$

where  $\delta V$  is an applied bias,  $\delta V_s = \delta V + \delta V_{xc}$  is the bias experienced by the KS system, and  $\delta I$  is the induced current in both. The formal result of Ref. [12] can be stated that  $\delta V_{xc} = 0$  due to the sum rule at zero temperature when the Kondo peak is present, and the pioneering work of Ref. [15] interpreted the XC corrections in  $\delta V_s$  as dynamical corrections arising from TDDFT, i.e., corrections that would not appear in any static DFT calculation.

Here we suggest that a static correction from ground-state DFT can explain the results of Kurth and Stefanucci[15] which they interpreted solely in terms of TDDFT. We propose the following approximation for a non-local XC bias:

$$\frac{\delta V_s^{\text{app}}}{\delta V} = \frac{n_1[1 - \cos(2\zeta)] + 2n_2/[1 + (2u + \cot \zeta)^2]}{2 \sin^2(n_2\pi)} \quad (11)$$

for  $n < 1$ , where  $\zeta = n_2(\pi + 2n_2 \tan^{-1} u/n_1)$  and  $n_1$  and  $n_2$  are swapped if  $n > 1$ . This specific choice will be justified shortly. For the present, we simply plot it in Fig. 4. For weak correlation at any filling, or for  $n_1$  or  $n_2 < 0.5$ , this KS bias is close to the applied bias. But for  $n$  near 1 and  $U \gg \Gamma$ ,  $\delta V_s$  is noticeably smaller than  $\delta V$ .

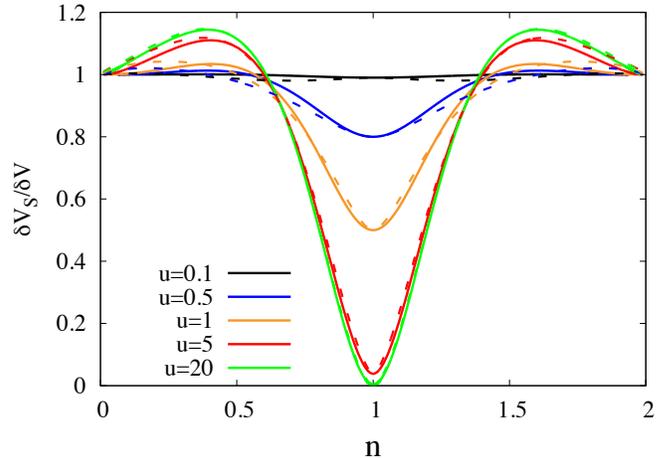


FIG. 4.  $\delta V_s^{\text{app}}$  as a function of  $n$  for various correlation strengths  $u = U/\Gamma$ . Solid lines are “exact”, as defined by Eq. (12). Dashed lines are approximate, as in Eq. (11).

Using  $\delta V_s^{\text{app}}$  in Eq. (11) with  $n$  calculated self-consistently from Eq. (8), we now plot the approximate conductance in Fig. 5. We see that it gives us essentially the correct conductance of the Anderson junction, including the severe corrections needed to reproduce the Coulomb blockade.

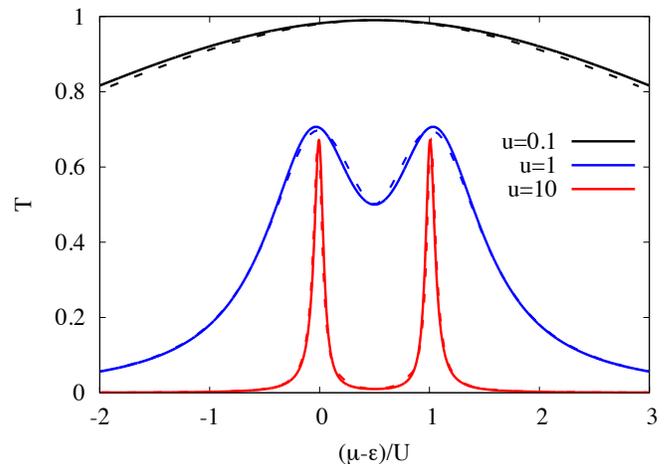


FIG. 5. Solid lines: physical conductances from Eq. (4). Dashed lines: conductances using approximations for both the local HXC potential Eq. (8) and non-local XC bias Eq. (11).

To understand how this was achieved, i.e., to derive  $\delta V_s^{\text{app}}$ , we first ask what XC drop would *exactly* reproduce the conductance implied by Eq. (4). From Eq. (10), we see

$$\delta V_s A_s(\omega = \mu) = \delta V A(\omega = \mu). \quad (12)$$

The  $\delta V_s/\delta V$  is an implicit functional of  $n$  via  $(\mu - \varepsilon)/U$ . For example, at particle-hole symmetry, we find explicitly

$$\left. \frac{\delta V_s}{\delta V} \right|_{n=1} = \frac{1}{1+u^2}, \quad \beta^{-1} \rightarrow 0. \quad (13)$$

This ‘‘exact’’  $\delta V_s$  is plotted in Fig. 4 as a function of  $n$ . The KS bias is close to the applied bias when the site is nearly empty or doubly-occupied. But near  $n = 1$ , as  $U$  increases,  $\delta V_s/\delta V$  drops rapidly from 1 to 0, i.e., the applied bias is almost entirely screened by the Coulomb blockade.

To use  $\delta V_{\text{xc}}$  to correct the KS conductance, one needs to express it as an explicit functional of the density  $n$ . The conductance is proportional to  $A(\omega = \mu)$ , which depends explicitly on  $\varepsilon$ , the external onsite potential (the strength of electron-electron interaction,  $u = U/\Gamma$ , enters into the formula as a parameter). We start with Eq. (3), and propose the following approximation:

$$\theta_2(n) \approx (n_1 - \frac{1}{2})\pi + 2n_2 \tan^{-1} u, \quad (14)$$

for  $n < 1$ , and  $n_1$  and  $n_2$  are swapped if otherwise. Then Eq. (3) can be inverted to find  $\varepsilon[n] = \mu + \Gamma \cot \zeta/2$ . After substituting  $\varepsilon[n]$  into Eqs. (2) and (4), we find our expression for  $\delta V_s/\delta V$ . One can verify that Eq. (11) satisfies the relation Eq. (13). The approximation used in Ref. [15] corresponds to  $\theta_2 \approx \pi/2$  [compared to Eq. (14)], which is accurate only in the large  $u$  limit, whereas Eq. (14) works wherever  $\delta V_{\text{xc}}$  is significant, even for small  $u$  or weak correlation [In the language of Ref. [15],  $R = 2n_2 \tan^{-1} u/(\pi n_1)$ ].

## V. ORIGIN OF NON-LOCAL CORRECTION

To understand how the XC bias drop might be extracted from a ground-state DFT calculation, we review the origin of Eq. (10). Start with Kubo response of the system to the external field, and here we follow the notation in Refs. [28] and [37]:

$$\delta \mathbf{j}(\mathbf{r}; \omega) = \int d\mathbf{r}' \hat{\sigma}_{\text{irr}}(\mathbf{r}, \mathbf{r}'; \omega) \delta \mathbf{E}_{\text{tot}}(\mathbf{r}'; \omega) \quad (15)$$

where the left-hand side is the current density in response to a perturbing external electric field at frequency  $\omega$ , and  $\hat{\sigma}_{\text{irr}}$  is the irreducible, frequency-dependent, nonlocal conductivity tensor of the many-electron problem. Since, in time-dependent current DFT (TDCDFT), the time-dependent KS system must produce the same current-

density response, we also have

$$\delta \mathbf{j}(\mathbf{r}; \omega) = \int d\mathbf{r}' \hat{\sigma}_s(\mathbf{r}, \mathbf{r}'; \omega) [\delta \mathbf{E}_{\text{tot}}(\mathbf{r}'; \omega) + \delta \mathbf{E}_{\text{xc}}(\mathbf{r}'; \omega)], \quad (16)$$

where  $\delta \mathbf{E}_{\text{tot}}$  contains both the external and Hartree electric fields. Here  $\hat{\sigma}_s$  is the KS conductivity tensor and  $\delta \mathbf{E}_{\text{xc}}$  is the exchange-correlation contribution to the field felt by the KS system.

The current is defined as an integral of the current density over a cross section:  $\delta I(z; \omega) = \int_S dS \delta \mathbf{j}(\mathbf{r}; \omega)$ , where  $z$  is the direction along the current flow. Great care with the order of limits must be taken when applying this formula to our problem[37]. The response formula is true for any  $\omega$ , but we wish to deduce the steady-state current. Thus  $\omega$  is kept finite, but reduced to 0 at the end of the calculation. In that limit, the nonlocal conductivity and the current become coordinate-independent[28, 37, 38], and are just the transmission  $T$  in Eq. (10). Integration of the fields over a large region including the device just yields the net voltage drop across the device,  $\delta V = \lim_{L \rightarrow \infty} \int_{-L}^L dz \int_S dS \delta \mathbf{E}(\mathbf{r}; \omega)$ . Thus we recover Eq. (10).

Now comes the tricky part. For any local (or semilocal) approximation to XC, if the density deep inside the leads is symmetric far from the molecule, the XC fields must be also symmetric, so that there can be no net XC bias drop. This is the case in all standard DFT calculations of transport[8, 28, 39]. But Ref. [28] argues that there are *two* possible sources of  $\delta V_{\text{xc}}$ : either highly nonlocal ground-state effects ( $\omega = 0$ ) or dynamical TDDFT corrections which fail to vanish as  $\omega \rightarrow 0$  (For any finite system, the dynamical effects must vanish in this limit, but our system is infinite).

Difficulties for DFT dealing with extended systems in electric fields first arose almost two decades ago. The famous GGG papers[40, 41] showed that there was, in principle, a long-range XC counterfield in insulators, that is missed by local and semilocal approximations. This is the same contribution that is needed to produce accurate exciton peaks in the optical response of solids[42, 43]. Contemporaneously, a similar effect was found in long chain polymers, whose polarizabilities and hyperpolarizabilities are greatly overestimated by LDA and GGA calculations[44–47].

This counteracting field is easily and accurately approximated by orbital-dependent functionals, such as Hartree-Fock or exact exchange using the OEP formalism[31]. It has also been found that the Vignale-Kohn approximation in TDCDFT, even taking the low-frequency limit, produces a finite correction, although the quantitative accuracy of such corrections has been questioned in some cases[48, 49]. The work of Ref. [50] suggests that either formalism might lead to approximations to the same feature.

For DFT calculations of transport through molecular junctions, the TDCDFT correction has been considered in several calculations and approximations, and differ-

ences between the KS and true conductance are often attributed to this. But there is no *a priori* reason to discount a non-local static contribution, which has proved much more straightforward (if expensive) to implement for both the optical response of insulators and polarizabilities of long-chain polymers. Thus it is important to understand if the effects seen in Ref. [15] can be understood in this manner. If so, then they can be searched for in orbital-dependent calculations of transport, such as GW, etc.

We note here that the crucial element for producing this counteracting XC field is *not* whether or not the system is a metal or insulator (traditional definitions based on bulk conductance[51] break down for nanoscale systems), but rather whether or not charge is localized on a site. This is exactly what is being modeled in the Anderson junction. Furthermore, while TDCDFT is needed to derive Eq. (10), the establishment of the steady current is done by the time-dependence of the KS equations themselves, without any need for dynamic XC contributions. As shown by Ref. [37], a steady current is established within even a simple Hartree calculation, i.e., one including no XC effects at all. This shows that the basic feature of a steady current occurs with the time-dependent KS equations in the absence of any dynamical XC contributions.

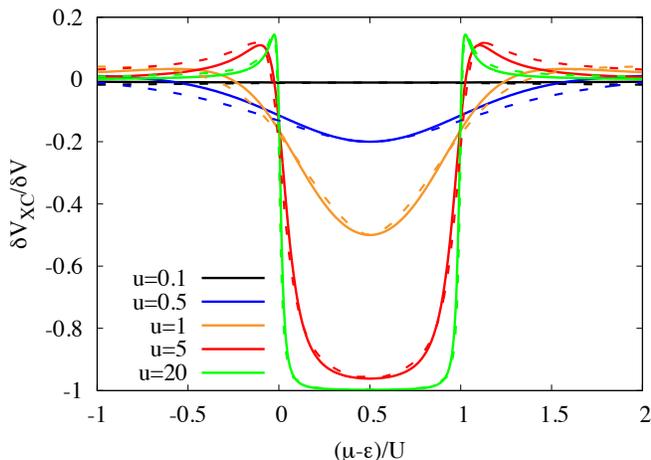


FIG. 6.  $\delta V_{XC}$  as a function of  $\mu$  for various correlation strengths  $u = U/\Gamma$ . Solid lines are “exact” as defined by Eq. (12) and dashed lines are approximations using both Eqs. (11) and (8).

To illustrate how this interpretation makes sense, we also plot  $\delta V_{XC}$  in Fig. 6 as a function of  $\mu - \epsilon$ . For large  $U$  the XC bias almost completely cancels the applied field, just as happens for well-separated molecules in response to applied fields[30]. Because we have performed our analysis for all  $U$ , we see that this remains true at all correlation strengths, for all  $\epsilon < \mu < \epsilon + U$ , i.e., in the region between the Coulomb peaks. Thus there is always an opposing field in this region, which can be un-

derstood as the origin of Coulomb blockade in terms of density functionals. Finally, we note that outside this region, we see regions where the XC bias has the same sign as the applied bias. We suspect this is an artifact of the simplicity of the model. Either the Anderson junction itself is oversimplified so its results cannot be trusted in this region, or possibly this is the non-applicability of our simple model for the spectral function [Eq. (2)] in this regime. In either case, this effect should be treated with caution unless it is also seen in a real-space calculation.

## VI. FINITE TEMPERATURE EFFECTS

The primary focus of our work has been the low-temperature limit, because of its relevance to standard electronic structure calculations. However, it is relatively straightforward to repeat our calculations at higher temperatures, as was done in Ref. [15]. To do that, Eq. (3) needs to be modified as:

$$n = 2 \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} f(\omega) A(\omega), \quad (17)$$

where  $f(\omega)$  is the Fermi function:  $f(\omega) = 1/(1 + \exp[(\omega - \mu)/\tau])$ , with  $\tau$  being the temperature. Also, the finite temperature version of Eq. (4) needs to be used, i.e.,

$$T = -\frac{\Gamma}{2} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \frac{df}{d\omega} A(\omega). \quad (18)$$

At finite temperature, we have no simple closed-form parametrization for the density or HXC potential and everything we show in this section is numerical. For ease of comparison, we use the same temperatures as those of Ref. [15], namely  $\tau = 0.1, 0.2$ , and  $1.0$ , respectively, with  $u = 10$ . We also show our low-temperature limit result.

In Fig. 7, we show conductance and occupation of the impurity site as a function of  $(\mu - \epsilon)/U$  for different temperatures (similar results can be found in Fig. 1 of Ref. [15]). In the lower panel, we see that for temperatures below about  $0.2$ , our low-temperature limit result is indistinguishable from the numerical result. On the other hand, the conductance shows substantially greater sensitivity, both exactly and at the KS level, due to the presence of the Fermi function in Eq. (18). The Friedel-Langreth sum rule applies only in the low-temperature limit. However, the figure also shows that our low-temperature result is approached as the temperature is reduced.

Finally, in Fig. 8 we show the XC drop  $\delta V_{XC}/\delta V$  as a function of  $n$ , for different temperatures. One can see that large temperatures wash out the sharp effects of the derivative discontinuity in the strongly correlated limit, as expected. The XC drop is less sensitive to temperature than the conductance. Overall, the qualitative features of the XC counterfield remain, but are weakened by increasing temperature, as the derivative discontinuity is rounded off.

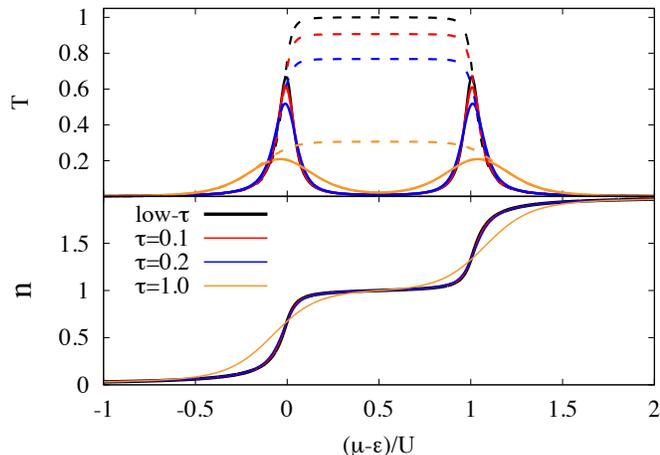


FIG. 7. Upper panel: conductance  $T$  as a function of  $(\mu - \epsilon)/U$ , plotted in unit of  $G_0$ , for different temperatures  $\tau$  at a fixed  $u = U/\Gamma = 10$ . Solid lines are “exact” and dashed lines are (uncorrected) KS conductance. The black line is for the low-temperature limit and is the same as the red line in Fig. 1. Lower panel:  $n$  as a function of  $(\mu - \epsilon)/U$ . By definition, the KS occupation always matches that of the exact occupation at all temperature.

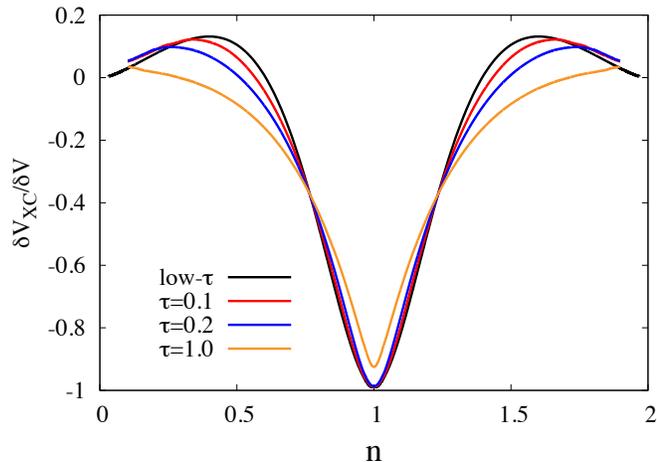


FIG. 8. Finite temperature generalization of Fig. 4 (but with  $\delta V_{XC}$  plotted rather than  $\delta V_S$ ):  $\delta V_{XC}$  as a function of  $n$ , for different temperatures  $\tau$  at a fixed  $u = U/\Gamma = 10$ . Black line is the low-temperature limit result.

## VII. CONCLUDING REMARKS

We conclude with a discussion of the relevance of these results for DFT calculations of transport. First we note that we have provided accurate parametrizations for both the onsite potential and the XC bias for the junction at low (but above  $T_K$ ) temperatures, that apply for all junctions, not just those strongly coupled to the leads.

These are available for any future calculations of impurity models of transport. If the parameters ( $\Gamma$ ,  $U$ ,  $\epsilon$ ) can be extracted from standard ground-state DFT calculations, the results could be compared with the accompanying DFT transport calculations to identify limitations of the pure DFT approximations. If  $U/\Gamma$  is large, the standard DFT approach will often yield a large overestimate of the conductance, as is often seen in comparison with experiment[8].

But, possibly more importantly, we have suggested that an alternative origin of the corrections to the KS conductance is non-local static XC effects. This is very important for understanding the limitations of standard DFT calculations of conductance and finding ways to improve them. Our reading suggests that, rather than looking to TDCDFT for corrections to the conductance, one could look instead at orbital-dependent *ground-state* approximations[30, 47, 52–54]. Such calculations can yield two important improvements in calculations in this area: (i) the correct positioning of orbital energies in the molecular region relative to the leads, as is already well-known[55], and (ii) a finite XC bias drop that corrects the KS conductance.

Unfortunately, due to the structureless nature of the leads in the Anderson model, there is no way at present to distinguish between the interpretation of the XC corrections presented in Ref. [15] and those presented here. In a more realistic model, the charge is depleted from the end of one lead and is increased at the end of the other, producing a net dipole. Such a dipole contributes to the net bias drop in the Hartree potential. But, with an orbital-dependent functional, a counteracting effect occurs in the exchange bias. This can be seen most clearly when the molecule is only weakly coupled to the leads. Then the form of this counteracting field is steps that are proportional to the applied field but that inhibit charge from moving from the molecule to the leads. Such steps are well-known in the absence of an applied field, between two distinct species, where they ensure dissociation into charge neutral fragments, and are consequences of the derivative discontinuity [22]. Our steps are field-induced versions of the same thing. Only a more detailed calculation, such as those of Refs. [56] and [17], can yield such information. But at least we have provided a reason to look for such corrections when non-local ground-state approximations are being applied.

To conclude, we have shown that, in the case of the Anderson junction, simple parametrizations of both the onsite HXC potential and the XC bias in linear response can reproduce the low-temperature Coulomb blockade, for all correlation strengths, not just the strongly correlated regime discussed in Ref. [15]. Furthermore, the XC bias can be interpreted as a non-local XC response to an applied electric field, and is not necessarily a dynamic TD-CDFT effect. Qualitatively similar effects should occur in more realistic descriptions of molecular transport[55]. Our approximate formulas could prove useful in other contexts, or as a check on XC approximations applied to

transport problems.

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- [1] H. J. W. Haug and A.-P. Jauho, *Quantum Kinetics in Transport and Optics of Semiconductors*, 2nd ed. (Springer, Berlin, 2007).
- [2] Y. Meir and N. S. Wingreen, Phys. Rev. Lett. **68**, 2512 (1992).
- [3] D. S. Fisher and P. A. Lee, Phys. Rev. B **23**, 6851 (1981).
- [4] J. Taylor, H. Guo, and J. Wang, Phys. Rev. B **63**, 245407 (2001).
- [5] M. Brandbyge, J.-L. Mozos, P. Ordejón, J. Taylor, and K. Stokbro, Phys. Rev. B **65**, 165401 (2002).
- [6] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
- [7] K. Burke, J. Chem. Phys. **136**, 150901 (2012).
- [8] M. Koentopp, C. Chang, K. Burke, and R. Car, J. Phys.: Condens. Matter **20**, 083203 (2008).
- [9] C. Toher, A. Filippetti, S. Sanvito, and K. Burke, Phys. Rev. Lett. **95**, 146402 (2005).
- [10] P. W. Anderson, Phys. Rev. **124**, 41 (1961).
- [11] G. Stefanucci and S. Kurth, Phys. Rev. Lett. **107**, 216401 (2011).
- [12] J. P. Bergfield, Z.-F. Liu, K. Burke, and C. A. Stafford, Phys. Rev. Lett. **108**, 066801 (2012).
- [13] Z.-F. Liu, J. P. Bergfield, K. Burke, and C. A. Stafford, Phys. Rev. B **85**, 155117 (2012).
- [14] P. Tröster, P. Schmitteckert, and F. Evers, Phys. Rev. B **85**, 115409 (2012).
- [15] S. Kurth and G. Stefanucci, Phys. Rev. Lett. **111**, 030601 (2013).
- [16] G. Stefanucci and S. Kurth, Phys. Status Solidi B **250**, 2378 (2013).
- [17] F. Evers and P. Schmitteckert, Phys. Status Solidi B **250**, 2330 (2013).
- [18] F. Evers and P. Schmitteckert, Eur. Phys. Lett. **103**, 47012 (2013).
- [19] P. B. Wiegmann and A. M. Tsvelick, J. Phys. C: Solid State Phys. **16**, 2281 (1983).
- [20] J. Friedel, Nuovo Cimento Suppl **7**, 287 (1958).
- [21] D. C. Langreth, Phys. Rev. **150**, 516 (1966).
- [22] J. P. Perdew, R. G. Parr, M. Levy, and J. L. Balduz, Phys. Rev. Lett. **49**, 1691 (1982).
- [23] K. Capelle, M. Borgh, K. Kärkkäinen, and S. M. Reimann, Phys. Rev. Lett. **99**, 010402 (2007).
- [24] S. Kurth, G. Stefanucci, E. Khosravi, C. Verdozzi, and E. K. U. Gross, Phys. Rev. Lett. **104**, 236801 (2010).
- [25] M. Pustilnik and L. Glazman, J. Phys.: Condens. Matter **16**, R513 (2004).
- [26] S. Kurth and G. Stefanucci, private communication. ().
- [27] N. Sai, M. Zwolak, G. Vignale, and M. Di Ventra, Phys. Rev. Lett. **94**, 186810 (2005).
- [28] M. Koentopp, K. Burke, and F. Evers, Phys. Rev. B **73**, 121403 (2006).
- [29] G. Vignale and M. Di Ventra, Phys. Rev. B **79**, 014201 (2009).
- [30] S. Kümmel, L. Kronik, and J. P. Perdew, Phys. Rev. Lett. **93**, 213002 (2004).
- [31] S. Kümmel and L. Kronik, Rev. Mod. Phys. **80**, 3 (2008).
- [32] In Refs. [12] and [13], we used  $\Gamma = \Gamma_L = \Gamma_R$ . Here, we use  $\Gamma = \Gamma_L + \Gamma_R$ , consistent with Ref. [15], which is more relevant to the discussions in this work. ().
- [33] R. N. Silver, J. E. Gubernatis, D. S. Sivia, and M. Jarrell, Phys. Rev. Lett. **65**, 496 (1990).
- [34] D. Carrascal, J. Ferrer, J. C. Smith, and K. Burke, “The Hubbard dimer: A density functional case study of a many-body problem,” ArXiv: 1502.02194 (2015).
- [35] A. C. Hewson, *The Kondo problem to heavy fermions* (Cambridge University Press, Cambridge, 1997).
- [36] N. D. Mermin, Phys. Rev. **137**, A1441 (1965).
- [37] A. Kamenev and W. Kohn, Phys. Rev. B **63**, 155304 (2001).
- [38] H. U. Baranger and A. D. Stone, Phys. Rev. B **40**, 8169 (1989).
- [39] G. Stefanucci, C.-O. Almbladh, S. Kurth, E. K. U. Gross, A. Rubio, R. van Leeuwen, N. E. Dahlen, and U. von Barth, in *Time-Dependent Density Functional Theory*, edited by M. A. L. Marques, C. A. Ullrich, F. Nogueira, A. Rubio, K. Burke, and E. K. U. Gross (Springer, 2006).
- [40] X. Gonze, Ph. Ghosez, and R. W. Godby, Phys. Rev. Lett. **74**, 4035 (1995).
- [41] X. Gonze, Ph. Ghosez, and R. W. Godby, Phys. Rev. Lett. **78**, 294 (1997).
- [42] R. Resta, Rev. Mod. Phys. **66**, 899 (1994).
- [43] G. Onida, L. Reining, and A. Rubio, Rev. Mod. Phys. **74**, 601 (2002).
- [44] B. Champagne, E. A. Perpète, S. J. A. van Gisbergen, E.-J. Baerends, J. G. Snijders, C. Soubra-Ghaoui, K. A. Robins, and B. Kirtman, J. Chem. Phys. **109**, 10489 (1998).
- [45] S. J. A. van Gisbergen, P. R. T. Schipper, O. V. Gritsenko, E. J. Baerends, J. G. Snijders, B. Champagne, and B. Kirtman, Phys. Rev. Lett. **83**, 694 (1999).
- [46] M. van Faassen, P. L. de Boeij, R. van Leeuwen, J. A. Berger, and J. G. Snijders, Phys. Rev. Lett. **88**, 186401 (2002).
- [47] C. D. Pemmaraju, S. Sanvito, and K. Burke, Phys. Rev. B **77**, 121204 (2008).
- [48] J. A. Berger, P. L. de Boeij, and R. van Leeuwen, Phys. Rev. B **75**, 035116 (2007).
- [49] J. Jung, P. Bokes, and R. W. Godby, Phys. Rev. Lett. **98**, 259701 (2007).
- [50] N. T. Maitra, I. Souza, and K. Burke, Phys. Rev. B **68**, 045109 (2003).
- [51] W. Kohn, Phys. Rev. **133**, A171 (1964).

- [52] T. Körzdörfer, M. Mundt, and S. Kümmel, *Phys. Rev. Lett.* **100**, 133004 (2008).
- [53] A. Ruzsinszky, J. P. Perdew, G. I. Csonka, G. E. Scuseria, and O. A. Vydrov, *Phys. Rev. A* **77**, 060502(R) (2008).
- [54] A. Ruzsinszky, J. P. Perdew, and G. I. Csonka, *Phys. Rev. A* **78**, 022513 (2008).
- [55] S. Y. Quek, L. Venkataraman, H. J. Choi, S. G. Louie, M. S. Hybertsen, and J. B. Neaton, *Nano Lett.* **7**, 3477 (2007).
- [56] P. Schmitteckert and F. Evers, *Phys. Rev. Lett.* **100**, 086401 (2008).