Kondo effect given exactly by density functional theory

Justin P. Bergfield, Zhen-Fei Liu, and Kieron Burke
Departments of Chemistry and Physics, University of California, Irvine, California 92697, USA

Charles A. Stafford
Department of Physics, University of Arizona, 1118 East Fourth Street, Tucson, AZ 85721
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Transport through an Anderson junction (two macroscopic electrodes coupled to an Anderson impurity) is dominated by a Kondo peak in the spectral function at zero temperature. The exact single-particle Kohn-Sham potential of density functional theory reproduces the linear transport exactly, despite the lack of a Kondo peak in its spectral function. Using Bethe ansatz techniques, we calculate this potential exactly for all coupling strengths, including the cross-over from mean-field behavior to charge quantization caused by the derivative discontinuity. A simple and accurate interpolation formula is also given.

It is a truth universally acknowledged that many-body effects in strongly correlated systems are not reproduced by mean-field theory. Although Kohn-Sham (KS) density functional theory (DFT) is formally exact, it is a non-interacting theory yielding only the ground-state energy and density of a system. No other information about the correlated many-body wavefunction is available. Dynamical properties, such as excitations and response functions, are also not predicted by ground-state DFT, even with the exact functional [1]. The hope is that, for weakly-correlated systems in which ground-state DFT approximations perform well for total energies, geometries, etc., the errors in such calculations are small. Nothing in the theorems of DFT guarantees that a ground-state KS calculation can describe transport correctly [2].

Consider transport through an Anderson junction [3, 4], composed of two macroscopic leads coupled to an Anderson impurity. As an integrable system, the Anderson model is a paradigm of many-body physics. It is also an accurate model of the low-energy spectrum of molecular radical-based junctions [5]. In Fig. 1, we show the zero-temperature transmission through an Anderson junction as a function of the energy \( \varepsilon \) of the resonant level using Bethe ansatz (BA), exact Kohn-Sham (KS) DFT, and Hartree-Fock (HF). In the figure, \( \mu \) is the chemical potential (Fermi energy) of the metal electrodes. Remarkably, the KS-DFT treatment of this problem reproduces the transmission exactly, apparently describing the non-perturbative Kondo effect whose spectral peak is the source of the perfect transmission when \( \varepsilon < \mu < \varepsilon + U \).

The inability to describe sharp steps in transmission is a well-understood failure of standard density functional approximations. In the limit of weak coupling to the leads, the system is a prototype example where the effects of the infamous derivative discontinuity is seen [6]. For such a system, the exchange-correlation (XC) energy of the molecule is strictly linear between integer values, and so the XC potential, its functional derivative, jumps discontinuously at such values [6]. This effect has been implicated in many well-known failures of DFT approximations such as strongly-correlated systems [7], charge-transfer excitations [8], and over-estimation of the current in organic junctions [9].

In this letter, we (a) solve the Anderson junction using BA and invert the KS equations to derive the exact KS potential, (b) show that the transport is recovered exactly, but only for zero temperature and weak bias, and (c) parametrize the XC potential, providing a unique interpolation formula that works for all correlation strengths. The exact and KS-DFT transport are intimately related via the Friedel sum-rule, a statement equating the occupancy and the transmission phase at the Fermi energy, as has been discussed for nearly isolated resonances [10, 11] or single-mode leads [11]. Since our system fits neither of these categories, it reopens the question of just when an accurate ground-state KS calculation will yield accurate transport.

Using BA [12, 13], we calculate the exact KS potential for the Anderson model, and investigate how the derivative discontinuity develops in the limit of weak impurity-lead coupling. From this solution, we extract the exact

FIG. 1. (Color online) Zero-temperature transmission of an Anderson junction as a function of \( \varepsilon \) using Bethe ansatz (exact), Kohn-Sham DFT with the exact functional (KS), and (spin-restricted) Hartree-Fock (HF). As \( U \) increases, HF misses the sharp structure, but the KS transport is always exact!
asymptotic scaling form of the derivative discontinuity and establish an interpolation formula for the KS potential which is accurate for all coupling strengths, computationally simple, and illustrates the crossover from mean-field behavior at strong impurity-lead coupling to charge quantization at weak coupling.

Consider a junction composed of a nanoscale central region (C) connected to two macroscopic electrodes, labeled left (L) and right (R). The Hamiltonian of the system is \( \mathcal{H} = \mathcal{H}_C + \mathcal{H}_T + \mathcal{H}_R + \mathcal{H}_L \), where \( \mathcal{H}_R/L \) describe Fermi gases in the electrodes and \( \mathcal{H}_T \) describes tunneling between the central region and the electrodes. The central region has the Hamiltonian [3]:

\[
\mathcal{H}_C = \varepsilon (\hat{n}_1 + \hat{n}_1) + U n_1 n_1,
\]

where \( \hat{n}_\sigma = d_\sigma^+ d_\sigma \) is the number operator for spin \( \sigma \) and the charging energy \( U \) is given by the Coulomb integral.

The exact Green’s function of an Anderson junction may be found using Dyson’s equation in an orthonormal basis:

\[
G(E) = \left[ E - \varepsilon - \Sigma_C(E) - \Sigma_T(E) \right]^{-1},
\]

where \( \Sigma_C \) is the Coulomb self-energy and \( \Sigma_T = \Sigma_R^2 + \Sigma_L^2 \) is the tunneling self-energy [14]. We consider transport in the broad-band limit where \( \Sigma_T(E) = -i \Gamma^\alpha/2 \) is pure imaginary and independent of energy, and define the mean tunneling-width \( \Gamma = (\Gamma^L + \Gamma^R)/2 \).

At zero temperature, the linear-response transmission function of an Anderson junction is given by [4, 13]

\[
T(E)\rvert_{\varepsilon = \mu} = \Gamma^L \Gamma^R | G(\mu) |^2 = \frac{4 \Gamma^L \Gamma^R}{(\Gamma^L + \Gamma^R)^2} \sin^2 \left( \frac{\theta(\mu)}{2} \right),
\]

where \( \theta(\mu) \) is the sum of transmission eigenphases evaluated at the Fermi energy \( \mu = \mu_L = \mu_R \). The total number of electrons on the central impurity is related to \( \theta(\mu) \) at zero temperature by the Friedel sum-rule [15–17]

\[
\langle n_C \rangle = \theta(\mu)/\pi.
\]

From the Bethe ansatz, one finds [12]

\[
\langle n_C(\mu) \rangle = 1 - \frac{i}{\pi \sqrt{2}} \int_{-\infty}^{\infty} \frac{d\omega}{\omega + i \eta} G^(-)(\omega) G^(+)(\omega) 
\]

with \( Q \) defined by the condition

\[
\frac{U - 2\mu}{\sqrt{2UT}} = \frac{i}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \frac{d\omega}{\omega + i \eta} G^(-)(\omega) G^(+)(\omega) \left( \sqrt{\omega^2 + 1} \right),
\]

making use of the following functions

\[
G^(-)(\omega) = \frac{\sqrt{2\pi}}{\Gamma(1/2 + i \omega/2\pi)} \left( \frac{i \omega + \eta}{2\pi} \right)^{i \omega/2\pi},
\]

\[
g(k) = (k + \mu - U/2)^2/(2UT), \quad \Delta(k) = (1/\pi)\Gamma/(\Gamma^2 + (k+\mu)^2), \quad \text{where} \quad \Gamma(x) \quad \text{is the Gamma function and} \quad \eta = 0^+.
\]

\( \langle n_C \rangle \) is plotted as a function of \( \varepsilon \) in Fig. 2.

![FIG. 2. (Color online) The occupancy of the Anderson junction as a function of \( \mu - \varepsilon \). The BA results (solid line) exhibit discrete charge steps when \( U \gg \Gamma \), whereas the mean-field RHF (dashed line) never does. The approximate occupancies calculated self-consistently within the KS-scheme using \( \varepsilon_{XC} \) (Eq. (15)) (dotted line) are nearly indistinguishable from the exact BA results. The exact occupancies were used to generate Fig. 1.](dft.uci.edu)

The KS ansatz of DFT employs an effective single-particle description, defined to reproduce the ground-state density of the interacting system. By the Hohenberg-Kohn theorem, this potential is unique if it exists (it usually does) [1]. The relationship between potential and density is fixed only in the full basis-set limit, but can be defined for lattice models. The leads of an Anderson model are non-interacting and characterized by a total charge, which remains constant. Thus the definition of the KS system in this extreme case is that of a non-interacting junction (\( U = 0 \)) with an on-site potential chosen to reproduce the on-site occupancy of the interacting system.

The KS Green’s function in the central region may be written as

\[
G^\sigma(E) = (E - \varepsilon^\sigma + i\Gamma)^{-1},
\]

where \( \varepsilon^\sigma \) is the KS potential for an electron on the impurity, and is written

\[
\varepsilon^\sigma = \varepsilon + U \langle n_C \rangle/2 + \varepsilon_{XC},
\]

where the second term is the Hartree contribution and the last is the correlation potential (there are no exchange contributions). The Anderson model has no internal molecular structure so the KS lead-molecule coupling is \( \Gamma [5, 18] \). For more complex systems, \( \Gamma \) need not be equal to the KS lead-molecule coupling. In a standard DFT calculation, \( \varepsilon_{XC} \) is approximated as a functional of the density [1]. The occupancy of the central region is

\[
\langle n_C \rangle = 2 \int_{-\infty}^{\infty} \frac{dE}{2\pi} \text{Im} [G(E)]^<,
\]

where the “lesser” Green’s function is found using the Keldysh relation [14]

\[
[G(E)]^< = 2if(E)\Gamma |G(E)|^2,
\]
Many-body
KS

FIG. 3. (Color online) Transmission through an Anderson junction at fixed $\mu = 3eV$ with $\varepsilon = 0$, $\Gamma = 0.5eV$ and $U = 10eV$, so that $T_K = 2mK$ [12, 13, 19]. The Doniach-Sunjić form [20] of the spectral function [21] is used near the Kondo peak, while the non-singular portion is calculated using the methods of Refs. [5, 14] with the exact occupancy. Logarithmic shifts of the charging resonances are also included [19]. More sophisticated numerical methods [22] reproduce the qualitative features shown here.

where at zero temperature, $f(E) \equiv \Theta(\mu - E)$ and $\Theta$ is the Heaviside function. Inserting the KS Green’s function and solving Eq. (10) for $\varepsilon^s$ gives

$$\varepsilon^s = \mu + \Gamma \cot \left( \frac{\pi}{2} \langle \bar{n}_C \rangle \right), \quad (12)$$

which defines the exact KS potential within the Anderson model. The KS transmission is then

$$T^s(E) = \frac{\Gamma^L - \Gamma^R}{(E - \varepsilon^s)^2 + \Gamma^2}. \quad (13)$$

Plugging Eq. (12) into Eq. (13), we find that $T^s(E)$ is identical to $T(E)$, as was shown in Fig. 1. Although this identity can be derived using, e.g., local Fermi liquid theory [4], nonetheless its significance is profound: If (and only if) a mean-field theory yields the exact occupation will it yield the exact transmission.

In an Anderson junction, the Friedel sum-rule connects the transmission at the Fermi energy to the occupancy at zero temperature. As shown in Fig. 3, the full transmission spectrum of an Anderson junction exhibits three peaks: Two Coulomb-blockade peaks of width $\sim \Gamma$ centered about $E \approx 0$ and $E \approx U$ and a third zero-bias Kondo peak of width $\sim k_BT_K$ pinned at $E = \mu$. In contrast, the KS-DFT transmission spectrum is a single Lorentzian of width $\Gamma$ peaked at $E = \mu$. As indicated in the figure, the KS value is a huge overestimate anywhere more than several $k_BT_K$ away from $\mu$, implying that the ground-state KS potential does not accurately predict transport at temperatures larger than $T_K$ or for bias voltages larger than $k_BT_K/e$.

From Eqs. (3), (4), (12) and (13) it is evident that the HF errors in transmission in Fig. 1 stem from errors in the occupancies of Fig. 2. When $U \lesssim \Gamma$, HF yields accurate occupancies and transmissions. But for $U \gg \Gamma$, the HF occupancies lack the distinct steps present in the exact solutions, causing corresponding discrepancies in the transport. Qualitatively similar errors would be found with any local or semilocal approximation for the XC potential, because such approximations are smooth functions of the interaction strength [23]. But the exact KS potential of an isolated system, infinitely weakly coupled to a reservoir, displays discontinuous jumps at integer particle number [6], just as ours does as $\Gamma/U \rightarrow 0$. The KS potential $\varepsilon^s$ is shown as a function of occupancy in Fig. 4a for several values of $U/\Gamma$. The HF potential is linear with a slope of $U/2$. For large but finite $U/\Gamma$, the KS potential is not discontinuous but has steps (of width $\sim \Gamma/U$) corresponding to the plateaus in the occupancy, becoming discontinuous in the limit. When $U/\Gamma$ is sufficiently small there is no step in the KS potential and the HF approximation is accurate.

We now show how the step develops as $\Gamma/U \rightarrow 0$. In Fig. 4a, $\varepsilon^s$ develops a step of height $U$ at $\langle \bar{n}_C \rangle = 1$ whose width decreases as $\Gamma/U \rightarrow 0$. Fig. 4b shows the exact derivative $\partial \varepsilon^s/\partial \langle \bar{n}_C \rangle$ in the vicinity of $\langle \bar{n}_C \rangle = 1$. The horizontal and vertical axes are rescaled to illustrate the scaling behavior of the step as $\Gamma/U \rightarrow 0$. From the BA solution, as $U \rightarrow \infty$ [24]:

$$\varepsilon_{XC} \approx \frac{U}{2} \left[ 1 - \langle \bar{n}_C \rangle - 2 \tan^{-1} \left( \frac{\pi U (1 - \langle \bar{n}_C \rangle)}{8\Gamma} \right) \right], \quad (14)$$

whose derivative yields a Lorentzian. In Fig. 4b, we show this limit and how it is approached as $U$ grows, but notice also that the Lorentzian shape is approximately correct for all $U$ down to $\Gamma$. We thus parametrize the XC potential for $U \gg \Gamma$ by the approximate form

$$\varepsilon_{XC} = \alpha \frac{U}{2} \left[ 1 - \langle \bar{n}_C \rangle - 2 \tan^{-1} \left( \frac{1 - \langle \bar{n}_C \rangle}{\sigma} \right) \right], \quad (15)$$

where $\alpha$ and $\sigma$ are functions of $\Gamma/U$ which $\rightarrow 1$ and $8\Gamma/\pi^2 U$, respectively, in the limit $\Gamma/U \rightarrow 0$, and determine the amplitude and width of the correlation contribution as a function of $\langle \bar{n}_C \rangle$. Varying $\alpha$ between 0 and 1 corresponds to “turning on” charge quantization, a nonperturbative interaction effect that would not be described by any local or semilocal approximation. To determine those parameterizations, we first note the behavior near $\langle \bar{n}_C \rangle = 0, 2$ for $\Gamma \neq 0$. This is not generic, but stems from the restricted Hilbert space of the Anderson model. For $U/\Gamma \rightarrow \infty$, Eqs. (12) and (10) imply that $\partial \varepsilon^s/\partial \langle \bar{n}_C \rangle \sim \Gamma \pi/(2 \sin^2 \pi \langle \bar{n}_C \rangle)$ near $\langle \bar{n}_C \rangle = 0$. However, $3 \times 10^{-5}[1/\langle \bar{n}_C \rangle^4]$ fits the data most accurately over the range $0.1 \leq U/\Gamma \leq 500$. Precisely the same form is applied at $\langle \bar{n}_C \rangle = 2$. Then a least-squares fit of Eq. (15) to the exact BA results, subtracting the features at $\langle \bar{n}_C \rangle = 0, 2$ and limiting the fit range to $0.1 \leq \langle \bar{n}_C \rangle \leq 1.9$, yields the values of $\alpha$ and $\sigma$ given in Fig. 4c by the points. We also found simple fits for these functions, with

$$\alpha = \frac{U}{U + 5.68 \Gamma},$$

$$\sigma = 0.811 \frac{\Gamma}{U} - 0.390 \frac{\Gamma^2}{U^2} - 0.168 \frac{\Gamma^3}{U^3}. \quad (16)$$

as shown by the smooth curves in Fig. 4c. The corresponding derivatives are given by dashed curves in Fig.
Our interpolation formula shows that the cross-over between weak and strong correlation occurs for $U/\Gamma \rightarrow \infty$, the exact (Lorentzian) asymptotic scaling form is recovered. The crossover from weakly to strongly correlated occurs for $U/\Gamma \approx 6$. (d) Exact and approximate $\partial \varepsilon^s / \partial \langle nC \rangle U$ spectra for several moderate $U/\Gamma$ values, highlighting the accuracy of Eq. (15). The dashed lines use Eq. (16).

Our results should prove useful for the development of density functional theory in general, and for its application to transport through molecular junctions. While much is known of the consequences of the derivative discontinuity to transport through molecular junctions, our results provide an exact limit for which both many-body and DFT approximations can be tested. Nor are these just theorists’ games with toy models. For example, for the archetypal Au-benzenedithiol single-molecule junction, $U > 8\Gamma$. In such a system, any approximate XC functional which fails to account for derivative discontinuity effects is unlikely to yield accurate results.

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[1] R. M. Dreizler and E. K. U. Gross, *Density functional theory: An approach to the quantum many-body problem* (Springer-Verlag, Berlin, 1990).

[2] M. Koentopp, C. Chang, K. Burke, and R. Car, *Density functional calculations of nanoscale conductance,* J. Phys.: Condens. Matter, 20, 083203 (2008).

[3] P. W. Anderson, *Localized magnetic states in metals,* Phys. Rev., 124, 41 (1961).

[4] M. Pustilnik and L. Glazman, *Kondo effect in quantum dots,* J. Phys.: Condens. Matter, 16, R513 (2004).

[5] J. P. Bergfield, G. C. Solomon, C. A. Stafford, and M. A. Ratner, *Novel quantum interference effects in transport through molecular radicals,* Nano Lett., 11, 2759 (2011).

[6] J. P. Perdew, R. G. Parr, M. Levy, and J. L. Balduz, “Density-functional theory for fractional particle number: derivative discontinuities of the energy,” Phys. Rev. Lett., 49, 1691 (1982).

[7] P. Mori-Sanchez, A. J. Cohen, and W. T. Yang, “Discontinuous nature of the exchange-correlation functional in strongly correlated systems,” Phys. Rev. Lett., 102, 066403 (2009).

[8] N. T. Maitra, “Undoing static correlation: Long-range charge transfer in time-dependent density-functional theory,” J. Chem. Phys., 122, 234104 (2005).

[9] F. Evers, F. Weigend, and M. Koentopp, “Conductance of molecular wires and transport calculations based on
density-functional theory,” Phys. Rev. B, 69, 235411 (2004).

[10] P. Schmitteckert and F. Evers, “Exact ground state density-functional theory for impurity models coupled to external reservoirs and transport calculations,” Phys. Rev. Lett., 100, 086401 (2008).

[11] H. Mera and Y. M. Niquet, “Are Kohn-Sham conductances accurate?” Phys. Rev. Lett., 105, 216408 (2010).

[12] P. B. Wiegmann and A. M. Tsvelick, “Exact solution of the Anderson model: I,” Journal of Physics C: Solid State Physics, 16, 2281 (1983).

[13] R. M. Konik, H. Saleur, and A. W. W. Ludwig, “Transport through quantum dots: Analytic results from integrability,” Phys. Rev. Lett., 87, 236801 (2001).

[14] J. P. Bergfield and C. A. Stafford, “Many-body theory of electronic transport in single-molecule heterojunctions,” Phys. Rev. B, 79, 245125 (2009).

[15] D. C. Langreth, “Friedel sum rule for Anderson’s model of localized impurity states,” Phys. Rev., 150, 516 (1966).

[16] J. Friedel, Nuovo Cimento Suppl, 7, 287 (1958).

[17] H. Mera, K. Kaasbjerg, Y. M. Niquet, and G. Stefanucci, “Assessing the accuracy of Kohn-Sham conductances using the Friedel sum rule,” Phys. Rev. B, 81, 035110 (2010).

[18] F. Evers and P. Schmitteckert, “Broadening of the Derivative Discontinuity in Density Functional Theory,” ArXiv e-prints (2011).

[19] F. D. M. Haldane, “Scaling theory of the asymmetric Anderson model,” Phys. Rev. Lett., 40, 416 (1978).

[20] S. Doniach and M. Sunjic, “Many-electron singularity in X-ray photoemission and X-ray line spectra from metals,” Journal of Physics C: Solid State Physics, 3, 285 (1970).

[21] R. N. Silver, J. E. Gubernatis, D. S. Sivia, and M. Jarrell, “Spectral densities of the symmetric Anderson model,” Phys. Rev. Lett., 65, 496 (1990).

[22] T. A. Costi, A. C. Hewson, and V. Zlatic, “Transport coefficients of the anderson model via the numerical renormalization group,” J. Phys.: Condens. Matter, 6, 2519 (1994).

[23] M. Koentopp, K. Burke, and F. Evers, “Zero-bias molecular electronics: Exchange-correlation corrections to Landauer’s formula,” Phys. Rev. B, 73, 121403 (2006).

[24] Z.-F. Liu, J. P. Bergfield, K. Burke, and C. A. Stafford, in preparation.

[25] P. Tröster, P. Schmitteckert, and F. Evers, “DFT-based transport calculations, Friedel’s sum rule and the Kondo effect,” ArXiv e-prints (2011).

[26] G. Stefanucci and S. Kurth, “Towards a description of the Kondo effect using time-dependent density functional theory,” ArXiv e-prints (2011).