Broadening of the Derivative Discontinuity in Density Functional Theory

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We clarify an important aspect of density functional theories, the broadening of the derivative discontinuity (DD) in a quantum system, with fluctuating particle number. Our focus is on a correlated model system, the single level quantum dot in the regime of the Coulomb blockade. We find that the DD-broadening is controlled by the small parameter Γ/U, where Γ is the level broadening due to contacting and U is a measure of the charging energy. Our analysis suggests, that Kondoesque fluctuations have a tendency to increase the DD-broadening, in our model by a factor of two.

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Introduction. Over the years the density functional theory (DFT) developed into an important tool to study transport properties of nano-systems and single molecules.\textsuperscript{1–5} This development occurred despite of the fact, that often the results are quantitatively sensitive to the approximations made for the \textit{exchange correlation} (XC) functional, $V_{\text{XC}}[n]$, underlying such calculations.\textsuperscript{6–14} In principle, dc-transport calculations should combine either long-time evolution of wavepackets or a KS-based quasistationary formalism, in both cases with special dynamical XC-functional.\textsuperscript{9,11,12} In practice, the available ground state functionals are being used.

The neglect of dynamical correlations for simulation of dc-transport was justified for spinless systems for which a Friedel-sum rule holds.\textsuperscript{15} In such systems, approximations to the XC-potential of the ground state introduce the largest numerical error in the regime of the Coulomb blockade (CB) where the system ("quantum dot", QD) is only weakly coupled to the electronic reservoirs and the filling is close to an integer. Its signature is an addition energy $U$, that largely exceeds the (single particle) level spacing of the QD.

In this Letter we exploit the observation that CB is intrinsically an \textit{equilibrium} phenomenon even though it is mostly discussed in its effect on transport measurements.\textsuperscript{15} In a broader context is it a typical manifestation of the reduced compressibility, $dn(r)/d\mu$, of repulsively interacting fermion gases. Therefore, it has a reincarnation in XC-functional of DFT where it appears as the \textit{derivative discontinuity} (DD).

Starting from the seminal work by Perdew et al.\textsuperscript{15} the DD was almost exclusively discussed in the limiting case of decoupled quantum dots, i.e. \textit{closed systems}. There, the XC-functional jumps discontinuously when tuning the particle number $N$, of a closed system in its ground state through an integer value

$$\Delta_{\text{XC}} = \lim_{\delta N \to 0} \left[ V_{\text{XC}}^{N+\delta N} - V_{\text{XC}}^{N-\delta N} \right],$$

hence the name. In this context the DD often makes a quantitatively relevant contribution to the band gap

$$\Delta = \lim_{\delta N \to 0} \left[ \mu^{N+\delta N} - \mu^{N-\delta N} \right].$$

where $\mu^N$ denotes the electrochemical potential of the $N$ particle system which (up to a sign) equals the workfunction $\mu^N_{\text{Fermi}}$. The relation between $\Delta$ and $\Delta_{\text{XC}}$ is easy to see. Due to Janak’s theorem the energy of a KS-orbital, index $M$, in the $N$-particle system, $\epsilon^N_M$ is related directly to the work functions: $\mu^{N+\delta N} = \epsilon^{N+\delta N}_N$, $\mu^{N+\delta N} = \epsilon^{N+\delta N}_{N+1}$. With Eq. (2) we conclude

$$\Delta = \Delta_{\text{KS}} + \Delta_{\text{XC}},$$

where $\Delta_{\text{KS}}$ is the energy spacing between the lowest unoccupied ($M = N+1$, LUMO) and the highest occupied ($M = N$, HOMO) KS states, $\Delta_{\text{KS}} = \epsilon^{N-\delta N}_{N+1} - \epsilon^{N-\delta N}_N$, and

$$\Delta_{\text{XC}} = \epsilon^{N+\delta N}_{N+1} - \epsilon^{N-\delta N}_{N+1}.$$  

It follows that the DD, $\Delta_{\text{XC}}$, accounts for the difference between the bare, single particle gap, $\Delta_{\text{KS}}$, and the addition energy, $\Delta$, for supplying one more particle. This extra energy cost, $\Delta_{\text{XC}}$, related to the repulsive interaction of fermions confined in a narrow region of space is also the origin of the CB and incompressibility. The DD in closed $N$-particle systems and ways to include it into approximate schemes have been a subject of intense research, recently.\textsuperscript{21–23} In local or semi-local approximations of XC-functional artifacts in the description of charge transfer and transport processes arise, because the DD is not accounted for.\textsuperscript{21–23}

In \textit{open systems} the understanding of the DD is still relatively poorly developed. In particular, its fate in a situation with weakly coupled subsystems, e.g., QD and electronic/thermal reservoirs, has not yet been studied systematically. This is our focus here. We investigate the equilibrium compressibility, $dn(r)/d\mu$, in a generic model system, the Anderson (or single site Hubbard) model with a repulsive on-site interaction $U$. The smearing of the discontinuity $\Delta$ as a consequence of coupling
to a reservoir, can be observed in simulations employing the density matrix renormalization group (DMRG)\textsuperscript{7}. Insight about parametrical dependency is drawn from analytical results that also allow the construction of “toy” XC-functionals to study CB in DFT.

Specifically, we report the compressibility \(dN/d\mu\) near integer filling, \(N = 1\), in three different temperature regimes. We summarize our findings. (i) For the isolated XC-functionals to study CB in DFT.

\[
\delta N = U dN/d\mu|_{N=1} = \beta U(e^{\beta U}/2+1)^{-1} \quad T_T \lesssim T \lesssim T_K
\]

In this perspective, the DD is the statement that in the zero temperature limit the amount of particles needed to drive the jump becomes arbitrarily small. (ii) In the presence of a weak coupling to an electronic reservoir, the single level acquires a width \(\Gamma\). Below a certain cross-over temperature, \(T_T\), we witness that \(\delta N\) stops to decrease and the lifetime broadening leads to an intermediate saturation; we obtain

\[
\delta N \approx 4\Gamma/\pi U(1 + O(\Gamma/U)) \quad T_K \ll T \ll T_T
\]

(iii) At even lower temperatures, below the Kondo scale, \(T_K\), where the Abrikosov-Suhl resonance if fully developed, we cite an exact asymptotic result:

\[
\delta N = 8\Gamma/\pi U(1 + O(\Gamma/U)) \quad T \ll T_K
\]

In cases (ii) and (iii) model XC-functionals are given, that reproduce the CB-features on a qualitative level.

\textit{Anderson model}. The Anderson model\textsuperscript{24} describes a single level QD coupled to a reservoir \((\mathcal{R})\):

\[
\hat{H} = \hat{H}_{\text{QD}} + \hat{H}_{\text{R}} + V \sum_{\sigma = \uparrow, \downarrow} \sum_{\mathbf{k}} (c_{\mathbf{k}\sigma}^\dagger d_{\sigma}^\dagger + d_{\sigma} c_{\mathbf{k}\sigma}),
\]

where \(\hat{H}_{\text{QD}} = \sum_{\mathbf{k}\sigma} \epsilon_{\mathbf{k}\sigma} c_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}\sigma}\), \(\epsilon_{\mathbf{k}\sigma} = -2t \cos(ka)\) (a: lattice spacing) and in the presence of spin-rotational invariance \((\hat{n}_{\sigma} = d_{\sigma}^\dagger d_{\sigma}, \langle \hat{n}_{\uparrow}, \hat{n}_{\downarrow} \rangle = N/2)\): \(\hat{H}_{\text{QD}} = \epsilon_d \hat{N} + U \hat{n}_{\uparrow} \hat{n}_{\downarrow}\)

The observable of interest in DFT is the local density and its variation with external parameters, e.g. \(\epsilon_d\) and \(\mu\): \(N(\mu)\) and \(dN/d\mu\) especially near integer fillings, \(N = 1\). The inverse, \(\mu(N)\), will then be related to the exchange-correlation potential on the QD via

\[
e_{\text{XC}}(N) = \mu(N) - U N/2 - \epsilon_d;
\]

where we have introduced the spectral function \(A_{\sigma}(E) = (1 - \langle n_{\sigma} \rangle)\delta(E - \epsilon_d) + \langle n_{\sigma} \rangle \delta(E - (\epsilon_d + U))\)

The two “Hubbard bands” are reflecting the energy cost, \(U\), for adding the second particle to the QD. Recalling \(\text{Eq. (11)}\) we obtain

\[
N/2 = f_{\epsilon_d}(f_{\epsilon_d} + f_{\epsilon_d - \epsilon_d - U})^{-1}, \quad (12)
\]

which implies that at integer filling, \(N=1\), we have \(\mu_1 = \epsilon_d + U/2\). Recalling \(\text{Eq. (12)}\) we conclude \(e_{\text{XC}}|_{N=1} = 0\). By inverting \(\text{Eq. (12)}\) we obtain the general answer

\[
\mu(N) = T \ln \left[ \frac{N-1}{2N} e^{\beta U} + \frac{a e^{\beta U^2}/2 - N}{2 - N} \right] + \epsilon_d \quad (13)
\]

and

\[
d\mu/dN|_{N=1} = T e^{\beta U}/2 + T - U/2 \quad (15)
\]

From this expression it is obvious how the DD emerges: at any nonzero value of the interaction parameter \(U\), the slope near \(N = 1\) diverges in the zero temperature limit. The divergence occurs in an exponential way because those fluctuations in particle numbers that give \(\mu\) a nonvanishing slope are suppressed by a factor of \(\exp \beta U/2\).

The diverging slope can also be interpreted in the following way. At low temperature and near integer filling a very small change in the local particle number, \(\delta N\), can increase the effective on-site potential by the finite \(\delta N\) falls below \(\Gamma\). The residual density fluctuations that give \(\mu\) a nonvanishing slope are suppressed by a factor of \(\exp \beta U/2\).

\(\text{b. The quantum limit: } T \to 0\). In the presence of the nonvanishing coupling, \(V > 0\), the occupation numbers \(n_{\sigma}\) no longer commute with the Hamiltonian, \(\hat{H}\), and the Anderson model becomes nontrivial. Two essential changes occur. First, the Hubbard bands acquire a finite width, \(\Gamma\). As a consequence, the decrease of \(\delta N(\beta U)\) stops when \(T\) falls below \(\Gamma\). The residual density fluctuations near integer filling then are no longer controlled by thermal but by quantum fluctuations. The control parameter for the latter is \(\Gamma/U\); it measures the overlap of the Hubbard bands with the Fermi-energy. Second, at lowest temperatures, \(T \ll T_K\), the spectral function acquires a third peak, the Abrikosov-Suhl resonance.
where \( \epsilon_d^* = \epsilon_d + \Re \Sigma \). Eq. (17) reveals that at \( N = 1 \) we still have \( \mu_1 = \epsilon_d^* + U/2 \) at arbitrary \( T, \Gamma \) values. The formulae (17,19) combine into a transcendental equation for \( \mu(N) \) and by virtue of Eq. (9) into a functional \( \nu_X \).

For calculating the \( dN/d\mu \) we notice, that \( \mu \) enters \( F_{\epsilon_d} \) and \( F_{2\epsilon_d-\epsilon_d-U} \) with the opposite sign, implying that the \( \mu \) derivative of the denominator of (17) vanishes at \( N = 1 \). Hence we derive

\[
\frac{dN}{d\mu} = F_{\epsilon_d}^{-1} \frac{dF_{\epsilon_d}}{d\mu} \bigg|_{N=1} = \frac{L(U/2)}{1/2 + \arctan(U/2\Gamma)/\pi} \tag{19}
\]

which implies

\[
\delta N = \frac{2\Gamma/U}{\pi (1 + (2\Gamma/U)^2/2 + \arctan(2\Gamma/U)/\pi)} \tag{20}
\]

Eq. (6) follows via expansion in \( \Gamma/U \).

d. The Kondo limit: \( T \ll T_K \). When the temperature decreases down to the Kondo scale, \( T \sim T_K \),

\[
T_K = c\sqrt{U}\text{e}^{-\left(\pi\mu-\epsilon_d\right)/\left|\mu-\epsilon_d+U\right|/2U\Gamma}, \quad \epsilon_d \leq \mu \leq \epsilon_d + U \tag{21}
\]

t he Abrikosov-Suhl (AS) resonance starts to build up.\( \epsilon_d \) (D: conduction electron bandwidth, \( c \approx (D^2/|\mu-\epsilon_d||\mu-\epsilon_d-U|)^{1/2}; c \approx 0.29 \) in the wide band limit, \( D \to \infty \)).

When it is fully developed, \( T \ll T_K \), its shape is roughly Lorentzian, \( A_{\text{AS}}(E) \approx \frac{1}{\pi} T_K \delta(\epsilon_d-U) \), and it adds a third resonance to the spectral function

\[
A(E) \approx \sum_p A_p(E) + pA_{\text{AS}}(E) \tag{22}
\]

with a normalizing coefficient, \( p=1/(1+T_K/2\Gamma) \). As written, Eq. (22) has an artificial feature in the sense that the peak values at all resonances coincide: \( 1/\pi\Gamma \). A slightly more accurate representation incorporates an increase in the shape of the Hubbard bands in the Kondo regime which we have accounted for by replacing the original width of \( A_p \) with another one, \( \Gamma \to \Gamma^p \), specified below. With this caveat we have \( \tau = \int dE f_E A_{\text{AS}}(E) = T_K/2\Gamma \):

\[
N = \frac{2}{1-p+p(F_{\epsilon_d}+F_{2\epsilon_d-\epsilon_d-U})} \frac{2F_{\epsilon_d}}{F_{\epsilon_d}+F_{2\epsilon_d-\epsilon_d-U}+\tau} \tag{23}
\]

Eq. (23) captures qualitative features of \( N(\mu) \) and it can be used to construct an LDA for a Kondo-system.

Eq. (24) suggests that the impact of the AS-resonance on the compressibility is small as \( T_K/\Gamma \). The main impact of Kondoesque fluctuations comes here from the renormalization of the shape of the Hubbard peaks. Indeed, the exact compressibility known from Bethe-Ansatz calculations reads in the limit of large \( U \):

\[
\frac{dN}{d\mu} \bigg|_{N=1} = \frac{8\Gamma}{\pi U^2} \left( 1 - \frac{6}{U} \frac{2\Gamma}{\pi U} + \ldots \right) \tag{24}
\]

implying Eq. (17). Analogous to Eq. (8), an estimate based on (24) would give \( 4\pi \Gamma^2/\pi U^2 \) which suggests \( \Gamma^2 \approx 2\Gamma \) when comparing with (24). We conclude that in the Kondo-regime \( dN/d\mu \) should be enhanced by a factor \( \sim 2 \) reflecting a stronger tendency for charge-fluctuations.
e. DMRG-calculation. To illustrate our analytical arguments DMRG-calculations have been performed on systems including \( M = 30, 50 \) sites. The available system sizes do not allow us to resolve the Kondo-scale, yet, but the expected finite slope of \( \frac{dN}{dm} \) at integer filling is clearly visible. The data also shows the collapse on a single curve when rescaled by \(|V|^{-2} \).

**Discussion.** Our survey of analytical results obtained in the symmetric Anderson model suggests that the DD is broadened in systems coupled to a reservoir: the particle transfer, \( \delta N \), needed to shift the local XC-potential by the on-site interaction energy \( \sim U \) is not infinitesimally small. Within the model considered, the particle transfer is a two-parameter function, \( \delta N(\beta U, \Gamma/U) \), that smoothly interpolates between a high temperature and a low-temperature (“quantum”) regime.

This result has implications for model studies of quantum transport within the framework of time dependent DFT. The importance of the DD for such transport simulations has been emphasized in several recent works.\(^{2,22,25}\) Our work implies, that effective functionals used in such simulations should exhibit a parametric dependency on \( \Gamma/U \). In particular, only terms quadratic in the coupling, \( V^2 \), appear in single channel quantum transport. The ABALDA-functional proposed in Ref. 25 does not adhere to this principle since it depends explicitly on the parameter \( U/V_{\text{link}} \).

Our results also have implications for molecules, i.e. systems where one subsystem couples weakly to a small number of other subsystems, but not to a (macroscopic) reservoir, proper. In this situation, the spectral function \( A_\sigma \), Eq. (11), will translate into the local spectral function of the given subsystem: each Hubbard peak acquires a splitting indicative of the hybridization of states with the environment. Again, the amount of charge needed to fill into the subsystem to drive \( \nu_{XC} \) up by \( U \) will not be zero but rather reflect this hybridization induced substructure.

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