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PAPER

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.

Introduction

Over the years the density functional theory (DFT) developed into an important tool to study transport properties of nano-systems and single molecules.[1–5] This development occured despite of the fact, that often the results are quantitatively sensitive to the approximations made for the *exchange correlation* (XC) functional, $V_{\rm XC}[n]$, underlying such calculations.[6–10] In principle, dc-transport calculations should combine either long-time evolution of wavepackets or a KS-based quasi-stationary formalism, in both cases with special dynamical XC-functionals.[9,11,12] In practice, the available ground state functionals are being used.

The neglect of dynamical correlations for simulation of dc-transport was justfied for spinless systems for which a Friedel-sum rule holds.[13] In such systems, approximations to the XC-potential of the ground state introduce the largest numerical error in the regime of *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 *equilibrium* phenomenon even though it is mostly discussed in its effect on transport measurements;[14,15] in a broader context it is a typical manifestation of the diminished compressibility, $dn(\mathbf{r})/d\mu$, of repulsively interacting fermion gases ($n(\mathbf{r}n)$: local particle density; μ: electrochemical potential). Therefore, it has a reincarnation in XC-functionals of DFT where it appears as the *derivative discontinuity* (DD).

Starting from the seminal work by Perdew *et al.*,[16] the DD was almost exclusively discussed in the limiting case of decoupled quantum dots, *i.e. 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

$$\Delta_{\rm XC} = \lim_{\delta N\to 0}[V_{\rm XC}^{N+\delta N} - V_{\rm XC}^{N-\delta N}], \qquad (1)$$

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

$$\Delta = \lim_{\delta N\to 0}[\mu^{N+\delta N} - \mu^{N-\delta N}], \qquad (2)$$

where $\mu^{\rm N}$ denotes the electrochemical potential of the N particle system which (up to a sign) equals the workfunction.[17,18] The relation between Δ and $\Delta_{\rm XC}$ is easy to see. Due to Janak’s theorem the energy of a KS-orbital, index M, in the N-particle system, ε_M^N is related directly to the work functions: $\mu^{N-\delta N} = \varepsilon_N^{N-\delta N}$, $\mu^{N+\delta N} = \varepsilon_{N+1}^{N+\delta N}$.[19,20] With eqn (2) we conclude

$$\Delta = \Delta_{\rm KS} + \Delta_{\rm XC}, \qquad (3)$$

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

$$\Delta_{\rm XC} = \varepsilon_{N+1}^{N+\delta N} - \varepsilon_{N+1}^{N-\delta N}. \qquad (4)$$

It follows that the DD, $\Delta_{\rm XC}$, accounts for the difference between the bare, single particle gap, $\Delta_{\rm KS}$, and the addition energy, Δ, for supplying one more particle. This extra energy cost, $\Delta_{\rm XC}$, 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.[21] In local or semi-local approximations of XC-functionals artifacts in the description of charge transfer and transport processes arise, because the DD is not accounted for.[21–23,31]

In *open systems* the understanding of the DD is still relatively poorly developed. In particular, its fate in a situation

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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, $\mathrm{d}n(\mathbf{r})/\mathrm{d}\mu$, in a generic model system, the *Anderson* (or single site Hubbard) model with a repulsive on-site interaction U. The smearing of the discontinuity (1), as a consequence of coupling to a reservoir, can be observed in simulations employing the density matrix renormalization group (DMRG).[13,24,25] 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 $\mathrm{d}N/\mathrm{d}\mu$ near integer filling, $N = 1$, in three different temperature regimes. We summarize our findings. (i) For the isolated level we have at nonzero temperatures ($\beta = 1/T$) the exact result: $\left.\frac{\mathrm{d}v_{\mathrm{XC}}}{\mathrm{d}N}\right|_{N=1} = Te^{\beta U/2} + T - U/2$. The derivative is finite as $T > 0$ and the discontinuity is broadened by temperature. A dimensionless measure of this smearing is provided by the number of particles δN that need to flow into the level in order to fascilitate the increase ("jump") of $\Delta(N)$ by $\Delta_{\mathrm{XC}} \approx U$:

$$\delta N = U\mathrm{d}N/\mathrm{d}\mu|_{N=1} = \beta U(e^{\beta U/2} + 1)^{-1} \qquad T_\Gamma \lesssim T \quad (5)$$

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 Γ. Below a certain cross-over temperature, $T_\Gamma \Gamma$, we witness that δN stops to decrease and the lifetime broadening leads to an intermediate saturation; we obtain

$$\delta N \approx 4\Gamma/\pi U + \mathcal{O}(1), \quad T_{\mathrm{K}} \ll T \lesssim T_\Gamma \qquad (6)$$

$$\left.\frac{\mathrm{d}v_{\mathrm{XC}}}{\mathrm{d}N}\right|_{N=1} \approx U(\pi U/4\Gamma + \mathcal{O}(1)).$$

The exponential growth of $\mathrm{d}v_{\mathrm{XC}}/\mathrm{d}(UN)$ in U/T gives way to a linear scaling in U/Γ in this temperature window. (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:

$$\delta N = 8\Gamma/\pi U + \mathcal{O}(1), \; T \ll T_{\mathrm{K}} \qquad (7)$$

$$\left.\frac{\mathrm{d}v_{\mathrm{XC}}}{\mathrm{d}N}\right|_{N=1} = U(\pi U/8\Gamma + \mathcal{O}(1))$$

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

Anderson model

The Anderson model[26] describes a single level QD coupled to a reservoir ($\mathscr{G}$):

$$\hat{H} = \hat{H}_{\mathrm{QD}} + \hat{H}_{\mathscr{R}} + V\sum_{\sigma=\uparrow,\downarrow}\sum_{\mathbf{k}}(c^\dagger_{\sigma\mathbf{k}}d_\sigma + d^\dagger_\sigma c_{\sigma k}), \qquad (8)$$

where $\hat{H}_{\mathscr{R}} = \sum_{\sigma\mathbf{k}} \varepsilon_{\mathbf{k}} c^\dagger_{\sigma\mathbf{k}} c_{\sigma\mathbf{k}}$, $\varepsilon_{\mathbf{k}} = -2t\cos(ka)$($a$: lattice spacing) and in the presence of spin-rotational invariance ($\hat{n}_\sigma = d^\dagger_\sigma d_\sigma$, $\hat{N} = \hat{n}_\uparrow + \hat{n}_\downarrow$, $\langle\hat{n}_\sigma\rangle = N/2$): $\hat{H}_{\mathrm{QD}} = \varepsilon_{\mathrm{d}}\hat{N} + U\hat{n}_\uparrow\hat{n}_\downarrow$. The observable of interest in DFT is the local density and its variation with exernal parameters, *e.g.* ε_{d} and μ: $N(\mu)$ and $\mathrm{d}N/\mathrm{d}\mu$ especially near integer fillings, $N = 1$. The inverse, $\mu(N)$, will then be related to the exchange–correlation potential on the QD *via*

$$v_{\mathrm{XC}}(N) = \mu(N) - UN/2 - \varepsilon_{\mathrm{d}}; \qquad (9)$$

Hartree and on site potential here must be subtracted. To calculate physical observables in the presence of reservoirs, thermal Green's functions provide a convenient formalism. For the thermal occupation numbers we have quite generally

$$N/2 = \langle\hat{n}_\sigma\rangle = T\sum_m \mathscr{G}_\sigma(\mathbf{i}\omega_m) = \int \mathrm{d}E f_E \mathscr{A}_\sigma(E) \qquad (10)$$

where we have introduced the spectral function $\mathscr{A}_\sigma(E) = (-1/\pi)\sum_\sigma \Im\mathscr{G}_\sigma(E)$ and $f_\varepsilon = (e^{\beta(\varepsilon-\mu)} + 1)^{-1}$.

a. Thermal coupling

In the absense of particle fluctuations, $V = 0$, the spectral function can be calculated exactly.[26] It is given by ($\bar{\sigma} = -\sigma$)

$$\mathscr{A}_\sigma(E) = (1 - \langle n_{\bar{\sigma}}\rangle)\delta(E - \varepsilon_d) + \langle n_{\bar{\sigma}}\rangle\delta(E - (\varepsilon_d + U)) \qquad (11)$$

The two "Hubbard bands" are reflecting the energy cost, U, for adding the second particle to the QD. Recalling (11) we obtain

$$N/2 = f_{\varepsilon_{\mathrm{d}}}(f_{\varepsilon_{\mathrm{d}}} + f_{2\mu-\varepsilon_{\mathrm{d}}} - U)^{-1}, \qquad (12)$$

which implies that at integer filling, $N = 1$, we have $\mu_1 = \varepsilon_{\mathrm{d}} + U/2$. Recalling eqn (9) we conclude $v_{\mathrm{XC}|N=1} = 0$. By inverting (12) we obtain the general answer

$$\mu(N) = T\ln\left[\frac{N-1}{2-N}e^{\beta U} + \frac{\boldsymbol{a}e^{\beta U/2}}{2-N}\right] + \varepsilon_{\mathrm{d}} \qquad (13)$$

and

$$\mathrm{d}\mu/\mathrm{d}N = T(e^{\beta U}-1)(\boldsymbol{a}e^{\beta U/2}-\boldsymbol{a}^2)^{-1} \qquad (14)$$

with $\boldsymbol{a}(\beta U, N) = \sqrt{1 + (e^{\beta U} - 1)(N-1)^2}$. It is implied that near integer filling $\mathrm{d}\mu/\mathrm{d}N|_{N=1} = T + Te^{\beta U/2}$ and

$$\left.\frac{\mathrm{d}v_{\mathrm{XC}}}{\mathrm{d}N}\right|_{N=1} = Te^{\beta U/2} + T - U/2 \qquad (15)$$

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 divergency occurs in an exponential way because those fluctuations in particle numbers that give μ 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, δN, can increase the effective on-site potential by the finite amount U: $\delta N \equiv U\mathrm{d}N/\mathrm{d}\mu = \beta U(e^{\beta U/2} + 1)^{-1}$. We have arrived at eqn (5).

b. The quantum limit

$T \to 0$: In the presence of the nonvanishing coupling, $V > 0$, the occupation numbers $\hat{n}_\sigma$ 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, Γ. As a consequence, the decrease of

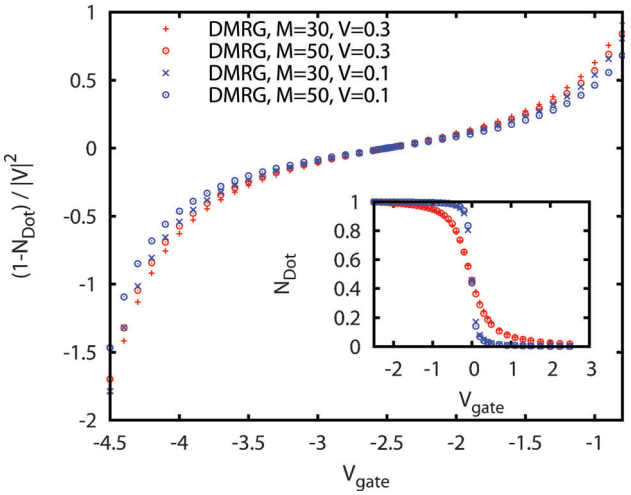

Fig. 1 The change of the dot filling rescaled by $|V|^{-2}$ in the Coulomb blockade regime for an on-site repulsion of $U = 5t$, a hybridization of $V = 0.3t(+)$ and $V = 0.1t(\times)$ for a $M = 30$ site system obtained from a ground state DMRG. For comparison results for a 50 site calculation are also shown (red,blue ○) emphasizing convergence with the system size. Data illustrates the scaling of $dN/d\mu$ with the hybridization $\Gamma \sim |V|^2$. Raw data is shown in the inset. Inset: dot occupation.

$\delta N(\beta U)$ stops when T falls below Γ. 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 Γ/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*.

c. Intermediate temperatures

$T_K \ll T \lesssim \Gamma, U$. We first imagine that the Kondo temperature is by far the smallest energy scale, in particular $T_K \ll T$, so that the Kondo effect can be ignored. This is justified in effectively finite systems, like large molecules, where the density of states (DoS) near the highest occupied molecular energy level is not truely continuous. In this situation the presence of the reservoirs is easily dealt with on a qualitative level by equipping the thermal Green's function eqn (10) with a self energy, $\Sigma(i\omega_m)$. It determines the inverse lifetime $\Gamma(E) = -\Im\Sigma(E)$ which evaluates to $\Gamma(E) = \pi|V|^2\rho_{\mathscr{R}}(E)$ for noninteracting reservoirs ($\rho_{\mathscr{R}}(E)$: reservoir DoS). The qualitative effect can be studied in the simplest approximation where we ignore the energy dependency of the self energy ("wide band limit"). Then, the spectral function for a given Hubbard subband takes the Lorentzian shape

$$\mathscr{L}(E) = \frac{1}{\pi}\frac{\Gamma}{E^2+\Gamma^2}. \tag{16}$$

As a consequence of the peak broadening, eqn (12) generalizes,

$$\frac{N}{2} = \frac{F_{\varepsilon_d^*}}{F_{\varepsilon_d^*} + F_{2\mu-\varepsilon_d^*-U}}, \quad F_u = \int_{-\infty}^{\infty} dE f_{E+u}\mathscr{L}(E), \tag{17}$$

with the zero temperature limit

$$F_u \underset{T\to 0}{=} 1/2 + \arctan[(\mu-u)/\Gamma]/\pi \tag{18}$$

where $\varepsilon_d^* = \varepsilon_d + \Re\Sigma$. Eqn (17) reveals that at $N = 1$ we still have $\mu_1 = \varepsilon_d^* + U/2$ at arbitrary T, Γ values. The formulae (17,19) combine into a transcendental equation for $\mu(N)$ and by virtue of eqn (9) into a functional v_{XC}.

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

$$\frac{dN}{d\mu} = F^{-1}_{\varepsilon_d^*}\frac{dF_{\varepsilon_d^*}}{d\mu}\bigg|_{N=1} \underset{T\to 0}{=} \frac{\mathscr{L}(U/2)}{1/2+\arctan(U/2\Gamma)/\pi} \tag{19}$$

which implies

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

Eqn (6) follows *via* expansion in Γ/U.

d. The Kondo limit

$T \ll T_K$. When the temperature decreases down to the Kondo scale, $T \sim T_K$,

$$T_K = c\sqrt{U\Gamma}e^{-\pi|\mu-\varepsilon_d^*||\mu-\varepsilon_d^*-U|/2U\Gamma}, \quad \varepsilon_d^* \lessapprox \mu \lessapprox \varepsilon_d^* + U \tag{21}$$

the Abrikosov-Suhl (AS) resonance starts to build up.[26,27] ($c \approx 0.29$ in the wide band limit). When it is fully developed, $T \ll T_K$, its shape is roughly Lorentzian, $\mathscr{A}_{AS}(E) \approx (1/\pi\Gamma)T_K^2/((E-\mu)^2 + T_K^2)^{-1}$ and it adds a third resonance to the spectral function

$$\mathscr{A}(E) \approx p\sum_\sigma \mathscr{A}_\sigma(E) + p\mathscr{A}_{AS}(E) \tag{22}$$

with a normalizing coefficient, $p = 1/(1 + T_K/2\Gamma)$. As written, eqn (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 a change in the shape of the Hubbard bands in the Kondo regime which we here account for by replacing the original width of $\mathscr{A}_\sigma$ with another one, $\Gamma \to \Gamma^K$, specified below. With this caveat we have ($c = \int dE f_E \mathscr{A}_{AS}(E) = T_K/2\Gamma$):

$$\begin{aligned} N &= \frac{2pF_{\varepsilon_d^*} + pc}{1 - p + p\left(F_{\varepsilon_d^*} + F_{2\mu-\varepsilon_d^*-U}\right)} \\ &= \frac{2F_{\varepsilon_d^*} + c}{F_{\varepsilon_d^*} + F_{2\mu-\varepsilon_d^*-U} + c}. \end{aligned} \tag{23}$$

Eqn (23) captures qualitative features of $N(\mu)$ and it can be used to construct an LDA for a Kondo-system. Eqn (23) suggests that the impact of the AS-resonance on the compressibility is small as T_K/Γ. 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[26] reads in the limit of large U:

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

implying eqn (7). Analogous to eqn (6), an estimate based on (23) would give $4\Gamma^K/\pi U^2$ which suggests $\Gamma^K \approx 2\Gamma$ when comparing with (24). We conclude that within the present framework in the Kondo-regime $dN/d\mu$ should be enhanced by a factor ~ 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, see Fig. 1. The available system sizes do not allow us to resolve the Kondo-scale T_K yet, see eqn (21), but the expected finite slope of $dN/d\mu$ at integer filling is clearly visible. The data also shows the collaps 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, δN, 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.[7,22,28] Our work implies, that effective functionals used in such simulations should exhibit a parametric dependency on Γ/U. In particular, only terms quadratic in the coupling, V^2, appear in single channel quantum transport. The ABALDA-functional proposed in ref. 28 does not adhere to this principle since it depends explicitly on the parameter U/V_{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 $\mathscr{A}_\sigma$, eqn (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 v_{XC} up by U will not be zero but rather reflect this hybridization induced substructure.

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31 Most current density functionals rely upon local (LDA) and semi-local (GGA) approximations[29]; they exhibit a continuous evolution with N which implies that the $\text{LUMO}^{N+\delta N}$ and the $\text{LUMO}^{N-\delta N}$ see essentially the same effective potential; therefore $\Delta_{\text{XC}}^{\text{LDA,GGA}} = 0$.

