Dynamical exchange-correlation corrections in transport

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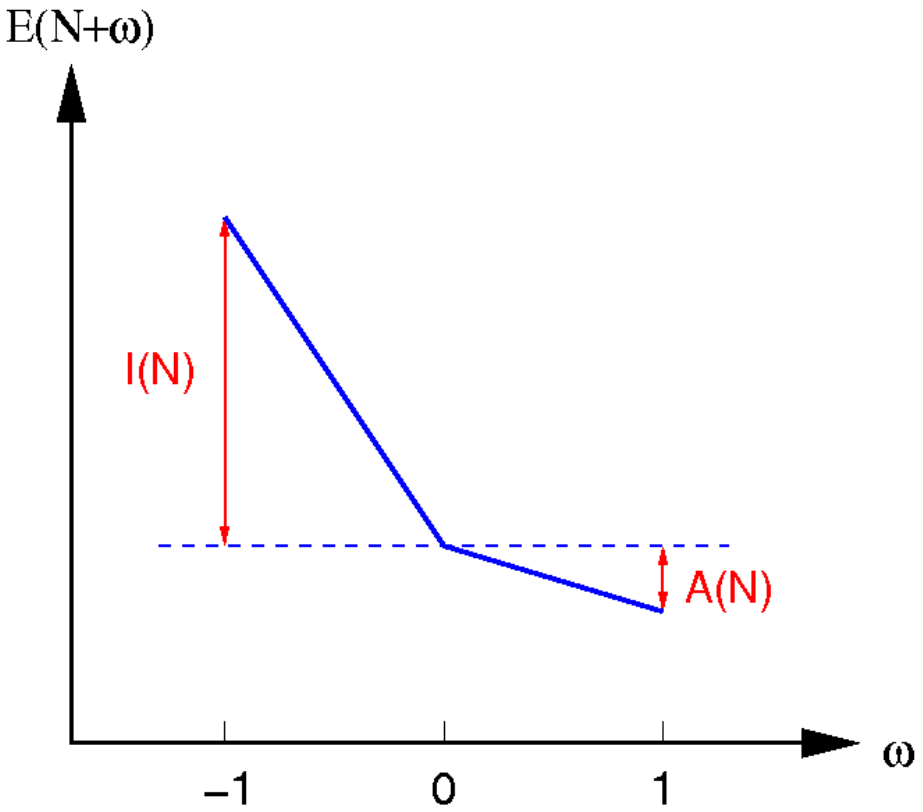
Outline

- Preliminaries
- The Kondo effect: what TDDFT has to say
- Dynamical corrections to KS conductances from static DFT
- Summary

Preliminaries

Derivative discontinuity in static DFT

total energy as function of (fractional) particle number is a series of straight lines (Perdew et al, PRL 49, 1691 (1982))



derivative discontinuity

$$\Delta = I(N) - A(N)$$

$I(N)$: ionization potential
$A(N)$: electron affinity
N : integer number of electrons

Derivative discontinuity in static DFT (cont.)

for given external potential $v(\mathbf{r})$, extend HK ground state energy functional to non-integer particle numbers:

derivative discontinuity

$$\Delta = \lim_{\omega \to 0} \left(\left. \frac{\delta E_v[n]}{\delta n(\mathbf{r})} \right|_{N+\omega} - \left. \frac{\delta E_v[n]}{\delta n(\mathbf{r})} \right|_{N-\omega} \right) = \Delta_{KS} + \Delta_{xc}$$

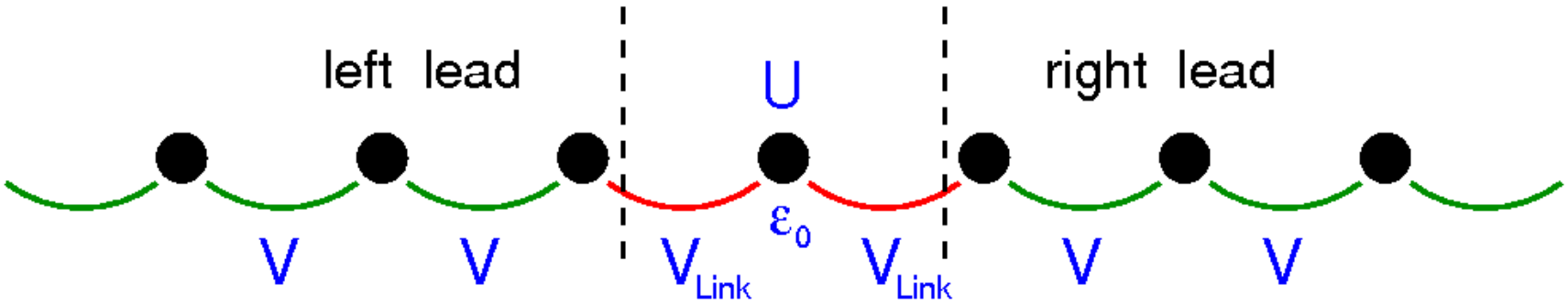
KS discontinuity $\Delta_{KS} = \varepsilon_{LUMO} - \varepsilon_{HOMO}$

xc contribution to discontinuity:

$$\Delta_{xc} = \lim_{\omega \to 0} \left(\left. \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} \right|_{N+\omega} - \left. \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} \right|_{N-\omega} \right)$$

note: for traditional functionals (LDA, GGA): $\Delta_{xc} = 0$!!

Simple impurity model for transport



one interacting impurity (level), on-site interaction U (charging energy of level), non-interacting leads, hopping V in leads and hopping V_{Link} from leads to impurity, on-site energy ε_0 at impurity, assume local KS potential only non-vanishing at impurity

interested in case of weak links $|V_{\mathrm{Link}}| < |V|$ and in wide-band limit: $|V_{\mathrm{Link}}| \to \infty$, $|V| \to \infty$ such that $\Gamma_\alpha = (V_{\mathrm{link}})^2/|V| = const$

Self-consistency condition for steady state density

Landauer approach:
assume for biased system there exists steady state with density n at impurity $\longrightarrow$ self-consistency condition for n

$$n = 2 \sum_{\alpha=L,R} \int_{-\infty}^{\infty} \frac{\mathrm{d}\omega}{2\pi} f_\beta(\omega - V_\alpha) \Gamma_\alpha |G(\omega)|^2$$

$$G(\omega) = [\omega - v_{KS}(n) - \Sigma_L - \Sigma_R]^{-1}$$

$$v_{KS}(n) = \varepsilon_0 + v_{Hxc}(n)$$

V_α: bias in lead α
$f_\beta(\omega)$: Fermi function at inverse temperature β
$\Sigma_\alpha = -\frac{i}{2}\Gamma_\alpha$: embedding self energy for lead α in wide-band limit

Landauer formula for steady state current

$$I = \int_{-\infty}^{\infty} \frac{\mathrm{d}\omega}{2\pi} T(\omega) \left[f_\beta(\omega - V_L) - f_\beta(\omega - V_R) \right]$$

with transmission function

$$T(\omega) = \mathrm{Tr} \left\{ \Gamma_L G(\omega) \Gamma_R G^*(\omega) \right\}$$

$\longrightarrow$ zero-bias conductance:

$$G/G_0 = - \int_{-\infty}^{\infty} \frac{\mathrm{d}\omega}{2\pi} T(\omega) \frac{\partial f_\beta(\omega)}{\partial \omega}$$

Landauer formalism originally derived for non-interacting electrons; often used together with *static* DFT for conductance calculations
but: static DFT is equilibrium theory, conductance is nonequilibrium property!!

TDDFT correction to Landauer conductance

TDDFT is a proper non-equilibrium theory; steady state (if achieved) is the long-time limit of a time evolution process where system initially in equilibrium is perturbed by time-dependent bias

$$I = \int_{-\infty}^{\infty} \frac{\mathrm{d}\omega}{2\pi} T(\omega) \left[f_\beta(\omega - \Delta V_L^{KS}) - f_\beta(\omega - \Delta V_R^{KS}) \right]$$

$$\Delta V_\alpha^{KS} = V_\alpha^{KS}(t=\infty) - V_\alpha^{KS}(t=0)$$

$$\longrightarrow \quad \delta I = (\delta V_L - \delta V_R + \delta V_{Hxc}^L - \delta V_{Hxc}^R) G_s$$

$$\delta V_{Hxc}^\alpha = \lim_{\omega\to 0} \lim_{z \to s_\alpha \infty} \int \mathrm{d}^3 r' \; f_{Hxc}(\mathbf{r}, \mathbf{r}', \omega) \delta n(\mathbf{r}', \omega)$$

with $s_L = -1$ and $s_R = +1$

TDDFT correction to Landauer conductance (cont.)

assume $\delta n(\mathbf{r}, \omega \to 0) = s_\alpha \delta n$ for $\mathbf{r}$ in lead α

def: $f_{Hxc}^{\alpha\beta} = \lim_{\omega\to 0} \lim_{z\to s_\alpha \infty} \int \mathrm{d}^3 r'_{\mathrm{lead}\beta}\ f_{Hxc}(\mathbf{r}, \mathbf{r}', \omega)$

$$\longrightarrow \quad \delta V_{Hxc}^{\alpha} = \sum_{\beta=L,R} f_{Hxc}^{\alpha\beta} s_\alpha \delta n \longrightarrow \delta I = (\delta V_L - \delta V_R) G_s - \Phi G_s \delta n$$

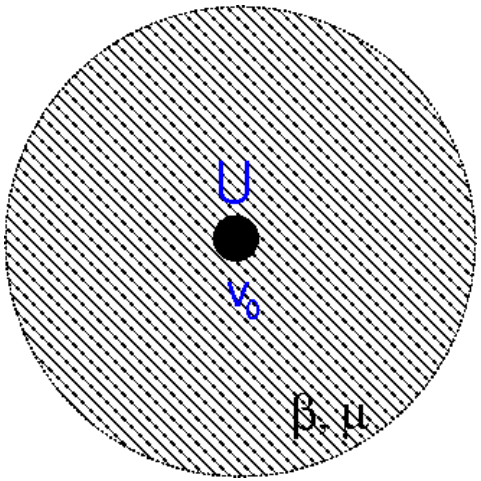
$$\text{with } \Phi = f_{Hxc}^{RL} + f_{Hxc}^{LR} - f_{Hxc}^{RR} - f_{Hxc}^{LL}$$

TDDFT expression for conductance

$$G = \frac{G_s}{1+\chi\Phi G_s} \qquad \text{with } \chi = \delta n / \delta I$$

note: $f_{Hxc}(\mathbf{r}, \mathbf{r}', \omega)$ is only defined up to addition of arbitrary function $g(\mathbf{r}) + g(\mathbf{r}')$ (Hellgren, Gross, PRA **85**, 022514 (2012)) but Φ is invariant under this transformation

Single-site model to construct finite temperature functional



4 states in Fock space: $|0\rangle$, $|\uparrow\rangle$, $|\downarrow\rangle$, $|\uparrow\downarrow\rangle$

calculate density $n(v_0 - \mu) = n(\tilde{v}_0)$
invert analytically $\longrightarrow \tilde{v}_0(n)$

non-interacting KS system: density $n_s(\tilde{v}_s)$
invert analytically $\longrightarrow \tilde{v}_s(n_s)$

Hartree-xc potential: $$v_{Hxc}(n) = \tilde{v}_s(n) - \tilde{v}_0(n)$$

Spectral function and smoothening

Spectral function of single-site model

$$A^{SSM}(\omega) = \lim_{\eta \to 0} \left[\frac{n}{2} L_{2\eta}(\omega - v_0 - U) + \left(1 - \frac{n}{2}\right) L_{2\eta}(\omega - v_0) \right]$$

with Lorentzian $L_\delta(\omega) = \frac{\delta}{\omega^2 + \left(\frac{\delta}{2}\right)^2}$

smoothen peaks by replacing $\eta \to \gamma/2$, the WBL emb. self energy

Spectral function of "smoothened" single-site model

$$A^{SSM-sm}(\omega) = \frac{n}{2} L_\gamma(\omega - v_0 - U) + \left(1 - \frac{n}{2}\right) L_\gamma(\omega - v_0)$$

often derived from EOM for Coulomb blockade regime

Hartree-xc potential from reverse engineering

density from spectral function

$$n(\tilde{v}_0) = 2\int \frac{\mathrm{d}\omega}{2\pi} f_\beta(\omega) A(\omega)$$

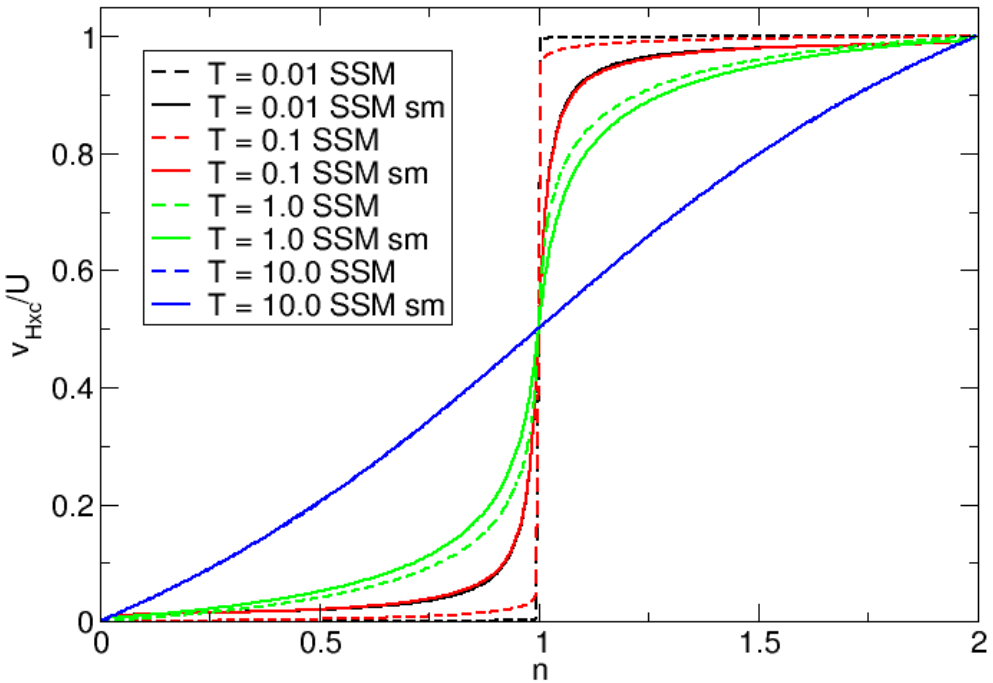
invert $n(\tilde{v}_0) \longrightarrow \tilde{v}_0(n)$; same for non-interacting density $n_s(\tilde{v}_s) \longrightarrow \tilde{v}_s(n_s)$

Hartree-xc potential

$$v_{\mathrm{Hxc}}(n) = \tilde{v}_s(n) - \tilde{v}_0(n)$$

Hartree-xc potential for (smoothened) single-site model

Hartree-xc potential for different temperatures and U=10 (energies in units of γ)



derivative "discontinuity" (better: step feature) emerges naturally in the zero-temperature limit

Kondo effect: what TDDFT has to say

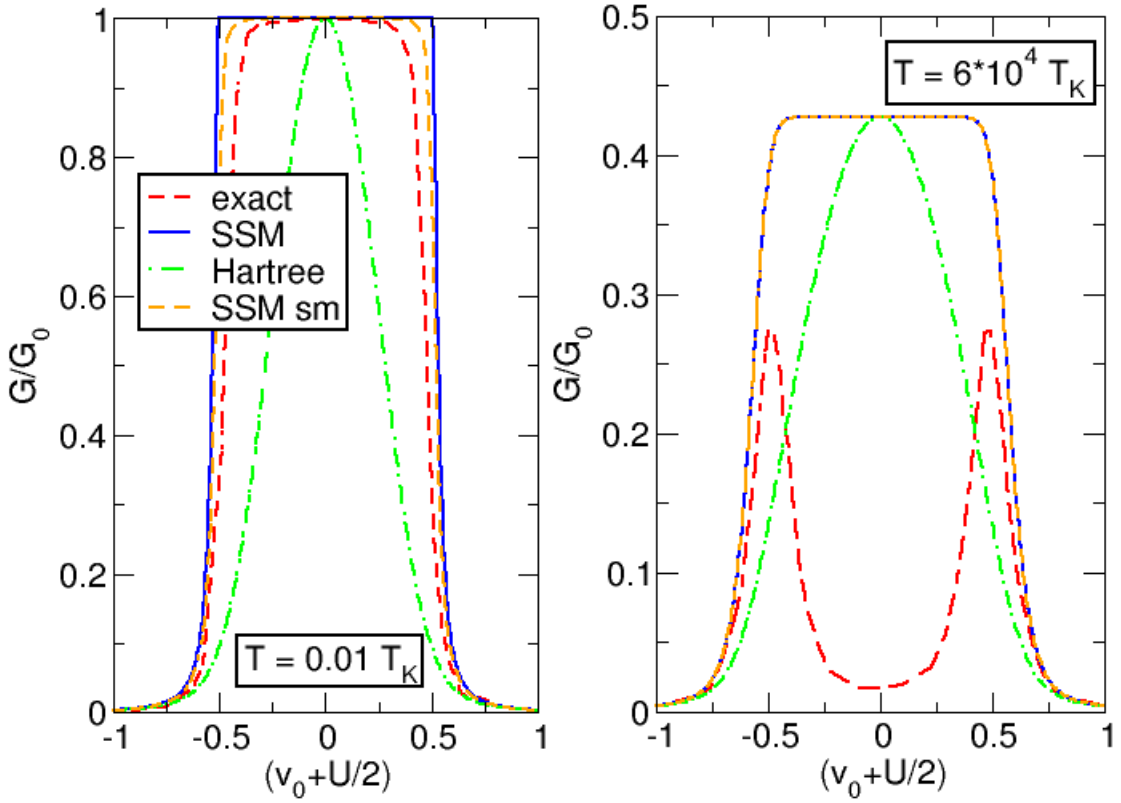
This work (finite temperature, TDDFT):

- Stefanucci, Kurth, PRL **107**, 216401 (2011)

Related work (zero temperature, DFT/Landauer):

- Bergfield, Liu, Burke, Stafford, PRL **108**, 066801 (2012)
- Tröster, Schmitteckert, Evers, PRB **85**, 115409 (2012)

Finite temperature conductance with Landauer



$T << T_{\mathrm{K}}$: Kondo plateau in conductance due to discontinuity;

$T >> T_{\mathrm{K}}$: plateau *not* destroyed; no Coulomb blockade peaks

exact data from: Izumida, Sakai, J. Phys. Soc. Jpn., 2005

Finite temperature conductance with Landauer

two ways to understand $T = 0$ result:

- Meir-Wingreen formula for conductance:

$$\frac{G}{G_0} = \gamma^2 |\mathcal{G}(\mu)|^2 \frac{\gamma - \mathrm{Im}\,\Sigma(\mu)}{\gamma}$$

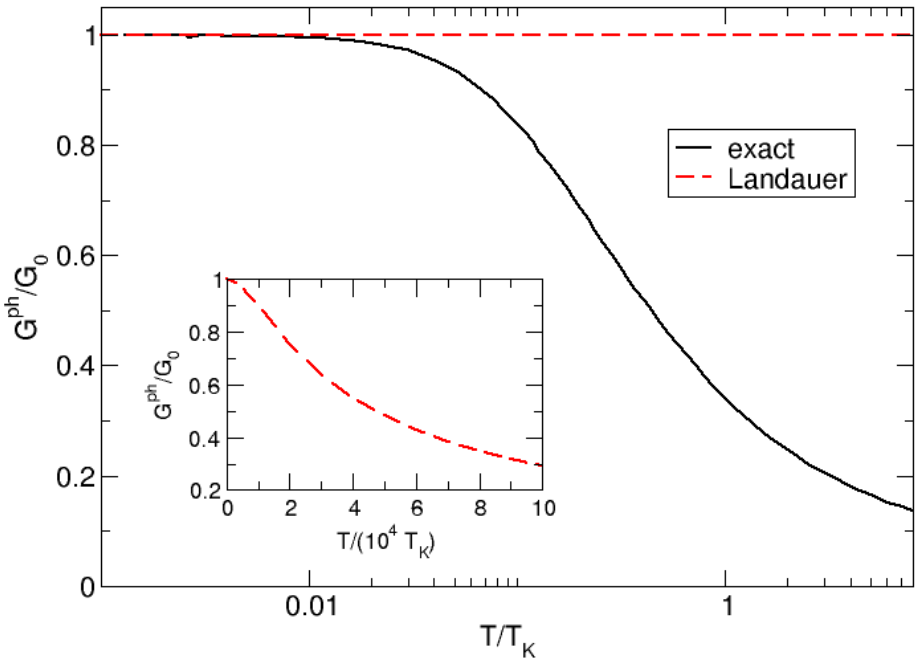
with many-body GF $\mathcal{G}(\omega)$ at impurity and self energy Σ
at Fermi energy: $\mathrm{Im}\,\Sigma(\mu) = 0 \longrightarrow$ can describe conductance by a KS potential $v_s = v_0 + \mathrm{Re}\Sigma(\mu)$

- Friedel sum rule (Langreth):

conductance determined by density n_0 on dot: $G = G(n_0)$
if KS potential gives good density $\longrightarrow$ good conductance

Finite temperature conductance with Landauer

note: at particle-hole symmetric point $v_0 = -U/2$ our approximation gives *exact* KS potential for all temperatures



for finite T: Landauer *does not* give correct conductance although static KS potential is exact!

exact results from T.A. Costi, PRL (2000)

difference between Landauer and exact results due to dynamical xc corrections!

Dynamical correction to KS conductances from static DFT

Reference:

- Kurth, Stefanucci, PRL **111**, 030601 (2013)
- Stefanucci, Kurth, Phys. Status Solidi B **250**, 2378 (2013)

Single-level model again

density and conductance from spectral function (in WBL)

$$n = 2 \int \frac{\mathrm{d}\omega}{2\pi} f_\beta(\omega) A(\omega)$$

$$G = -\frac{\gamma}{2} \int \frac{\mathrm{d}\omega}{2\pi} f'_\beta(\omega) A(\omega)$$

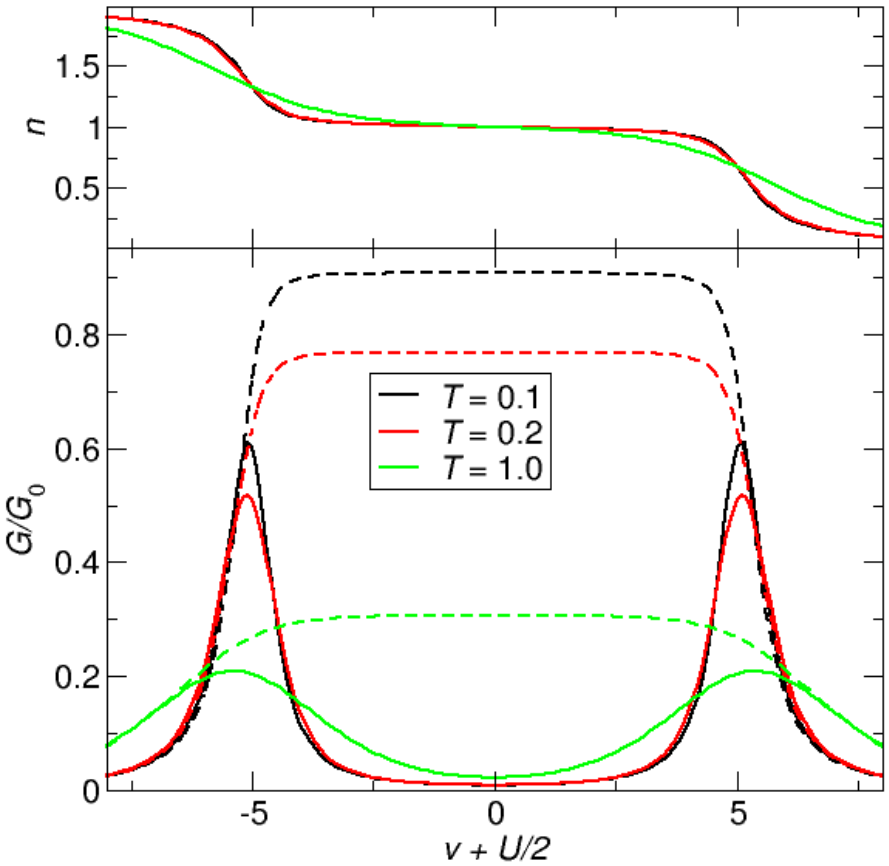
Kohn-Sham system

$$n_s = n = 2 \int \frac{\mathrm{d}\omega}{2\pi} f_\beta(\omega) A_s(\omega) \qquad A_s(\omega) = L_\gamma(\omega - v_s(n))$$

$$G_s = -\frac{\gamma}{2} \int \frac{\mathrm{d}\omega}{2\pi} f'_\beta(\omega) A_s(\omega)$$

Density and conductance from spectral function

use spectral function of smoothened single-site model



MB and KS density identical

MB (solid) and KS (dashed) conductances very different

KS: Kondo-plateau persists
MB: Coulomb blockade peaks

Dynamical corrections for single-level model

compressibility

$$\kappa = \frac{\partial n}{\partial \mu} = \frac{4}{\gamma} G + 2 \int \frac{\mathrm{d}\omega}{2\pi} f_\beta(\omega) \frac{\partial A(\omega)}{\partial n} \frac{\partial n}{\partial \mu} = \frac{4}{\gamma} G \frac{1}{1+R}$$

where

$$R = -2 \int \frac{\mathrm{d}\omega}{2\pi} f_\beta(\omega) \frac{\partial A(\omega)}{\partial n}$$

KS compressibility

$$\kappa_s = \kappa = \frac{\partial n}{\partial \mu} = \frac{4}{\gamma} G_s + 2 \int \frac{\mathrm{d}\omega}{2\pi} f_\beta(\omega) \frac{\partial A_s(\omega)}{\partial n} \frac{\partial n}{\partial \mu}$$

$$= \frac{4}{\gamma} G_s - 2 \int \frac{\mathrm{d}\omega}{2\pi} f_\beta(\omega) \frac{\partial A_s(\omega)}{\partial \omega} \frac{\mathrm{d}v_{Hxc}(n)}{\mathrm{d}n} \frac{\partial n}{\partial \mu}$$

Dynamical corrections for single-level model (cont.)

exact conductance in terms of KS conductance (no approx!)

$$\frac{G}{G_s} = \frac{1+R}{1+\frac{4}{\gamma}G_s\frac{\mathrm{d}v_{Hxc}(n)}{\mathrm{d}n}}$$

Remarks:

- for $T \ll T_K$ (Kondo temperature) at ph symm. point: $R = 4G_s/\gamma\frac{\mathrm{d}v_{Hxc}(n)}{\mathrm{d}n}$
- for $T \gtrsim T_K$: Abrikosov-Suhl resonance broadens and height decreases; no simple relation for dynamical correction
- for $T \gg T_K$: spectral function of smoothened SSM is good approximation to true spectral function

Dynamical corrections for single-level model (cont.)

for $T \gg T_K$ use smoothened SSM spectral function:

$n = \frac{2I(v_0)}{1+I(v_0)-I(v_0+U)}$ where $I(E) = \int \frac{\mathrm{d}\omega}{2\pi} f_\beta(\omega) L_\gamma(\omega - E)$
$1 + R = 2I(v_0)/n$ implicit density functional due to $v_0 = v_0(n)$

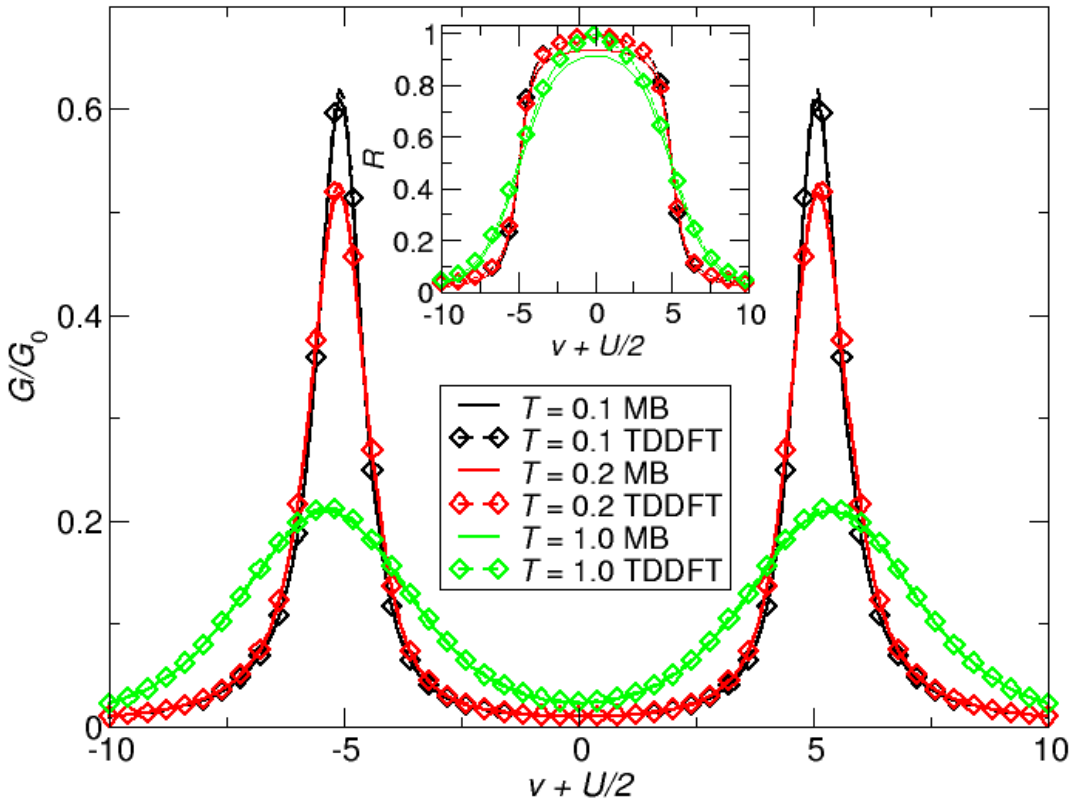
for $n < 1$: good approximation $n \approx \frac{2I(v_0)}{1+I(v_0)}$ and use particle-hole symmetry to deduce expression also for $n > 1$: $1 + R \approx \frac{2}{1+|\delta N|}$ where $\delta N = n - 1$

conductance in terms of DFT quantities (approximate)

$$\frac{G}{G_s} = \frac{2}{1+|\delta N|} \frac{1}{1 + \frac{4}{\gamma} G_s \frac{\mathrm{d}v_{Hxc}(n)}{\mathrm{d}n}}$$

note: dynamical xc corrections (from δV^α_{Hxc} deep inside the leads) expressed *completely* in terms of static DFT quantities on the dot!

Dynamical corrections for single-level model (cont.)



MB and TDDFT conductances very close!

Application to physical, multi-level systems

multiple levels: for general broadening matrix Γ_α, no relation between N (number of electrons on molecule) and G (conductance);

but for $\Gamma_{\alpha,ml} = (\gamma_\alpha/2)\delta_{ml}$: $N = 2\int \frac{\mathrm{d}\omega}{2\pi} f_\beta(\omega)\mathrm{Tr}\{A(\omega)\}$ and $G = -\frac{\gamma}{2}\int \frac{\mathrm{d}\omega}{2\pi} f'_\beta(\omega)\mathrm{Tr}\{A(\omega)\}$ and arguments can be repeated

$\longrightarrow$ correction formula should also be applicable for multiple levels

in real molecules write $v_{Hxc}(\mathbf{r}) = \delta v_{Hxc}(\mathbf{r}) + \bar{v}_{Hxc}$ with $\bar{v}_{Hxc} = \int \mathrm{d}^3 r_V \; v_{Hxc}(\mathbf{r})$ (V: volume of molecule)
weak dependence of $\delta v_{Hxc}(\mathbf{r})$ on $N \rightarrow$ neglect $\delta v_{Hxc}(\mathbf{r})$;
weakly coupled molecules: $\bar{v}_{Hxc}$ has sharp steps at integer $N \longrightarrow$ correction dominated by $\frac{\mathrm{d}\bar{v}_{Hxc}}{\mathrm{d}N}$.

conductance including dynamical corrections for multiple levels

$$\frac{G}{G_s} = \frac{2}{1+|\delta N|}\frac{1}{1+\frac{4}{\gamma(N)}G_s\frac{\mathrm{d}\bar{v}_{Hxc}(N)}{\mathrm{d}N}}$$

for $\gamma(N)$: $\gamma(N) \approx 1/2\Gamma_{\alpha,HH}$ for $\mu \approx \varepsilon_H$ (resonance, open shell)
$\gamma(N) \approx 1/4(\Gamma_{\alpha,HH}+\Gamma_{\alpha,LL})$ for $\mu \approx (\varepsilon_H+\varepsilon_L)/2$ (off resonance, closed shell)

$\delta N = N - \mathrm{Int}[N] - 1$

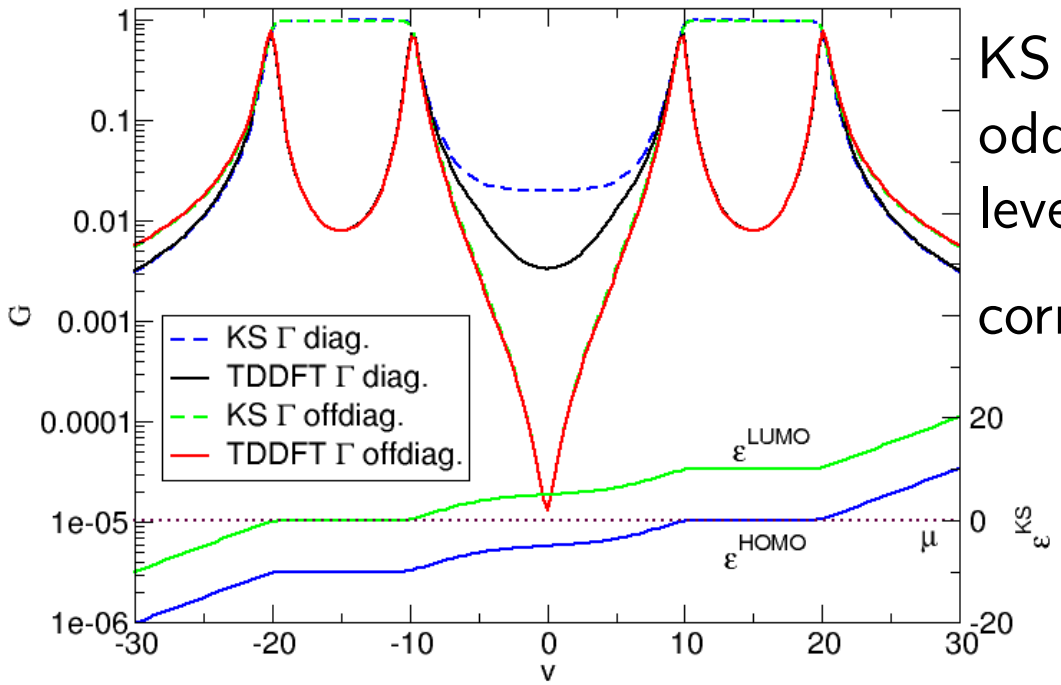
model for xc potential in multi-level case

$$\bar{v}_{Hxc}(N) = \sum_K \frac{\Delta_{xc}(K)}{\pi}\arctan\left(\frac{N-K}{W(K)}\right)$$

with: $\Delta_{xc}(N)$ xc part of derivative discontinuity of isolated molecule with N electrons and $W(N) = 0.16\gamma(N)/\Delta_{xc}(N)$

HOMO-LUMO model

$\varepsilon_H = -\varepsilon_L = -5\gamma$, $\Delta_{xc}(N) = 10\gamma$, $\beta = 10\gamma^{-1}$, $\Gamma_L = \Gamma_R$



KS conductance plateaus for odd N (Kondo; pinned KS levels)

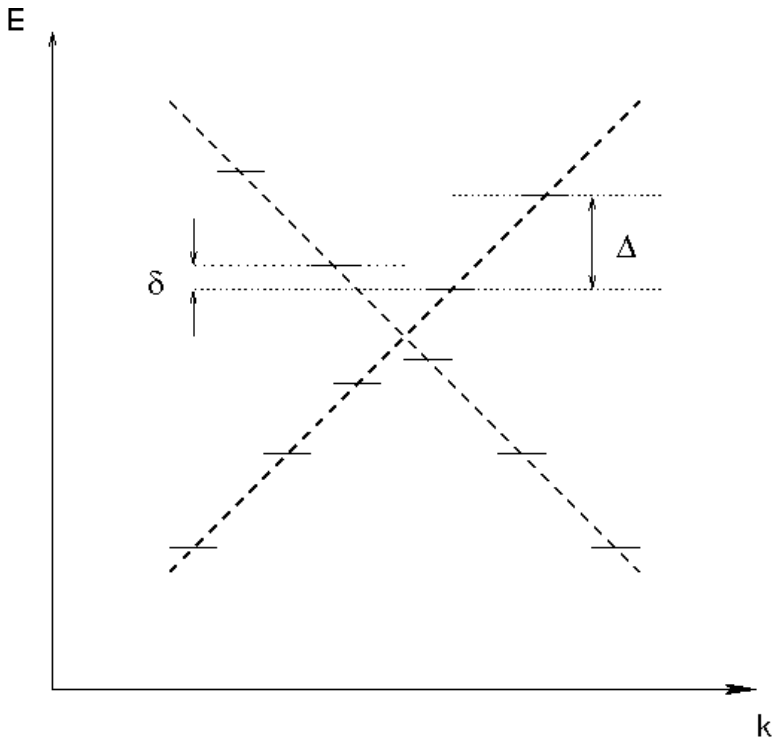
correction restores CB peaks

opening of conductance gap by discontinuity for even electron number also discussed in Toher et al, PRL **95**, 146402 (2005)

Single-wall carbon nanotube quantum dot

model for level structure: S.Sapmaz et al, PRB **71**, 153402 (2005)

single-particle energy spectrum of single-wall carbon nanotube (SWNT) quantum dots: $\varepsilon_{0l\nu} = l\Delta + l(\nu - 1)\delta$ (band $\nu = 0, 1$)

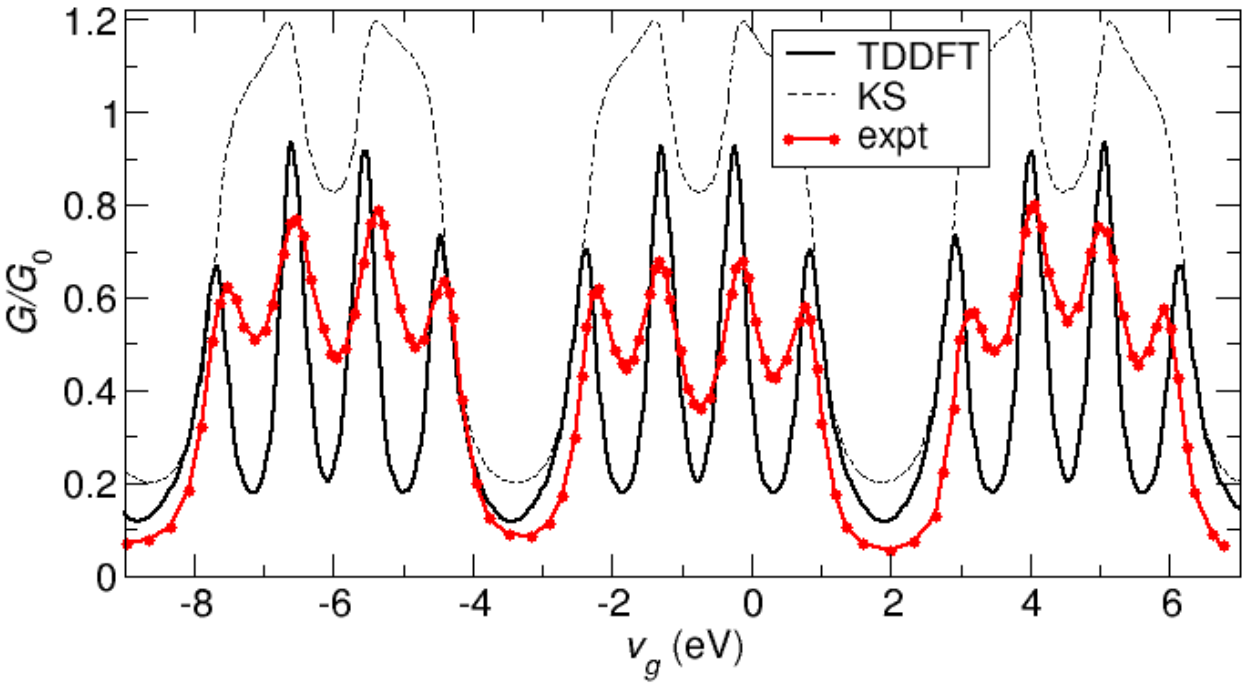


diagonal $\Gamma_{lm} = \gamma\delta_{lm}$
charging energies:
$\Delta_{xc}(1) = \Delta_{xc}(3) = E_C + U + J$
$\Delta_{xc}(2) = \Delta_{xc}(4) = E_C - U$
and periodic $\Delta_{xc}(K) = \Delta_{xc}(i)$
for $K - i = 0 \bmod 4$

parameter values (in meV):
$\Delta = 9.2$, $\delta = 2.27$, $\gamma = 1$
$E_C = 2.485$, $J = 0.7$, $U = 0.37$

our simulation: 22 single-particle levels

Single-wall carbon nanotube quantum dot



- KS conductance with deformed Kondo plateaus at odd N
- TDDFT conductance with correct fourfold periodicity
- expt. results: W. Liang et al, PRL **88**, 126801 (2001)

Summary

- importance of derivative discontinuity in transport
- at $T = 0$ discontinuity is responsible for Kondo plateau in G_s for odd electron numbers
- dynamical correction of KS conductance in terms of static DFT quantities for single and multi-level systems
- for $T \gg T_K$ dynamical correction leads to suppression of Kondo plateau (Coulomb blockade peaks) in TDDFT corrected conductance

Collaborator:

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