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Filling gaps in our understanding of gaps

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Filling gaps in our understanding of gaps

Klaus Capelle, UFABC, Brazil

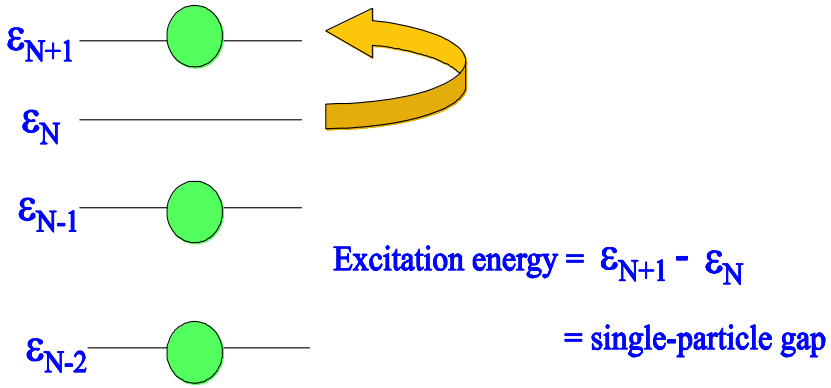
Gaps in our understanding of gaps

- Brief review of some basic terminology and concepts

- Can there be purely local functionals with a derivative discontinuity?
- What is the effect of self-interaction on Mott gaps and band gaps?
- How about spin gaps? Are they similar to charge gaps? Are there spin discontinuities?

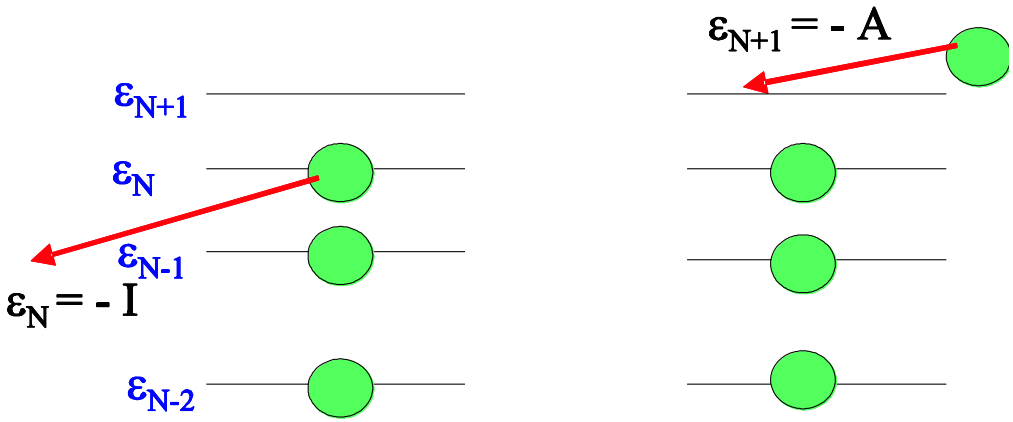
Excitation gap vs. fundamental gap

Electron excitation



Excitation gap: $E^{exc} - E$

Electron addition and removal



Fundamental gap:I-A

These gaps are the same for noninteracting particles, but NOT for interacting particles

A useful single-particle gap: Kohn-Sham gap

$$\left(-\frac{\hbar^2\nabla^2}{2m}+v_s(\mathbf{r})\right)\phi_k(\mathbf{r})=\epsilon_k\phi_k(\mathbf{r})$$

$$E_g^{KS}=\epsilon_{N+1}(N)-\epsilon_N(N)$$

KS single-particle gap

The KS gap is not an excitation gap and neither the fundamental gap, but a zero-order approximation to both

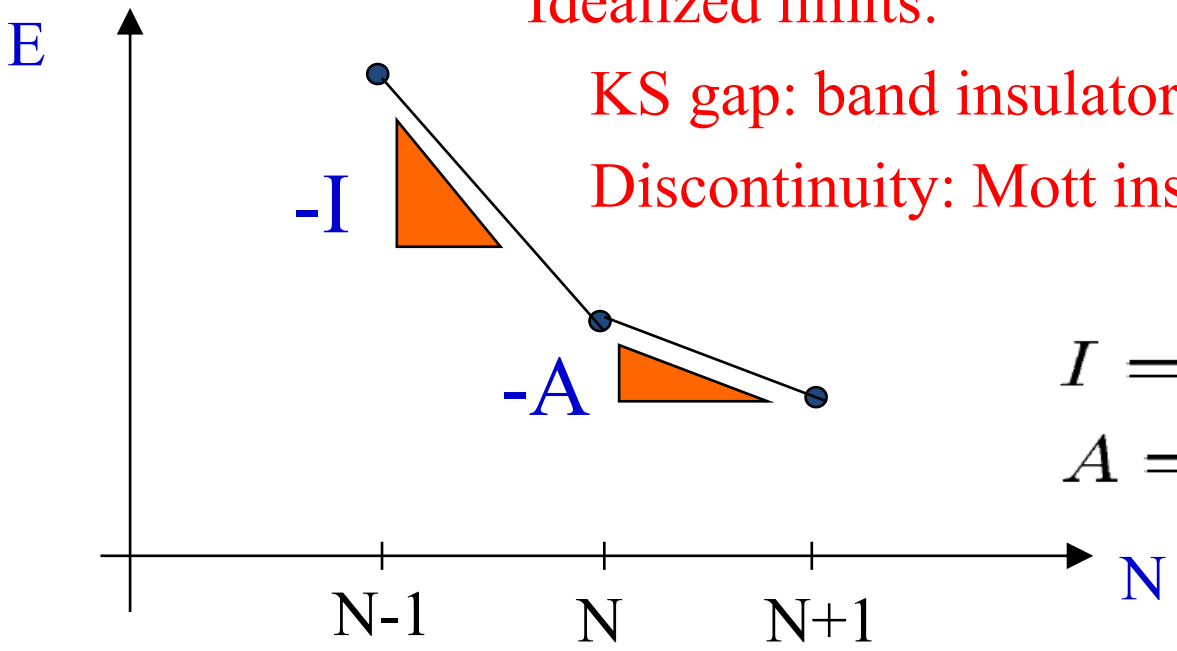
Fundamental gap

$$E_g = E_g^{KS} + \Delta_{xc}$$

Idealized limits:

KS gap: band insulator

Discontinuity: Mott insulator (not in LDA/GGA)



$$I = E(N-1) - E(N)$$
$$A = E(N) - E(N+1)$$

$$E_g = I - A = \mu_+ - \mu_- = \left.\frac{\delta E[n]}{\delta n}\right|_{N+\eta} - \left.\frac{\delta E[n]}{\delta n}\right|_{N-\eta}$$

Gaps in our understanding of gaps

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To answer first two questions: use theoretical laboratory

Hubbard model

Inhomogeneous 1D Hubbard model: a theoretical laboratory for DFT

Standard 1D Hubbard model

$$\hat{H}_{hom} = -t \sum_{i\sigma} (\hat{c}^{\dagger}_{i\sigma} \hat{c}_{i+1\sigma} + H.c.)$$

$$+U \sum_{i} \hat{c}^{\dagger}_{i\uparrow} \hat{c}_{i\uparrow} \hat{c}^{\dagger}_{i\downarrow} \hat{c}_{i\downarrow} + \mu \sum_{i\sigma} \hat{c}^{\dagger}_{i\sigma} \hat{c}_{i\sigma}$$

Inhomogeneous 1D Hubbard model

$$\hat{H}_{inhom} = -t \sum_{i\sigma} (\hat{c}^{\dagger}_{i\sigma} \hat{c}_{i+1,\sigma} + H.c.)$$

$$+ \sum_{i} U_i \hat{c}^{\dagger}_{i\uparrow} \hat{c}_{i\uparrow} \hat{c}^{\dagger}_{i\downarrow} \hat{c}_{i\downarrow} + \sum_{i\sigma} v_i \hat{c}^{\dagger}_{i\sigma} \hat{c}_{i\sigma}$$

XC energy of the homogeneous 1D Hubbard model

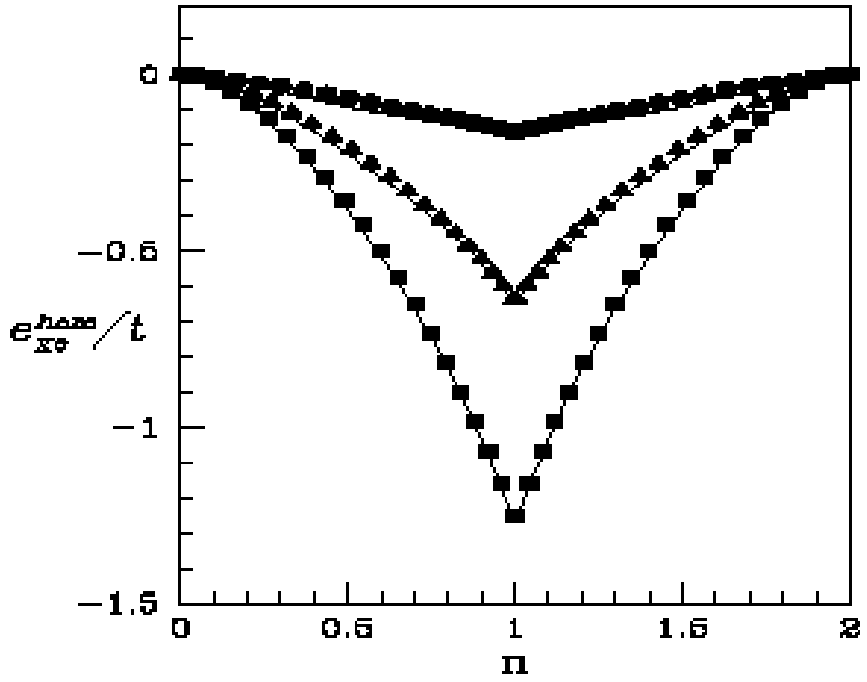

Figure 1. Exchange-correlation energy per site of the homogeneous infinite 1DHM as obtained by numerically solving the Lieb-Wu integral equations resulting from the Bethe Ansatz. Circles: $U = 3$, triangles: $U = 6$, squares: $U = 9$. The full lines are obtained from our expression (8) with (9) and (10). The band filling n ranges from $n = 0$ (empty band) over $n = 1$ (half-filled band) to $n = 2$ (filled band). The form of the curves reflects particle-hole symmetry, and the kinks at $n = 1$ signal the Mott metal-insulator transition.

DFT for the Hubbard model: Bethe-Ansatz LDA not: LDA+U, rather: U+LDA

$$E_{xc}^{BA-LDA}(n,U) = \sum_i e_{xc}^{BA}(n,U)|_{n\to n_i}$$

parametrization of XC energy

$$\frac{e^{BA}(n,U)}{tN_s} = -\frac{2\beta}{\pi}\sin\left(\frac{\pi n}{\beta}\right)$$

$$\beta\sin\left(\frac{\pi}{\beta}\right) = 2\pi\int_0^\infty dx \frac{J_0(x)J_1(x)}{x(1+\exp(xU/2)}$$

(i) $U \to 0$ and any $n \leq 1$

(ii) $U \to \infty$ and any $n \leq 1$

(iii) for $n = 1$ and any U

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Density Functionals Not Based on the Electron Gas: Local-Density Approximation for a Luttinger Liquid

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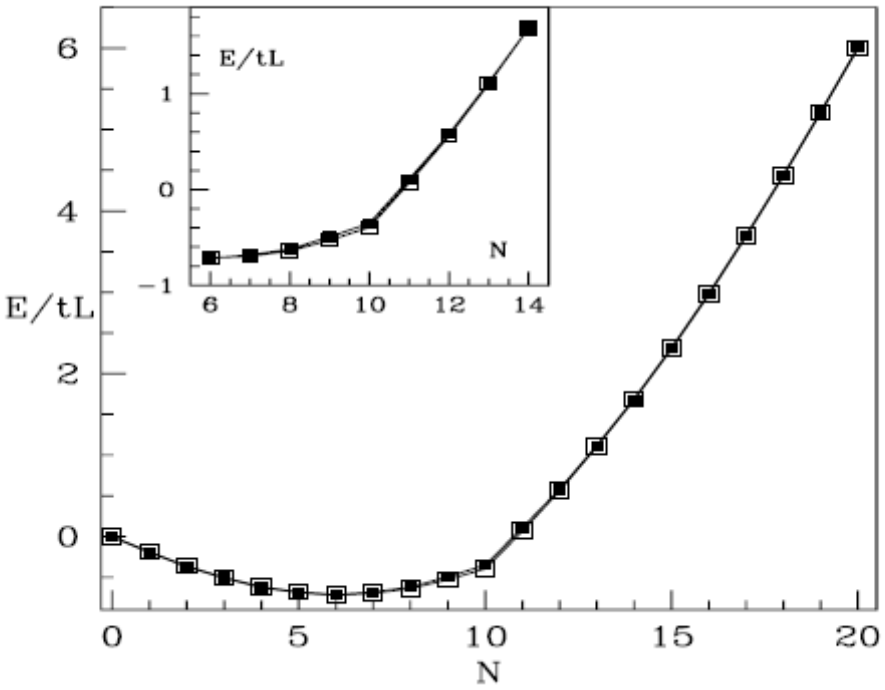
Energy depends on particle number



EUROPHYSICS LETTERS

Europhys. Lett., **60** (4), pp. 601–607 (2002)

Density-functional study of the Mott gap in the Hubbard model

N. A. Lima[1], L. N. Oliveira[1] and K. Capelle[2]

$$\Delta_{xc} = \left.\frac{\delta E_{xc}[n]}{\delta n}\right|_{N+\delta} - \left.\frac{\delta E_{xc}[n]}{\delta n}\right|_{N-\delta}$$

$$\Delta(U) = U + 4t\cos\left(\frac{\pi}{\beta(U/t)}\right)$$

Proof: derivative discontinuity of DFT = Mott gap

Filling gaps in our understanding of gaps

- Can there be purely local functionals with a derivative discontinuity?

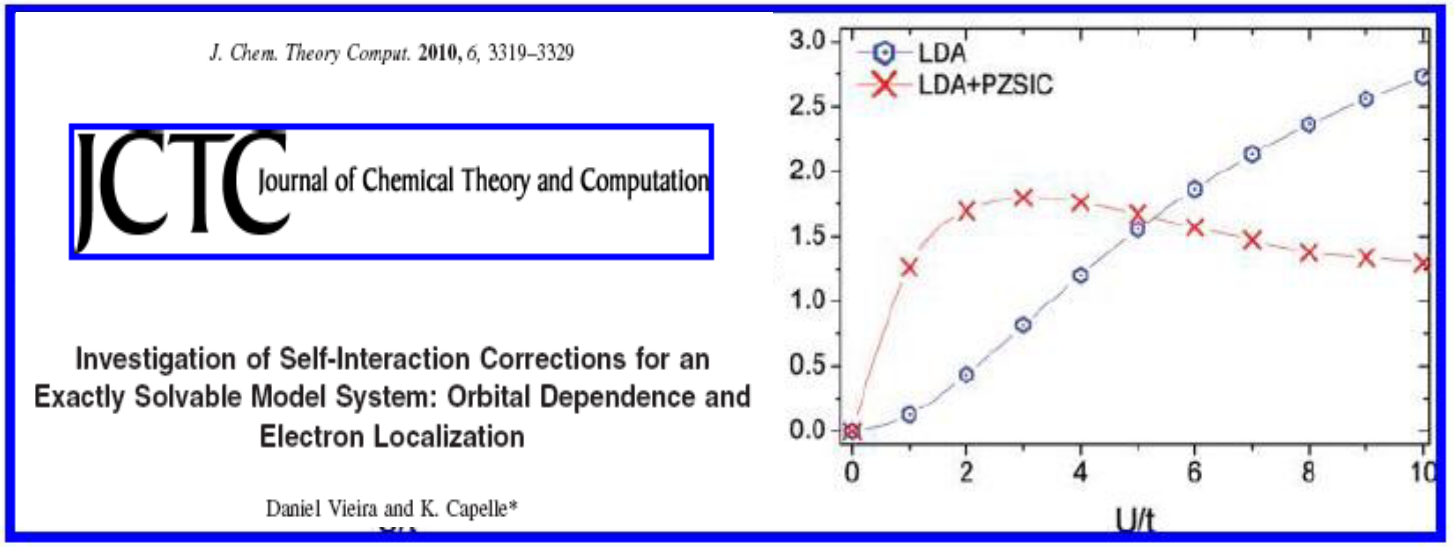
  Yes, but our example is a model Hamiltonian with a gap in its spatially homog. phase

- What is the effect of self-interaction on Mott gaps and band gaps?

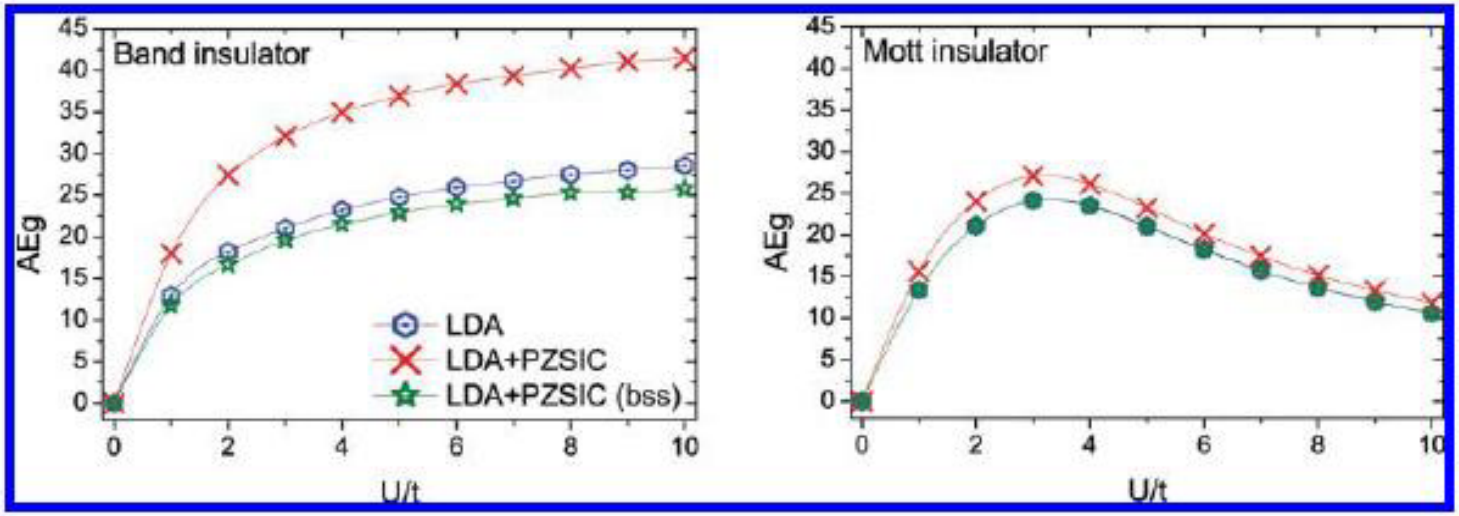
- How about spin gaps? Are they similar to charge gaps? Are there spin discontinuities?

Effect of self-interaction on gaps

average error
in total energy:
LDA vs. PZ-SIC



average error
in fund. gap:
LDA vs. PZ-SIC



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  Yes, but our example is a model Hamiltonian with a gap in its spatially homog. phase

- What is the effect of the (PZ) self-interaction on Mott gaps and band gaps?

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Spin gaps

Spintronics aims at controlling spin degrees of freedom

- How shall we define spin gaps in DFT?
- Are there spin deriative discontinuities?

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Spin gaps and spin-flip energies in density-functional theory

K. Capelle,[1,2] G. Vignale,[3] and C. A. Ullrich[3]
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(Received 9 November 2009; revised manuscript received 18 February 2010; published 16 March 2010)

Some analogies between spin and charge

$$A(N) = E(N) - E(N+1)$$

$$I(N) = E(N-1) - E(N).$$

$$E^{sf+}(N) = E(N,S+1) - E(N,S)$$

$$E^{sf-}(N) = E(N,S-1) - E(N,S)$$

Excitation energies!

$$E_{g,KS}(N) = \epsilon_{N+1}(N) - \epsilon_N(N)$$

$$E_{KS}^{sf+} = \epsilon_{l(\uparrow)} - \epsilon_{H(\downarrow)}$$

$$E_{KS}^{sf-} = \epsilon_{l(\downarrow)} - \epsilon_{H(\uparrow)}$$

$$E_g = E_g^{KS} + \Delta_{xc}$$

$$E^{sf-} = E_{KS}^{sf-} + \Delta_{xc}^{sf-}$$

$$E^{sf+} = E_{KS}^{sf+} + \Delta_{xc}^{sf+}$$

Formal introduction of "discontinuity"

- But is this a true derivative discontinuity?
- Is it nonzero?

Atomic spin gaps from exact energies

TABLE II. Single-particle spin-flip energies [Eqs. (34) and (35)] and spin stiffness [Eq. (29)], their experimental (Expt.) counterparts, Eqs. (20), (21), and (26), and the resulting *xc* corrections defined in Eqs. (30)–(32), for the lithium atom. In the columns labeled KS we employ KS eigenvalues obtained from near-exact densities, while in the columns labeled XX, KLI-XX, and LSDA we use approximate eigenvalues obtained from standard SDFT calculations. The experimental values were obtained using spectroscopic data for the lowest quartet state $^4P^0$ from Ref. 15 as well as accurate wave-function based theory from Ref. 16. All values are in eV.

	KS[a]	KS[b]	XX[a]	KLI-XX	LSDA	Expt.
E^{sf+}	60.87	60.87	63.70	63.64	49.47	57.41
E^{sf-}	−2.77	−0.48	−2.91	−2.89	1.07	0
E_s	58.10	60.39	60.79	60.75	50.54	57.41
Δ_{xc}^{sf+}	−3.46	−3.46	−6.29	−6.23	7.94	
Δ_{xc}^{sf-}	2.77	0.48	2.91	2.89	−1.07	
Δ_{xc}^{s}	−0.69	−2.98	−3.38	−3.34	6.87	

negative

"discontinuity"!

Spin discontinuities: ensemble theory

$$E^w = (1-w)E_A + wE_B \qquad n^w = (1-w)n_A + wn_B$$

But which ensemble should we use ?

Not: Perdew, Parr, Levy, Balduz, (PPLB) ensemble of fractional particle numbers

Not: Yang ensemble of fractional spins

But: Oliveira-Gross-Kohn ensemble of excited states

$$E_B - E_A = \epsilon^w_{M+1} - \epsilon^w_M + \left.\frac{\partial E^w_{xc}[n]}{\partial w}\right|_{n=n_w}$$

E. K. U. Gross, L. N. Oliveira, and W. Kohn, Phys. Rev. A **37**, 2805 (1988); **37**, 2809 (1988); L. N. Oliveira, E. K. U. Gross, and W. Kohn, *ibid.* **37**, 2821 (1988).

$$\left.\frac{\partial E^w_{xc}[n]}{\partial w}\right|_{n=n^w} = \left.\frac{\delta E^{w=0}_{xc}[n]}{\delta n(\mathbf{r})}\right|_{n=n^{w=0}} - \left.\frac{\delta E^w_{xc}[n]}{\delta n(\mathbf{r})}\right|_{n=n^w}$$

M. Levy, Phys. Rev. A **52**, R4313 (1995)

Spin discontinuities: ensemble theory

$$E^{sf+}(N) = E(N,S+1) - E(N,S)$$

The difference between KS spin gaps and many-body spin gaps is a derivative discontinuity

$$= \epsilon^{w}_{l(\uparrow)} - \epsilon^{w}_{H(\downarrow)} + \left.\frac{\partial E^{w}_{xc}[n_\uparrow, n_\downarrow]}{\partial w}\right|_{\substack{n_\uparrow = n^{w}_\uparrow \\ n_\downarrow = n^{w}_\downarrow}}$$

$$= \epsilon^{w}_{l(\uparrow)} - \epsilon^{w}_{H(\downarrow)} + \left.\frac{\delta E^{w=0}_{xc}[n_\uparrow, n_\downarrow]}{\delta n_\downarrow(\mathbf{r})}\right|_{\substack{n_\uparrow = n^{w=0}_\uparrow \\ n_\downarrow = n^{w=0}_\downarrow}}$$

$$- \left.\frac{\delta E^{w}_{xc}[n_\uparrow, n_\downarrow]}{\delta n_\downarrow(\mathbf{r})}\right|_{n_\uparrow = n^{w}_\uparrow}$$

$$= E^{sf+}_{w,KS}(N) + \Delta^{sf+}_{w,\mathrm{xc}}$$

But this is not a practical expression for calculating it

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Spin gaps: time-dependent DFT

$$E^{sf+} = \omega_{\uparrow\downarrow} + M_{\uparrow\downarrow,\uparrow\downarrow}$$

$$E^{sf-} = \omega_{\downarrow\uparrow} + M_{\downarrow\uparrow,\downarrow\uparrow}$$

$$M_{\alpha\alpha',\sigma\sigma'} = K^{\alpha'\alpha,\sigma'\sigma}_{H\alpha i\alpha',H\sigma i\sigma'}(\omega)$$

$$K^{\alpha\alpha',\sigma\sigma'}_{i\alpha a\alpha',i'\sigma a'\sigma'}(\omega) = \int d^3r \int d^3r'\, \psi_{i\alpha}(\mathbf{r})\psi_{a\alpha'}(\mathbf{r}) \times f^{Hxc}_{\alpha\alpha',\sigma\sigma'}(\mathbf{r},\mathbf{r}',\omega)\psi_{i'\sigma}(\mathbf{r}')\psi_{a'}$$

$$f^{xc}_{\uparrow\uparrow,\uparrow\uparrow} = \frac{\partial^2(ne^h_{\rm xc})}{\partial n^2} + 2(1-\zeta)\frac{\partial^2 e^h_{\rm xc}}{\partial n\,\partial\zeta} + \frac{(1-\zeta)^2}{n}\frac{\partial^2 e^h_{\rm xc}}{\partial\zeta^2}$$

$$f^{xc}_{\downarrow\downarrow,\downarrow\downarrow} = \frac{\partial^2(ne^h_{\rm xc})}{\partial n^2} - 2(1+\zeta)\frac{\partial^2 e^h_{\rm xc}}{\partial n\,\partial\zeta} + \frac{(1+\zeta)^2}{n}\frac{\partial^2 e^h_{\rm xc}}{\partial\zeta^2}$$

$$f^{xc}_{\uparrow\uparrow,\downarrow\downarrow} = \frac{\partial^2(ne^h_{\rm xc})}{\partial n^2} - 2\zeta\frac{\partial^2 e^h_{\rm xc}}{\partial n\,\partial\zeta} - \frac{(1-\zeta^2)}{n}\frac{\partial^2 e^h_{\rm xc}}{\partial\zeta^2},$$

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$$f^{xc}_{\uparrow\downarrow,\uparrow\downarrow} = \frac{2}{n\zeta}\frac{\partial e^h_{\rm xc}(n,\zeta)}{\partial\zeta},$$

TD-DFT calculation of spin gaps

TABLE III. Top part: lowest spin-conserving and spin-flip excitation energies for the lithium atom, calculated with LSDA and KLI-XX using differences of KS eigenvalues and TDDFT in the single-pole approximation (51)–(53). Bottom part: TDDFT *xc* corrections to the KS spin-flip excitation energies, from Eqs. (52) and (53), and to the KS spin gap, Eq. (54). All numbers are in eV.

	LSDA		KLI-XX		Exact	
	KS	TDDFT	KS	TDDFT	KS[a]	Expt.[b]
$E^{sc\uparrow}$	1.83	2.00	1.84	2.01	1.85	1.85
$E^{sc\downarrow}$	48.72	48.89	58.90	59.31	56.25	56.36
E^{sf+}	49.47	48.23	63.64	62.12	60.87	57.41
E^{sf-}	1.07	0.99	−2.89	−2.97	−2.77	0.0
Δ_{xc}^{sf+}		−1.24		−1.52		−3.46
Δ_{xc}^{sf-}		−0.08		−0.07		+2.77
Δ_{xc}^{s}		−1.32		−1.59		−0.69

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- How about spin gaps? Are they similar to charge gaps? Are there spin discontinuities?

  Similar: * can define KS and many-body spin gaps, and related quantities
  * there are spin discontinuities

  Different: * spin gaps are excitation energies
  * spin discontinuities may be negative (KS spin gap > many-body spin gap)