

The derivative discontinuity in the strong-interaction limit of density functional theory

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GENERAL CO-MOTION FUNCTIONS FOR ONE-DIMENSIONAL DENSITIES

Integer electron numbers

Given a one-dimensional (1D) N -electron density $\rho(x)$, we aim at building $N-1$ co-motion functions $f_2(x), \dots, f_N(x)$ that satisfy the condition of total suppression of fluctuations [1, 2],

$$\int_{f_{i-1}(x)}^{f_i(x)} \rho(x') dx' = 1, \quad (1)$$

and minimize the expectation of \hat{V}_{ee} , yielding the functional $V_{ee}^{\text{SCE}}[\rho]$ [2–4],

$$V_{ee}^{\text{SCE}}[\rho] = \int_{-\infty}^{\infty} \frac{\rho(x)}{N} \sum_{i=1}^{N-1} \sum_{j=i+1}^N w_b(|f_i(x) - f_j(x)|) dx = \frac{1}{2} \int_{-\infty}^{\infty} \rho(x) \sum_{i=2}^N w_b(|x - f_i(x)|) dx, \quad (2)$$

where we have used the convention $f_1(x) \equiv x$, and $w_b(x)$ is the electron-electron interaction. Equation (1) is equivalent to

$$\int_x^{f_i(x)} \rho(x') dx' = i - 1. \quad (3)$$

If we define the function

$$N_e(x) = \int_{-\infty}^x \rho(x') dx', \quad (4)$$

we see that Eq. (3) becomes

$$N_e[f_i(x)] - N_e(x) = i - 1, \quad (5)$$

yielding the to co-motion functions

$$f_i(x) = N_e^{-1}[N_e(x) + i - 1]. \quad (6)$$

Equation (3) is actually only valid for $f_i(x) > x$ restricting the domain of x to $x < N_e^{-1}(N + 1 - i)$. We can find the second branch of $f_i(x)$, for $x > N_e^{-1}(N + 1 - i)$, by considering that in this case Eq. (3) becomes

$$\int_{f_i(x)}^x \rho(x') dx' = N - (i - 1). \quad (7)$$

The co-motion functions for the entire domain then read

$$f_i(x) = \begin{cases} N_e^{-1}[N_e(x) + i - 1] & x \leq a_{N+1-i} \\ N_e^{-1}[N_e(x) + i - 1 - N] & x > a_{N+1-i}, \end{cases} \quad (8)$$

where $a_k = N_e^{-1}(k)$.

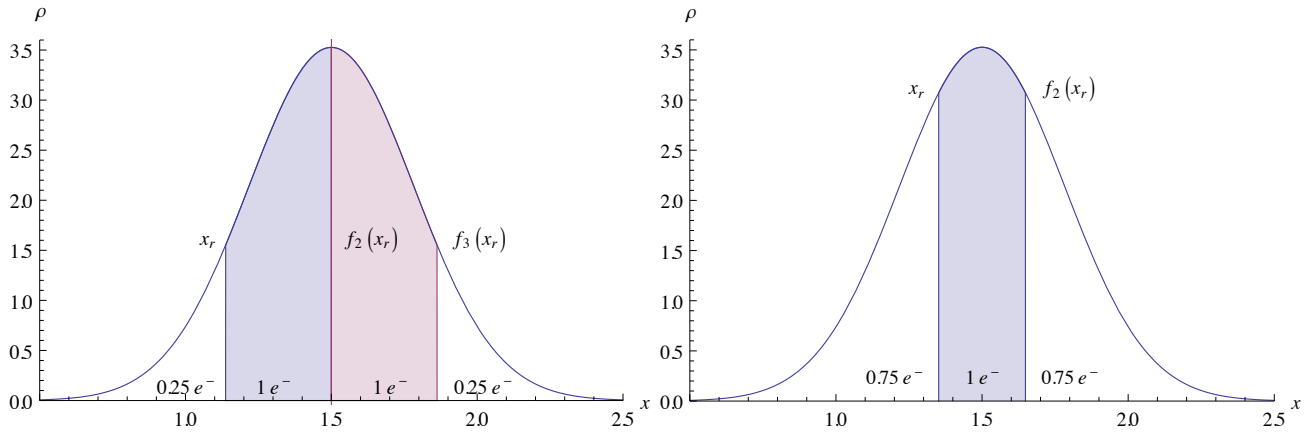


FIG. 1: (color online) The SCE solution for a density integrating to $Q = 2.5$ electrons. For some values of $x = x_r$ we find 2 other strictly correlated positions (the density contains 3 electrons; case in the left panel), but for other values of $x = x_r$ we can only find one co-motion function (we find only 2 electrons in the density, the 3rd one is pushed to infinity; case in the right panel).

Extension to Fractional Electron Numbers

If the density $\rho(x)$ integrates to $Q = N + \eta$ electrons, with $0 \leq \eta \leq 1$, we see that Eq. (1) can be satisfied for certain values of x up to $i = N + 1$ (so that there are $N + 1$ electrons in the density) and for certain values of x only up to $i = N$ (only N electrons can be found in the density). This is illustrated in Fig. 1 for the case $Q = 2.5$ electrons. By inspection, we see that Eqs. (8) become now Eqs. (8) of the paper,

$$f_i(x) = \begin{cases} N_e^{-1}[N_e(x) + i - 1] & x < a_{N+1+\eta-i} \\ N_e^{-1}[N_e(x) + i - N - 2] & x > a_{N+2-i} \\ \infty & \text{otherwise,} \end{cases} \quad (9)$$

with the same definitions of $N_e(x)$ and a_k and $i \in [2, \dots, N + 1]$. Notice that in this case it is crucial to use the second expression of $V_{ee}^{\text{SCE}}[\rho]$ in Eq. (2), as discussed in the paper (with the sum now running up to $N + 1$).

The functional derivative of $V_{ee}^{\text{SCE}}[\rho]$ can be obtained exactly by integrating the 1D equivalent of Eq. (4) of the paper [5–7],

$$\tilde{v}'_{\text{SCE}}[\rho](x) = \sum_{i=2}^{N+1} w'_b(|x - f_i(x)|) \text{sgn}(x - f_i(x)), \quad (10)$$

with boundary condition $\tilde{v}_{\text{SCE}}[\rho](|x| \rightarrow \infty) = 0$. For fractional electron numbers $Q = N + \eta$ this equation yields the functional derivative of $V_{ee}^{\text{SCE}}[\rho_Q]$ if the co-motion functions of Eqs. (9) are used.

CO-MOTION FUNCTIONS FOR A SYMMETRIC 1D DENSITY WITH $N + \eta$ ELECTRONS

If the density is symmetric with respect to the origin, $\rho(x) = \rho(-x)$, we can define the co-motion functions in a way that allows for a straightforward generalization to the two- and three-dimensional spherically-symmetric cases. Consider now the function $\tilde{N}_e(x)$ defined only for $x \geq 0$,

$$\tilde{N}_e(x) = 2 \int_0^x dx' \rho(x'), \quad (11)$$

where the factor 2 takes into account the 1D volume element, and $\lim_{x \rightarrow \infty} \tilde{N}_e(x) = N + \eta$. The positive co-motion functions define now only the distance of the N electrons from the origin. We can obtain these “radial” co-motion functions from Eq. (9) by using the identities

$$N_e(x) = \frac{\tilde{N}_e(x)}{2} + \frac{N + \eta}{2}, \quad N_e^{-1}(x) = \tilde{N}_e^{-1}(|2x - N - \eta|). \quad (12)$$

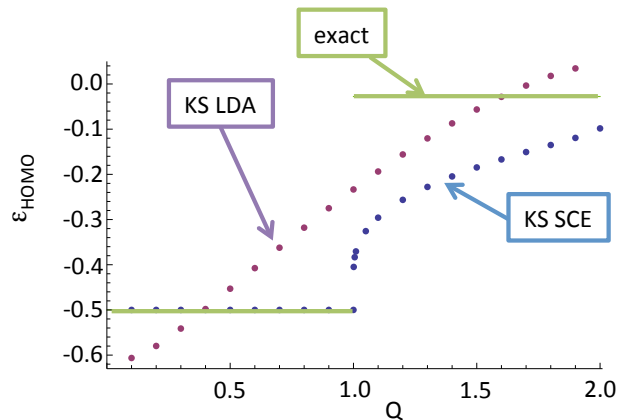


FIG. 2: (color online) The spin-restricted self-consistent KS highest occupied eigenvalue (HOMO) for the H atom, when the number of electrons Q varies continuously between 0 and 2. The KS SCE and KS LDA results are compared with the exact values.

This yields

$$f_i(x) = \begin{cases} \tilde{N}_e^{-1}[\tilde{N}_e(x) + 2i - 2] & x < \tilde{a}_{N+2-2i+\eta} \\ \tilde{N}_e^{-1}[|\tilde{N}_e(x) - 2(N + 2 - i)|] & x > \tilde{a}_{N+4-2i-\eta} \\ \infty & \text{otherwise,} \end{cases} \quad (13)$$

where $\tilde{a}_k = \tilde{N}_e^{-1}(k)$ with the convention that $\tilde{a}_k = 0$ when $k < 0$. When $\eta = 1$, these co-motion functions agree with the ones of Eqs. (44)-(46) in Ref. [3] for $N + 1$ electrons. Minimization of the electron-electron repulsion $V_{ee}(x)$ for a given reference position x ,

$$V_{ee}(x) = \sum_{i=1}^N \sum_{j=i+1}^{N+1} w_b(|f_i(x) - f_j(x)|), \quad (14)$$

decides whether the functions $f_i(x)$ are at the left or at the right of the origin. This is the 1D equivalent of the 3D angular minimization of Ref. [3], which (only in the 1D case) can be simplified by using the co-motion functions of Eqs. (9).

GENERALIZATION TO SPHERICALLY SYMMETRIC DENSITIES

As discussed in Ref. [3], for spherically symmetric densities we can define radial co-motion functions $f_i(r)$ that give the distances from the center of symmetry of the density as a function of the distance r of the first electron. The relative angles can then be minimized for every r [3].

By defining in three-dimensions

$$N_e(r) = \int_0^r 4\pi u^2 \rho(u) du, \quad (15)$$

we obtain again the same Eqs. (13) with x replaced by r , thus generalizing the radial equations found in Ref. [3] to fractional electron numbers $N + \eta$.

HARMONIC AND COULOMB EXTERNAL POTENTIALS

When the external potential of a finite many-electron system is Coulombic, it is not possible to reach the extreme low-density (or strong-interaction) limit, because the system becomes unbound. We will present an extensive study of

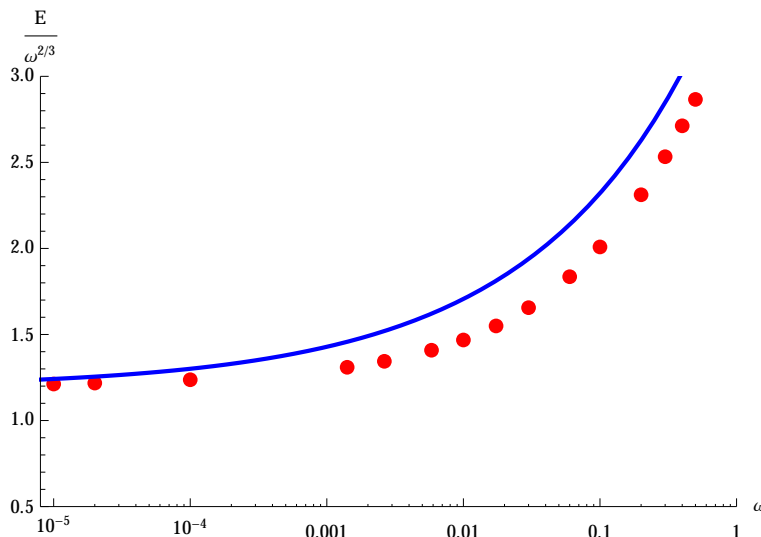


FIG. 3: (color online) The Hooke's atom ($N = 2$ electrons in the external harmonic potential $\frac{1}{2}\omega^2 r^2$) self-consistent KS SCE energies (red dots) are compared with the exact energies (blue curve, [9]) as a function of the spring constant ω . We see that when $\omega \rightarrow 0$ KS SCE approaches asymptotically the exact curve.

negative ions with the KS SCE approach elsewhere. Here, we show the KS SCE result for the H atom when we vary the number of electrons between 0 and 2 (Fig. 2). This result is, as in all our work, obtained in the spin-restricted formalism, so that the vertical change in Fig. 2 of the KS SCE results at $Q = 1$ is exactly the same we would observe in the H atom with $\frac{1}{2}$ spin-up and $\frac{1}{2}$ spin-down electrons, which is often considered a paradigmatic model for a Mott insulator [8]. In other words, the KS SCE energy (of which the HOMO in Fig. 2 is the derivative with respect to Q) has the correct behavior in the spin degree of freedom (flat plane), but, as we see from Fig. 2, it is not perfectly linear for $1 < Q < 2$. Notice also that KS SCE is able to bind H^- (negative HOMO at $Q = 2$) something that neither Hartree-Fock nor DFT with local or semilocal functionals is able to do.

The reason why KS SCE does not yield the exact result in this case is that H^- is a system which is not close enough to the regime in which the SCE functional becomes very accurate. The Hooke's atom with very small spring constant, instead, supports bound states with very low density, where KS SCE becomes asymptotically exact, as shown in Fig. 4 of the Letter. In Fig. 3 of this Supplemental Material we also show that, energetically, the KS SCE result approaches indeed the exact one in the limit of small ω .

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