



# Discontinuities of the exchange-correlation kernel and charge-transfer excitations in time-dependent density functional theory

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Density functional theory (DFT) owes its great success to the fact that the highly intricate many-body wave function is replaced by the much simpler electronic density. In addition, the density is calculated from a system of non-interacting electrons known as the Kohn-Sham (KS) system. The effective KS potential is composed of the external, the Hartree and the so-called exchange-correlation (XC) potential  $v_{xc}$ , where the latter is given by the functional derivative of the XC energy  $E_{xc}$  with respect to the density, and incorporates all the effects of the Coulomb interaction beyond the Hartree level. The difficulties in using DFT lies in finding good approximations to  $E_{xc}$ . Many works have therefore been devoted to study its exact properties. One of the most intriguing features is the existence of derivative discontinuities at integral particle numbers [1], a property which turns out to have several important physical implications.

It is not hard to see that a derivative discontinuity in  $E_{xc}$  gives rise to a singularity in  $v_{xc}$  in the form of a jump by a constant  $\Delta_{xc}$ , i.e.,  $v_{xc}^+(\mathbf{r}) = v_{xc}^-(\mathbf{r}) + \Delta_{xc}$ , where  $\pm$  refers to  $N \rightarrow N_0^\pm$ , and  $N_0$  is an integer. A classic example where the jump in  $v_{xc}$  becomes important is in the dissociation of closed-shell molecules composed of open-shell atoms. In order to get the correct dissociation limit a step in  $v_{xc}$  has to develop over the atom with the lower ionization energy (a similar situation but with closed-shell fragments is depicted in Fig. 1).

With the advent of time-dependent DFT (TDDFT) the variation of  $v_{xc}$  with respect to the density, i.e., the XC kernel  $f_{xc}(\mathbf{r}, \mathbf{r}', \omega)$ , has become another central quantity of interest. The reason is the possibility of extracting excitation energies from the linear density response function, which in TDDFT can be expressed [2] in terms of the KS response function  $\chi_s$ , the Coulomb interaction  $v$ , and  $f_{xc}$

$$\chi(\omega) = \chi_s(\omega) + \chi_s(\omega)[v + f_{xc}(\omega)]\chi(\omega). \quad (1)$$

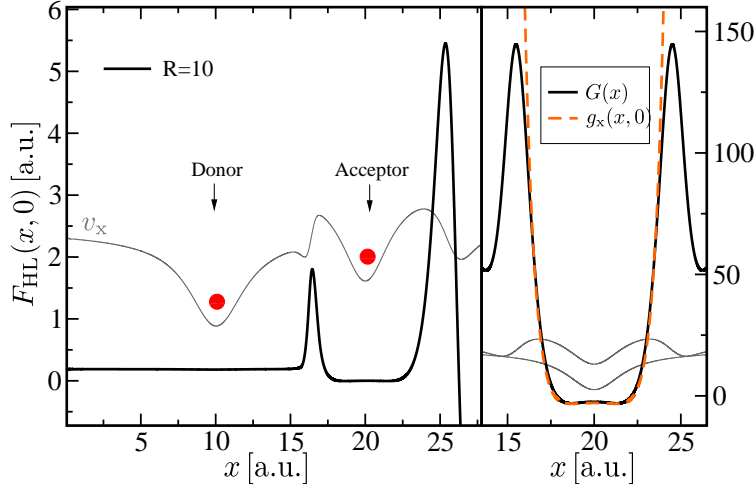


FIG. 1: Left:  $f_{xc}$  and  $v_{xc}$  of a dissociating He-Be<sup>2+</sup> system. Right: Discontinuity of the Be<sup>2+</sup> atom.

In this work we have evaluated the discontinuities of  $f_{xc}$  in order to increase the understanding of its exact behavior [3]. The discontinuities of  $f_{xc}$  turned out to be of a more complex nature than those of  $v_{xc}$ , where the general structure is an  $\mathbf{r}$ - and  $\omega$ -dependent function  $g_{xc}(\mathbf{r}, \omega)$ , which may diverge. In order to obtain an exact expression for the discontinuity we study the limiting behavior of  $E_{xc}$  as a function of particle number  $N$  around an integer  $N_0$ . The constant jump in  $v_{xc}$  can then formally be written as

$$\Delta_{xc} = \left. \frac{\partial E_{xc}}{\partial N} \right|_+ - \int d\mathbf{r} v_{xc}^-(\mathbf{r}) f^+(\mathbf{r}), \quad (2)$$

where  $f(\mathbf{r}) = \partial n(\mathbf{r}) / \partial N$  is the Fukui function. The same idea can then be used for the static XC kernel and we find an expression for  $g_{xc}$

$$\begin{aligned} \int d\mathbf{r} \chi(\mathbf{r}_1, \mathbf{r}) g_{xc}(\mathbf{r}) &= \frac{\delta}{\delta w(\mathbf{r}_1)} \left. \frac{\partial E_{xc}}{\partial N} \right|_+ \\ &\quad - \int d\mathbf{r} v_{xc}^+(\mathbf{r}) \frac{\delta f^+(\mathbf{r})}{\delta w(\mathbf{r}_1)} \\ &\quad - \int d\mathbf{r} d\mathbf{r}' \chi(\mathbf{r}_1, \mathbf{r}) f_{xc}^-(\mathbf{r}, \mathbf{r}') f^+(\mathbf{r}'). \end{aligned} \quad (3)$$

After performing a common denominator approximation to the response functions it is easy to see that the second term exhibits a diverging behavior  $g_{xc}(\mathbf{r}) \propto e^{2(\sqrt{I} - \sqrt{A_s})r}$  which depends on the difference between the ionization energy  $I$  and the KS affinity  $A_s$ . This divergency can be seen in  $f_{xc}$  of the dissociating system in Fig. 1 where the calculations have been made in the exact-exchange approximation, which is known to have a discontinuity. The

right panel of Fig. 1 displays  $g_{xc}$ , calculated in the same approximation but defined on an ensemble which allows for fractional charges. A striking similarity can be seen and we can conclude that the peaked structure in the XC kernel of a dissociating system is just the discontinuity of the kernel.

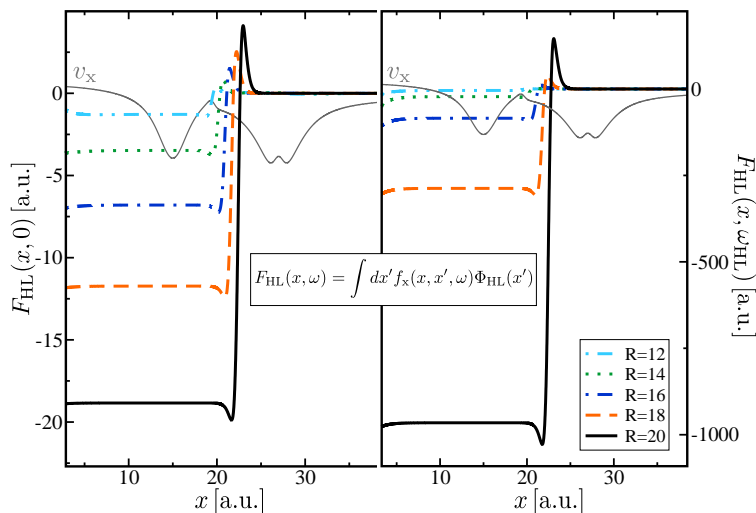


FIG. 2:  $v_{xc}$  and  $f_{xc}$  at  $\omega = 0$  and  $\omega_{KS}$  of a dissociating He-Be system.

A diverging behavior of the kernel is exactly what is needed in order to describe charge-transfer (CT) excitations. The reason is that Eq. (1) involves only matrix elements of  $f_{xc}$  between so-called excitation functions, i.e., products of occupied and unoccupied KS orbitals. As the distance between the fragments increases these products vanish exponentially and thus there is no correction to the KS eigenvalue differences unless the kernel diverges. The formulation of TDDFT for fractional charges has to allow the particle number to change in time and we have therefore proposed an ensemble of the form  $\hat{\rho}(t) = \sum_k \alpha_k(t) |\Psi_k(t)\rangle \langle \Psi_k(t)|$ , where  $\Psi_k(t)$  is the  $k$ -particle many-body state at time  $t$  and  $\alpha_k(t)$  are given TD probabilities. A Runge-Gross theorem can be proved also in this case allowing for an analysis of the same kind as in the static case. The function  $g_{xc}$  acquires an  $\omega$ -dependence and Fig. 2 illustrates the difference compared to the static case showing mainly an increase of the exponential growth. This increase is, however, crucial for the description of CT excitations, as seen in Fig. 3, where AEXX uses  $f_x(\omega = 0)$  and TDEXX uses  $f_x(\omega_{KS})$ .

Apart from playing an important role for the excitation energies also the orbitals are affected by the discontinuity. Within chemical reactivity the Fukui function  $f(\mathbf{r})$  as defined above is an important reactivity indicator. The Fukui function can be expressed as [4]  $f^\pm = f_0^\pm + \chi f_{Hxc}^\pm f_0^\pm$ , and we see that a discontinuity of  $f_{xc}$  does not cancel when determining

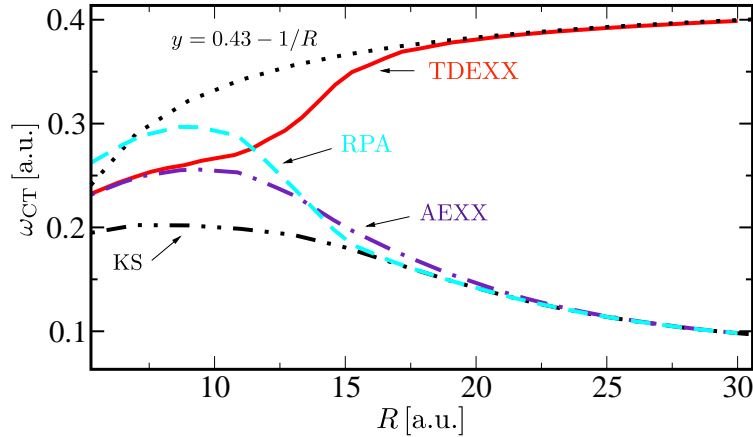


FIG. 3: CT excitation energies of system in Fig. 2 in different approximations.

$f^+$ . This contribution can be very large for certain molecules as shown in Fig. 4.

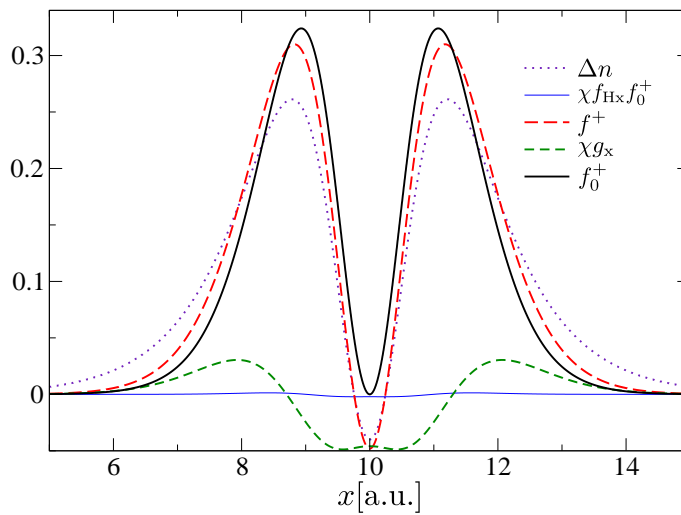


FIG. 4: The Fukui function  $f^+$  of a 1D  $\text{Be}^{2+}$  atom.

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