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The linear response function $\chi(r, r')$: another perspective

Samir Kenouche[1] · **Jorge I. Martínez-Araya**[2]

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Abstract

In this paper, we propose a conceptual approach to assign a "mathematical meaning" to the non-local function $\chi(\mathbf{r}, \mathbf{r}')$. Mathematical evaluation of this kernel remains difficult since it is a function depending on six Cartesian coordinates. The idea behind this approach is to look for a limit process in order to explore mathematically this non-local function. According to our approach, the bra $\langle \chi_{r'}^{\xi}|$ is the linear functional that corresponds to any ket $|\psi\rangle$, the value $\langle \mathbf{r}'|\psi\rangle$. In condensed writing $\langle \chi_{r'}^{\xi}|\,\langle \mathbf{r}|\psi\rangle = \langle \mathbf{r}'|\psi\rangle$, and this is achieved by exploiting the sifting property of the delta function that gives it the sense of a measure, i.e. measuring the value of $\psi(\mathbf{r})$ at the point $\mathbf{r}'$. It is worth noting that $\langle \chi_{r'}^{\xi}|$ is not an operator in the sense that when it is applied on a ket, it produces a number $\psi(\mathbf{r} = \mathbf{r}')$ and not a ket. The quantity $\chi_{r'}^{\xi}(\mathbf{r})$ proceed as nascent delta function, turning into a real delta function in the limit where $\xi \to 0$. In this regard, $\chi_{r'}^{\xi}(\mathbf{r})$ acts as a limit of an integral operator kernel in a convolution integration procedure.

Keywords Conceptual DFT · Linear response function · Dirac distribution

1 Introduction

Conceptual Density Functional Theory (noted C-DFT) is defined as the theory of chemical reactivity aimed to extract chemical concepts from the DFT [1]. This formalism constitutes a paradigm for understanding chemical reactivity and selectivity in chemistry. Its foundation was established in 1978 by Parr et al. [2], through the identification of the Lagrange multiplier $\mu = \left[\frac{\partial E}{\partial \rho(r)}\right]_{\upsilon(r)}$ with the electronic chemical potential. This

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✉ Jorge I. Martínez-Araya
jorge.martinez@unab.cl

[1] Modeling of Chemical Systems Using Quantum Calculations, LCA Laboratory, University of Biskra, 07000 Biskra, Algeria

[2] Departamento de Ciencias Químicas, Facultad de Ciencias Exactas, Universidad Andres Bello (UNAB), Av. República 275, 8370146 Santiago, Chile

thermodynamic quantity refers to the stabilization or destabilization during the addition or subtraction of an electron and its is linked to fundamental concepts in chemistry such as electronegativity, electronic affinity and ionization potentials [3]. The C-DFT is originally built on the energy functional in the canonical set: $E[\rho(\mathbf{r})] = E[N, \upsilon(\mathbf{r})]$, where E refers to the energy of the system, N its number of electrons and $\upsilon(\mathbf{r})$ represents the external potential at position $\mathbf{r}$. However, there are other equivalent sets of representations that involve different variables [4]. The consequences of derivative discontinuity for C-DFT have already been examined [5], since the number of electrons is a discrete variable. The Taylor series of the energy functional $E[N, \upsilon(\mathbf{r})]$ provides several response functions expressed in the canonical set [4]:

$$\begin{aligned} E[N, \upsilon(\mathbf{r})] \; &= \left[N \left(\frac{\partial E}{\partial N} \right)_{\upsilon(\mathbf{r})} + \int d\mathbf{r} \left(\frac{\partial E}{\partial \upsilon(\mathbf{r})} \right)_N \upsilon(\mathbf{r}) \right] \\ &\quad - \frac{1}{2} \left[N^2 \left(\frac{\partial^2 E}{\partial N^2} \right)_{\upsilon(\mathbf{r})} + 2N \int d\mathbf{r} \frac{\partial}{\partial N} \left(\frac{\partial E}{\partial \upsilon(\mathbf{r})} \right)_N \upsilon(\mathbf{r}) \right. \\ &\quad \left. + \int d\mathbf{r} d\mathbf{r}' \underbrace{\left(\frac{\partial^2 E}{\partial \upsilon(\mathbf{r}) \upsilon(\mathbf{r}')} \right)_N}_{\chi(\mathbf{r},\mathbf{r}')} \upsilon(\mathbf{r}) \upsilon(\mathbf{r}') + \cdots \right] \end{aligned} \tag{1}$$

This formula is not a perturbation expansion, the negative signs are very instructive for its implications in this theory. For the interested reader, the perturbative formula is available at the reference [6]. The general expression for successive partial derivatives is given by [7]:

$$\frac{\delta^b}{\delta \upsilon(\mathbf{r_1}) \delta \upsilon(\mathbf{r}_2) \cdots \delta \upsilon(\mathbf{r}_b)} \left[\frac{\partial^a E}{\partial N^a} \right] \tag{2}$$

The non-local second order derivative ($a = 0, b = 2$) of the canonical set corresponds to the linear response function $\chi(\mathbf{r}, \mathbf{r}')$ (noted LRF). It is a non-local descriptor depending on two positions $\mathbf{r}$ and $\mathbf{r}'$.

$$\chi(\mathbf{r}, \mathbf{r}') = \left[\frac{\delta^2 E}{\delta \upsilon(\mathbf{r}) \delta \upsilon(\mathbf{r}')} \right]_N \tag{3}$$

The function $\chi(\mathbf{r}, \mathbf{r}')$ is defined as the electron density response at $\mathbf{r}$ induced by a change in the external potential at $\mathbf{r}'$ (and vice versa) [7]:

$$\chi(\mathbf{r}, \mathbf{r}') = \left[\frac{\delta \rho(\mathbf{r})}{\delta \upsilon(\mathbf{r}')} \right]_N \tag{4}$$

Mathematical evaluation of this kernel remains difficult since it is a function depending on six Cartesian coordinates. Concerning its chemical interpretation, the LRF is related to the structure of the atomic electronic layers [8, 9], to the polarisability [10], to the inductive and mesomeric effects [11, 12] as well as to the aromaticity [13, 14] in molecules. The LRF has also proved a valuable tool for assessing and interpreting molecular conductivity [15]. Furthermore, many other interesting applications have been reported in the biological/pharmaceutical field, on the decomposition mechanism of explosives, and transferability of functional groups [16–20]. The LRF can be evaluated at several levels of approximation using the perturbative approach within a Kohn–Sham formalism [21–25]. This approach is very helpful because it is consistent with the chemical intuition that chemical reactivity is examined according to a perturbation undergone by a molecule when it is approached by another molecule. In the present study, we attempt to assign a mathematical "meaning" to LRF by combining both the properties of delta function and the formalism inherent in quantum mechanics.

2 Mathematical meaning of $\chi(\mathbf{r}, \mathbf{r}')$

Some fundamental notions of quantum mechanics are given in ESI (Electronic Supporting Information). These notions are helpful especially for readers who are not familiar with the notation of quantum mechanics and will also be useful to make the link with the subject treated in this study. Moreover, all the basic mathematical details on the functional derivatives are rigorously defined in the following references [26–28]. For simplification purposes, let us consider $\mathcal{F}$ as a set of continuous and real-valued functions ($g : \mathbb{R}^3 \to \mathbb{R}$). For assessing the "action" of a distribution, we rely on sufficiently regular functions with compact support. We denote by $D_c^{\infty}(\mathbb{R})$ the space of functions $g(\mathbf{r})$ of class $D^{\infty}(\mathbb{R})$ which vanish, as well as all their derivatives, outside a closed and bounded interval. Such functions form a set of infinitely-differentiable functions of compact support. Then, consider any functional F that maps each $g \in \mathcal{F}$ to a number: $F : \mathcal{F} \to \mathbb{R}$. By using the derivation rules of the density functionals, we obtain:

$$\delta F := F\big[g(\mathbf{r}) + \delta g(\mathbf{r})\big] - F\big[g(\mathbf{r})\big] \quad \equiv \quad \delta F := F\big[g(\mathbf{r}) + h\eta(\mathbf{r})\big] - F[g(\mathbf{r})] \tag{5}$$

The variation of $g(\mathbf{r})$ by $\delta g(\mathbf{r})$ generates $\delta F[g(\mathbf{r})]$. The functional $F\big[g(\mathbf{r})+h\eta(\mathbf{r})\big]$ is expanded in terms of powers of h according to the Taylor series:

$$F\big[g(\mathbf{r}) + h\eta(\mathbf{r})\big] = \sum_{k=0}^{K} \frac{1}{k!} \left.\frac{d^k F\big[g(\mathbf{r}) + h\eta(\mathbf{r})\big]}{dh^k}\right|_{h=0} h^k + \mathcal{O}(h^{K+1}) \tag{6}$$

where K being either finite or infinite, h is a scalar and η is an arbitrary function in $\mathcal{F}$. The functional derivative of k^{th} order is defined by:

$$\left.\frac{d^k F\big[g(\mathbf{r}) + h\eta(\mathbf{r})\big]}{dh^k}\right|_{h=0} =: \int d\mathbf{r}_1 \cdots d\mathbf{r}_k \frac{\delta^k F\big[g(\mathbf{r})\big]}{\delta g(\mathbf{r}_1)\cdots\delta g(\mathbf{r}_k)}\, \eta(\mathbf{r}_1)\cdots\eta(\mathbf{r}_k) \tag{7}$$

For $k = 1$ we obtain:

$$\lim_{h\to 0}\frac{F\big[g(\mathbf{r}) + h\eta(\mathbf{r})\big] - F[g(\mathbf{r})]}{h} =: \left.\frac{dF\big[g(\mathbf{r}) + h\eta(\mathbf{r})\big]}{dh}\right|_{h=0} =: \int d\mathbf{r}\frac{\delta F\big[g(\mathbf{r})\big]}{\delta g(\mathbf{r})}\, \eta(\mathbf{r}) \tag{8}$$

By reducing h to an infinitesimally small number, $g(\mathbf{r})+h\eta(\mathbf{r})$ will become close to $g(\mathbf{r})$, since the quantity $h\eta(\mathbf{r})$ describes the infinitesimal change to $g(\mathbf{r})$. A functional for which (8) is verified is considered differentiable. From another point of view, the functional can be expressed in integral form as:

$$F\big[g(\mathbf{r})\big] = \int d\mathbf{r}\, \delta(\mathbf{r} - \mathbf{r}_0)\, g(\mathbf{r}) = g(\mathbf{r}_0) \tag{9}$$

where the generalized function $\delta(\mathbf{r} - \mathbf{r}_0)$ plays the role of a weight function. In the same way, we can also write:

$$F\big[g(\mathbf{r})\big]^n = \int d\mathbf{r}\, \delta(\mathbf{r} - \mathbf{r}_0)\, g(\mathbf{r})^n = g(\mathbf{r}_0)^n \tag{10}$$

The variation of this functional is calculated by a simple Taylor expansion, then:

$$\delta F\big[g(\mathbf{r})\big]^n = \int d\mathbf{r}\, \delta(\mathbf{r} - \mathbf{r}_0)\left[\, (g(\mathbf{r}) + h\eta(\mathbf{r}))^n - g(\mathbf{r})^n\right] \tag{11}$$

$$= \int d\mathbf{r}\, \delta(\mathbf{r} - \mathbf{r}_0)\left[ng(\mathbf{r})^{n-1}\, h\eta(\mathbf{r}) + \frac{n(n-1)}{2} g(\mathbf{r})^{n-2}\, (h\eta(\mathbf{r}))^2 + \cdots\right] \tag{12}$$

By comparing (8) and (12), the result is:

$$\frac{\delta F\big[g(\mathbf{r})\big]^n}{\delta g(\mathbf{r})} = \frac{\delta g(\mathbf{r}_0)^n}{\delta g(\mathbf{r})} = \delta(\mathbf{r} - \mathbf{r}_0)\, n\, g(\mathbf{r})^{n-1} \tag{13}$$

$$\text{For} \quad n = 1 \quad \Rightarrow \quad = \frac{\delta g(\mathbf{r}_0)}{\delta g(\mathbf{r})} = \delta(\mathbf{r} - \mathbf{r}_0) = \delta(\mathbf{r}_0 - \mathbf{r}) \tag{14}$$

Applying this definition to LRF within the C-DFT framework, we find:

$$\chi(\mathbf{r}, \mathbf{r}') = \left[\frac{\delta^2 E}{\delta v(\mathbf{r})\delta v(\mathbf{r}')}\right]_N = \delta(\mathbf{r} - \mathbf{r_0})\delta(\mathbf{r}' - \mathbf{r_0}) = \delta(\mathbf{r} - \mathbf{r}') \tag{15}$$

This equality means that one of the members can be replaced by the other when it is under an integration symbol with respect to $\mathbf{r}$. Suppose a set of functions of $\mathbf{r}$, $\chi_{r'}(\mathbf{r})$, marked by the continuous index $\mathbf{r}'$ and defined by:

$$\chi_{r'}(\mathbf{r}) = \delta(\mathbf{r} - \mathbf{r}') = \delta(x - x')\, \delta(y - y')\, \delta(z - z') \tag{16}$$

Actually, $\chi_{r'}(\mathbf{r})$ represents the set of functions centered at $\mathbf{r}'$. We have already written the following equality (see Eq. 5 in ESI):

$$\psi(\mathbf{r}) = \int \psi(\mathbf{r}')\, \delta(\mathbf{r} - \mathbf{r}')\, d^3 r' \tag{17}$$

The integration bounds $-\infty$ and $+\infty$ have been issued to avoid unnecessarily burdening the mathematical writings. The integral (17) is a functional of $\psi(\mathbf{r}')$ depending on $\mathbf{r}$ as a parameter. The terms "function of a function" or "functional transform" are commonly used for functions that themselves depend on variables. Then,

$$\psi(\mathbf{r}') = \int \delta(\mathbf{r}' - \mathbf{r})\, \psi(\mathbf{r})\, d^3 r \tag{18}$$

That we can also write as:

$$\psi(\mathbf{r}) = \int \psi(\mathbf{r}')\, \chi_{r'}(\mathbf{r})\, d^3 r' \tag{19}$$

And,

$$\psi(\mathbf{r}') = \int \chi_{r'}(\mathbf{r})^*\, \psi(\mathbf{r})\, d^3 r \tag{20}$$

The relation (19) states that any wave function can be expanded in a unique way along $\chi_{r'}(\mathbf{r})$. In contrast, the relation (20) denotes that the component of $\psi(\mathbf{r})$ on $\chi_{r'}(\mathbf{r})$ is specifically $\psi(\mathbf{r}') = \psi(\mathbf{r} = \mathbf{r}')$. In this regard, the relation (20) is equivalent to that of c_n (see ESI for more details):

$$c_n = \int n(\mathbf{r})^*\, \psi(\mathbf{r})\, d^3 r \tag{21}$$

Therefore, $\psi(\mathbf{r}')$ is the equivalent of c_n, these two complex numbers represent the coordinates of the same $\psi(\mathbf{r})$ function in two different basis $\{\chi_{r'}(\mathbf{r})\}$ and $\{n(\mathbf{r})\}$. Let us also mention that the functions of the basis $\{\chi_{r'}(\mathbf{r})\}$ are orthonormal and verify the closure relation:

$$\int \chi_{r'}(\mathbf{r})\, \chi_{r'}(\mathbf{r}'')^*\, d^3 r' = \int \delta(\mathbf{r} - \mathbf{r}')\, \delta(\mathbf{r}'' - \mathbf{r}')\, d^3 r' = \delta(\mathbf{r} - \mathbf{r}'') \tag{22}$$

And,

$$\langle \chi_{r'} | \chi_{r''} \rangle = \int \delta(\mathbf{r} - \mathbf{r}')\, \delta(\mathbf{r} - \mathbf{r}'')\, d^3r = \delta(\mathbf{r}' - \mathbf{r}'') \tag{23}$$

Strictly speaking, $|\chi_r\rangle$ is not square integrable and therefore $\notin \mathcal{H}$ (does not belong to the state space), since:

$$\mathbf{r} = \mathbf{r}' \Rightarrow \int \underbrace{\delta(\mathbf{r} - \mathbf{r}')}_{\delta(0)}\, d^3r \longrightarrow \infty \tag{24}$$

It is indispensable that any acceptable function be square integrable, otherwise the inner product is inexistent. Although $|\chi_r\rangle$ does not describe the state of a system, it is a very useful computational intermediate for operations on $\psi(\mathbf{r})$, which can describe a physical state. However, it is still possible to assign a very localized summable square function around $\mathbf{r}'$: $\chi^{\xi}_{r'}(\mathbf{r}) = \delta^{\xi}(\mathbf{r} - \mathbf{r}')$, where $\chi^{\xi}_{r'}(\mathbf{r})$ exhibits a peak of width ξ and height $1/\xi$ centered at $\mathbf{r}'$, such that:

$$\int \chi^{\xi}_{r'}(\mathbf{r})\, d^3r = 1 \tag{25}$$

In such situation $\chi^{\xi}_{r'}(\mathbf{r})$ denotes a function in the usual meaning, which can be a Gaussian, Lorentzian in absorption or a retangular function. The set of functions $\chi^{\xi}_{r'}(\mathbf{r})$ then naturally takes the name of the set of trial functions or nascent delta function [29, 30]. These few examples of trial functions have a width of order ξ and a maximum amplitude of order ξ^{-1}, which systematically gives an integral of $\xi \times \xi^{-1} = 1$. When $\lim_{\xi \to 0} \chi^{\xi}_{r'}(\mathbf{r}) = \chi_{r'}(\mathbf{r})$ which is not square integrable, then if $\xi \neq 0 \Rightarrow |\chi^{\xi}_{r'}\rangle \in \mathcal{H}$ and $\langle \chi^{\xi}_{r'}| \in \mathcal{H}^*$ (the dual space). Then we can write $\forall\, |\psi\rangle \in \mathcal{H}$:

$$\langle \chi^{\xi}_{r'} | \psi \rangle = \int \chi^{\xi}_{r'}(\mathbf{r}) \psi(\mathbf{r})\, d^3r \tag{26}$$

In addition,

$$\psi(\mathbf{r}) = \psi(\mathbf{r}') \;\Rightarrow\; \langle \chi^{\xi}_{r'} | \psi \rangle = \psi(\mathbf{r}') \int \chi^{\xi}_{r'}(\mathbf{r})\, d^3r \tag{27}$$

The relation (27) should be perceived as the result of a limiting process. In particular,

$$\xi \to 0 \Rightarrow \int \chi^{\xi}_{r'}(\mathbf{r})\, d^3r = 1 \Rightarrow \langle \chi^{\xi}_{r'} | \psi \rangle = \langle \mathbf{r}' | \psi \rangle \tag{28}$$

Which can also be written as,

$$\langle \chi^{\xi}_{r'} |\, \langle \mathbf{r} | \psi \rangle = \langle \mathbf{r}' | \psi \rangle \quad \equiv \quad \langle \chi^{\xi}_{r'} | \mathbf{r} \rangle \langle \mathbf{r} | \psi \rangle = \langle \mathbf{r}' | \psi \rangle \quad \equiv \quad \chi^{\xi}_{r'}(\psi(\mathbf{r})) = \psi(\mathbf{r}') \tag{29}$$

Therefore, the bra $\langle \chi^{\xi}_{r'}|$ is the linear functional (or linear form) that corresponds to any ket $|\psi\rangle$, the value $\psi(\mathbf{r})$ taken at $\mathbf{r}'$. The relation (28) indicates that $\chi^{\xi}_{r'}$ is homogeneous to the inverse of the dimension of $\mathbf{r}$. It is worth noting that $\langle \chi^{\xi}_{r'}|$ is not an operator in the sense that when it is applied on a ket, it produces a number $\psi(\mathbf{r} = \mathbf{r}')$ and not a ket. The set of all linear functionals form a dual vector space. More generally, we can write for all regular functions, as small as ξ ($\xi << b - a$):

$$\int_a^b \chi^{\xi}_{r'}(\mathbf{r})\, \psi(\mathbf{r})\, d^3r \simeq \psi(\mathbf{r}') \tag{30}$$

And then,

$$\lim_{\xi \to 0} \int_a^b \chi^{\xi}_{r'}(\mathbf{r})\, \psi(\mathbf{r})\, d^3r = \psi(\mathbf{r}') \tag{31}$$

The displacement of the peak does not affect the total area if the interval from a to b contains the peak. From this point of view, $\chi^{\xi}_{r'}(\mathbf{r})$ is related to $\psi(\mathbf{r})$ in an integral whose integration interval contains not only $\mathbf{r}$ but also the finite interval ξ, for which $\chi^{\xi}_{r'}(\mathbf{r})$ is not null. Thus, $\chi^{\xi}_{r'}(\mathbf{r})$ is only defined in terms of a limit, and/or in terms of how it behaves inside integrals, it is not actually a function but rather a generalized function or a functional. This is equivalent to a physical system where its linear response to the functions $\chi^{\xi}_{r'}(\mathbf{r})$ is known for any $\psi(\mathbf{r})$ input, whatever its complexity. This is even more true as ξ tends to zero. Moreover, the variables $\mathbf{r}$ and $\mathbf{r}'$ are obviously defined on the same interval and play a symmetrical role since $\chi^{\xi}_{r'}(\mathbf{r}) = \chi^{\xi}_{r}(\mathbf{r}')$ (or equivalently $\delta(\mathbf{r} - \mathbf{r}') = \delta(\mathbf{r}' - \mathbf{r})$). This last equality shows that $\chi^{\xi}_{r'}$ is an even function. These two last integrals correspond to a translation of the initial wave function by one value of $\mathbf{r}'$, which can be seen as a convolution product by $\chi^{\xi}_{r'}(\mathbf{r})$. The wave function $\psi(\mathbf{r})$ is invariant, it is just shifted. Provided that it exists, the convolution between $\chi^{\xi}_{r'}(\mathbf{r})$ and $\psi(\mathbf{r})$ has the Fourier transform $\sqrt{2\pi}\, F(u)\, G(u)$, where $F(u)$ and $G(u)$ are the Fourier transforms of $\chi^{\xi}_{r'}(\mathbf{r})$ and $\psi(\mathbf{r})$ respectively, and this transformation is reciprocal.

3 Conclusion

In this study, we have attempted to clarify the mathematical meaning of the linear response function (LRF) through a purely conceptual approach. The idea behind this approach is to look for a limit process in order to explore mathematically this non-local function. Formally, LRF has been defined from classical tools of mathematical analysis through a limit process. The limit process has been presented in a somewhat general way, but it is relatively easy to make it explicit by choosing a function (a kind of trial function) reproducing $\chi^{\xi}_{r'}$. For instance, this function can be a Gaussian or a Lorentzian, one thing is certain whatever the chosen function, at the limit all these functions generate the Dirac distribution. Moreover, by reasoning before the limit step, it is possible to analyze the operational role of the $\chi^{\xi}_{r'}$ functions, if a difficulty arises after the application of this rule of thumb, it is still possible to go back and introduce a new $\chi_{r'}^{\xi}$ with the appropriate physical scales of the analyzed problem and to perform the limit step correctly. The introduction of $\chi_{r'}^{\xi}$ is justified since all measuring instruments exhibit a spatial extension. Convolution of $\psi(\mathbf{r})$ with $\chi_{r'}^{\xi}$ at $\mathbf{r}'$ is equivalent to shifting ψ by $\mathbf{r}'$. The idea of convolution by $\chi_{r'}^{\xi}$ is consistent with an electron density ($\rho(\mathbf{r}) = |\psi(\mathbf{r})|^2$) shift that is physically similar to a polarization and electron delocalization phenomenon.

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Data availability Not applicable.

Declarations

Conflict of interest There are no financial interests.

Ethical approval Not applicable.

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