Relationships between charge density response functions, exchange holes and localized orbitals

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Abstract

The charge density response function and the exchange hole are closely related to each other via the fundamental fluctuation-dissipation theorem of physics. A simple approximate model of the static response function is visually compared on several examples in order to demonstrate this relationship. This study is completed by illustrating the well-known isomorphism between the exchange hole and the square of the dominant localized orbital lying in the space region of the reference point of the exchange hole function. The implications of these relationships for the interpretation of common chemical concepts, such as delocalization, are discussed.

Keywords: charge density response function, Fermi-hole, localized orbitals, electron localization, topological analysis

1. Introduction

To establish links between the wave function and chemical concepts characterizing the structure and reactivity of atoms, molecules, solids and interfaces has always been a considerable challenge for computational and theoretical chemistry. Although this is a subject which has been in the focus of scientists since the very beginning of quantum chemistry, the development of Conceptual Quantum Chemistry tools remains even in our days a dynamically developing domain, producing new ideas and leading to a deeper understanding of old concepts. This research activity betrays a natural need for having a sound basis of quantitative or semi-quantitative characterization of chemical objects and their interaction in the framework of concepts, which are most often deeply rooted in chemical thinking. Technically it means that one has to extract specific parameters from many-electron wave functions of high complexity, which are able to quantify or illustrate concepts.

If we are to identify some trends in the evolution of conceptual tools over the decades, one of the most remarkable feature is that the definition of extracted quantities become more and more independent of any specific approximation scheme and are rooted more and more in true observables. On the one hand, at the beginning, quantities like bond orders and atomic populations were constructed directly from intermediate quantities of popular quantum chemical approximations (molecular orbitals, populations analysis in a given basis set, valence bond configurations, . . .) which could not be interpreted outside the scope of a given computational scheme. On the other hand, in the course of the last 20 years, researchers made an effort to define generally applicable conceptual measures and indices, which are valid independently of any quantum chemical approximation method. Emblematic examples of such approximation-independent concepts are atomic multipoles defined on the basis of the topological partitioning of the electron density [1], delocalization indices between topologically defined atoms [2–6] or, more recently, the total position spread (TPS) [7], based on the localization tensor of Resta [8]. Various measures of electron localization, like the electron localization function (ELF) [9–11], and other analogous functions of the three-dimensional space [12–14] are also defined in a universal manner, without referring to specific notions which would be valid only in the realm of a particular approximate electronic structure method. Such a philosophy has not only the advantage of making possible a judicious comparison of results obtained from different electronic structure methods (e.g. atomic charges obtained from Gaussian and plane-wave basis set calculations), but opens the way to the comparison of theoretical values directly with the experiment. For instance, atomic charges and Laplacians derived from the QTAIM (Quantum Theory of Atoms In Molecules) of Bader can be derived not only from computed, but also from experimental electron densities obtained from high-resolution X-ray diffraction data [15–18].

Inspired by the works of Parr and his coworkers [19], a whole family of functions have been defined in the framework of the Conceptual Density Functional Theory, leading to a formally rigorous interpretation of the chemical potential of an electronic system as the functional derivative of the electronic energy with respect to the number of electrons, and of the linear charge density response function as the functional derivative of

the electronic energy with respect to the external potential [20]. One can define quantities like hardness, softness, Fukui function, ... *via* various higher order and mixed derivatives [21]. It has to be stressed that these definitions are fully general and valid not only in DFT but, in principle, at any level of modern electronic structure theory. Among all these quantities, we are going to be concerned mainly by the softness, more precisely by the softness kernel.

The relevance of the linear charge density response function, which is called by some authors *linear response kernel* and which is equal to the negative of the softness kernel, for the characterization of localization/delocalization properties of an electronic system has been recognized in the past by several authors. The remarkable correlation between atom-atom softnesses *i.e.* atomic partition of the linear response functions and atom-atom delocalization indices have been pointed out through the example of Y-conjugated compounds [22, 23]. The properties of the linear density-density response and its eigenvalue decomposition have been used by Savin and his coworkers to analyze the strong density-dependence of the Kohn-Sham potential in density functional theory [24] and the radial density-density response function has been analyzed for a series of atoms along the adiabatic connection path [25].

More recently, in a series of papers [26–32], Geerlings and his coworkers have analyzed the distribution of the charge density response in the space for atoms and molecules. One possibility to study this quantity is to calculate the atom-condensed linear response parameters, corresponding to the charge-flow polarizabilities in the general distributed polarizability theory of Stone [33, 34]. Distributed polarizabilities can be implemented in the context of various definitions of atoms in molecules (AIM). The possibilities cover a wide range of definitions of AIM, going from the partition of the basis functions to the Hirshfeld-like fuzzy [35] or to the QTAIM [1] discontinuous partitioning of the space. QTAIM charge-flow polarizabilities have been introduced first in [36].

The full non-expanded density-density response kernel, calculated in the uncoupled perturbed Hartree-Fock theory, has been plotted in Ref. [30] for a few planar metallic and simple organic systems in view of characterizing their aromaticity. The connection of the response kernel to the delocalization and to induction and resonance effects have been discussed in Refs. [26, 27].

In the present contribution, we discuss not only a few more examples to illustrate the behavior of the linear density-density response kernel for molecular systems as plots of the charge deformation due to a perturbation in a fixed point in the space, but we attempt to point out and to demonstrate the possible relationships between the response kernel and the exchange (or Fermi) hole function. Furthermore, the well-known connection between the exchange hole and localized orbitals is also illustrated.

2. Basic relationships

2.1. *Exact response and exchange-correlation hole functions*

Using the definition of the two-particle (pair) density operator $\hat{n}_2(\mathbf{r}_1, \mathbf{r}_2)$ in terms of the one-particle density operator $\hat{n}(\mathbf{r}_1)$ and of $\delta(\mathbf{r}_1, \mathbf{r}_2)$, the Dirac delta function defined later:

$$\hat{n}_2(\mathbf{r}_1, \mathbf{r}_2) = \hat{n}(\mathbf{r}_1)\hat{n}(\mathbf{r}_2) - \delta(\mathbf{r}_1, \mathbf{r}_2)\hat{n}(\mathbf{r}_1), \qquad (1)$$

and the definition of the exchange-correlation hole in terms of the expectation values $n(\mathbf{r}_1)$ and $n_2(\mathbf{r}_1, \mathbf{r}_2)$:

$$h_{xc}(\mathbf{r}_1, \mathbf{r}_2) = \frac{n_2(\mathbf{r}_1, \mathbf{r}_2)}{n(\mathbf{r}_1)} - n(\mathbf{r}_2), \qquad (2)$$

one can deduce the following relationship:

$$\begin{aligned} n(\mathbf{r}_1)h_{xc}(\mathbf{r}_1, \mathbf{r}_2) &= n_2(\mathbf{r}_1, \mathbf{r}_2) - n(\mathbf{r}_1)n(\mathbf{r}_2) \\ &= \langle \hat{n}_2(\mathbf{r}_1, \mathbf{r}_2) \rangle - \langle \hat{n}(\mathbf{r}_1) \rangle \langle \hat{n}(\mathbf{r}_2) \rangle \\ &= \langle \hat{n}(\mathbf{r}_1)\hat{n}(\mathbf{r}_2) \rangle - \delta(\mathbf{r}_1, \mathbf{r}_2)\langle \hat{n}(\mathbf{r}_1) \rangle - \langle \hat{n}(\mathbf{r}_1) \rangle \langle \hat{n}(\mathbf{r}_2) \rangle \\ &= \langle \delta\hat{n}(\mathbf{r}_1)\delta\hat{n}(\mathbf{r}_2) \rangle - \delta(\mathbf{r}_1, \mathbf{r}_2)\langle \hat{n}(\mathbf{r}_1) \rangle, \end{aligned} \qquad (3)$$

where $\langle \hat{O} \rangle = \langle \Psi_0 | \hat{O} | \Psi_0 \rangle$ denotes a ground state expectation value, and we use the decomposition of the density operator as a fluctuation $\delta\hat{n}(\mathbf{r}_1)$ around its mean: $\hat{n}(\mathbf{r}_1) = n(\mathbf{r}_1) + \delta\hat{n}(\mathbf{r}_1)$. The Dirac delta function $\delta(\mathbf{r}_1, \mathbf{r}_2) = \delta(\mathbf{r}_2 - \mathbf{r}_1)$ is usually defined in the most general terms via its sifting property [37]

$$\int d\mathbf{r}_1 \, f(\mathbf{r}_2) \, \delta(\mathbf{r}_2 - \mathbf{r}_1) = f(\mathbf{r}_1). \qquad (4)$$

There are numerous options to represent $\delta(\mathbf{r}_2 - \mathbf{r}_1)$ by the limiting value of a series of functions, like in Eq. (13).

Eq. (3) leads to:

$$\langle \delta\hat{n}(\mathbf{r}_1)\delta\hat{n}(\mathbf{r}_2) \rangle = \delta(\mathbf{r}_1, \mathbf{r}_2)n(\mathbf{r}_1) + n(\mathbf{r}_1)h_{xc}(\mathbf{r}_1, \mathbf{r}_2). \qquad (5)$$

The right-hand side of the above equation is usually referred to as the static form factor (cf. Ref. [38]). As we can see, Eq. (5) establishes a relationship between the density-weighted hole function and the *fluctuations* of the charge density, fluctuations that are themselves related to the response function by the virtue of the (zero-temperature) fluctuation-dissipation theorem. In the following we derive an approximate relationship between Eq. (5) and the *static* response function.

We proceed by the technique of effective denominators, usually related to the name of Unsöld [39] and which has been later generalized by others, e.g. [40–42]. The aim of this technique is to replace the state-specific energy denominator in the sum-over-states expression of the response function by a constant and to transform the sum over the excited states in the numerator to a ground state expectation value by invoking the resolution of identity.

Using the shorthand notation for the transition density associated with the α excited state $n_\alpha(\mathbf{r}_1) = \langle \Psi_0 | \hat{n}(\mathbf{r}_1) | \Psi_\alpha \rangle$ and
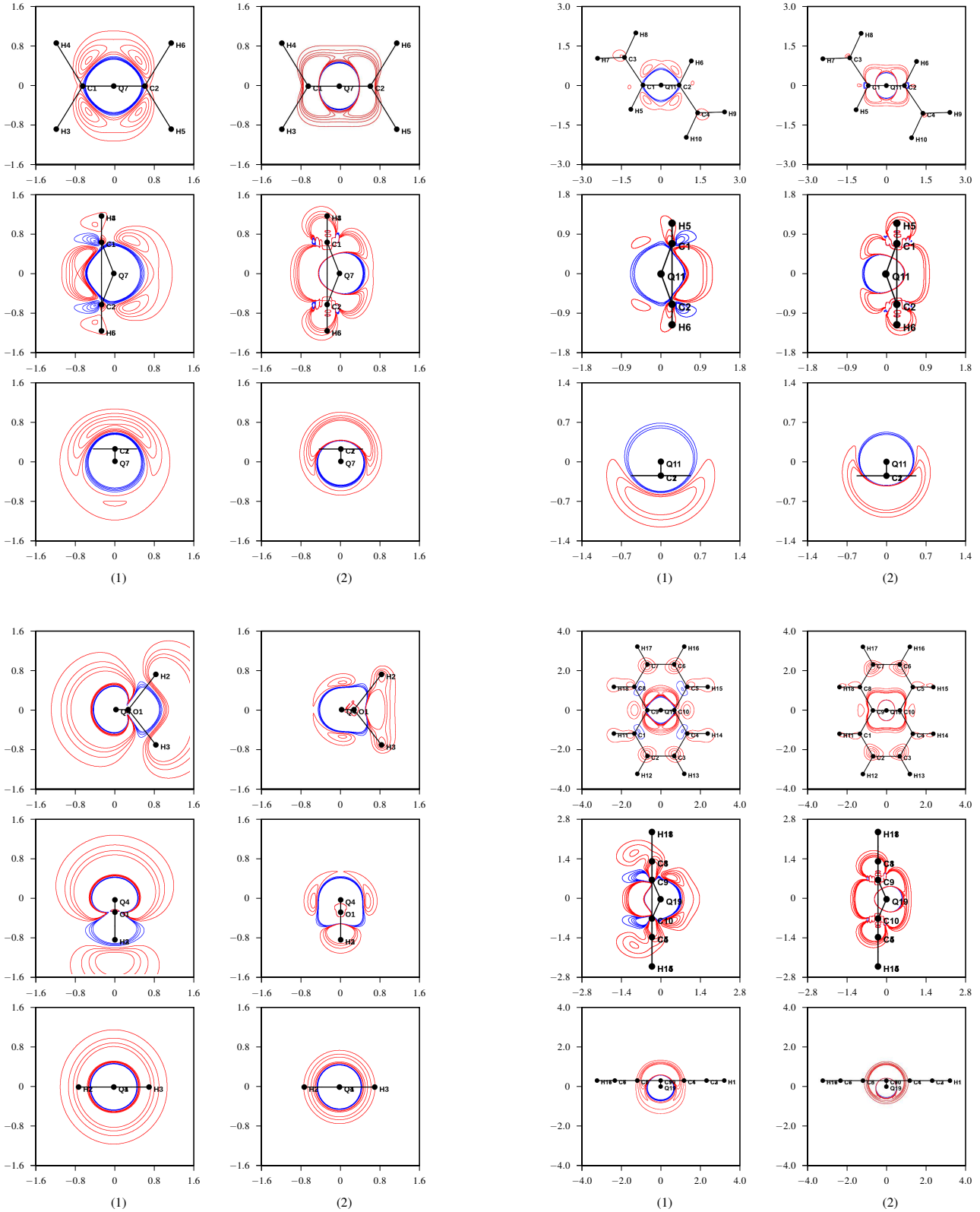
Figure 1: Sectional drawings, for the molecules of ethylene (top left), butadiene (top right), water (bottom left) and naphthalene (bottom right), along three orthogonal planes of the isocontours of (1) the response function corresponding to the reference point $\mathbf{r}_0$ indicated by the black dot labelled "Q" and of (2) the mathematical object defined by the right-hand side of equation Eq. (8), shown for the same reference point $\mathbf{r}_0$. The isocontour levels are in the range ±0.002 for the response function and static form factor of the ethylene and butadiene molecules, in the range ±0.005 for the response function and static form factor of the water molcule, in the range ±0.0005 for the response function of the naphthalene and ±0.00025 for the static form factor of the naphthalene. The isocontours are separated by 0.0005 in the cases of the ethylene, butadiene and water molecule, by 0.0001 for the response function of the naphthalene and 0.00005 for its static form factor.

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with the excitation energy ω_α, the *static* response function can be written as:

$$
\begin{aligned}
\chi(\mathbf{r}_1, \mathbf{r}_2; 0) &= 2 \sum_{\alpha \neq 0} \frac{n_\alpha(\mathbf{r}_1) n_\alpha(\mathbf{r}_2)}{\omega_\alpha} \\
&= \frac{2}{\omega(\mathbf{r}_1, \mathbf{r}_2)} \sum_{\alpha \neq 0} n_\alpha(\mathbf{r}_1) n_\alpha(\mathbf{r}_2) \\
&= \frac{2}{\omega(\mathbf{r}_1, \mathbf{r}_2)} \langle \delta\hat{n}(\mathbf{r}_1) \delta\hat{n}(\mathbf{r}_2) \rangle \quad (6) \\
&\approx \frac{2}{\overline{\omega}} \langle \delta\hat{n}(\mathbf{r}_1) \delta\hat{n}(\mathbf{r}_2) \rangle, \quad (7)
\end{aligned}
$$

where, disregarded the hypothesis of working with real wave functions, only the last step involves an approximation. While the position-dependent effective denominator function $\omega(\mathbf{r}_1, \mathbf{r}_2)$ in line (6) is able to maintain the equality, its reduction to a position-independent constant $\overline{\omega}$ necessarily leads to an approximate expression of the response function. We have used similar approximations in earlier works [23, 38]. Comparing equations Eq. (5) and Eq. (7) allows us to write:

$$
\frac{\overline{\omega}}{2} \chi(\mathbf{r}_1, \mathbf{r}_2; 0) = \delta(\mathbf{r}_1, \mathbf{r}_2) n(\mathbf{r}_1) + n(\mathbf{r}_1) h_{xc}(\mathbf{r}_1, \mathbf{r}_2), \quad (8)
$$

which is the desired (approximate) relationship between the static response function and the right-hand side of Eq. (5), the static form factor. Note that the two contributions to the static form factor, corresponding to the density multiplied, on the one hand, by the Dirac delta function and on the other hand, by the xc-hole function, ensure the correct charge conservation sumrule. Indeed, the response function on the left-hand side of Eq. (8) integrates to zero, while, on the right hand side, the Dirac delta function integrates to plus one and the exchange-correlation hole function to minus one.

In the following we are going to simplify the problem and instead of working with the exact response function and the exchange-correlation hole function, we are going to consider the noninteracting (or bare) response function and the exchange hole function, which arises in an independent particle model.

2.2. Noninteracting response and exchange hole functions

In this subsection we are going to apply the effective denominator technique to the zero-frequency bare or noninteracting response function:

$$
\chi_0(\mathbf{r}_1, \mathbf{r}_2) = 2 \sum_i^{occ} \sum_a^{virt} \frac{\phi_a^*(\mathbf{r}_2) \phi_i(\mathbf{r}_2) \phi_i^*(\mathbf{r}_1) \phi_a(\mathbf{r}_1)}{\epsilon_a - \epsilon_i}, \quad (9)
$$

where ϕ_i, ϵ_i (ϕ_a, ϵ_a) are occupied (virtual) orbitals and orbital energies. Using a position-dependent effective denominator, $\omega(\mathbf{r}_1, \mathbf{r}_2)$, this yields:

$$
\omega(\mathbf{r}_1, \mathbf{r}_2) \chi_0(\mathbf{r}_1, \mathbf{r}_2) = 2 \sum_i^{occ} \sum_a^{virt} \phi_a^*(\mathbf{r}_2) \phi_i(\mathbf{r}_2) \phi_i^*(\mathbf{r}_1) \phi_a(\mathbf{r}_1). \quad (10)
$$

The summation over the virtual orbitals is transformed into a sum over all the orbitals minus a sum over occupied orbitals:

$$
\begin{aligned}
\omega(\mathbf{r}_1, \mathbf{r}_2) \chi_0(\mathbf{r}_1, \mathbf{r}_2) = {}& 2 \sum_i^{occ} \sum_p^{all} \phi_p^*(\mathbf{r}_2) \phi_i(\mathbf{r}_2) \phi_i^*(\mathbf{r}_1) \phi_p(\mathbf{r}_1) \\
&- 2 \sum_i^{occ} \sum_j^{occ} \phi_j^*(\mathbf{r}_2) \phi_i(\mathbf{r}_2) \phi_i^*(\mathbf{r}_1) \phi_j(\mathbf{r}_1),
\end{aligned}
$$
$$(11)$$

where ϕ_j is an occupied orbital and ϕ_p designates an arbitrary (virtual or occupied) orbital. In this last expression, we recognize the usual definition of the exchange hole $h_x(\mathbf{r}_1, \mathbf{r}_2)$ for a single determinant wave function:

$$
n(\mathbf{r}_1) h_x(\mathbf{r}_1, \mathbf{r}_2) = -2 \sum_{ij} \phi_i^*(\mathbf{r}_1) \phi_j(\mathbf{r}_1) \phi_j^*(\mathbf{r}_2) \phi_i(\mathbf{r}_2), \quad (12)
$$

and the resolution-of-identity expression of the Dirac delta function:

$$
\delta(\mathbf{r}_1, \mathbf{r}_2) = \sum_p \phi_p^*(\mathbf{r}_2) \phi_p(\mathbf{r}_1). \quad (13)
$$

Note that the above representation of the Dirac delta function holds strictly only in the case of a complete orbital basis. We obtain:

$$
\omega(\mathbf{r}_1, \mathbf{r}_2) \chi_0(\mathbf{r}_1, \mathbf{r}_2) = 2\delta(\mathbf{r}_1, \mathbf{r}_2) \sum_i \phi_i(\mathbf{r}_2) \phi_i^*(\mathbf{r}_1) + n(\mathbf{r}_1) h_x(\mathbf{r}_1, \mathbf{r}_2),
$$
$$(14)$$

where we can use the Dirac delta function to see the expression of the charge density $n(\mathbf{r}_1)$ emerge in the first term:

$$
\omega(\mathbf{r}_1, \mathbf{r}_2) \chi_0(\mathbf{r}_1, \mathbf{r}_2) = \delta(\mathbf{r}_1, \mathbf{r}_2) n(\mathbf{r}_1) + n(\mathbf{r}_1) h_x(\mathbf{r}_1, \mathbf{r}_2). \quad (15)
$$

As seen before, the simplest approximation to this potentially exact relation is to replace $\omega(\mathbf{r}_1, \mathbf{r}_2)$ by a position-independent constant, $\overline{\omega}$:

$$
\overline{\omega} \chi_0(\mathbf{r}_1, \mathbf{r}_2) \approx \delta(\mathbf{r}_1, \mathbf{r}_2) n(\mathbf{r}_1) + n(\mathbf{r}_1) h_x(\mathbf{r}_1, \mathbf{r}_2). \quad (16)
$$

Compared to Eq. (8), which relates the exact interacting static response function to the exchange-correlation hole, equation (16) involves the noninteracting static response function and the exchange hole.

Our average energy denominator approximation is expected to fail in reproducing the nodal structure of the response function in all its details, but the major features are expected to be preserved. In the present article all the numerical examples will be limited to the noninteracting (bare) response function and to the corresponding exchange hole.

2.3. Exchange-hole and localized orbitals

The idea that localized orbitals are closely related to the exchange hole has probably first appeared in the work of Luken [43, 44] at the beginning of the eighties and it has been later reiterated by Tschinke and Ziegler [45] as well as by others [46]. The central idea is that the definition of the exchange hole for a single determinant wave function of Eq. (12) can be considerably simplified if it were possible to use strictly localized orbitals. Indeed, strictly localized orbitals are such that the "differential overlap" $\phi_i^*(\mathbf{r}_1)\phi_j(\mathbf{r}_1)$ is (almost) zero for $i \neq j$ and it is $|\phi_i(\mathbf{r}_1)|^2$ for $i = j$. Therefore we can write the hole function as:

$$h_x(\mathbf{r}_1, \mathbf{r}_2) = -2 \sum_i \frac{|\phi_i(\mathbf{r}_1)|^2}{n(\mathbf{r}_1)} |\phi_i(\mathbf{r}_2)|^2. \qquad (17)$$

Let us consider a partition of the physical space to approximately disjoint regions Ω_i [38], each belonging to a strictly localized orbital ϕ_i. In every region only one localized orbital contributes to the electron density, *i.e.* $|\phi_i(\mathbf{r}_1)|^2 \approx n(\mathbf{r}_1)$. Using the window function $\Theta_i(\mathbf{r}_1)$ (which is equal to unity if $\mathbf{r}_1$ is in Ω_i and zero otherwise) it is possible to write that:

$$h_x(\mathbf{r}_1, \mathbf{r}_2) = -2 \sum_i \Theta_i(\mathbf{r}_1) |\phi_i(\mathbf{r}_2)|^2, \qquad (18)$$

i.e. that the exchange hole associated with a reference point $\mathbf{r}_1$ is approximated as the negative of the square of the localized orbital k which is situated in the space domain of this point and satisfies $\Theta_k(\mathbf{r}_1) = 1$, that is to say:

$$h_x(\mathbf{r}_1, \mathbf{r}_2) = -2 |\phi_k(\mathbf{r}_2)|^2 \qquad \text{for } \mathbf{r}_1, \mathbf{r}_2 \in \Omega_k. \qquad (19)$$

In Section 3, it is shown in several illustrations how far this reasoning holds in different systems characterized by different degree of localization of their electrons.

3. Picturial comparison of response functions, exchange holes and localized orbitals

3.1. Computational details

A software has been written to calculate the two-variable functions $\chi_0(\mathbf{r}_k, \mathbf{r}_0)$, $\delta(\mathbf{r}_k, \mathbf{r}_0)$ and $h_x(\mathbf{r}_k, \mathbf{r}_0)$ appearing in equations (9), (13) and (12) on regular grids $\{\mathbf{r}_k\}$, for a fixed reference point $\mathbf{r}_0$, permitting us to generate visual representations of both sides of Eq. (8) and Eq. (19). The program takes as input the orbitals and the total electronic density of a system in the CUBE file format using the MOLPRO program [47]. The calculations have been done at the Kohn-Sham level using the LDA functional and the aug-cc-aVTZ basis set. The sum rules $\int d\mathbf{r}_k \; \chi_0(\mathbf{r}_k, \mathbf{r}_0) = 0$, $\int d\mathbf{r}_k \; h_x(\mathbf{r}_k, \mathbf{r}_0) = -1$ and $\int d\mathbf{r}_k \; \delta(\mathbf{r}_k, \mathbf{r}_0) = 1$ have been checked to verify the suitability of the grid by simple summation over the grid points. The

Dirac delta function has been represented by a spherical Gaussian model: $\delta(\mathbf{r}_k, \mathbf{r}_0) \approx \frac{w}{2\pi} e^{\left(-\frac{1}{2} w^2 |\mathbf{r}_k - \mathbf{r}_0|^2\right)}$. The half-width parameter $w = 2.5$ has been found on our grids to produce a normalization integral closest to 1 for all studied systems. Localized orbitals were generated using the Foster-Boys localization criterium [48, 49].

3.2. Response function and exchange hole

In order to visualize the relationship between the response function and the hole function, we present contour plots of the noninteracting response function,

$$\chi_0(\mathbf{r}_k, \mathbf{r}_0; 0) \quad \text{and} \quad \delta(\mathbf{r}_k, \mathbf{r}_0) n(\mathbf{r}_k) + n(\mathbf{r}_k) h_x(\mathbf{r}_k, \mathbf{r}_0),$$

in cross sections of the molecule lying in the *xy*, *yz* and *zx* planes.

Figure 1 shows the correspondance between the static response function $\chi(\mathbf{r}_k, \mathbf{r}_0; 0)$ and the static form factor, *i.e.* the function appearing on the right-hand side of Eq. (8). We have used as example the ethylene, butadiene, water and naphthalene molecules. The reference points $\mathbf{r}_0$ are labelled with a "Q" on the Figures. The quality of the ressemblance between the static response function and the static form factor does not depend on the choice of the reference points, but these are placed on symmetry planes or axis for each molecule and are chosen such that they coincide with a grid point. Due to the relatively rough grids, an arbitrarily placed reference point would have destroyed the symmetry of the resulting figure. For the ethylene and butadiene molecule the reference point is near the C-C single bond, outside of the plane of the molecule. In the case of the water molecule, the reference point is on the bisector of the H-O-H angle. The reference point for the naphthalene molecule is near the central C-C bond, above the molecular plane.

Overall, the correspondance between the two functions is of rather acceptable visual quality, in spite of some discrepancies, which can be attributed to the relative crude model of the response function, supposing a simple, position independent, proportionality with the form factor. The incompleteness of the model can be conjectured from the fact that linear response functions possess a richer topological structure, as compared to the form factor based model. The mathematical structure of the form factor makes clear that the dominant feature in both functions should be a positive peak centered on the reference point $\mathbf{r}_0$ and an essentially negative region corresponding to the exchange hole.

The comparison of the butadiene and the naphthalene clearly shows the difference in the extent of the delocalization in these two systems. While in the former case the response function describes an induced change of the charge which extends out only slightly from a central perturbation to the terminal carbon atoms, in the case of the naphthalene the charge density is quite significantly perturbed on the entire molecular skeleton. We can observe also an alternating sign of the charge density variations. The topology of the corresponding independent particle form factor function shows a reasonable resemblance with the behavior of the linear response function, although some features seem to be different on the two contour plots. For instance,
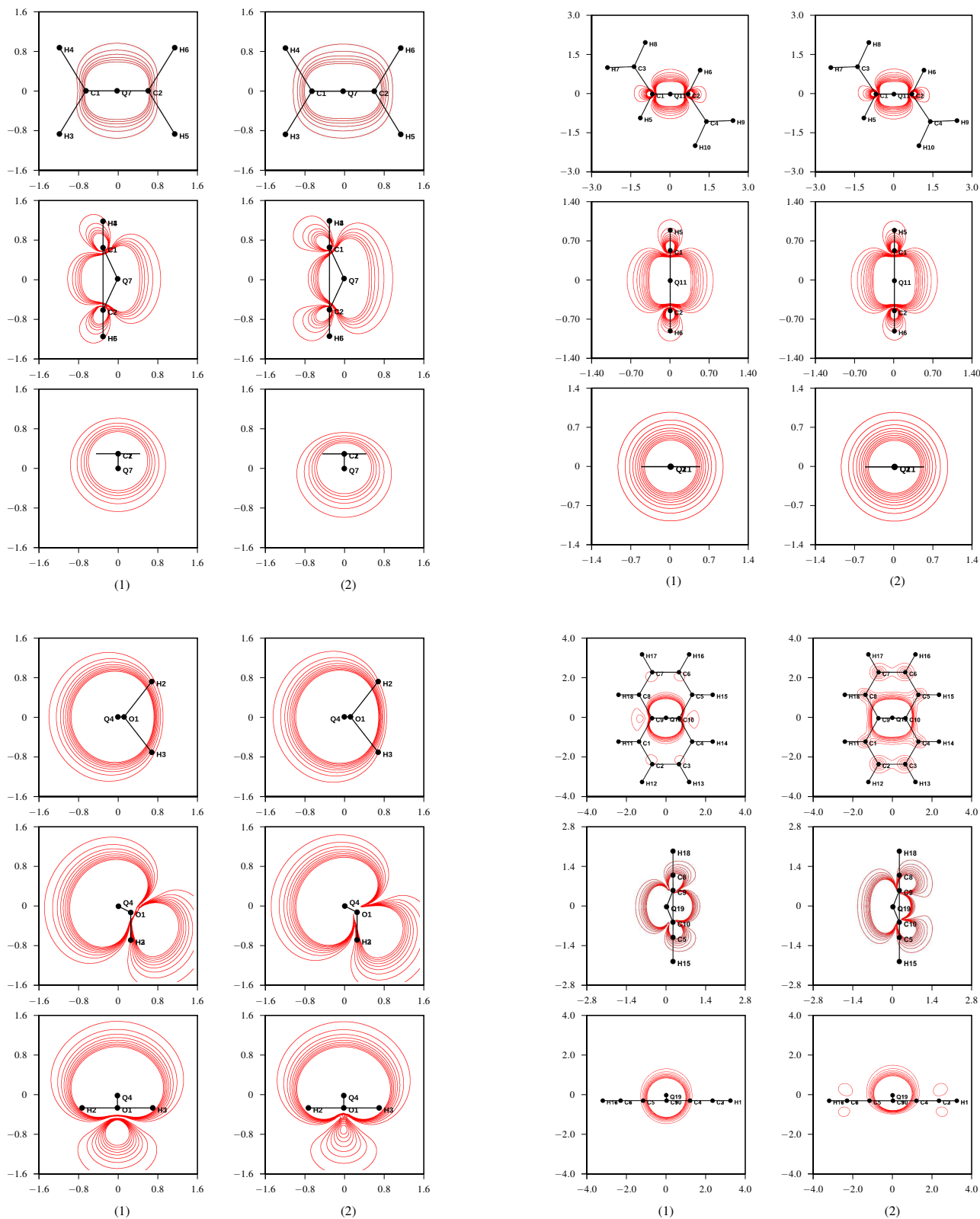
Figure 2: Sectional drawings, for the molecules of ethylene (top left), butadiene (top right), water (bottom left) and naphthalene (bottom right), along three orthogonal planes of the isocontours of (1) the exchange hole corresponding to the reference point $\mathbf{r}_0$ indicated by the black dot labelled "Q" and of (2) the square of the localized orbital which centroid is situated in this space domain. The isocontours are in the range ±0.03 and separated by 0.005 for the ethylene molecule, in the range ±0.05 and separated by 0.005 for the butadiene, and in the range ±0.005 and separated by 0.0005 for both the water and naphthalene molecule.
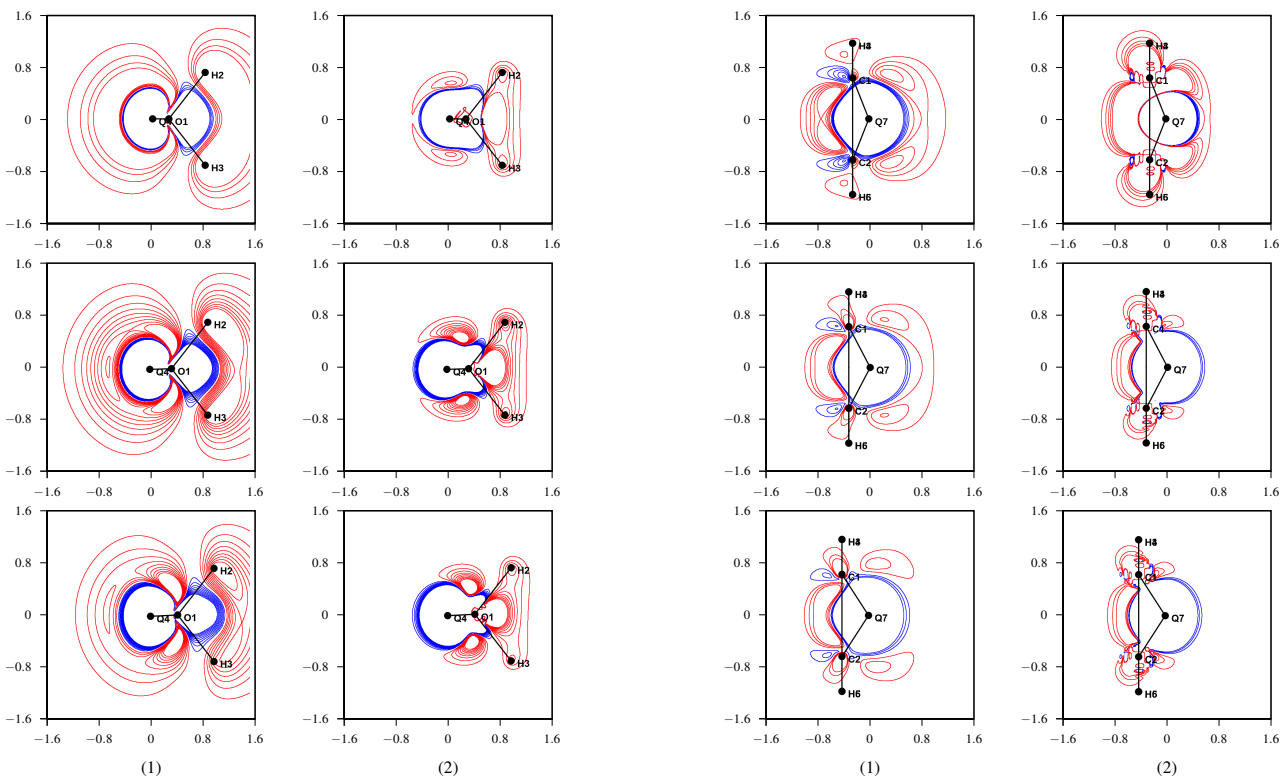
Figure 3: Effect of the choice of the reference point, $\mathbf{r_0}$, denoted by Q4 and Q7, respectively for the water (left) and ethylene (right) molecules. The reference point is moving outwards along a symmetry axis of the molecules, remaining in the same bond domain. Column (1) represents the response function in the *xy* plane, column (2) illustrate the mathematical object defined by the rhs of Eq. (8), both shown for the reference point $\mathbf{r_0}$.

the multiple maxima observed in the response function plot of the naphthalene molecule seems to be absent on the form factor plot. In the case of the butadiene the strong positive peaks at the on the opposite side of the molecular plane with respect to the reference point under the C1 and C2 carbon atoms are almost invisible on the form factor plot.

The contour plots in Figure 1 depend on the choice of the reference point. We have examined the sensitivity of the response function and of the form factor with respect to the position of the reference point. Since the shape of these functions is expected to change radically if the reference point is moved from one electron pair domain to another, we focused our attention to relatively small displacements within the same domain. As illustrated by Figure 3, the shape of the response function does not change appreciably; we have the positive peak, associated in the form factor model with the Dirac delta function and a negative region related to the exchange hole in the form factor model. However, according to the selected examples, the water and ethylene molecules, some details may change in the case of a shift of the reference point along the symmetry axis and additional critical points may appear in the negative (red) regions of both the response function and the form factor model.

3.3. Exchange hole and localized orbitals

Figure 2 illustrates the relationship seen Eq. (19) between the localized orbital and the exchange hole, by plotting

$$h_x(\mathbf{r}_k, \mathbf{r}_0) \quad \text{and} \quad -|\phi_k(\mathbf{r}_k)|^2 .$$

The reference points $\mathbf{r}_0$ for the exchange hole have been chosen at the centroids of the localized orbital ϕ_k, obtained by the Foster-Boys localization criterium. The following orbitals were selected: the C-C bonds for the case of the ethylene molecule, the C-C simple bond of the butadiene molecule, one of the oxygen lone pairs for the water molecule and the central C-C bond of the naphthalene molecule. The grids are constructed such that the reference points coincide with one of the grid points.

In the case of the small water and ethylene molecules and even in butadiene the contour plots of the exchange hole and of the square of the localized orbital are practically indistinguishable. Although the agreement is very good in naphthalene as well, the squared localized orbital seems to be slightly more extended on the naphthalene rings than the exchange hole.

It has been observed for a long time that *bond polarizabilities* are remarkably transferable from one system to another. This point was discussed from the theoretical chemistry viewpoint by Claverie [50] by identifying bond polarizabilities and localized orbital polarizabilities. The isomorphism of the localized orbitals and of the exchange hole, which in turn is related to the local charge density response puts this observation in a new context a provides a sort of explanation in terms of the model independent exchange hole through its close relationship with the linear response function itself.

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3.4. Discussion

From a conceptual point of view it is quite obvious that the notion of delocalization is primarily connected to the question "How electrons respond to an external disturbance?". The basic physical observable in this respect is the charge density response function, unfortunately its direct use in routine studies is made difficult by some obstacles.

The main difficulty is that the response function depends on two space variables so its full pictorial representation in the three dimensional space or in any lower dimensional cross-section (plane or line) should be done as a function of the reference point, which should, in principle, scan the whole space. Geerlings and his co-workers have recently published a series of articles, which present and discuss response functions (linear response kernels) for a series of systems [32]. These studies have been done most often on the noninteracting response function, which requires significantly less computational resources, than the analogous plots of the interacting response, e.g. at the coupled perturbed Kohn-Sham or Hartree-Fock or correlated (coupled cluster) level.

A way to get rid of the second variable would be to construct domain-averaged quantities, in analogy to the domain-averaged Fermi holes (DAFH) [51–53]:

$$\chi_{\Omega_A}(\mathbf{r}_1) = \int_{\Omega_A} d\mathbf{r}_2 \chi(\mathbf{r}_1, \mathbf{r}_2). \qquad (20)$$

To the best of our knowledge this quantity constructed from the response function has not yet been proposed in the literature. For instance, it is expected that the shape of the atomic domain-averaged response function provides information about space regions where the electrons of this particular atom are expected to be delocalized. A detailed study of such domain-averaged response functions will be be the subject of a forthcoming publication.

A further simplification in the characterization of the linear response function can be achieved by a double domain average, leading to a quantity identical to the charge-flow polarizability in the distributed polarizability formalism:

$$\chi_{\Omega_A,\Omega_B} = \int_{\Omega_A} d\mathbf{r}_2 \int_{\Omega_B} d\mathbf{r}_1 \chi(\mathbf{r}_1, \mathbf{r}_2). \qquad (21)$$

χ_{Ω_A,Ω_B} measures the propensity of the charge density in Ω_A to flow towards the domain Ω_B under the effect of an electric potential difference between the two domains. Application of the above definition to QTAIM domains defined by Bader [1] leads to atom-atom charge flow polarizabilities [36, 54]. Although relatively small systems were studied in these works, clear signatures of strong delocalization have been observed for the dicyan (NCCN) and benzene molecules. In the former case, the end-to-end charge flow is remarkably high (-0.499) which is to be compared to the charge flow polarizability between bonded nitrogen and carbon atoms (-1.256) while the charge flow between non bonded carbon and nitrogen atoms is very small (-0.042). In the benzene, the strong para charge-flow is remarkable (-0.316) and the opposite sign meta charge flow (+0.103).

Such a behavior is in good agreement with well-known reactivity rules in substituted benzenes.

Our attempt to model the main features of the response function in terms of the density-weighted exchange hole was motivated in a great extent by the observation that the charge flow derived from the linear response function by a double atomic domain average correlates well with delocalization indices, which can be calculated from the exchange hole. Although the model presented in this work does correctly reflect the main trends, it can and should be improved in the future. One possible way consists in finding a simple model for the position-dependent effective excitation energies. Work in this direction is in progress.

A recent exhaustive review by Geerlings and his coworkers [32] came to our knowledge after completing our work. Their paper discusses in depth various chemical applications of the linear response function, like mesomeric effects, delocalization, aromaticity, reactivity, *etc* of the response functions and quantities derived therefrom.

One of the roles of the density-weighted exchange hole is to establish a link between the most general delocalization measures, the response function and the localized orbitals, which are usually considered as outdated. The quality of the conventional localized orbitals depends on the localization criteria. It is interesting to notice that one can derive one-electron functions, which play an analogous role as the localized orbitals, directly from the exchange hole. In this respect, one should mention the Fermi hole based localized orbitals of Luken and Culberson [44, 55], the natural orbitals derived from the domain-averaged Fermi hole by Poneč [53], the domain natural orbitals (DNO) [56], which were further generalized by diagonalization of the *n*-th order cumulant density matrices, leading to Natural Adaptive Orbitals (NAdOs) [57]. In this respect one should mention Cioslowski's isopycnic transformation method to obtain localized natural orbitals from correlated (many-determinantal) wave functions, based on the invariance of the Fermi hole [58].

4. Conclusions

The basic physical model that the (de)localization of electrons is intimately related to fundamental physical observables like the charge density response function of the system on the one hand and to the exchange-correlation hole function on the other, has been illustrated on a few selected examples. Note that in independent particle theories we can consider the exchange hole and the noninteracting linear response function, which are much simpler to calculate than the full linear response and the full many-body exchange-correlation hole.

Pictures of two-dimensional cross-sections of the molecular space provide a detailed insight to the relationships which have been established earlier between charge-flow polarizabilities and atom-atom delocalization indices. Further and more rigorous comparisons should be done in the future, since the visual shape of the contour plots may be strongly dependent on the choice of the contours, selected here on a linear scale and uniformly for all the presented pictures. The still objectively existing discrepancies are expected to be removed by an

improved, position-dependent effective excitation energy modulating the form factor function, as indicated previously.

The relationship between localized orbitals and the exchange hole, first observed by Luken more than 30 years ago, permits an *a posteriori* justification of the use of localized orbitals in qualitative interpretations of bonding and localization. In the mean time this analysis underlines some inherent limitations of the localized orbital picture.

There are several physical implications of the relationships which we attempted to make more plausible via graphical illustrations. First, we can see that the charge density of an electronic system at point $\mathbf{r}_2$ responding to an external perturbation applied in $\mathbf{r}_1$ can be quite reasonably predicted from the exchange hole. Roughly speaking, the response will be nonzero essentially in those region where the exchange hole is nonzero too. Furthermore, it may be surprising that the charge density response in genuinely localized systems remains local in real space: it extends only to a few-atom region around the perturbation. An implication of this observation is that the charge-flow between such regions, which are in close resemblance with the exchange hole and by consequence to localized orbital domains, can be relatively small. Selecting such domains for a multi-center, distributed description of intermolecular forces, in particular in the case of induction and dispersion interactions, leads naturally to models without significant charge-flow contributions. In contrast, in metal-like strongly delocalized systems the possible necessity of including charge-flow contributions [59] becomes obvious by the failure of finding localized orbitals or in more general terms, by the inherently delocalized nature of the density-weighted exchange hole. Since the Resta localization tensor [8] or using a recently suggested alternative name [7], the Total Position Spread Tensor (TPST), is the second moment of the density-weighted exchange hole, one can establish also a direct link [60] to the well-known near-sightedness concept of Walter Kohn [61, 62], which provides a general framework to discuss localization and delocalization in solids but also in finite molecular systems.

Acknowledgement

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