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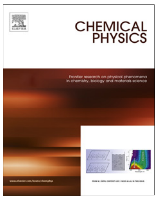

Spatial localization of electron pairs in molecules using the Fisher information density

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ABSTRACT

Starting from the quasi-probability distribution function by electron positions **r** and momenta **p** and applying the minimum information principle subject to the certain physically-grounded constrains, we obtained the approximate expression for phase-space-defined Fisher information density (PS-FID). It provides information about an electron momentum in the position representation and reveals the electronic shell structure for atoms with $Z \leqslant 20$ as well as the regions of maximal concentration of bonding and lone electron pairs in molecules. Also, this function enables to recognize the different types of chemical bonds as polar and non-polar covalent bonds, the charge-shift bond as well as the weak non-covalent molecular interactions. We found that the PS-FID behavior results from the local electron momentum uncertainty that is linked with both information about electron real-space position (which, in turn, is related with electronic steric factor) and the Pauli principle.

1. Introduction

The Lewis concept of electron pairs [1] is one of the most important in chemistry [2–4]. Physical basis for electron pairing is as follows [5–7]. In addition to Coulomb electron–electron repulsion, the presence of a given electron in some spatial region excludes from this region all other electrons with the same spin due to Pauli principle. Because such a behavior is peculiar to each electron with any spin, all electrons are maximally removed from a given region, except the pair of the 'spin-up' and 'spin-down' electrons. Eventually, all electrons in the closed-shell systems are proved to be distributed in the pairs with different degree of localization.

However, the direct-space one-electron density, the recognized source of the information about the chemical bonding [8,9], does not show any signatures of the electron pairing: the electrons are indistinguishable and distributed over a whole molecule or a crystal. Therefore, the different tools have been suggested to detect the electron localization/concentration regions. Among them are the Laplacian of electron density [5,8,10], one-electron potential [11], electron localization function (ELF) [12–14], localized orbital locator [15,16], electron localizability indicator (ELI) [17–19], maximum probability domains (MPD) [20–22] and conditional pair density [23]. They have been recently supplemented by localized electron detector (LED) [24–27], single exponential decay detector (SEDD) [28] and information-theoretic ELF (IT-ELF) [29], steric [30] and Pauli potentials [31]. Some of these functions are also approximately derived from experimental electron density and its derivatives [32–34]. These electron localization tools play nowadays an important role in the chemical bonding analysis despite some disadvantages. For example, Laplacian of electron density does not display the electronic shells for many heavy atoms [35,36] while the LED and SEDD do not show the electron lone pairs.

The concepts of Shannon information entropy [37] and Fisher information [38], which are nowadays widely used in physics and chemistry [39–44], provide another general approach to electronic structure of atoms, molecules and crystals [29,45–47]. Especially, Nalewajski [29] has presented the Fisher information-based ELF to demonstrate the electron localization in molecules (IT-ELF). In this work we show that the evidence about electron localization in chemical systems can be derived from the phase-space-(PS) defined Fisher information. We demonstrate that the PS-Fisher information density reveals the electronic shells for atoms and detects the most probable positions of the bonding and lone electron pairs in molecules.

2. Method

Ghosh, Berkowitz and Parr (GBP) [48] have reformulated the density functional theory (DFT) [49] considering the electron cloud

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in molecular systems as an electron gas in the effective external potential. The N-electron quasi-probability distribution function by positions $\mathbf{r}$ and momenta $\mathbf{p}$ is defined in a $6N$-dimensional phase space [50,51] as

$$F(\mathbf{r}_1,\ldots,\mathbf{r}_N,\mathbf{p}_1,\ldots,\mathbf{p}_N)=(2\pi)^{-6N}\sum_{\sigma}\int g(\{\mathbf{h}_i\},\{\mathbf{s}_i\})\prod_{i}^{N}e^{-i\mathbf{s}_i\cdot\mathbf{p}_i}e^{-i\mathbf{h}_i\cdot(\mathbf{r}_i-\mathbf{u}_i)}\times\Psi^*\left(\left\{\mathbf{r}_i-\frac{\mathbf{s}_i}{2}\right\},\sigma_i\right)\Psi\left(\left\{\mathbf{r}_i+\frac{\mathbf{s}_i}{2}\right\},\sigma_i\right)\prod_{i}^{N}d\mathbf{h}_i d\mathbf{s}_i d\mathbf{u}_i. \quad (1)$$

Here $\Psi(\{\mathbf{r}_i\},\{\sigma_i\})$ is a wave function in the coordinate representation, $\mathbf{r}_i$ and σ_i stand for the position and spin of ith electron, correspondingly; $\mathbf{h}_i$, $\mathbf{s}_i$ and $\mathbf{u}_i$ are real-space vectors and $g(\{\mathbf{h}_i\},\{\mathbf{s}_i\})$ is any function satisfying the condition $g(\{\mathbf{h}_i\},\{0\})=g(\{0\},\{\mathbf{s}_i\})=1$. When $g(\{\mathbf{h}_i\},\{\mathbf{s}_i\})=1$, function $F(\mathbf{r}_1,\ldots,\mathbf{r}_N,\mathbf{p}_1,\ldots,\mathbf{p}_N)$ is the so-called Wigner function [50]. However, by virtue of indistinguishability of particles, the electron interactions in a system are described by the only two-particle phase-space distribution function, $F(\mathbf{r}_1,\mathbf{r}_2,\mathbf{p}_1,\mathbf{p}_2)$. Moreover, within the framework of DFT, $F(\mathbf{r}_1,\ldots,\mathbf{r}_N,\mathbf{p}_1,\ldots,\mathbf{p}_N)$ can be reduced to the distribution function $f(\mathbf{r},\mathbf{p})$ depending on a position and momentum of only one electron [14]:

$$f(\mathbf{r},\mathbf{p})=\int\sum_{i=1}^{N}\delta(\mathbf{r}-\mathbf{r}_i)\delta(\mathbf{p}-\mathbf{p}_i)F(\mathbf{r}_1,\ldots,\mathbf{r}_N,\mathbf{p}_1,\ldots,\mathbf{p}_N)\prod_{i=1}^{N}d\mathbf{r}_i d\mathbf{p}_i. \quad (2)$$

The non-interacting electronic properties are extracted from $f(\mathbf{r},\mathbf{p})$ by integration over the dynamical variables $\mathbf{r}$ and $\mathbf{p}$. Especially, electron density $\rho(\mathbf{r})$ is expressed in terms of $f(\mathbf{r},\mathbf{p})$ as

$$\rho(\mathbf{r})=\int d\mathbf{p}f(\mathbf{r},\mathbf{p}) \quad (3)$$

and Kohn–Sham electron kinetic energy density is

$$t_s(\mathbf{r})=\int d\mathbf{p}\,\frac{\mathbf{p}^2}{2}f(\mathbf{r},\mathbf{p}). \quad (4)$$

Unlike the function (1), which is normalized to unity, $f(\mathbf{r},\mathbf{p})$ in (2) is normalized to the number of electrons N. There are infinite numbers of functions $f(\mathbf{r},\mathbf{p})$ which satisfy Eqs. (3) and (4), and not all of them are non-negative everywhere [51,52–54]. GBP [48] have found the most probable form of $f(\mathbf{r},\mathbf{p})$ by applying *the maximum entropy principle* [55]. They define the local phase-space information entropy as

$$s_f(\mathbf{r})=-\int d\mathbf{p}f(\mathbf{r},\mathbf{p})\ln f(\mathbf{r},\mathbf{p}) \quad (5)$$

and its global form is

$$S_f=\int d\mathbf{r}\,s_f(\mathbf{r}). \quad (6)$$

Quantity S_f is recognized as the Shannon information entropy [37], which characterizes the information content of the function $f(\mathbf{r},\mathbf{p})$. Maximum information entropy principle subject to constrains (3) and (4) leads to the Maxwell–Boltzmann distribution function for an ideal electron gas [48]:

$$f(\mathbf{r},\mathbf{p})=\rho(\mathbf{r})[2\pi kT(\mathbf{r})]^{-3/2}\exp\left\{-\frac{\mathbf{p}^2}{2kT(\mathbf{r})}\right\}. \quad (7)$$

Here $T(\mathbf{r})$ is the local *information electron gas temperature* [48,14]. Within the non-interacting particle approximation, GBP have associated $T(\mathbf{r})$ with electronic kinetic energy density using the relation

$$t_s(\mathbf{r})=\frac{3}{2}\rho(\mathbf{r})kT(\mathbf{r}), \quad (8)$$

which is analog to the main equation of the molecular kinetic theory [56]. The presence of the Boltzmann constant k just emphasizes the formal analogy between the information and thermodynamic temperature. As opposed to the thermodynamic entropy, S_f does not vanish for quantum–mechanical electronic ground state. It is also not linked with the energy of the system. Note that in any system at equilibrium the thermodynamic temperature is the same everywhere in the $\mathbf{r}$-space, while information temperature $T(\mathbf{r})$ varies with the position $\mathbf{r}$.

Fisher information minimum principle [39] is another expression of the general principle of physical information extreme. Now we extend the GBP approach to minimize the Fisher information [38], which quantitatively characterizes spatial structuredness of some distribution function [39] and plays important role in the information theory. We consider the phase-space-defined Fisher information density (PS-FID)

$$i_f(\mathbf{r})=\int d\mathbf{p}\,\frac{\nabla_{\mathbf{p}}f(\mathbf{r},\mathbf{p})\cdot\nabla_{\mathbf{p}}f(\mathbf{r},\mathbf{p})}{f(\mathbf{r},\mathbf{p})}. \quad (9)$$

Here the subscript $\mathbf{p}$ stands for the gradient, which is taken by only momentum variables. The function $i_f(\mathbf{r})$ contains information about *structuredness* (or *sharpness*) of electronic momentum distribution in the position representation. The global form of the PS-Fisher information

$$I_f=\int d\mathbf{p}\,i_f(\mathbf{r}), \quad (10)$$

characterizes the total structuredness of $f(\mathbf{r},\mathbf{p})$ relative to the electron momentum.

Let us express I_f as a functional of quasi-probability amplitude $\eta(\mathbf{r},\mathbf{p})=\sqrt{f(\mathbf{r},\mathbf{p})}$:

$$I_f=4\int d\mathbf{r}d\mathbf{p}\,\nabla_{\mathbf{p}}\eta(\mathbf{r},\mathbf{p})\cdot\nabla_{\mathbf{p}}\eta(\mathbf{r},\mathbf{p}). \quad (11)$$

Minimization of I_f (11) subject to the constrains (3) and (4) leads to the second-order differential equation

$$\nabla^2_{\mathbf{p}}\eta(\mathbf{r},\mathbf{p})-\left[\alpha(\mathbf{r})+\beta(\mathbf{r})\frac{\mathbf{p}^2}{2}\right]\eta(\mathbf{r},\mathbf{p})=0 \quad (12)$$

in which $\alpha(\mathbf{r})$ and $\beta(\mathbf{r})$ are $\mathbf{r}$-depending Lagrange multipliers. Differentiation in (12) is only in the momentum variables, therefore the position $\mathbf{r}$ can be regarded as a parameter. Eq. (12) is formally similar to the Schrödinger equation for a harmonic oscillator, $\alpha(\mathbf{r})$ being the ‘information energy’ and $\beta(\mathbf{r})\frac{\mathbf{p}^2}{2}$ the ‘information harmonic potential’ [57]. Solution of (12) leads to the set of the functions including Hermite polynomials and depending on values of three integer numbers: n_1, n_2 and n_3. Minimum information is provided by the solution with $n_1=n_2=n_3=0$; it yields

$$f(\mathbf{r},\mathbf{p})=A(\mathbf{r})\exp\{-\xi(\mathbf{r})\mathbf{p}^2\}, \quad (13)$$

where $\xi(\mathbf{r})=\sqrt{\beta(\mathbf{r})}$ and $A(\mathbf{r})$ is $\mathbf{r}$-depending normalization factor. Substituting (13) into (3) and (4) and taking into account Eq. (8), we get function $f(\mathbf{r},\mathbf{p})$ in the form (7) with $A(\mathbf{r})=\rho(\mathbf{r})[2\pi kT(\mathbf{r})]^{-3/2}$ and $\xi(\mathbf{r})=\frac{1}{2kT(\mathbf{r})}$. Thus, minimization of I_f (11) subject to the constrains (3) and (4) yields the same distribution function as it has been obtained by GBP [48].

It is well-known that the exact Wigner distribution function can attain the negative values [50], i.e., it is not probability distribution function (in this sense we employ the term ‘quasi-probability’), while the function $f(\mathbf{r},\mathbf{p})$ (13) is non-negative everywhere since the multiplier $A(\mathbf{r})$ is not defined if $T(\mathbf{r})<0$. Thus $f(\mathbf{r},\mathbf{p})$ (13) is just Wigner-like function which correctly yields the electron density and electronic kinetic energy density in accordance with (3) and (4), however it does not necessary provide any other local properties. Nevertheless, calculations of electron exchange energy and