Quantum similarity, volume functions and generalized Carbó indices

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Abstract   In this paper it is described a new family of homothetic functions, derived from quantum mechanical density functions (DF), which here are called volume functions (VF), appearing with such a sufficient entity level as to merit description. Shape functions become the first term of the VF collection. VFs are elements of the unit shell of the DFs generated collection of tensorial product spaces. Besides these properties, here is shown that the construction of generalized Carbó indices can be proved to be feasible, as a consequence of the use of generalized scalar products and the appropriate definition of another alternative kind of homothetic DFs.

1 Introduction

The homothetic scaling of electronic density functions (DF) by the number of electrons, the Minkowski norm of any first order DF, has been proposed by Parr and Bartolotti several years ago [1] and called *shape function* (ShF). Such apparently trivial DF transformation was put later on in evidence by the author in another context [2], as a mean to transform DF into a probability function and to simplify the numeric structure of electronic properties of atoms and molecules. Other authors (see reference [3] as an example) have been interested into such a homothetic DF (HDF) transformation. More recently, the structure of ShF has been studied in deep with respect of vector semispace shell formalism [4].

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The present study pretends to describe a collection of HDF transformations, which will be called *volume functions* (VF), closely related to the structure of vector semi-spaces [5] and the generalized scalar products [6,7], which can be defined among their elements. For more details about all these simple concepts related to quantum similarity mathematical foundation see a recent résumé [8].

Definition of such a VF sequence permits to classify the ShF as the first term of it and afterwards clearly design the structure of the unit shells [4], which can be attached to the tensorial product of the previously and properly defined vector semispaces. A related feature of such a development, which permits to construct another sequence of HDFs, allows to clearly define the nature of the generalized Carbó indices, see for example [5,8], thus connecting this kind of normalized DFs with quantum similarity.

In order to achieve the previous prospect, this work will provide first a section dealing with volume functions, followed by a simple Gaussian function example to illustrate the previous definition. A brief description on a possible interpretation of the VF will follow the mentioned previous introductory sections, and as a final part, the connection between VF and generalized Carbó indices will be discussed.

2 Volume functions

2.1 Preliminaries

When analyzing the way by which ShF are defined and the nature of the implicit homothetic transformation, which converts any quantum mechanical electronic DF into a ShF, one can try to study the use of other norms to transform DF in a similar although not completely equivalent way.

In fact a ShF: $\sigma(\mathbf{r})$ is simply defined from any arbitrary DF: $\rho(\mathbf{r})$, according to the next algorithm, which can be written in several ways as follows:

$$\forall \rho(\mathbf{r}) : \langle \rho \rangle = \int_D \rho(\mathbf{r}) \, d\mathbf{r} = N \rightarrow \sigma(\mathbf{r}) = N^{-1} \rho(\mathbf{r}) = \langle \rho \rangle^{-1} \rho(\mathbf{r}), \qquad (1)$$

being N the number of electrons and the integral $\langle \rho \rangle$ is the Minkowski norm of the DF $\rho(\mathbf{r})$. Because of this definition, a ShF like $\sigma(\mathbf{r})$ behaves as a probability distribution:

$$\forall \sigma(\mathbf{r}) : \langle \sigma \rangle = \int_D \sigma(\mathbf{r}) \, d\mathbf{r} = 1 \wedge \int_{d \subset D} \sigma(\mathbf{r}) \, d\mathbf{r} \in [0, 1].$$

2.2 Euclidian norms

Keeping in mind the fact that ShF are simply obtained normalizing any DF by a first order norm like Minkowski's, it is not difficult to realize that there is a large field of possible DF normalizations to be exploited: by just employing norms of any order to obtain normalized DFs, which will obviously become a new collection of HDFs.

An evident second order homothetic term, candidate to become the second element of a HDF collection, can be associated to the Euclidian norm of any DF, providing the algorithm:

$$\forall \rho\left(\mathbf{r}\right) : \langle \rho | \rho \rangle = \left\langle \rho^2 \right\rangle = \int_D |\rho\left(\mathbf{r}\right)|^2 \, d\mathbf{r} \to \upsilon^{(2)}\left(\mathbf{r}\right) = \left\langle \rho^2 \right\rangle^{-1} |\rho\left(\mathbf{r}\right)|^2, \qquad (2)$$

where the integrals of type $\left\langle \rho^2 \right\rangle$ have been used from the early times of quantum similarity [9–15] with the name of quantum selfsimilarity measures.

2.3 Homothetic sequence and volume functions

Taking into account the previous definition of ShF in Eq. (1) and the second order one in Eq. (2), it is not difficult to assign to ShFs the role of first order terms of a possible sequence of normalized DFs:

$$\upsilon^{(1)}\left(\mathbf{r}\right) = \sigma\left(\mathbf{r}\right).$$

It is straightforward to define the nth order term of the normalized DF collection by means of the algorithm:

$$\forall \rho\left(\mathbf{r}\right) : \left\langle \rho^n \right\rangle = \int_D |\rho\left(\mathbf{r}\right)|^n \, d\mathbf{r} \to \upsilon^{(n)}\left(\mathbf{r}\right) = \left\langle \rho^n \right\rangle^{-1} |\rho\left(\mathbf{r}\right)|^n. \qquad (3)$$

The integrals: $\langle \rho^n \rangle$ can be immediately interpreted as nth order norms of the DF $\rho\left(\mathbf{r}\right)$. Within the quantum similarity theoretical framework they can be associated to $n-$tuple DF selfsimilarities.

Thus, the collection of normalized DFs: $\left\{ \upsilon^{(p)}\left(\mathbf{r}\right) | p = 1, 2, \ldots, n \ldots \right\}$ is perfectly defined in the way described as in Eq. (3).

These normalized DFs will be called here from now on *volume functions* (VF). VFs have obviously an order or rank attached, corresponding to the generalized norm employed to compute a specific term of the sequence. Accordingly, as previously commented the first order VF is the ShF.

3 A simple gaussian function example

As a way to have a schematic picture of what is described beforehand about VF, one can choose as a simple model for such a DF manipulation a monovariate Gaussian function, which initially will be written as:

$$\gamma\left(\alpha | x\right) = \exp(-\alpha x^2). \qquad (4)$$

If from the Gaussian function defined above it is wanted to simulate the DF of a monodimensional atom with charge Z, then as the Minkowski norm of the function (4) has to fulfill the following sequence of implications:

$$\langle \gamma \rangle = \int_{-\infty}^{+\infty} \gamma \left(\alpha \,|x\, \right) dx = \sqrt{\frac{\pi}{\alpha}} = Z \to \alpha = \frac{\pi}{Z^2} \to \gamma \left(Z \,|x \right) = \exp \left(-\frac{\pi}{Z^2} x^2 \right),$$

(5)

providing the schematic atomic density function: $\gamma \left(Z \,|x \right)$.

The first rank VF or ShF is defined in this simple case immediately as:

$$\upsilon^{(1)} \left(Z \,|x \right) = Z^{-1} \exp \left(-\frac{\pi}{Z^2} x^2 \right) \to \left\langle \upsilon^{(1)} \right\rangle = 1.$$

The VF of higher rank may be written, first using the product of any number of type (5) functions:

$$\left(\gamma \left(Z \,|x \right) \right)^n = \exp \left(-n \frac{\pi}{Z^2} x^2 \right)$$

in this way, the generalized norm of this product will be in this case:

$$\left\langle \left(\gamma \left(Z \,|x \right) \right)^n \right\rangle = \int_{-\infty}^{+\infty} \exp \left(-n \frac{\pi}{Z^2} x^2 \right) dx = \sqrt{\frac{n\pi}{Z^2}} = \frac{\sqrt{n\pi}}{Z}$$

and the nth rank volume function can be written as:

$$\upsilon^{(n)} \left(Z \,|x \right) = \frac{Z}{\sqrt{n\pi}} \exp \left(-n \frac{\pi}{Z^2} x^2 \right) \to \left\langle \upsilon^{(n)} \left(Z \,|x \right) \right\rangle = 1.$$

One can see that the volume functions will be more sharp peaked as the ratio: $a = \frac{n\pi}{Z^2}$ becomes greater than one and approaches infinite, while will be flattened as a becomes nearest to zero. That means that for a given fixed atomic charge Z, the volume function will become sharper at the origin as higher the function rank grows, and flatter when for a fixed rank n the atomic charge grows and becomes: $Z^2 \gg n\pi$.

This kind of trend will certainly be similar in real atoms and by extension in molecules. That means for molecules with a small fixed number of electrons, the higher rank volume functions will become sharper around the nuclei, while for a fixed rank the same function will become flatter for molecules with increasing number of electrons.

4 Interpretation of the VF

Using the generic VF definition as provided in Eq. (3), and with the experience of the Gaussian example of the previous section in mind, it is easy to see that:

$$\forall \upsilon^{(n)} \left(\mathbf{r} \right) : \left\langle \upsilon^{(n)} \left(\mathbf{r} \right) \right\rangle = \left\langle \left\langle \rho^n \right\rangle^{-1} \left| \rho \left(\mathbf{r} \right) \right|^n \right\rangle = \left\langle \rho^n \right\rangle^{-1} \left\langle \left| \rho \left(\mathbf{r} \right) \right|^n \right\rangle = 1.$$

That is: nth rank VFs are normalized functions within the space where they belong and because of its positive definiteness in addition they can be considered as probability distributions.

The space where VF can be attached it is easy to define, by employing the vector semispace [5]: $P\left(\mathbf{R}^{+}\right)$ containing the DFs as elements. The unit shell: S_1, see also [4,8] for more details on unit shells, of such a space contains the ShF or the first rank VF:

$$S_1 \subset P\left(\mathbf{R}^{+}\right) \wedge \forall \theta\left(\mathbf{r}\right) \in S_1 : \langle \theta\left(\mathbf{r}\right) \rangle = 1 \rightarrow \sigma\left(\mathbf{r}\right) = \upsilon^{(1)}\left(\mathbf{r}\right) \in S_1.$$

Constructing the tensorial product of the vector semispace: $P\left(\mathbf{R}^{+}\right)$, such that:

$$P^{(n)}\left(\mathbf{R}^{+}\right) = \overset{n}{\underset{I=1}{\otimes}} P\left(\mathbf{R}^{+}\right) \rightarrow |\rho\left(\mathbf{r}\right)|^{n} \in P^{(n)}\left(\mathbf{R}^{+}\right),$$

and then defining the unit shell of such a tensorial product of vector semispaces as:

$$\forall \theta\left(\mathbf{r}\right) \in P\left(\mathbf{R}^{+}\right) \wedge$$
$$S_1^{(n)} \subset P^{(n)}\left(\mathbf{R}^{+}\right) : \forall \theta^{(n)}\left(\mathbf{r}\right) = |\theta\left(\mathbf{r}\right)|^{n} \in P^{(n)}\left(\mathbf{R}^{+}\right) \wedge$$
$$\langle |\theta\left(\mathbf{r}\right)|^{n} \rangle = 1 \rightarrow \theta^{(n)}\left(\mathbf{r}\right) \in S_1^{(n)},$$

Therefore, this implies that any VF will fulfill by construction:

$$\forall \upsilon^{(n)}\left(\mathbf{r}\right) \in S_1^{(n)}.$$

Hence, nth order VF are nothing else, but elements of the unit shell of the tensorial product of the vector semispace where they belong. ShFs are a particular case of VF. Alternatively, reversing the previous statement: VFs are generalized ShF. Moreover, as it has been previously noted: the whole VF collection can be seen as a probability distribution assembly.

5 Volume functions and generalized Carbó indices

Going beyond what has been described until now, one can start on the fact the integral of the product of several DF, correspond to a generalized scalar product [6,7], which can produce a generalized Carbó index, see for example [8,9].

Suppose an indefinite number of DF collected into a set: $P = \{\rho_I\left(\mathbf{r}\right) | I = 1, n\}$. A generalized scalar product [7], involving the elements of the set P, can be defined in a similar way as the norms giving rise to the initially defined VF:

$$\langle \rho_1 \rho_2 \ldots \rho_n \rangle = \int_{D} \rho_1\left(\mathbf{r}\right) \rho_2\left(\mathbf{r}\right) \ldots \rho_n\left(\mathbf{r}\right) d\mathbf{r}.$$

The above defined integral is nothing else than a n-tuple DF quantum similarity measure, see for example [5,8,16]. The nth norms defined in the previous sections, can be employed to obtain HDF not belonging to the unit shell though. In this case one can define the collection of HDF by means of the algorithm:

$$\forall \rho\left(\mathbf{r}\right): \left\langle \rho^n \right\rangle = \int_D \left| \rho\left(\mathbf{r}\right) \right|^n d\mathbf{r} \to p^{(n)}\left(\mathbf{r}\right) = \left\langle \rho^n \right\rangle^{-\frac{1}{n}} \rho\left(\mathbf{r}\right),$$

which can be considered belonging to some shell of the semispace $P(\mathbf{R}^+)$:

$$\forall p^{(n)}\left(\mathbf{r}\right): \lambda = \left\langle p^{(n)}\left(\mathbf{r}\right)\right\rangle = \left\langle \rho^n \right\rangle^{-\frac{1}{n}} \left\langle \rho\left(\mathbf{r}\right)\right\rangle = N \left\langle \rho^n \right\rangle^{-\frac{1}{n}} \to p^{(n)}\left(\mathbf{r}\right) \in S_{\lambda;}$$

A generalized product involving n homothetic functions of such kind: $\Pi^{(n)} = \left\{ p_I^{(n)}\left(\mathbf{r}\right) | I = 1, n \right\}$, can be expressed as the nth rank tensor:

$$\begin{aligned} r_{1,2,\ldots,n}^{(n)} &= \left\langle p_1^{(n)}\left(\mathbf{r}\right) p_2^{(n)}\left(\mathbf{r}\right) \ldots p_n^{(n)}\left(\mathbf{r}\right)\right\rangle \\ &= \left(\left\langle \rho_1^n \right\rangle \left\langle \rho_2^n \right\rangle \ldots \left\langle \rho_n^n \right\rangle\right)^{-\frac{1}{n}} \left\langle \rho_1\left(\mathbf{r}\right) \rho_2\left(\mathbf{r}\right) \ldots \rho_n\left(\mathbf{r}\right)\right\rangle, \end{aligned} \quad (6)$$

which has the structure of a generalized Carbó index.

This can be assumed in this way because when all the involved functions are the same: $r_{1,2,\ldots,n}^{(n)} = 1$. Expression (6) can be thus interpreted as the cosine of the collective n-dimensional angle, subtended by all the involved DF. Moreover, according to this generalized collective cosine interpretation, Eq. (6) is *invariant* if initially defined DFs are substituted by the associated ShFs.

The sets of HDF like $\Pi^{(n)}$, describe another generalization of ShFs, because when their order is the unit: $p^{(1)}\left(\mathbf{r}\right) = \left\langle \rho \right\rangle^{-1} \rho = N^{-1} \rho = \sigma$, so the first order scaled functions become ShF. Thus, nth order HDF of this kind are well adapted to compute n-tuple DF generalized Carbó indices. Somehow this kind of HDF functions corresponds to another complementary generalization of ShF, but as they do not belong to a homogeneous unit shell as VFs are, it is perhaps not worth to name them specifically.

6 Conclusions

ShFs can be easily generalized by using tensorial products of vector semispaces, where DFs belong. In this way, they originate a VF collection. Alternative HDFs can be also defined, obtaining another generalization of ShF, which can be employed to effortlessly produce generalized Carbó indices.

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