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Generation of molecular fields, quantum similarity measures and related questions

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A straightforward discussion on how to generate molecular fields is developed within the postulates of quantum mechanics. The theoretical formalism points towards the generalization and extension of the well-known molecular field forms, associated to density function and electrostatic molecular potential (EMP), including another category of fields associated to quantum molecular similarity measures. The results show that the new formalism can be easily applied to obtain an unlimited number of new information about molecular behavior.

KEY WORDS: quantum molecular fields, quantum similarity measures, density functions, electrostatic molecular potential, quantum similarity fields

1. Introduction

Since many years ago, numerous authors have increasingly employed molecular fields to obtain information on molecular chemical behavior, see for a recent comprehensive review reference [1]; also, molecular field values within a grid have been currently used as a source of parameters in QSPR studies, see for example references [2–4] and, finally, they have been employed as a source of information in quantum similarity studies [5]. Molecular fields can have diverse origins as the ones generated empirically for molecular mechanics purposes, see for example the first chapter of reference [1] or can be constructed according to quantum mechanical postulates [6–9]. Here, in a systematic way, will be described the generation of molecular fields within quantum mechanical rules, by means of integral transforms and quantum similarity measures. Furthermore,

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it will be discussed a possible way to use them for similar purposes than the ones already studied in the current literature, but trying to go beyond the present usage, looking for new techniques and applications.

2. Preliminary definition

In order to avoid from the start a fuzzy description of the subject of this work, a definition of molecular field follows:

Definition 1. A molecular field is a function whose variables are the three-dimensional space coordinates, embedding a known molecular structure.

Thus, the first order density function and the electrostatic molecular potential (EMP) are well known examples of molecular fields, which fit the Definition 1. However, the on purpose definition has a formally unrestricted setup in order to contain EMP and similar related functions too. However, it is well known that the total density or the EMP, when considered as a sum of electronic and nuclear contributions, possesses discontinuities at the nuclear coordinates of any molecule, due to the point-like structure of nuclear charge contributions. Despite of this, EMP has been employed in several occasions without considering this drawback, for example in molecular similarity studies [2,4]. Another important problem, which shall concern potential users of molecular fields, corresponds to their use as providers of parameters in QSPR studies, as it has been commented before. Employing molecular fields for this purpose is usually performed taking a point grid surrounding the molecule and computing the molecular field at the grid points. Such a procedure do not takes into account the fact that such sampling of the molecular field for its use as molecular parameters will produce a matrix or vector, which will vary completely, even catastrophically in the case of EMP, when the molecular coordinate frame is rotated or translated, within three-dimensional space. This specially occurs if some grid coordinates are coincident with the nuclear ones.

The first aim of this paper is to describe systematically the way to set up a set of possible molecular fields, void of discontinuities, whose use has to be no longer dependent of a grid, thus becoming rotationally and translationally invariant. The subsidiary purpose of this study is to comment and give complementary information about some aspects of quantum molecular fields.

3. Generalization of usual molecular fields

A molecular field family can always be generated within quantum mechanical theoretical structure by knowing the molecular first or higher order density function. This statement corresponds to the customary setup of quantum mechanics, stating that the density function contains all the information about a given quantum object.

Therefore, Definition 1, could be modified to include the elements discussed so far, providing the following:

Definition 2. A molecular field is *a continuous function, derivable up to any order, deduced from the quantum mechanical density function,* whose variables are the three dimensional space coordinates, embedding a known molecular structure.

The italics denote the difference between former Definition 1 and the present one.

3.1. Generation of usual molecular fields

In order to construct molecular fields according to Definition 2, then, initially one can recognize that the first order density function and the *electronic* part of the EMP can be considered included within the standards of the new definition form and follow the quantum path with them.

3.2. General integral generation

A mathematical formulation of Definition 2 can be set up in the following way. Suppose known the quantum mechanical density function, $\rho_F(\mathbf{r}\,|\mathbf{R}_F)$, of a given molecule F, possessing atomic coordinates $\mathbf{R}_F$, fixed in space. The expectation value of some function or Hermitian operator, $M(\mathbf{r},\mathbf{R})$, acting as an integral transformation kernel, can be written as:

$$\mu(\mathbf{R}) = \langle M(\mathbf{R})\rangle = \int_D M(\mathbf{r}\,|\mathbf{R})\,\rho_F(\mathbf{r}\,|\mathbf{R}_F)\,\mathrm{d}\mathbf{r}, \tag{1}$$

where, $\mathbf{r}$ and $\mathbf{R}$ correspond to some three-dimensional space coordinates. Thus, in this manner a molecular field can be generated as an integral transform of the density function, as described in equation (1).

3.3. Generation of the density function

The density function itself can be generated in this way, just using a three-dimensional Dirac's delta function as kernel in the expectation value as described in the integral equation (1):

$$M(\mathbf{r}\,|\mathbf{R}) = \delta(\mathbf{r}-\mathbf{R}) \rightarrow \mu(\mathbf{R}) = \rho_F(\mathbf{R}\,|\mathbf{R}_F)\,. \tag{2}$$

The choice of the type (2) kernel can be generalized using a Gaussian function:

$$M(\mathbf{r}\,|\mathbf{R};\alpha) = N(\alpha)\exp\left(-\alpha\,|\mathbf{r}-\mathbf{R}|^2\right)$$
$$\rightarrow \mu(\mathbf{R};\alpha) = N(\alpha)\int_D \exp\left(-\alpha\,|\mathbf{r}-\mathbf{R}|^2\right)\rho_F(\mathbf{r}\,|\mathbf{R}_F)\,\mathrm{d}\mathbf{r},$$

where $N(\alpha)$ is a normalization constant. The expectation value above has the property:

$$\lim_{\alpha\to\infty}\mu(\alpha;\mathbf{R}) = \mu(\mathbf{R})\,.$$

3.4. The Atomic Shell Approximation (ASA) for the atomic density

It is well known that the atomic density function can be accurately described by means of a spherical distribution, within the context, which was called ASA distribution, employing a linear combination of normalized s-type functions fitted to the *ab initio* first order atomic density function [10,11]. The ASA density function can be written as:

$$\rho_A(\mathbf{r}\,|\mathbf{R}) = \sum_{I\in A}|x_{AI}|^2\,|s_{AI}(\mathbf{r}-\mathbf{R})|^2\,,$$

where the set of coefficients $\{x_{AI}\}$ as well the non-linear parameters of the normalized s-type functions $\{s_{AI}(\mathbf{r}-\mathbf{R})\}$, centered at point $\mathbf{R}$, have been optimally fitted to some atomic density function. For the optimization it is necessary that the set of real positive coefficients $\left\{\omega_{AI} = |x_{AI}|^2\right\}$ remains convex in order that the Minkowski norm of the ASA density functions becomes unit:

$$1 = \langle\rho_A\rangle = \sum_{I\in A}\omega_{AI}\left\langle|s_{AI}|^2\right\rangle = \sum_{I\in A}\omega_{AI}\,.$$

This is a well-known subject, more details can be found in the literature [12,13]. The ASA approach will be employed later on in this paper.

3.5. Analytic form of the holographic theorem

The interesting topological description of the holographic theorem by Mezey [14], can be also discussed at this point. Being the density function the generator of molecular fields, in accord with the usual quantum mechanical theoretical framework and accepting, as it has been discussed at the beginning, that the density function is the source of all the information about the attached molecular system. The analytic holographic theorem, which can be viewed as an enrichment of the topological formulation of Mezey, applies to any kind of density function order.

Suppose it is known a density function of any order in the neighborhood of a given reference point, $\mathbf{R_0}$, of the particle coordinate space. Provided that the derivatives up to any order with respect the particle coordinates are also known at the reference point, then to show the analytical holographic theorem applies in any case, it is just a matter of properly defining the following Taylor series:

$$\rho(\mathbf{R}) = \sum_{p=0}^{\infty} T^{(p)}\left[\rho(\mathbf{R_0})\right],$$

where the set of operators: $\tau = \left\{T^{(p)}\right\}$ is defined as a complete sum of the inward matrix product (inward product) of two pth order tensors:

$$T^{(p)}\left[\rho\left(\mathbf{R_0}\right)\right] = \frac{1}{p!}\left\langle \mathbf{P}^{(p)} * \mathbf{D}^{(p)}\left[\rho\left(\mathbf{R_0}\right)\right]\right\rangle,$$

except for the zeroth order, which is equivalent to the unit operator, that is: $T^{(0)}\left[\rho\left(\mathbf{R_0}\right)\right] = 1\rho\left(\mathbf{R_0}\right)$, the two involved tensors can be defined respectively as the tensor product of the particle coordinates vector referred to the reference point:

$$\mathbf{P}^{(p)} = \bigotimes_{k=1}^{p}\left(\mathbf{R} - \mathbf{R}_0\right),$$

and the tensor product of the gradient operator applied over the density function and evaluated at the reference point:

$$\mathbf{D}^{(p)}\left[\rho\left(\mathbf{R_0}\right)\right] = \bigotimes_{k=1}^{p}\left(\frac{\partial}{\partial \mathbf{R}}\right)\left[\rho\left(\mathbf{R_0}\right)\right] = \left\{\frac{\partial^{p}\left[\rho\left(\mathbf{R_0}\right)\right]}{\partial R_{i_1}\partial R_{i_2}\cdots\partial R_{ip}}\right\} \equiv \left.\frac{\partial^{p}\left[\rho\left(\mathbf{R}\right)\right]}{\partial \mathbf{R}^{p}}\right|_{\mathbf{R}=\mathbf{R_0}}.$$

The complete sum of the inward product of two pth order tensors is defined as a generalized scalar product:

$$\langle \mathbf{A} * \mathbf{B}\rangle = \sum_{i_1}\sum_{i_2}\cdots\sum_{i_p} a_{i_1 i_2 \cdots i_p} b_{i_1 i_2 \cdots i_p},$$

although the summation symbols can be obviated employing Einstein's convention, there they have been preserved to connect the complete summation symbol with the nested sum formalism [15–18].

3.6. *Derivatives of the density function*

The analytic holographic theorem set up has made necessary an easy formal structure for the derivatives, up to any order, of the density function. In the current MO theoretical practice density functions are built by basis sets of Gaussian type orbitals, thus assuring the basic property of derivation, up to any order, associated to Definition 2. It has been Bader, by means of a continued work on the description of bonding throughout the first order density function analysis [9] that has put forward the use of the first and second order derivatives of such density function. But it is interesting to point out that no higher order derivatives had been employed in the literature for such a purpose, as far as the authors know. At least one can perhaps consider that third and fourth order derivatives could provide interesting information too.

4. Generation of the electrostatic molecular potential

The same as in the density function can be said of the electronic part of the EMP, which can be generated by simply using the Coulomb operator as kernel:

$$M(\mathbf{r}\,|\mathbf{R}) = |\mathbf{r}-\mathbf{R}|^{-1} \rightarrow \mu(\mathbf{R}) = V(\mathbf{R}) = \int_D |\mathbf{r}-\mathbf{R}|^{-1}\, \rho_F(\mathbf{r}\,|\mathbf{R}_F)\,\mathrm{d}\mathbf{r}.$$

This general formalism encompassing both density and EMP encourages the development of some discussion on EMP, like the one, which will follow here.

4.1. Generation of the family of the electronic Coulomb-moment molecular fields

However, while looking at the previous EMP construction one becomes aware that a more general situation can be obviously described. Just by using as kernels in the integral (1) anyone of the following operator set or the related to electronic moments or powers other than one of the Coulomb operator; that is, for any value of n:

$$M^{(\pm n)}(\mathbf{r}\,|\mathbf{R}) = |\mathbf{r}-\mathbf{R}|^{\pm n} \rightarrow M^{(\pm n)}(\mathbf{R}) = \int_D |\mathbf{r}-\mathbf{R}|^{\pm n} \rho_F(\mathbf{r}\,|\mathbf{R}_F)\,\mathrm{d}\mathbf{r},$$

where the $n = 0$ value will give a constant no other than the Minkowski norm of the density function. Although some of these fields above defined are related to well-known molecular observables, as far as the authors know, none has been employed in the current literature, except for quantum similarity purposes [19]. It will be quite interesting to observe the behavior of some dipole or quadrupole fields, as well as, besides the everywhere popular EMP, the electrostatic third or fifth power of the coulomb operator could provide alternative information on molecular behavior.

4.2. Electronic part of EMP

The old idea of the electrostatic molecular potential described by Scrocco and coworkers [6,7] and further systematically applied by Politzer et al. [8], can be studied from the point of view of the present work. The electrostatic part of the EMP is defined as:

$$V_F(\mathbf{R}) = -\int_\Delta |\mathbf{r}-\mathbf{R}|^{-1}\, \rho_F(\mathbf{r})\,\mathrm{d}\mathbf{r}, \tag{3}$$

and has been interpreted as the Coulomb interaction energy between the electronic density of system F and a positive point charge, a proton located at the position $\mathbf{R}$.

5. Quantum similarity molecular fields (QSMF)

In the previous introduction it has been provided an easy way to describe the usual molecular fields, and in this manner the possibility to generate new fields has been trivially made. The option to rewrite the generation of EMP, as in the integral (8) permits to take a next step, which could be the description of new field generation under the ideas of quantum similarity, so this section will be devoted to this task.

5.1. Generation of molecular fields as quantum similarity measures

The brief introduction on the generation of well-known molecular fields and their easy generalization permits to consider cases that are even more general. Suppose known the first order density function of two molecules F and M : $\rho_F(\mathbf{r}\,|\mathbf{R}_F) \wedge \rho_M(\mathbf{r}\,|\mathbf{R}_M)$, where in both functions are explicitly given the coordinate framework symbols of both molecular structures, noted by: $\mathbf{R}_F \wedge \mathbf{R}_M$, while by $\mathbf{r}$ is noted the three-dimensional space coordinates acting as variables. The molecular frame $\mathbf{R}_F$ is left fixed in the construction procedure, while the molecular coordinates of the structure M can be varied by means of any rotation–translation transformation, which can formally be expressed as:

$$\mathbf{R}_M \rightarrow \mathrm{R}[\Theta]\,(\mathbf{R}_M) + \mathbf{R} = \mathbf{R}_M\,(\Theta, \mathbf{R}).$$

Then, the measure:

$$z_{FM}\,(\Omega, \Theta, \mathbf{R}) = \int_D \int_{D'} \rho_F(\mathbf{r}\,|\mathbf{R}_F)\Omega\left(\mathbf{r}, \mathbf{r}'\right) \rho_M\!\left(\mathbf{r}'\,|\mathbf{R}_M\,[\Theta, \mathbf{R}]\right) \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}', \tag{4}$$

when the positive definite operator $\Omega\left(\mathbf{r}, \mathbf{r}'\right)$ is chosen once for all, is a function of the rotation angles Θ and translation coordinates $\mathbf{R}$. This is the same as to have employed a kernel in equation (1) made by the integral operator:

$$M\,(\mathbf{r}, \Theta, \mathbf{R}) = \int_{D'} \Omega\left(\mathbf{r}, \mathbf{r}'\right) \rho_M\!\left(\mathbf{r}'\,|\mathbf{R}_M\,[\Theta, \mathbf{R}]\right) \mathrm{d}\mathbf{r}'.$$

In the additional choice that the rotation angles are maintained constant: $\Theta = \Theta_0$, then the measure (4) becomes a function of the translation variables $\mathbf{R} \equiv (x, y, z)$:

$$z_{FM}\,(\Omega, \Theta_0, \mathbf{R}) \rightarrow z_{FM}\,(\Omega, \Theta_0\,|\mathbf{R}) \rightarrow \theta_{FM}\,(\Omega, \mathbf{R}) \equiv \theta_{FM}\,(\mathbf{R}), \tag{5}$$

therefore the measure $\theta_{FM}\,(\mathbf{R})$ is a molecular field according to definition 2.

However, whenever the operator chosen is positive definite, the construction (4) with or without the constraint (5) produces a positive definite field. Thus, the possibility of the following definition is set:

Definition 3. A quantum similarity molecular field is a positive definite molecular field defined as in Definition 2, constructed by means of the measure (4).

6. Quantum similarity atomic molecular fields

As a particular case of the Definition 3, which in any circumstance avoids the use of the rotation angles, one can use as the moving density function any *atomic density*, ρ_A, in this case:

$$\rho_M(\mathbf{r}\,|\Theta,\ \mathbf{R}) \to \rho_A(\mathbf{r}\,|\mathbf{R}),$$

so the molecular field generated by the atomic density function becomes defined by the measure:

$$z_{FA}\,(\Omega\,|\mathbf{R}) = \int_D \int_{D'} \rho_F(\mathbf{r}\,|\mathbf{R}_F)\Omega\left(\mathbf{r},\mathbf{r}'\right)\rho_A\left(\mathbf{r}'\,|\mathbf{R}\right)\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'. \tag{6}$$

Furthermore, in case one wants to avoid the explicit use of a positive definite operator it is sufficient to choose it in the form of an appropriate Dirac's function:

$$\Omega\left(\mathbf{r},\mathbf{r}'\right) = \delta\left(\mathbf{r}-\mathbf{r}'\right),$$

so the simplified final molecular field becomes:

$$z_{FA}\,(\Omega\,|\mathbf{R}) \to \theta_{FA}(\mathbf{R}) = \int_D \rho_F(\mathbf{r}|\mathbf{R}_F)\,\rho_A(\mathbf{r}\,|\mathbf{R})\,\mathrm{d}\mathbf{r}, \tag{7}$$

which only depends of the space points $\mathbf{R}$.

Thus for a given molecule F, one can have a set of molecular fields according to the chosen atom density function: $\theta_{FA}(\mathbf{R})$. It is also easy to obtain the first order density functions for atomic ions, so the polarized molecular fields: $\theta_{FA^+}(\mathbf{R}) \wedge \theta_{FA^-}(\mathbf{R})$ can be also available. One can name such atomic generated molecular fields as: *Quantum Similarity Atomic Molecular Fields* (QSAMF).

The molecular fields of type (7) have been for a long time described [20] but its use has been limited to few applications.

6.1. Electronic part of the EMP as a QSAMF

It is obvious that the function: $-V_F(\mathbf{R})$ as expressed in equation (3) is a smooth positive definite function; thus, a good candidate to be considered a particular case of a QSAMF, as appears according to definition 3. This can be done easily taking into account that the corresponding atomic density becomes in this situation a Dirac function with the appropriate sign. The integral (3) can be written in a more interesting way within this context as:

$$-V_F(\mathbf{R}) = \int_{\Delta}\int_{\Delta'} \rho_F(\mathbf{r}) \left|\mathbf{r}-\mathbf{r}'\right|^{-1} \delta\left(\mathbf{r}'-\mathbf{R}\right) \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'.$$

Thus, the electronic part of the EMP is just a QSAMF with the atomic density function described as a point-like charge and the integral defining the field has explicitly a weighting Coulomb operator. Of course, one can easily generalize this last representation employing instead of the Dirac delta function a Gaussian function, so:

$$-V_F(\alpha;\mathbf{R}) = N(\alpha)\int_{\Delta}\int_{\Delta'} \rho_F(\mathbf{r}) \left|\mathbf{r}-\mathbf{r}'\right|^{-1} \exp\left(-\alpha\left|\mathbf{r}'-\mathbf{R}\right|^2\right) \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}', \qquad (8)$$

where $N(\alpha)$ is a normalization factor, then the EMP will be obtained as the limit:

$$\lim_{\alpha\to\infty} V_F(\alpha;\mathbf{R}) = V_F(\mathbf{R}).$$

Both discussed generalizations of the density function and of EMP, have originated the possibility of constructing the nuclear part of both molecular fields as a superposition of Gaussian charges, centered at the molecular nuclei [21]. This possibility will not be further discussed here, in order to keep the main unlimited subject and precise purpose of this paper within limits. It will be only commented that, in this manner, the total nuclear and electronic part of the molecular fields will become within the framework of Definition 2.

7. Comparison of two quantum similarity atomic molecular fields

Suppose now that two QSAMF generated by the densities of atoms A and B, for a given molecule are known, that is they can be defined as the measures:

$$\theta_{FA}(\mathbf{R}) = \int_D \rho_F(\mathbf{r}\,|\mathbf{R}_F)\,\rho_A(\mathbf{r}\,|\mathbf{R})\,\mathrm{d}\mathbf{r} \wedge \theta_{FB}(\mathbf{R}) = \int_D \rho_F(\mathbf{r}\,|\mathbf{R}_F)\,\rho_B(\mathbf{r}\,|\mathbf{R})\,\mathrm{d}\mathbf{r},$$

then, one can find the associated p-th order norms

$$N_{FX}^{(p)} = \int_{\Delta} |\theta_{FX}(\mathbf{R})|^p \mathrm{d}\mathbf{R} = \int_{\Delta}\left|\int_D \rho_F(\mathbf{r}\,|\mathbf{R}_F)\,\rho_X(\mathbf{r}\,|\mathbf{R})\,\mathrm{d}\mathbf{r}\right|^p \mathrm{d}\mathbf{R}\,(X=A,B),$$

and normalize them in order to assign both fields to the unit shell of some vector semispace. Choosing a Euclidian norm with $p = 2$, then normalization will provide the new fields:

$$\theta^N_{FX}(\mathbf{R}) = \left(N^{(2)}_{FX}\right)^{-\frac{1}{2}} \theta_{FX}(\mathbf{R})\,(X = A, B),$$

and an overlap-like comparison will yield the measure:

$$\left\langle \theta^N_{FA} \mid \theta^N_{FB} \right\rangle = \int_\Delta \theta^N_{FA}(\mathbf{R})\,\theta^N_{FB}(\mathbf{R})\,\mathrm{d}\mathbf{R},$$

which in the most simplified form not only can be made intramolecular but associated to the same atom, becoming the measure the Euclidian norm, that is:

$$\left\langle \theta^N_{FA} \mid \theta^N_{FA} \right\rangle = \int_\Delta \left|\theta^N_{FA}(\mathbf{R})\right|^2 \mathrm{d}\mathbf{R} = N^{(2)}_{FA} = 1.$$

Moreover, the same type of comparison can be made between two different molecular structures, F and G, say and the same atomic density to generate both molecular fields:

$$\left\langle \theta^N_{FA} \mid \theta^N_{GA} \right\rangle = \int_\Delta \theta^N_{FA}(\mathbf{R})\,\theta^N_{GA}(\mathbf{R})\,\mathrm{d}\mathbf{R},$$

constituting in this way a set of intramolecular or intermolecular field comparisons respectively.

The comparison of the QSAMF can be performed within the usual description of quantum similarity measures.

7.1. QSAMF using ASA density functions

Taking into account the ASA form, which can be written using the following symbols for the squared modules of the s-type functions:

$$\sigma_{AI}(\mathbf{r} - \mathbf{R}) = |s_{AI}(\mathbf{r} - \mathbf{R})|^2,$$

then an ASA derived QSAMF can be written as:

$$\begin{aligned}\theta_{FA}(\mathbf{R}) &= \sum_{I \in A} \omega_{AI} \int_\Delta \rho_F(\mathbf{r})\,\sigma_{AI}(\mathbf{r} - \mathbf{R})\mathrm{d}\mathbf{r} \\ &= \sum_{I \in A} \omega_{AI} \langle \rho_F \mid \sigma_{AI} \rangle = \sum_{I \in A} \omega_{AI} \theta_{FA;I}.\end{aligned} \tag{9}$$

The molecular field obtained in that way can be compared with a density of another molecule G, $\rho_G(\mathbf{r})$, say, producing the measure:

$$\begin{aligned}\langle\theta_{FA} \mid \rho_G\rangle &= \int_\Delta \theta_{FA}(\mathbf{R})\rho_G(\mathbf{R})\,\mathrm{d}\mathbf{R}\\ &= \sum_{I\in A}\omega_{AI}\int_\Delta\left[\int_D \rho_F(\mathbf{r})\,\sigma_{AI}(\mathbf{r}-\mathbf{R})\,d\mathbf{r}\right]\rho_G(\mathbf{R})\mathrm{d}\mathbf{R}\\ &= \sum_{I\in A}\omega_{AI}\int_D \rho_F(\mathbf{r})\left[\int_\Delta \sigma_{AI}(\mathbf{r}-\mathbf{R})\,\rho_G(\mathbf{R})\,\mathrm{d}\mathbf{R}\right]\mathrm{d}\mathbf{r}\\ &= \sum_{I\in A}\omega_{AI}\int_D \rho_F(\mathbf{r})\theta_{GA;I}(\mathbf{r})\,\mathrm{d}\mathbf{r}\\ &= \int_D \rho_F(\mathbf{r})\theta_{GA}(\mathbf{r})\,\mathrm{d}\mathbf{r} = \langle\rho_F \mid \theta_{GA}\rangle, \end{aligned} \qquad (10)$$

which appears to be symmetrical with respect of the molecular density functions in such a way that the QSAMF can be associated to either the molecular structure F or to the G, without altering the comparison measure.

This behavior can be explained because one can rewrite the comparison measure (10) as a triple density measure:

$$\begin{aligned}\langle\theta_{FA} \mid \rho_G\rangle &= \langle\rho_F \mid \theta_{GA}\rangle\\ &= \int_\Delta\int_D \rho_F(\mathbf{r})\,\rho_A(\mathbf{r}-\mathbf{R})\,\rho_G(\mathbf{R})\,d\mathbf{R}d\mathbf{r} = \langle\rho_F|\,\rho_A\,|\rho_G\rangle\,,\end{aligned}$$

thus, the measures (10) can be interpreted as a quantum similarity measure involving the density functions of both molecular structures F and G, weighted by the atomic density, which acts as an operator [22].

The Euclidian norm of the QSAMF (9) is related to the atomic selfsimilarity computed with the involved atomic densities at the points $\{\mathbf{R};\mathbf{R}'\}$, that is:

$$\theta_{AA}(\mathbf{R};\mathbf{R}') = \int_\Delta \rho_A(\mathbf{r}-\mathbf{R})\rho_A(\mathbf{r}-\mathbf{R}')\,\mathrm{d}\mathbf{r}. \qquad (11)$$

In the ASA approach the expression (11) above can be written as:

$$\theta_{AA}(\mathbf{R};\mathbf{R}') = \sum_{I\in A}\sum_{J\in A}\omega_{AI}\omega_{AJ}\int_D \sigma_{AI}(\mathbf{r}-\mathbf{R})\,\sigma_{AJ}(\mathbf{r}'-\mathbf{R}')\,\mathrm{d}\mathbf{r},$$

which collecting the convex coefficient set into a unit shell column vector:

$$\mathbf{w}_A = \{\omega_{AI}\}\,,$$

can be written as:

$$\theta_{AA}(\mathbf{R};\mathbf{R}') = \mathbf{w}_A^T\mathbf{S}_{AA}(\mathbf{R};\mathbf{R}')\,\mathbf{w}_A,$$

and the matrix elements can be written in turn as:

$$\mathbf{S}_{AA}\left(\mathbf{R};\mathbf{R}'\right)=\left\{\mathbf{S}_{AA;IJ}\left(\mathbf{R};\mathbf{R}'\right)=\int_D \sigma_{AI}\left(\mathbf{r}-\mathbf{R}\right)\sigma_{AJ}\left(\mathbf{r}'-\mathbf{R}'\right)\mathrm{d}\mathbf{r}\right\}. \tag{12}$$

The matrix elements (12) in the case that only 1s GTO are used become a Gaussian function, like:

$$\mathbf{S}_{AA;IJ}\left(\mathbf{R};\mathbf{R}'\right)=K_{A;IJ}\exp\left(\gamma_{A;IJ}\left|\mathbf{R}-\mathbf{R}'\right|^2\right),$$

where: $K_{A;IJ}\wedge\gamma_{A;IJ}$ are constants depending of the normalization factors and the exponents of the functions involved in the definition of the integral in equation (12).

Then, with this information, the QSAMF norm can be written as:

$$\begin{aligned}N_{FA}^{(2)}&=\int_\Delta|\theta_{FA}\left(\mathbf{R}\right)|^2\mathrm{d}\mathbf{R}\\&=\int_\Delta\left[\int_D\rho_F\left(\mathbf{r}\right)\rho_A\left(\mathbf{r}-\mathbf{R}\right)\mathrm{d}\mathbf{r}\int_{D'}\rho_F\left(\mathbf{r}'\right)\rho_A\left(\mathbf{r}'-\mathbf{R}\right)\mathrm{d}\mathbf{r}'\right]\mathrm{d}\mathbf{R}\\&=\int_D\rho_F\left(\mathbf{r}\right)\int_{D'}\rho_F\left(\mathbf{r}'\right)\left[\int_\Delta\rho_A\left(\mathbf{r}-\mathbf{R}\right)\rho_A\left(\mathbf{r}'-\mathbf{R}\right)\mathrm{d}\mathbf{R}\right]\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\\&=\int_D\rho_F\left(\mathbf{r}\right)\int_{D'}\rho_F\left(\mathbf{r}'\right)\left[\theta_{AA}\left(\mathbf{r};\mathbf{r}'\right)\right]\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\\&=\left\langle\rho_F\right|\theta_{AA}\left|\rho_F\right\rangle,\end{aligned}$$

which can be interpreted as a selfsimilarity measure of the molecular structure F weighted by the atomic selfsimilarity as defined in the measure (11).

8. Ion generated QSAMF

In this section it will be studied a simple approach for ionic QSMF generators. Suppose written the total first order density of some closed shell molecule or atom as:

$$\rho^{(0)}\left(\mathbf{r}\right)=2\sum_{I\in O}\rho_I\left(\mathbf{r}\right),$$

where the set: $\{\rho_I\,|I\in O\}$ are the contributions of each occupied MO to the total density, and O represents the set of subindices associated to occupied MO. A Koopmans-like description can be used for a positive ion:

$$\forall K\in O:\rho_K^{(+)}\left(\mathbf{r}\right)\approx\rho^{(0)}\left(\mathbf{r}\right)-\rho_K\left(\mathbf{r}\right),$$

while the same idea can be applied to negative ions, so if one represents by V the subindices attached to the virtual MO's, then:

$$\forall L\in V:\rho_L^{(-)}\left(\mathbf{r}\right)\approx\rho^{(0)}\left(\mathbf{r}\right)+\rho_L\left(\mathbf{r}\right).$$

Thus, three kinds of QSMF of type (4) can be generated for a given molecule M:
(A)

$$z_{FM}(\Omega,\Theta,\mathbf{R})=\int_D\int_{D'}\rho_F(\mathbf{r},\mathbf{R}_F)\Omega\left(\mathbf{r},\mathbf{r}'\right)\rho_M^{(0)}\left(\mathbf{r}',\mathbf{R}_M[\Theta,\mathbf{R}]\right)\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}',$$

(B)

$$\begin{aligned}z_{FM;K}^{(+)}(\Omega,\Theta,\mathbf{R})&=\int_D\int_{D'}\rho_F(\mathbf{r},\mathbf{R}_F)\Omega\left(\mathbf{r},\mathbf{r}'\right)\rho_{M;K}^{(+)}\left(\mathbf{r}',\mathbf{R}_M[\Theta,\mathbf{R}]\right)\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\\&=z_{FM}^{(0)}(\Omega,\Theta,\mathbf{R})-\int_D\int_{D'}\rho_F(\mathbf{r},\mathbf{R}_F)\Omega\left(\mathbf{r},\mathbf{r}'\right)\rho_{M;K}\left(\mathbf{r}',\mathbf{R}_M[\Theta,\mathbf{R}]\right)\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}',\end{aligned}$$

(C)

$$\begin{aligned}z_{FM;L}^{(-)}(\Omega,\Theta,\mathbf{R})&=\int_D\int_{D'}\rho_F(\mathbf{r},\mathbf{R}_F)\Omega\left(\mathbf{r},\mathbf{r}'\right)\rho_{M;L}^{(-)}\left(\mathbf{r}',\mathbf{R}_M[\Theta,\mathbf{R}]\right)\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\\&=z_{FM}^{(0)}(\Omega,\Theta,\mathbf{R})+\int_D\int_{D'}\rho_F(\mathbf{r},\mathbf{R}_F)\Omega\left(\mathbf{r},\mathbf{r}'\right)\rho_{M;L}\left(\mathbf{r}',\mathbf{R}_M[\Theta,\mathbf{R}]\right)\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'.\end{aligned}$$

From the cases (B) and (C) above one can deduce that the relevant information generated by the ionic Koopmans-like QSMF, are the integrals:

$$\theta_{FM;P}^{(\lambda)}=-\lambda\int_D\int_{D'}\rho_F(\mathbf{r},\mathbf{R}_F)\Omega\left(\mathbf{r},\mathbf{r}'\right)\rho_{M;P}\left(\mathbf{r}',\mathbf{R}_M[\Theta,\mathbf{R}]\right)\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}',$$

where, when $P\in O\rightarrow\lambda=+1$ and if $P\in V\rightarrow\lambda=-1$. For a given molecular system F, the set of ionic Koopmans QSMF: $\left\{\theta_{FM;P}^{(\lambda)}[\Omega,\Theta,\mathbf{R}]\right\}$ can provide with a quite large information on the nature of the interaction with the ionic system M.

The obvious conclusion is that every MO belonging to system M can be used to generate an appropriate QSMF.

9. Other possibilities to generate molecular fields, associated to the Mulliken projection of the density function

Although the present and final commentary has a vast potential, in order to do not enlarge in a tedious manner this paper, it will only be briefly sketched the possible way to use projected density functions for the purpose to describe molecular fields.

Recently, has been described within the MO theory a natural way to project the density function by means of some well defined operators, which can be called Mulliken projectors [23]. It has been proved that Mulliken projectors can be used to construct Mulliken charges as expectation values of these operators. Tensor products of them, applied to the exchange part of the density functions of any order, generate bond orders or bond indices, involving an indefinite number of atoms also as quantum mechanical expectation values. Besides to link the empirical lore, associated in theoretical chemistry to charges and bond indices, with sound quantum mechanical procedures, Mulliken projectors permit to project the density functions over a chosen molecular fragment or a set of MO. The theoretical construction is trivial and is based in the simple Mulliken projector over a basis function $\chi_\mu(\mathbf{r})$, which can be written as:

$$\Pi_\mu(\mathbf{r}) = \sum_\nu S_{\mu\nu}^{(-1)} \left|\chi_\mu(\mathbf{r})\right\rangle \left\langle \chi_\nu(\mathbf{r})\right| ,$$

where the elements of the inverse overlap matrix $\mathbf{S}^{-1} = \left\{S_{\mu\nu}^{(-1)}\right\}$ act as the superposition coefficients of the direct product of the basis set functions $\left\{\chi_\mu(\mathbf{r})\right\}$. Employing the Mulliken operator over the first order density function, which within MO theory can be written in terms of the basis set functions and the charge and bond order matrix: $\mathbf{D} = \left\{D_{\mu\nu}\right\}$:

$$\rho(\mathbf{r}) = \sum_\mu \sum_\nu D_{\mu\nu} \left|\chi_\mu(\mathbf{r})\right\rangle \left\langle \chi_\nu(\mathbf{r})\right|,$$

produces the density part associated to the chosen basis set function:

$$\begin{aligned}\Pi_\mu[\rho(\mathbf{r})] &= \sum_\alpha \sum_\beta D_{\alpha\beta} \sum_\nu S_{\mu\nu}^{(-1)} S_{\alpha\nu} \left|\chi_\mu\right\rangle \left\langle \chi_\beta\right| \\ &= \sum_\beta D_{\mu\beta} \left|\chi_\mu\right\rangle \left\langle \chi_\beta\right| = \rho_\mu(\mathbf{r}) ,\end{aligned}$$

in such a way that the original density function can be reconstructed as:

$$\rho(\mathbf{r}) = \sum_\mu \Pi_\mu[\rho(\mathbf{r})] = \sum_\mu \sum_\beta D_{\mu\beta} \left|\chi_\mu\right\rangle \left\langle \chi_\beta\right| = \sum_\mu \rho_\mu(\mathbf{r}).$$

From the definition of the basis set function parts: $\left\{\rho_\mu(\mathbf{r})\right\}$ of the density function, it can be seen atomic density function parts: $\{\rho_A(\mathbf{r})\}$ can be defined in the same way as the superposition of the basis set parts belonging to a given atomic center:

$$\rho_A(\mathbf{r}) = \sum_{\mu \in A} \rho_\mu(\mathbf{r}) \rightarrow \rho(\mathbf{r}) = \sum_A \rho_A(\mathbf{r}).$$

Thus any subdivision of the density function can be performed in this way, for instance in aromatic hydrocarbons the π-type orbital part of the density function and so on.

These Mulliken operator fragments of the density function can be employed in turn as field generators, in the way it has been commented in this study so far. So, as a possible example, the electronic π-type part of the EMP can be easily described, to mention one of innumerable possibilities open to the imagination of quantum chemists.

10. Conclusions

The prospect to generate molecular fields, other than the usual first order density function and the EMP, has been briefly described. The authors wonder about how this widely unlimited set of possibilities, which can be used to learn more, in the analytical and pictorial sense of the words, about molecular behavior, have not been exploited systematically in quantum chemistry. While the literature repeats incessantly the pictures of density function and EMP analysis without any new point of view, which as it has been shown here, other choices can be equally well defined in many appealing ways under the theoretical coverage of quantum theory. The authors hope that this paper can stimulate the use of alternative ways to visualize molecular structure.

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