# Mathematical aspects of the LCAO MO first order density function (2): Relationships between density functions

Ramon Carbó-Dorca

*Department of Inorganic and Physical Chemistry, Ghent University, Krijgslaan 281, Gent 9000, Belgium*
E-mail: quantumqsar@hotmail.com
Institut de Química Computacional, Universitat de Girona, Girona 17071, Catalonia, Spain

In this paper use is made of the Mulliken atomic density basis set to build up matrix descriptions of the density function and to construct algorithms which permit to express one density function with the atomic basis set of another in the most accurate way possible.

**KEY WORDS:** density functions, Mulliken projectors, Mulliken atomic basis set, density function fitting

## 1. Introduction

In a first paper of a self-contained series dedicated to comment several aspects of the density functions [1], including the comparison of two of them, the description and generation of two possible atomic basis sets was the main task. In the present work, the second paper of the series, the Mulliken atomic basis set will be used for constructing matrix representations of the density function and further details on density functions relationships, will be studied. Extension to second order density problems will be finally sketched.

## 2. First order density function in LCAO MO theory

It is well known that first order molecular density can be expressed within LCAO MO theory in a very general manner, first with the form:

$$\rho_M(\mathbf{r}) = \langle \Gamma * |\mathbf{m}_0\rangle \langle \mathbf{m}_0| \rangle = \sum_i \sum_j \gamma_{ij} |i_0\rangle \langle j_0|, \qquad (1)$$

where $\Gamma = \{\gamma_{ij}\}$ is a Hermitian coefficient matrix, whose elements depend on the computational level employed to obtain the molecular wave function, and $|\mathbf{m}_0\rangle = \{|i_0\rangle\}$ a column vector the whose elements are the one-electron MO functions, which is used to construct a tensor product, yielding an object of the same dimension as the coefficient matrix $\Gamma$. In the form used within equation (1), the coefficient matrix and the MO tensor product are multiplied using an inward matrix product[1] and submitted to a complete sum [2].[2]

The first order density function has a Minkowski norm equal to the number of electrons, $N_M$, of the molecule $M$ considered, that is one can write:

$$\langle \rho_M \rangle = \int_D \rho_M(\mathbf{r}) \, d\mathbf{r} = N_M.$$

In a further step, the matrix $\Gamma$ can be diagonalized by means of a unitary matrix $\mathbf{U}$, fulfilling: $\mathbf{U}^+\mathbf{U} = \mathbf{U}\mathbf{U}^+ = \mathbf{I}$, such that:

$$\Gamma\mathbf{U} = \mathbf{U}\Delta \rightarrow \Delta = Diag(\omega_i) \wedge \Gamma = \mathbf{U}^+\Delta\mathbf{U};$$

in this manner, substituting the coefficient matrix by its spectral decomposition, as written above, the first order density matrix can be expressed as:

$$\rho_M(\mathbf{r}) = \langle \mathbf{U}^+\Delta\mathbf{U}^* |\mathbf{m}_0\rangle \langle \mathbf{m}_0| \rangle = \sum_i \sum_j \left( \sum_k u_{ki}^* u_{kj} \omega_k \right) |i_0\rangle \langle j_0|$$

$$= \langle \Delta^*\mathbf{U}^+ |\mathbf{m}_0\rangle \langle \mathbf{m}_0| \mathbf{U}\rangle = \sum_i \omega_i |i\rangle \langle i|$$

where it has been used the new transformed MO column matrix:

$$\mathbf{U}^+ |\mathbf{m}_0\rangle = |\mathbf{m}\rangle = \{|i\rangle\} \wedge |i\rangle = \sum_k u_{ki}^* |k_0\rangle.$$

As a result of these previous considerations, the diagonal form of the density function can be used in general for any purpose. Hence, in this paper without loss of generality the first order density function diagonal form:

$$\rho_M(\mathbf{r}) = \sum_i \omega_i |i\rangle \langle i| \tag{2}$$

will be employed thereafter.

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[1]The *inward matrix product* between two matrices: $\mathbf{A} = \{a_{ij}\} \wedge \mathbf{B} = \{b_{ij}\}$ of dimension $(m \times n)$, is defined as a matrix of the same dimension by means of the algorithm: $\mathbf{A}^*\mathbf{B} = \mathbf{P} = \{p_{ij}\} \rightarrow \forall i, j : p_{ij} = a_{ij}b_{ij}$.
[2]The *complete sum* of the elements of a matrix of arbitrary dimension $(m \times n)$: $\mathbf{A} = \{a_{ij}\}$, is described according to the algorithm: $\langle \mathbf{A} \rangle = \sum_{i=1}^{m} \sum_{j=1}^{n} a_{ij}$.

## 3.    Density function in the LCAO framework

Now it can be considered that MO are usually expressed in the LCAO formalism; that is, knowing a one-electron basis set, which can be expressed in a column vector form: $|\mathbf{x}\rangle = \{|\mu\rangle\}$, then the MO set is expressed as a linear combination of the basis functions:

$$\forall i : |i\rangle = \langle \mathbf{c}_i^* |\mathbf{x}\rangle = \sum_{\mu} c_{\mu i} |\mu\rangle,$$

where: $\mathbf{c}_i = \{c_{\mu i}\}$ are the coordinates of the $i$th MO with respect to the basis set $|\mathbf{x}\rangle$. Substituting the LCAO MO expansion into the density function (2), one arrives to the well-known expression:

$$\rho_M(\mathbf{r}) = \langle \mathbf{D}^* |\mathbf{x}\rangle \langle \mathbf{x}| \rangle = \sum_{\mu} \sum_{\nu} D_{\mu\nu} |\mu\rangle \langle \nu|, \tag{3}$$

with the so-called charge and bond order matrix $\mathbf{D}$, defined as follows:

$$\mathbf{D} = \{D_{\mu\nu}\} = \sum_{i} \omega_i \mathbf{c}_i \mathbf{c}_i^+.$$

## 4.    Metric matrix and Mulliken projectors

Then, one can take into account that the AO basis set $|\mathbf{x}\rangle$ is customarily attached to the atomic centers, $I$ say, of a given molecule, $M$, so formally one can write:

$$\forall \mu \in I \wedge I \in M : |\mu\rangle \equiv \chi_\mu(\mathbf{r}|\mathbf{R}_I) \rightarrow |\mu\rangle \in I$$

where $\mathbf{R}_I$ are the position coordinates of atomic center $I$. Thus, there can be computed a positive definite metric or overlap matrix for the AO basis set, which can be formally written as:

$$\mathbf{S} = \int_D |\mathbf{x}\rangle \langle \mathbf{x}| d\mathbf{r} = \{S_{\mu\nu}\}.$$

For a given molecular structure, a set of Mulliken projectors can be constructed in such a way that, applied to the molecular density function, yield a density function associated to the AO belonging to a given atomic center [3]:

$$\prod_I = \sum_{\alpha \in I} \sum_J \sum_{\beta \in J} S_{\alpha\beta}^{(-1)} |\alpha\rangle \langle \beta|,$$

that is:

$$
\begin{aligned}
\prod_I [\rho_M] &= \sum_{\alpha \in I} \sum_J \sum_{\beta \in J} S_{\alpha\beta}^{(-1)} |\alpha\rangle \langle\beta| \left[ \sum_\mu \sum_\nu D_{\mu\nu} |\mu\rangle \langle\nu| \right] \\
&= \sum_{\alpha \in I} \sum_J \sum_{\beta \in J} \sum_\mu \sum_\nu D_{\mu\nu} S_{\alpha\beta}^{(-1)} S_{\mu\beta} |\alpha\rangle \langle\nu| \\
&= \sum_{\alpha \in I} \sum_\mu \sum_\nu D_{\mu\nu} \delta_{\alpha\mu} |\alpha\rangle \langle\nu| = \sum_{\alpha \in I} \sum_\nu D_{\alpha\nu} |\alpha\rangle \langle\nu| = \rho_I
\end{aligned}
$$

The result of the Mulliken projectors over the density function can be related to the quantum mechanical background of the Mulliken atomic populations [3B].

## 5. Density function as a superposition of atomic contributions

Therefore, as the Mulliken projectors fulfill:

$$
\sum_{I \in M} \prod_I = \hat{I},
$$

being $\hat{I}$ the unit operator, then, it can be written:

$$
\rho_M(\mathbf{r}) = \sum_{I \in M} \rho_I(\mathbf{r}).
$$

The set of Mulliken atomic density functions obtained in this way: $\{\rho_I(\mathbf{r}) \,|\, I = 1, n_M\}$, has to necessarily form a basis set, able to construct the molecular first order density function with coordinates equal to the unity vector: $|\mathbf{1}\rangle = \{1_k = 1\}$, a vector whose elements are the real unit element. The Mulliken atomic density functions basis sets are necessarily dependent on the computational level and on the completeness of the AO basis set employed in order to obtain the molecular wave function, but for a given molecular structure, the dimension of the subtended semispace will be always the same, $n_M$, the number of atoms or AO centers present in molecule $M$. For that reason, the semispace generated by the atomic density basis set in a given molecular frame is $n_M$-dimensional.

## 6. The Mulliken atomic density functions as basis sets

Here some consequences of the definition of the Mulliken atomic density basis sets are analyzed [1]. First the metric properties of the space generated by the Mulliken atomic densities will be studied, then the Mulliken metric matrices, which will represent in a discrete fashion the density function of a molecule, will be constructed for some simple systems, finally the diagonalization of the metric matrices will be put forward.

(a) The Mulliken atomic density metric matrix as a similarity matrix.

The set of Mulliken atomic density functions seen as a basis set, has to possess a positive definite metric matrix of dimension $(n_M \times n_M)$ in the Euclidian scalar product sense. It is easy to find out that the Mulliken atomic similarity matrix:

$$\mathbf{Z} = \{z_{IJ} \mid \forall I, J \in M\}, \tag{4}$$

where:

$$z_{IJ} = \int_D \rho_I(\mathbf{r}) \, \rho_J(\mathbf{r}) d\mathbf{r} = \langle \rho_I | \rho_J \rangle \tag{5}$$

constitute an adequate Euclidean metric, associated to the Mulliken atomic density basis set functions: $\{\rho_I\}$.

Alternatively, from a formal point of view, the construction of the Mulliken atomic similarity matrix can be described in the following manner. The set of Mulliken atomic density basis set functions can be ordered into a $n_M$-dimensional column vector as:

$$|\rho\rangle = \{\rho_I(\mathbf{r})\}. \tag{6}$$

Then it can be formally written:

$$\mathbf{Z} = \int_D |\rho\rangle \langle \rho| \, d\mathbf{r}.$$

The molecular density function is consequently expressible in terms of the complete sum of the atomic density vector:

$$\rho_M = \langle |\rho\rangle \rangle;$$

moreover, the molecular self-similarity can be written as the complete sum of the elements of the Mulliken atomic similarity matrix:

$$z_M = \int_D |\rho_M(\mathbf{r})|^2 d\mathbf{r} = \langle \mathbf{Z} \rangle.$$

To illustrate the previous discussion, a set of simple examples will be given.

(b) Elementary atomic similarity matrices.

 (i) Homonuclear Diatomic Molecules.

In homonuclear diatomic molecules the density basis set vector can be written in this case as:

$$|\rho\rangle = \begin{pmatrix} \rho_{A_1}(\mathbf{r} - \mathbf{R}_{A_1}) \\ \rho_{A_2}(\mathbf{r} - \mathbf{R}_{A_2}) \end{pmatrix},$$

then the molecular density can be written as:

$$\rho_{A-A}\left(\mathbf{r}\right) = \langle|\rho\rangle\rangle = \rho_{A_1}\left(\mathbf{r} - \mathbf{R}_{A_1}\right) + \rho_{A_2}\left(\mathbf{r} - \mathbf{R}_{A_2}\right)$$

and the atomic similarity matrix can be written in any case as:

$$\mathbf{Z}_{A-A} = \int_D \begin{pmatrix} \rho_{A_1} \\ \rho_{A_2} \end{pmatrix} \begin{pmatrix} \rho_{A_1} & \rho_{A_2} \end{pmatrix} d\mathbf{r} \tag{7}$$
$$= \begin{pmatrix} \int_D \rho_{A_1}\rho_{A_1} d\mathbf{r} & \int_D \rho_{A_1}\rho_{A_2} d\mathbf{r} \\ \int_D \rho_{A_2}\rho_{A_1} d\mathbf{r} & \int_D \rho_{A_2}\rho_{A_2} d\mathbf{r} \end{pmatrix} = \begin{pmatrix} \alpha & \beta \\ \beta & \alpha \end{pmatrix}$$

and the eigenvalues of $\mathbf{Z}_{A-A}$ are: $\theta_\pm = \alpha \pm \beta$. Taking into account that the selfsimilarity $\alpha$, located into the diagonal, will be always greater than the off-diagonal term $\beta$, which heavily depends on interatomic distance; otherwise, the equality $\alpha = \beta$ will mean both molecular centers are collapsed into a unique coordinate. Therefore, this situation will always yield: $\theta_\pm > 0$. Thus, the atomic density functions similarity matrix for homonuclear diatomic molecules is positive definite.

The molecular self-similarity can be easily written in this case as:

$$z_{A-A} = \int_D |\rho_{A-A}|^2 \, d\mathbf{r} = \langle \mathbf{Z}_{A-A} \rangle = 2\left(\alpha + \beta\right) = 2\theta_+.$$

This kind of development reminds of Hückel MO theory, although there is quite a great difference when HMO is compared with the basic theoretical background of the present atomic density basis set theory.

(ii) Homonuclear simplex molecules: equilateral $A_3$ and tetrahedral $A_4$ molecules

The resemblance with HMO theory can go further on if one sets up the Mulliken atomic density similarity matrices for simplex structures made of three or four atoms.

In this case, again it shall be taken into account that the atomic density vector for $A_3$ can be written as:

$$|\rho\rangle = \begin{pmatrix} \rho_{A_1}\left(\mathbf{r} - \mathbf{R}_{A_1}\right) \\ \rho_{A_2}\left(\mathbf{r} - \mathbf{R}_{A_2}\right) \\ \rho_{A_3}\left(\mathbf{r} - \mathbf{R}_{A_3}\right) \end{pmatrix} 3,$$

so the Mulliken atomic density similarity matrix can be easily be written as in the diatomic case, but adding a new row and column:

$$\mathbf{Z} = \begin{pmatrix} \alpha & \beta & \beta \\ \beta & \alpha & \beta \\ \beta & \beta & \alpha \end{pmatrix}$$

A similar structure can be obtained for both density vector and similarity matrix for the tetrahedral form. The similarity matrix can be written in both cases, including even the diatomic studied example, as:

$$\mathbf{Z} = \alpha\mathbf{I} + \beta(\mathbf{1} - \mathbf{I}) = (\alpha - \beta)\mathbf{I} + \beta\mathbf{1}, \tag{8}$$

where $\mathbf{1} = \{1_{IJ} = 1\}$ is a unity matrix of appropriate dimension. The secular equation of such matrices can be written as:

$$\mathbf{Z}\mathbf{u}_I = \theta_I\mathbf{u}_I,$$

so, using the definition (8) it can be transformed into the secular equation of the unity matrix:

$$\mathbf{1}\mathbf{u}_I = \beta^{-1}(\theta_I - (\alpha - \beta))\mathbf{u}_I = \mu_I\mathbf{u}_I,$$

which has two kinds of eigenvalues: $\mu_1 = n_M \wedge \forall I = 2; n_M : \mu_I = 0$, thus the eigenvalues of the similarity matrix will be:

$$\theta_1 = \alpha + (n_M - 1)\beta \wedge \forall I = 2; n_M : \theta_I = \alpha - \beta,$$

which proves that for this kind of structures the atomic density similarity matrix will be positive definite.

(c) Diagonalization of the Mulliken atomic density metric matrix.

As a positive definite matrix, the Mulliken atomic density similarity matrix is a symmetric one. Due that such a metric matrix is defined over the Mulliken atomic density functions, which are positive definite functions, and then their elements are in any case real and positive. Also, this means there exists an orthogonal matrix: $\mathbf{U} \rightarrow \mathbf{U}\mathbf{U}^T = \mathbf{U}^T\mathbf{U} = \mathbf{I}$, which diagonalizes the matrix $\mathbf{Z}$, or that the matrix eigensystem:

$$\mathbf{Z}\mathbf{U} = \mathbf{U}\Theta \rightarrow \Theta = Diag\left(\theta_1; \theta_2; \ldots \theta_{n_M}\right)$$

holds, with the diagonal matrix $\Theta$ containing the real positive eigenvalues.

## 7.    Mulliken atomic density basis set relationships

Given two distinct density functions: $\{\rho_{0;M}; \rho_{1;M}\}$, associated to a given molecule with fixed geometry, there can be constructed two basis sets made of atomic density functions:

$$(\mu = 0, 1) : \rho_{\mu;M} = \sum_{I \in M} \rho_{\mu;I} \rightarrow |\rho_\mu) = \{\rho_{\mu;I}\}.$$

Every atomic density basis set generates an atomic similarity metric matrix:

$$(\mu = 0, 1) : \mathbf{Z}_{\mu\mu} = \int_D |\rho_\mu\rangle\langle\rho_\mu| \, d\mathbf{r}.$$

Also, as a result of a well-known property of vector spaces, a non-singular transformation matrix, $\mathbf{T}$ say, shall connect the known basis sets. To obtain such a transformation matrix, one can write for instance:

$$|\rho_1\rangle = \mathbf{T}|\rho_0\rangle, \tag{9}$$

which can be formally changed into:

$$\int_D |\rho_1\rangle\langle\rho_0| d\mathbf{r} = \mathbf{T} \int_D |\rho_0\rangle\langle\rho_0| d\mathbf{r} \rightarrow \mathbf{Z}_{10} = \mathbf{T}\mathbf{Z}_{00},$$

therefore, the transformation matrix can be obtained by means of:

$$\mathbf{T} = \mathbf{Z}_{10}\mathbf{Z}_{00}^{-1} \tag{10}$$

and at the same time the inverse transformation can be obtained as:

$$\mathbf{Z}_{11} = \mathbf{T}\mathbf{Z}_{01} \rightarrow \mathbf{T}^{-1} = \mathbf{Z}_{01}\mathbf{Z}_{11}^{-1}$$

taking into account that:

$$\mathbf{Z}_{01} = \mathbf{Z}_{10}^T.$$

As an example of this possible relationship, one can use the molecular density $\rho_{0;M}$ as the HF density matrix, computed with a given basis set, and $\rho_{1;M}$ as a KS density for the same molecule using the same nuclear coordinates as in the HF calculation. According to the previous discussion both density functions shall be related, as the respective atomic basis set vectors are related by means of a relationship of the kind (9):

$$|\rho_1\rangle = \mathbf{T}|\rho_0\rangle \rightarrow \forall I \in M : \rho_{1;I} = \sum_{J \in M} T_{IJ} \rho_{0;J}$$

so it can be written:

$$\rho_{1;M} = \sum_{I \in M} \rho_{1;I} = \sum_{I \in M} \sum_J T_{IJ} \rho_{0;J} = \sum_{J \in M} \left[ \sum_{I \in M} (T_{IJ}) \right] \rho_{0;J} = \sum_{J \in M} t_J \rho_{0;J}.$$

The coefficients, which are the sums of the columns of the transformation matrix:

$$\forall J \in M : t_J = \sum_{I \in M} T_{IJ}$$

are the coordinates of the molecular density function $\rho_{1;M}$ with respect to the basis set $|\rho_0\rangle$.

The values of the final coefficients can be expressed in terms of the atomic similarity matrices involved:

$$\forall J \in M : t_J = \sum_I T_{IJ} = \sum_I \sum_K z_{10;IK} z^{(-1)}_{00;KJ} \tag{11}$$

the coefficients can be ordered as elements of a column vector, $|t\rangle = \{t_J \,|\, J=1; n_M\}$, and thus the molecular density function can be written compactly as:

$$\rho_{1;M} = \langle t | \rho_0 \rangle.$$

## 8.   Least squares fitting

The previous procedure although correct from an algebraic point of view, cannot provide an exact relationship between both density functions due to the nature of the Hilbert semispace involved, because of this the density function relationship previously found, can be proved equal to an approximate unconstrained fitting of one density function with respect the atomic basis set of the other. In this section this possibility will be discussed.

### 8.1.   Unconstrained fitting

Suppose one tries to obtain a relationship between both densities in an approximate way, using the atomic density basis set generating another density function for the same molecular structure, or:

$$\rho^{(a)}_{1;M} \approx \sum_{I \in M} a_I \rho_{0;I} \tag{12}$$

then, the quadratic error can be introduced:

$$\varepsilon^{(2)} = \int_D \left| \rho_{1;M} - \rho^{(a)}_{1;M} \right|^2 d\mathbf{r} = \theta_{1;M} + \sum_{I \in M} \sum_{J \in M} a_I a_J z_{00;IJ} - 2 \sum_{I \in M} a_I z_I$$

where the elements $\{z_I\}$ are defined as:

$$z_I = \int_D \rho_{1;M} \rho_{0;I} d\mathbf{r} = \sum_{J \in M} \int_D \rho_{1;J} \rho_{0;I} d\mathbf{r} = \sum_{J \in M} z_{10;JI} \rightarrow |z\rangle = \{z_I\}.$$

The quadratic error can be also expressed as:

$$\varepsilon^{(2)} = \theta_{1;M} + \langle a | \mathbf{Z}_{00} | a \rangle - 2 \langle z | a \rangle, \tag{13}$$

after collecting the fitting coefficients into a column vector: $|a\rangle = \{a_I\}$. From the above expression (13), it is obtained for the optimal coefficient vector, the trivial result:

$$|a\rangle = \mathbf{Z}_{00}^{-1} |z\rangle. \tag{14}$$

This is the same as to write:

$$\begin{aligned}
\forall I \in M : a_I &= \sum_{J \in M} z_{00;IJ}^{(-1)} z_J = \sum_{J \in M} z_{00;IJ}^{(-1)} \left( \sum_{K \in M} z_{10;KJ} \right) \\
&= \sum_{K \in M} \sum_{J \in M} z_{00;IJ}^{(-1)} z_{10;KJ} = \sum_{K \in M} \sum_{J \in M} z_{10;KJ} z_{00;JI}^{(-1)}
\end{aligned}$$

however, this result is exactly the same, as it shall be expected, as the previous one in equation (11), or:

$$\forall I \in M : a_I = t_I \rightarrow |a\rangle = |t\rangle.$$

Therefore the transformation (10) corresponds to an unconstrained least squares fitting between both density functions.

## 8.2. Constrained least squares

The previous result indicates that the sum of coefficients relating both density functions has in general no other definite value than the following one, which can be easily computed as:

$$\langle |a\rangle \rangle = \sum_{I \in M} a_I = \sum_{I \in M} \sum_{K \in M} \sum_{J \in M} z_{10;KJ} z_{00;JI}^{(-1)} = \left\langle \mathbf{Z}_{10} \mathbf{Z}_{00}^{(-1)} \right\rangle,$$

providing a Minkowski norm of the fitted density different from the number of electrons, $N_M$, in the associated molecule:

$$\left\langle \rho_{1;M}^{(a)} \right\rangle = \sum_{I \in M} a_I \langle \rho_{0;I} \rangle = \sum_{I \in M} a_I N_{0;I},$$

where the set of atomic density Minkowski norms:

$$\forall I \in M : N_{0,I} = \langle \rho_{0;I} \rangle \rightarrow |N_0\rangle = \{N_{0,I}\}$$

coincide with the Mulliken atomic charges, and thus: $\langle |N_0\rangle \rangle = N_M$. For the exact density function $\rho_{1;M}$, the Minkowski norm will produce the same result:

$$\langle \rho_{1;M} \rangle = \sum_I \langle \rho_{1,I} \rangle = \sum_I N_{1,I} = N_M.$$

It seems plausible, when optimizing the quadratic error (13), in a first instance, that a constraint like:

$$\sum_{I \in M} a_I N_{0;I} = N_M$$

for the coefficients $|a\rangle$ shall be taken into account. Such a constraint can be included by means of a Lagrange multiplier and constructing the augmented function:

$$L = \varepsilon^{(2)} - \lambda \left( \langle N_0 | a \rangle - N_M \right),$$

the null gradient condition will be now written:

$$2\mathbf{Z}_{00} |a\rangle - 2 |z\rangle - \lambda |N_0\rangle = |0\rangle;$$

from where one can obtain the constrained coefficients as:

$$|a\rangle = \mathbf{Z}_{00}^{-1} \left( |z\rangle + \frac{1}{2}\lambda |N_0\rangle \right) \tag{15}$$

from equation (15), the Lagrange multiplier is readily found to be expressed as:

$$N_M = \langle N_0 | a \rangle = \langle N_0 | \mathbf{Z}_{00}^{-1} |z\rangle + \frac{1}{2}\lambda \langle N_0 | \mathbf{Z}_{00}^{-1} |N_0\rangle$$

implying that:

$$\lambda = 2 \left( \langle N_0 | \mathbf{Z}_{00}^{-1} |N_0\rangle \right)^{-1} \left( N_M - \langle N_0 | \mathbf{Z}_{00}^{-1} |z\rangle \right). \tag{16}$$

Substituting equation (16) into (15) it is easily obtained:

$$|a\rangle = \mathbf{Z}_{00}^{-1} \left( |z\rangle + \left( \langle N_0 | \mathbf{Z}_{00}^{-1} |N_0\rangle \right)^{-1} \left( N_M - \langle N_0 | \mathbf{Z}_{00}^{-1} |z\rangle \right) |N_0\rangle \right).$$

The appropriate coefficients possess the unconstrained least squares result in a first part, as discussed in the unconstrained case above, plus a correction including the number of molecular electrons and the vector of Mulliken atomic populations. They can be rewritten in the following manner, using the symbol $|a_U\rangle$ for the unconstrained solution (14):

$$|a\rangle = \mathbf{L}\mathbf{Z}_{00}^{-1} |z\rangle = \mathbf{L} |a_U\rangle$$

where the matrix $\mathbf{L}$ is defined with the expression:

$$\mathbf{L} = (\mathbf{I} + \eta |N_0\rangle [\langle 1| - \langle N_0|]) \wedge \eta = N_M \left( \langle N_0 | \mathbf{Z}_{00}^{-1} |N_0\rangle \right)^{-1}. \tag{17}$$

Using these last expressions it can be further written:

$$|a\rangle = |a_U\rangle + \sigma\,|N_0\rangle \wedge \sigma = \eta\,(\langle\langle a_U\rangle\rangle - \langle N_0|a_U\rangle), \tag{18}$$

which proves that the correction to the unconstrained least squares solution is just made of the scaled Mulliken atomic population vector.

### 8.3. Convex constrained coefficients

A final remark is due now. As it has been proved and subsequently used in several previous work [1, 4], the above discussed constrained least squares procedure do not provide a set of more tightly constrained coefficients $|a\rangle$, which can be proved positive definite for any molecule in general. In order to obtain such a further constrained coefficient set some additional scheme shall be followed. In fact the algorithm used to obtain approximate promolecular atomic densities has been employed in various cases, producing the so-called ASA form of atomic density functions [4].

In order to work the appropriate algorithm to obtain the least squares coefficients relating a given molecular density with the atomic density basis set of another calculation, there is better to transform the densities as to become members of the unit shell of the vector semispace where they belong. So, the implied density functions of equation (12) may be written as:

$$\sigma_{1;M}^{(a)} \approx \sum_{I \in M} \alpha_I \sigma_{0;I},$$

where unit shell shape functions [shape functions] are used, that is:

$$\left\langle \sigma_{1;M}^{(a)} \right\rangle = 1 \wedge \forall I : \left\langle \sigma_{0;I} \right\rangle = 1 \rightarrow \sum_{I \in M} \alpha_I = 1$$

In these circumstances the augmented quadratic error function can be written as:

$$L = \theta_{1;M}^{(1)} + \langle\alpha|\,\mathbf{Z}_{00}^{(1)}\,|\alpha\rangle - 2\left\langle z^{(1)}|\alpha\right\rangle - \lambda\,(\langle v_0|\alpha\rangle - 1),$$

where the superscript (1) means that the corresponding matrix elements are computed over the shape functions, and the scaled population vector is defined as:

$$|v_0\rangle = N_M^{-1}\,|N_0\rangle \rightarrow \langle|v_0\rangle\rangle = 1;$$

that is: the population vector has been converted into a discrete probability distribution. This can be seen as a natural consequence of using shape functions.

One can envisage the task of obtaining the coefficient vector $|\alpha\rangle$ as a convex vector, belonging to the unit shell of the appropriate semispace. In order to consider this possibility, there one can generate it by means of:

$$R\left(|x\rangle \rightarrow |\alpha\rangle\right): |\alpha\rangle = |x\rangle * |x\rangle = \left|x^2\right\rangle \rightarrow \forall I : \alpha_I = x_I^2.$$

And in order to have the convex conditions: $K\left(|\alpha\rangle\right)$ fulfilled, it is only necessary that the generating vector $|x\rangle$ become normalized in the Euclidean sense: $\langle x|x\rangle = 1$. So, the augmented function can be written:

$$L = \theta_{1;M}^{(1)} + \left\langle x^2 \left| \mathbf{Z}_{00}^{(1)} \right| x^2 \right\rangle - 2\left\langle z^{(1)}|x^2\right\rangle - \lambda \left(\left\langle v_0|x^2\right\rangle - 1\right),$$

and its gradient can be written as:

$$\frac{\partial L}{\partial |x\rangle} = 4\,|x\rangle * \left(\mathbf{Z}_{00}^{(1)} \left|x^2\right\rangle - \left|z^{(1)}\right\rangle - \frac{1}{2}\lambda\,|v_0\rangle\right).$$

The null gradient condition provides:

$$\mathbf{Z}_{00}^{(1)} \left|x^2\right\rangle - \left|z^{(1)}\right\rangle - \frac{1}{2}\lambda\,|v_0\rangle = |0\rangle,$$

from where the coefficient vector can be obtained:

$$|\alpha\rangle = \left|x^2\right\rangle = \left(\mathbf{Z}_{00}^{(1)}\right)^{-1}\left(\left|z^{(1)}\right\rangle + \frac{1}{2}\lambda\,|v_0\rangle\right)$$

which permits in turn to evaluate the Lagrange multiplier, taking into account that: $\langle v_0|\alpha\rangle = 1$, as:

$$\lambda = 2\,\langle v_0|\left(\mathbf{Z}_{00}^{(1)}\right)^{-1}|v_0\rangle^{-1}\left(1 - \langle v_0|\left(\mathbf{Z}_{00}^{(1)}\right)^{-1}\left|z^{(1)}\right\rangle\right).$$

Now, calling:

$$|\gamma\rangle = \left(\mathbf{Z}_{00}^{(1)}\right)^{-1}|v_0\rangle \wedge |\eta\rangle = \left(\mathbf{Z}_{00}^{(1)}\right)^{-1}\left|z^{(1)}\right\rangle,$$

then it can be written:

$$|\alpha\rangle = |\eta\rangle + \left(\langle\gamma|v_0\rangle^{-1}\left(1 - \langle v_0|\eta\rangle\right)\right)|v_0\rangle. \tag{19}$$

In turn, calling the coefficient in the second term:

$$\chi = \langle\gamma|v_0\rangle^{-1}\left(1 - \langle v_0|\eta\rangle\right)$$

allows to write the constrained coefficients as:

$$|\alpha\rangle = |\eta\rangle + \chi\,|v_0\rangle,$$

a result similar to the former constrained procedure described above.

In this case, however, one can also further develop the structure of the coefficient vector rearranging terms in expression (19), renaming the coefficient:

$$\theta = \langle \gamma | v_0 \rangle^{-1}.$$

then it can be written:

$$|\alpha\rangle = |\eta\rangle + \theta \left( |v_0\rangle - |v_0\rangle \langle v_0 | \eta\rangle \right) \rightarrow \theta \left[ \left( \theta^{-1}\mathbf{I} - |v_0\rangle \langle v_0| \right) |\eta\rangle + |v_0\rangle \right];$$

furthermore, constructing the matrix:

$$\mathbf{K} = \langle \gamma | v_0 \rangle \, \mathbf{I} - |v_0\rangle \langle v_0| \,,$$

then it can be written:

$$|\alpha\rangle = \theta \left[ \mathbf{K} |\eta\rangle + |v_0\rangle \right].$$

## 9. Mulliken charges and expectation values

Another question, which will arise to the reader's mind, is how the expectation values of both density functions will be related. However, with the information provided so far such a question is readily answered. Starting from the relationship:

$$\rho_{1;M} \approx \langle a | \rho_0 \rangle,$$

then any expectation value of a one- electron operator, $\Omega\,(\mathbf{r})$, including the Mulliken atomic populations [6], which can be considered expectation values of the unit operator, as discussed at the beginning, can be associated to the integrals:

$$\langle \Omega \left[ \rho_{1;M} \right] \rangle = \sum_{I \in M} \langle \Omega \left[ \rho_{1;I} \right] \rangle \approx \langle a | \, \Omega \, | \rho_0 \rangle = \sum_{I \in M} a_I \langle \Omega \left[ \rho_{0;I} \right] \rangle. \tag{20}$$

One can follow several paths for obtaining the optimal relationships between the results associated to both density functions. The most straightforward is to use the unconstrained coefficient vector as previously discussed; the alternative is to use a constraint associated to equation (20), which includes the operator but then, the fitting coefficients will depend on every operator studied, as equations (17) and (18) suggest. In fact, the new coefficients can be deduced from these expressions just substituting the Mulliken population symbol by the appropriate atomic expectation value:

$$\forall I \in M : N_{0;I} \rightarrow \langle \Omega \left[ \rho_{0;I} \right] \rangle \wedge N_M \rightarrow \langle \Omega \left[ \rho_{1;M} \right] \rangle.$$

## 10. Higher order density functions

It has been easily proved that with an appropriate unitary transformation the density function form up to any order can be written in a similar way as equation (2) as it has been known in quantum chemistry for a long time [7]. This fact was also well known in the case of second order density functions, but it has been proved that the extension to higher order density functions is trivial [8]. The second order case is interesting for the obvious reason that it enters the electronic energy expression for atomic and molecular systems. It will be studied first; in an attempt to prove that the relationships between second order density functions shall obey to the same rules as the first order ones. Proving so, it is a problem of formalism details to extend such a property to any order.

A second order density function can be written using the same notation as in the first order case, like:

$$\rho_M (\mathbf{r}_1; \mathbf{r}_2) = \langle \Gamma * | \mathbf{m}_0 \otimes \mathbf{m}_0 \rangle \langle \mathbf{m}_0 \otimes \mathbf{m}_0 | \rangle = \sum_i \sum_j \sum_k \sum_l \gamma_{ijkl} |i_0 j_0\rangle \langle k_0 l_0|,$$

where $\Gamma = \{\gamma_{ijkl}\}$ is a Hermitian coefficient hypermatrix, whose elements depend on the computational level employed to obtain the molecular wave function, and $|\mathbf{m}_0 \otimes \mathbf{m}_0\rangle = \{|i_0\rangle \otimes |j_0\rangle \equiv |i_0 j_0\rangle\}$ a column hypervector formed by the tensor product of the one-electron MO functions. It can be adopted a convention such that the first MO index corresponds to the coordinates of the first electron, $\mathbf{r}_1$, and the second index to the coordinates of the second electron, $\mathbf{r}_2$, taking into account that in the bra representation: $\{\langle j_0 i_0|\}$ such an association of indices and coordinates will be reversed. Then, a unitary transformation can be found in order to diagonalize the coefficient matrix; in such a way that the second order density function can be written:

$$\rho_M (\mathbf{r}_1; \mathbf{r}_2) = \sum_i \sum_j \omega_{ij} |ij\rangle \langle ji|, \tag{21}$$

with now $\{\omega_{ij}\}$ being the eigenvalues of the second order coefficient matrix and the two-electron MO basis functions $\{|ij\rangle\}$ unitary transformations of the initial tensor product of MO.

As in the first order case, the two-electron MO functions can be expressed as linear combinations of the tensor product of basis functions, which can be expressed in a column vector form:

$$|\mathbf{x} \otimes \mathbf{x}\rangle = \{|\mu\rangle |\nu\rangle \equiv |\mu\nu\rangle\},$$

then the MO set is expressed as a linear combination of the basis functions:

$$\forall (i; j) : |ij\rangle = \left\langle \mathbf{c}_{ij}^* |\mathbf{x} \otimes \mathbf{x}\rangle \right\rangle = \sum_\mu \sum_\nu c_{\mu\nu;ij} |\mu\nu\rangle,$$

where $\mathbf{c}_{ij} = \{c_{\mu\nu;ij}\}$ are the coordinates of the ij-th MO tensor product with respect to the basis set $|\mathbf{x} \otimes \mathbf{x}\rangle$. Substituting the LCAO MO expansion into the density function (21), one arrives to the expression:

$$\rho_M(\mathbf{r}_1; \mathbf{r}_2) = \langle \mathbf{D}* | \mathbf{x} \otimes \mathbf{x}\rangle \langle \mathbf{x} \otimes \mathbf{x}| \rangle = \sum_\mu \sum_\nu \sum_\lambda \sum_\sigma D_{\mu\nu\lambda\sigma} |\mu\nu\rangle \langle\lambda\sigma|,$$

where a second order equivalent of the charge and bond order matrix can be defined:

$$\mathbf{D} = \{D_{\mu\nu\lambda\sigma}\} = \sum_i \sum_j \omega_{ij} \mathbf{c}_{ij} \mathbf{c}_{ij}^+,$$

and in the second order projector tensor the same convention, as in the MO case, for the assignment of the electron coordinates can be also used. Thus, a formally equivalent development as in the first order case can be designed, just with the additional complication that two indices have to be used instead of one. At the same time the atomic projectors and the atomic density basis set have to be adapted to the new situation, where diatomic density basis set functions shall be operative. That is, the second order density function can be written as a superposition of diatomic contributions:

$$\rho_M(\mathbf{r}_1; \mathbf{r}_2) = \sum_{I \in M} \sum_{J \in M} \rho_{IJ}(\mathbf{r}_1; \mathbf{r}_2).$$

The diatomic density basis set $\{\rho_{IJ}(\mathbf{r}_1; \mathbf{r}_2)\}$ can be easily written as:

$$\forall (I; J) \in M : \rho_{IJ}(\mathbf{r}_1; \mathbf{r}_2) = \sum_{\mu \in I} \sum_{\nu \in J} \sum_{K \in M} \sum_{L \in M} \sum_{\lambda \in K} \sum_{\sigma \in L} D_{\mu\nu\lambda\sigma} |\mu\nu\rangle \langle\lambda\sigma|.$$

As the correspondence between this result and the first order density one is obvious, the rest of the first order properties and discussion can be applied into the second order case without problems. Extension to higher order density functions is, therefore, a matter of developing the adequate and, as simple as possible, formalism. An analysis similar to the first order density can be also performed at the light of the present results, that is: a two-center two-electron density basis set can be defined, a metric matrix composed and thus the self similarity calculation of second order densities can be expressed by means of such basis set, as well as two different densities associated to the same molecule can be compared throughout the procedures already developed in the first order case.

## 11.    Conclusions

First order density functions in LCAO framework are analyzed from the point of view of their description as a superposition of one-center densities. This

permits the description of an atomic density basis set, which leads to the definition of a metric, whose elements are the similarity integrals associated to the atomic density basis set. The metric plays a relevant role into the definition of selfsimilarity measures and also in the way two density functions, belonging to the same molecular structure, can be compared and related. Extension to two-electron and higher order density functions appears to be associated to equivalent procedures.

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