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Descriptors and probability distributions in MO theory: Weighted Mulliken matrices and molecular quantum similarity measures

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Starting from the original Mulliken study on population analysis, it is shown how these initial ideas not only are expressible as expectation values of a projector, but also how they can be extended and generalized into the domain of non-singular Hermitian operators using the same technique. Some examples of this possibility are given. The formalism is studied in deep, proving that the Mulliken populations are a zero-th order approach to the description of condensed density functions and their connection with quantum similarity measures is analyzed. Employing positive definite operators as natural weights to compute atomic condensed density terms, lead to produce elements of vector semispaces. Such vectors can be subject to Minkowski normalization becoming discrete probability distributions, which can be gathered using several weight operators into stochastic arrays as molecular fingerprint descriptors.

KEY WORDS: Mulliken population analysis, weighted Mulliken matrices, weighted Mulliken populations, molecular discrete probability distributions, molecular descriptors

1. Preface

Since Mulliken published his work about population analysis [1], a large amount of studies has been put forward in the literature [2]. Recently, a stepwise comprehensive review of this essential subject, in order to enlarge the understanding of chemistry and chemical processes, has been underwent by Bultinck and Carbó-Dorca in a set of two studies tending to demonstrate how atomic charges, diatomic bond orders and polyatomic bond indices can be constructed within the quantum mechanical framework [3]. These authors had recently shown that, within the MO theoretical structure Mulliken populations can be deduced under the quantum mechanical usual rules, associated to density functions of arbitrary order, as expectation values of Hermitian operators which, in turn, can be built up by means of tensor products of projectors over the atomic basis functions [4]. The final result can be seen as the possibility to refer to a unique quantum mechanically based procedure for the computation of bond indices, attached to a polyatomic set possessing a given molecular structure. Thus, from now on, derivation of Mulliken atomic charges can be attached to first order projected-condensed density function, bond orders to second order projected-condensed density, and so on ... up to any order bond index.

However, the development of these previous ideas is based in several simple but basic definitions, which together with the quantum mechanical expectation value fundamental statistical scheme can lead to a real generalization of the population analysis framework. That is, such a generalized formalism can direct not only to a correct quantum mechanical definition of molecular atomic charges and bond indices, as expectation values of a Hermitian operator, attached to some system observable, but to the definition of other molecular expectation values decomposition in atomic, diatomic... polyatomic contributions.

According to this, the aim of this study is to put forward the initial definitions for the understanding of the possible ways of this generalization, which will be proposed in a manner as broad as possible, connecting the theoretical background with other descriptive tools, like quantum similarity. Thus, after some initial definitions this work will describe the structure and properties of the classical Mulliken matrices as a first step to define the condensed atomic densities as expectation values of well defined projectors. This preparatory material permits to define a generalized kind of Mulliken matrices and thus of condensed densities, weighted by positive definite operators. Next, several choices of such weighting operators are discussed and a section is devoted afterwards to the effect on condensed densities of unitary and other transformations of the MO. A discussion of the zero-th order nature of the classical Mulliken condensed densities will be put forward and a connection of the generalized Mulliken condensed densities with quantum similarity measures will be given. A section providing approximate implementation of the condensed densities in the general framework is given and finally two sections dealing respectively with the off-diagonal elements of the density function, demonstrating this is a source of irrelevant information for condensed densities, and a discussion of the role of the shape function as source of atomic charges close this work. Two appendixes provide complementary details about classical Mulliken projectors and permanents.

2. Initial definitions

In a first place the necessary definitions, well known by the community of theoretical chemists, but with possible quite diverse formalism choices, will be presented in order to set up the notation, which will be employed with the aim to ease the understanding of the mathematical arguments contained within this study.

2.1. Classical Mulliken matrix

The elements of the initial definitions correspond essentially to the components of an array structure, which will be named from now on classical Mulliken matrix (CMM) according to the definition:

$$\mathbf{M} = \mathbf{DS}. \tag{1}$$

The definitions that follow are usually attached to the LCAO MO schemes [5], and thus to the usual Hartree–Fock results [6,7], but can be employed equally well to Kohn–Sham MO sets [8], although taking into account some possible limitations, associated to the MO vectors in DFT [9].

Being also necessary that both elements of the CMM composition become unambiguously defined and the notation which will be used thereafter described, there follow some auxiliary definitions:

2.1.1. Overlap or metric matrix

$$\mathbf{S} = \left\{ S_{\mu\nu} = \langle \mu \mid \nu \rangle = \int_D \chi_\mu^* (\mathbf{r})\, \chi_\nu (\mathbf{r})\, \mathrm{d}\mathbf{r} \right\}. \tag{2}$$

With the symbols of the monoelectronic basis set functions defined as:

$$\{|\mu\rangle\} \equiv \left\{\chi_\mu (\mathbf{r})\right\} \rightarrow \langle X| = \left(\chi_1; \chi_2; \ldots, \chi_\mu; \ldots,\right),$$

where **r** stands for the coordinates of the attached electron.

Moreover, being the overlap matrix a metric matrix it has to be supposed to be positive definite, then there exists a non-singular upper triangular matrix, permitting the Cholesky decomposition [10–12]:

$$\mathbf{S} = \mathbf{T}^T \mathbf{T},$$

so the inverse of the overlap matrix can be easily computed as:

$$\mathbf{S}^{-1} = \mathbf{T}^{-1}\mathbf{T}^{-T}.$$

2.1.1.1. Alternative overlap matrix. The previous Cholesky decomposition permits to construct an alternative positive definite matrix by means of the following manipulation:

$$\mathbf{Z} = \mathbf{T}\mathbf{T}^T \rightarrow \mathbf{Z}^{-1} = \mathbf{T}^{-T}\mathbf{T}^{-1}, \tag{3}$$

which has the same eigenvalues as the original overlap:

$$\begin{aligned}
\exists \mathbf{U} \rightarrow \mathbf{U}^T\mathbf{U} = \mathbf{U}\mathbf{U}^T &= \mathbf{I} : \\
&\mathbf{S}\mathbf{U} = \mathbf{U}\boldsymbol{\Sigma} \rightarrow \mathbf{T}^T\mathbf{T}\mathbf{U} = \mathbf{U}\boldsymbol{\Sigma} \\
&\rightarrow \mathbf{T}\mathbf{T}^T\mathbf{T}\mathbf{U} = \mathbf{T}\mathbf{U}\boldsymbol{\Sigma} \rightarrow \mathbf{Z}\mathbf{V} = \mathbf{V}\boldsymbol{\Sigma} \\
&\rightarrow \mathbf{V}^T\mathbf{V} = \mathbf{U}^T\mathbf{T}^T\mathbf{T}\mathbf{U} = \mathbf{U}^T\mathbf{S}\mathbf{U} = \boldsymbol{\Sigma} \\
&\rightarrow \mathbf{V}_1 = \mathbf{V}\boldsymbol{\Sigma}^{-\frac{1}{2}} \rightarrow \mathbf{Z}\mathbf{V}_1 = \mathbf{V}_1\boldsymbol{\Sigma} \\
&\rightarrow \mathbf{V}_1{}^T\mathbf{V} = \mathbf{V}\mathbf{V}_1^T = \mathbf{I}.
\end{aligned}$$

In fact, the Cholesky decomposition of both matrices implies:

$$\begin{aligned}
\alpha \leqslant \beta : S_{\alpha\beta} &= \sum_{\lambda} T_{\alpha\lambda}^{(T)} T_{\lambda\beta} = \sum_{\lambda\leqslant\alpha} T_{\lambda\alpha} T_{\lambda\beta} \\
\wedge Z_{\alpha\beta} &= \sum_{\lambda} T_{\alpha\lambda} T_{\lambda\beta}^{(T)} = \sum_{\lambda\geqslant\beta} T_{\alpha\lambda} T_{\beta\lambda},
\end{aligned}$$

which proves that the elements of the matrix **Z** still possess preserved the AO locations in the same order than the overlap matrix. Both matrices also possess the same trace as shows the following equality sequences:

$$\begin{aligned}
Tr\,|\mathbf{S}| &= \sum_{\alpha} S_{\alpha\alpha} = \sum_{\alpha}\sum_{\lambda} T_{\alpha\lambda}^{(T)} T_{\lambda\alpha} = \sum_{\alpha}\sum_{\lambda\leqslant\alpha} |T_{\lambda\alpha}|^2 = \langle \mathbf{T} * \mathbf{T} \rangle \\
Tr\,|\mathbf{Z}| &= \sum_{\alpha} Z_{\alpha\alpha} = \sum_{\alpha}\sum_{\lambda} T_{\alpha\lambda} T_{\lambda\alpha}^{(T)} = \sum_{\alpha}\sum_{\lambda\geqslant\alpha} |T_{\alpha\lambda}|^2 = \langle \mathbf{T} * \mathbf{T} \rangle,
\end{aligned}$$

according to the previous result concerning the equality of the spectra of both arrays. By the symbol $\langle \mathbf{A} * \mathbf{A} \rangle$ it is meant the Euclidian norm of the involved array, for instance if $\mathbf{A} = \{a_{ij}\}$ is a matrix, then:

$$\langle \mathbf{A} * \mathbf{A} \rangle = \sum_{i}\sum_{j} |a_{ij}|^2.$$

Two symbols in this case have been put forward, first the inward matrix product and the complete sum of an array [13]. A short description follows. By an inward matrix product of two arrays possessing the same dimension it is understood another array with the same dimension whose elements are products of the array elements in the same position, for example, when two matrices $\mathbf{A}, \mathbf{B}$, say, of dimension $(m \times n)$ are inwardly multiplied, a new matrix $\mathbf{P}$ of the same dimension is created:

$$\mathbf{P} = \mathbf{A} * \mathbf{B} \rightarrow \forall i, j : p_{ij} = a_{ij} b_{ij}.$$

By the complete sum of an array it is understood the sum of all the elements of such an array, for example it could be written for the previous inward product matrix:

$$\langle \mathbf{P} \rangle = \sum_i \sum_j p_{ij}.$$

The complete sum of an array, whenever is different of zero, can be used as a scale factor to normalize in the Minkowski sense the array, for instance:

$$\mathit{iff}\ \langle \mathbf{P} \rangle \neq 0 : \mathbf{P}^{(1)} = \langle \mathbf{P} \rangle^{-1} \mathbf{P} \rightarrow \left\langle \mathbf{P}^{(1)} \right\rangle = 1.$$

2.1.2. LCAO MO charge and bond order matrix

The following array will be named *charge and bond order* (CBO) matrix(*):

$$\mathbf{D} = \sum_i w_i \mathbf{c}_i \mathbf{c}_i^{+} \rightarrow \mathbf{D} = \left\{ D_{\mu\nu} = \sum_i w_i c_{\mu i} c_{\nu i}^{*} \right\} \tag{4}$$

with $\{\omega_i\}$ being the MO occupation numbers fulfilling:

$$\sum_i w_i = N, \tag{5}$$

being N in turn the total number of electrons in the system studied, also: $\mathbf{C} = \{\mathbf{c}_i\} \rightarrow \{c_{\mu i}\}$ note the LCAO MO column vector coefficients; that is, if $\{\varphi_i(\mathbf{r}) \equiv |i\rangle\}$ corresponds to the monoelectronic functions forming the MO set, then:

$$\varphi_i = \sum_\mu c_{\mu i} \chi_\mu \equiv |i\rangle = \sum_\mu c_{\mu i} |\mu\rangle \equiv |i\rangle = \langle X | \mathbf{c}_i, \tag{6}$$

where the electron coordinates have been dropped to ease notation.

2.1.2.1. General form of CBO matrix. The CBO matrix can be also written in a general manner by using a symmetrical occupation number matrix: $\mathbf{W} = \{w_{ij}\}$, as:

$$\mathbf{D} = \mathbf{C}\mathbf{W}\mathbf{C}^T. \tag{7}$$

(*)Such an array is also called in the literature a *Density Matrix*, but this produces some confusion with the same description given to the matrix, whose elements are the density functions. In order to avoid confusing terms, here has been chosen the use of this longer description in acronym form.

However, if the full occupation number matrix is symmetrical there exists an orthogonal matrix: $\mathbf{U} \rightarrow \mathbf{U}^T\mathrm{U} = \mathbf{U}\mathbf{U}^T = \mathbf{I}$, which diagonalize it:

$$\mathbf{U}^T\mathbf{W}\mathbf{U} = \Omega = \mathrm{Diag}\,(w_i) \rightarrow \mathbf{W} = \mathbf{U}\Omega\mathbf{U}^T, \tag{8}$$

substituting expression (8) into the general expression (7) transforms the MO coordinates while producing an expression for the CBO matrix with a diagonal occupation number matrix, equivalent to expression (4):

$$\mathbf{D} = \mathbf{C}\mathbf{U}\Omega\mathbf{U}^T\mathbf{C}^T,$$

using the MO coordinates transformation:

$$\mathbf{C}_U = \mathbf{C}\mathbf{U},$$

then the CBO matrix will remain invariant:

$$\mathbf{D} = \mathbf{C}_U\Omega\mathbf{C}_U^T.$$

Due to this property, from now on it will be considered in this paper that the CBO matrices will always possess the diagonal occupation number form (4). This is the usual transformation structure when any localization procedure is envisaged to be performed into the MO [14].

2.1.3. MO coefficients orthonormalization

The set of the MO coefficients, which can be ordered as columns in a square $(n \times n)$ matrix: $\mathbf{C} = (\mathbf{c}_1, \mathbf{c}_2, \ldots, \mathbf{c}_n)$ are considered to be orthonormalized in the sense:

$$\forall i, j : \mathbf{c}_i^+\mathbf{S}\mathbf{c}_j = \delta_{ij} \rightarrow \mathbf{C}^+\mathbf{S}\mathbf{C} = \mathbf{I}. \tag{9}$$

2.1.4. First order density function

The CBO matrix (4) can be used to construct the first order density function, as follows:

$$\begin{aligned} \rho(\mathbf{r}) &= \sum_i \omega_i \, |i\rangle \, \langle i| = \sum_i \omega_i \varphi_i(\mathbf{r}) \, \varphi_i^*(\mathbf{r}) \\ &= \sum_\mu \sum_\nu D_{\mu\nu} \, |\mu\rangle \, \langle \nu| = \sum_\mu \sum_\nu D_{\mu\nu} \chi_\mu(\mathbf{r}) \, \chi_\nu^*(\mathbf{r}), \end{aligned} \tag{10}$$

where, into the expression (10) above, several equivalent formulae of the density function have been written. The first order density function (10), when integrated over the appropriate domain will provide N, the number of electrons in the associated molecular system:

$$\begin{aligned}\langle \rho(\mathbf{r})\rangle &= \int_D \rho(\mathbf{r})\, d\mathbf{r} = \sum_\mu \sum_\nu D_{\mu\nu} \int_D \chi_\mu(\mathbf{r})\, \chi_\nu^*(\mathbf{r})\, d\mathbf{r} = \sum_\mu \sum_\nu D_{\mu\nu} S_{\mu\nu} \\ &= \sum_\mu \sum_\nu \left(\sum_i \omega_i c_{\mu i} c_{\nu i}^*\right) S_{\mu\nu} = \sum_i \omega_i \mathbf{c}_i^+ \mathbf{S} \mathbf{c}_i = \sum_i \omega_i = N.\end{aligned}$$

Due to this property, the first order density can be normalized, producing the so called *shape function* [15]:

$$\sigma(\mathbf{r}) = N^{-1}\rho(\mathbf{r}) \rightarrow \langle \sigma(\mathbf{r})\rangle = 1.$$

The relationship of both functions and their algebraic properties, connected with the unit shell in vector semispaces have been recently studied [16]. Therefore, to construct a shape function becomes equivalent to scale the CBO matrix by a scalar factor equal to the inverse of the number of electrons, and this corresponds to scale by the same factor the occupation numbers.

2.1.5. Idempotency of the CMM

The CMM (1) becomes an idempotent matrix [17], under the MO orthonormalization, as:

$$\begin{aligned}\mathbf{M}^2 = (\mathbf{DS})^2 = \mathbf{DSDS} &= \sum_i \sum_j \omega_i \omega_j \mathbf{c}_i \left(\mathbf{c}_i^+ \mathbf{S} \mathbf{c}_j\right) \mathbf{c}_j^+ \mathbf{S} \\ &= \sum_i \sum_j \delta_{ij} \omega_i \omega_j \mathbf{c}_i \mathbf{c}_j^+ \mathbf{S} = \sum_i \omega_i \mathbf{c}_i \mathbf{c}_i^+ \mathbf{S} = \mathbf{DS} = \mathbf{M},\end{aligned} \tag{11}$$

alternatively, the following proof of the CMM idempotency can be also used:

$$\begin{aligned}\left[(\mathbf{DS})^2\right]_{\alpha\beta} &= \sum_\lambda \sum_\mu \sum_\nu D_{\alpha\mu} S_{\mu\lambda} D_{\lambda\nu} S_{\nu\beta} \\ &= \sum_i \omega_i \sum_j \omega_j \sum_\lambda \sum_\mu \sum_\nu c_{\alpha i} \left(c_{\mu i} S_{\mu\lambda} c_{\lambda j}\right) c_{\nu j} S_{\nu\beta} \\ &= \sum_i \omega_i \sum_j \omega_j \sum_\lambda \sum_\mu \sum_\nu c_{\alpha i} \delta_{ij} c_{\nu j} S_{\nu\beta} \\ &= \sum_i \omega_i \sum_\nu c_{\alpha i} c_{\nu i} S_{\nu\beta} = \sum_\nu D_{\alpha\nu} S_{\nu\beta} = [\mathbf{DS}]_{\alpha\beta}\,.\end{aligned}$$

The idempotent property of the CMM is extensible to any power of the CMM, or it is the same to say that the following equality also holds:

$$\forall p > 0 : \mathbf{M}^p = \mathbf{M},$$

a result which, starting with the previous one in equation (11), can be easily proved by recurrence.

2.1.6. Eigenvalues and eigenvectors of a CMM

The secular equation of any CMM,

$$\mathbf{MX} = \mathbf{X}\Delta,$$

where in the columns of the matrix **X** are the ordered eigenvectors of the CMM, while in the elements of the diagonal matrix Δ, have to be found the eigenvalues in the same order. The solution can be described in the following way, using previous results concerning the CBO and overlap matrices:

$$\begin{aligned}\mathbf{M} = \mathbf{DS} = \mathbf{C}\Omega\mathbf{C}^T\mathbf{S} \\ &\rightarrow \mathbf{DSC} = \mathbf{C}\Omega\mathbf{C}^T\mathbf{SC} = \mathbf{C}\Omega \\ &\rightarrow \mathbf{X} = \mathbf{C} \wedge \Delta = \Omega.\end{aligned}$$

An alternative form of the secular equation of the CMM can be found in the following manner:

$$\forall J : \mathbf{DSc}_J = \sum_I \omega_I \mathbf{c}_I \mathbf{c}_I^T \mathbf{Sc}_J = \sum_I \omega_I \mathbf{c}_I \delta_{IJ} = \omega_J \mathbf{c}_J.$$

Thus the right eigenvectors of a CMM are the MO coordinates and the associated eigenvalues the occupation numbers.

2.1.7. Alternative CMM

Then, it can be interesting to analyze which results will provide the matrix **Z** defined in equation (3), when used in the CMM definition instead of the overlap matrix **S**.

$$\mathbf{M}_Z = \mathbf{DZ}.$$

Contrarily to the usual CMM, the matrix $\mathbf{M}_Z$ is no longer idempotent, nor has the same properties in its secular equation. However, such a possibility precludes the development of the section 4 below and constitutes the first step towards a general formalism of Mulliken matrices.

3. CMM and atomic condensed densities: charges and bond orders

The CMM is customarily employed to obtain atomic charges and bond orders in the molecular LCAO MO framework. In the context of the previous definitions and using equations (5) and (9) it can be easily found the following property of the CMM trace:

$$Tr\,|\mathbf{M}| = \sum_{\lambda}\sum_{\mu} D_{\lambda\mu}S_{\mu\lambda} = \sum_{i}\omega_i \mathbf{c}_i^{+}\mathbf{S}\mathbf{c}_i = \sum_{i}\omega_i = N. \tag{12}$$

3.1. Atomic charges

Also, it is well known that a gross atomic population [1], briefly, the charge or condensed density Q_A on atom A, was defined by Mulliken by means of:

$$Q_A = \sum_{\alpha\in A} M_{\alpha\alpha} = \sum_{\alpha\in A}\sum_{\mu} D_{\alpha\mu}S_{\mu\alpha}. \tag{13}$$

Atomic charges are also associated to the obvious property:

$$\sum_{A} Q_A = \sum_{A}\sum_{\alpha\in A} M_{\alpha\alpha} = Tr\,|\mathbf{M}| = N. \tag{14}$$

The set of Mulliken populations or the condensed atomic counterpart can be normalized in the same sense as the density matrix and the shape function are related. It is just needed to scale the CMM by the number of particles:

$$\mathbf{M}^{(1)} = N^{-1}\mathbf{M},$$

then,

$$Tr\left|\mathbf{M}^{(1)}\right| = 1,$$

a result implying that the scaled atomic charges and the diagonal elements of the CMM constitute a pair of convex sets [18]:

$$\sum_{A} Q_A^{(1)} = \sum_{A}\sum_{\alpha\in A} M_{\alpha\alpha}^{(1)} = Tr\left|\mathbf{M}^{(1)}\right| = 1.$$

That is, defining a *convexity symbol* as:

$$K\left(\{x_\alpha\}\right) = \left[\forall\alpha : x_\alpha \in \mathbf{R}^{+} \wedge \sum_{\alpha} x_\alpha = 1\right],$$

then one can write:

$$K\left(\left\{Q_A^{(1)}\right\}\right) \wedge K\left(\left\{M_{\alpha\alpha}^{(1)}\right\}\right).$$

3.2. *Ordering atomic charges as a semispace unit shell vector*

The Mulliken gross atomic populations for a given molecular structure can be associated to a condensed form of the first order density function as it has been commented, however, after ordering the atomic charge values into a column vector:

$$|\mathbf{Q}_M\rangle = \{Q_A \,|\forall A \in M\} \in V_\nu\left(\mathbf{R}^+\right), \tag{15}$$

one can consider that such vectors are members of some vector semispace [18, 19] $V_\nu\left(\mathrm{R}^+\right)$of the same dimension, ν, as many atomic centres possess the associated molecule. It is obvious that the complete sum of the molecular charge vector is the number of electrons N in the molecule, which is moreover coincident with its Minkowski norm [19]:

$$\langle|\mathbf{Q}\rangle\rangle = N \rightarrow |\mathbf{Q}\rangle \in S(N) \subset V_\nu\left(\mathbf{R}^+\right),$$

therefore, the charge vector belongs to the N shell of the vector semispace and the normalized vector:

$$|\mathbf{q}\rangle = N^{-1}\,|\mathbf{Q}\rangle \rightarrow \langle|\mathbf{q}\rangle\rangle = 1 \rightarrow |\mathbf{q}\rangle \in S(1) \subset V_\nu\left(\mathbf{R}^+\right), \tag{16}$$

corresponds to an element of the unit shell of the same vector semispace, so it can be associated to the condensation of the shape function. The normalized charge vector can be taken as a discrete descriptor of the corresponding molecule. Section 11 below will study again the possibility of constructing a probability distribution from atomic populations at the light of the following development of generalized Mulliken matrices.

3.3. *Bond orders*

According to well-known and old quantum chemical descriptions [1], the bond order P_{AB} between atoms A and B it is obtained as:

$$P_{AB} = \frac{1}{2}\sum_{\alpha\in A}\sum_{\beta\in B}\left(M_{\alpha\beta} + M_{\beta\alpha}\right). \tag{17}$$

These definitions are related to the possible partition of the CMM into submatrices involving atomic pairs:

$$\mathbf{M} = \{\mathbf{M}_{IJ}\} \rightarrow \mathbf{M}_{IJ} = \left\{M_{\alpha\beta}^{IJ}\,|\alpha \in I \wedge \beta \in J\right\}. \tag{18}$$

With this partition in mind, equation (13) can be rewritten as:

$$Q_A = Tr\,|\mathbf{M}_{AA}| = \sum_{\alpha\in A} M_{\alpha\alpha}^{AA}, \tag{19}$$

and equation (17) may be expressed more explicitly as:

$$P_{AB} = \frac{1}{2} \sum_{\alpha \in A} \sum_{\beta \in B} \left(M_{\alpha\beta}^{AB} + M_{\beta\alpha}^{BA} \right). \tag{20}$$

3.4. Charges and bond orders as expectation values

It has been recently shown that the Mulliken definitions can be obtained throughout using appropriate Hermitian operators, acting over the first and second order density functions respectively [3]. Also, bond orders involving a higher number of atoms can be deduced in the same way, however in this case the corresponding operators shall be applied to the pure exchange terms attached to higher order density functions [4]. These Hermitian operators which shall be employed over the adequate density function, are made in such a way that, in any case, both atomic charge (13), using one electron operators: $\{\Pi_A(\mathbf{r}_1)\}$, and bond order (17), using a two electron operator set: $\{\Pi_{AB}(\mathbf{r}_1; \mathbf{r}_2)\}$, items can be produced as their expectation values.

For example, for atomic charges one has:

$$Q_A = \langle \Pi_A[\rho] \rangle = \int_D \Pi_A \left[\rho^{(1)}(\mathbf{r}) \right] \mathrm{dr}, \tag{21}$$

with a similar expression for the bond orders, such a procedure constitutes in this manner a concept which can be easily extended up to any number of atoms producing polyatomic bond orders [4].

In particular, the operator, which permits to obtain atomic charges as expectation values, is defined by means of the projector [3], see also Appendix 1 for more details:

$$\Pi_A = \sum_{\alpha \in A} \Pi_\alpha = \sum_{\alpha \in A} \sum_{\beta} S_{\alpha\beta}^{-1} |\alpha\rangle \langle\beta|, \tag{22}$$

where $\mathbf{S}^{-1} = \left\{ S_{\alpha\beta}^{(-1)} \right\}$ is the inverse of the overlap matrix defined as in equation (2). Ahlrichs have put a similar idea forward in order to compute efficiently two-electron integrals [20], also Pipek and Mezey [14d] used them as a basic operators for delocalization procedures.

Mulliken projectors for the computation of diatomic and multiple atom bond orders can be made by tensor products of projectors of type (22), applied over the pure exchange part of the appropriate higher order density functions [4].

Such a property, like the one shown in expressions (12) and (14), amounts the same as to take into account that the property (12) corresponds to obtain the expectation value of the unit operator, I, as:

$$\langle I \rangle = \langle I[\rho] \rangle = \langle \rho \rangle = N \tag{23}$$

and equation (23) implies and, at the same time, it is implied by equation (14), being the projectors (22) nothing else than parts of the resolution of the identity.

4. Generalized Mulliken matrices

To start the procedure in order to show the nature of Mulliken charges and bond orders, as well as, to generalize such a pair of conceptual parameters, in this section some considerations about Mulliken matrices will be first put forward.

4.1. Weighted Mulliken matrices

By a weighted Mulliken matrix (WMM) it will be understood hereafter the matrix defined in the same way as shown in the CMM definition in equation (1):

$$\mathbf{M}[\Theta] = \mathbf{DZ}, \tag{24}$$

but using, instead of the overlap matrix, the matrix representation of a positive-definite monoelectronic operator$\Theta(\mathbf{r}) > 0$, that is:

$$\mathbf{Z} = \left\{ Z_{\mu\nu} = \langle\mu|\,\Theta\,|\nu\rangle = \int_D \chi_\mu^*(\mathbf{r})\,\Theta(\mathbf{r})\,\chi_\nu(\mathbf{r})\,\mathrm{d}\mathbf{r} \right\}. \tag{25}$$

In fact this matrix construction can involve any non-singular operator:R, by using the fact that a positive definite operator can be easily deduced by the multiplication:

$$\Theta = R^+ R \equiv |R|^2;$$

within this particular construction, the matrix elements (25) can be written as a generalized overlap:

$$Z_{\mu\nu} = \langle\mu|\,|R|^2\,|\nu\rangle = \int_D \left(R\left[\chi_\mu(\mathbf{r})\right]\right)^* \left(R\left[\chi_\nu(\mathbf{r})\right]\right)\mathrm{d}r.$$

In this way, the expectation value of the operator Θ could be easily defined as:

$$\langle\Theta\rangle = \langle\Theta[\rho]\rangle = Tr\,|\mathbf{M}[\Theta]| > 0. \tag{26}$$

4.2. Weighted atomic charges

Thus, the weighted atomic charges for a given molecular structure can be defined now as:

$$Q_A[\Theta] = \sum_{\alpha\in A} M_{\alpha\alpha} = \sum_{\alpha\in A}\sum_{\mu} D_{\alpha\mu} Z_{\mu\alpha}, \tag{27}$$

with a straightforwardly deducible expression for the weighted bond orders of any order.

The sum of weighted atomic charges will provide:

$$\sum_A Q_A[\Theta] = \sum_A\sum_{\alpha\in A} M_{\alpha\alpha} = Tr\left|\mathbf{M}[\Theta]\right| = \langle\Theta\rangle,$$

which is coincident thus with a Minkowski norm and therefore a vector of type (15) can be constructed, in the same way as the Minkowski normalized vector (16), with the difference that the normalization factor will be this time:$\langle\Theta\rangle^{-1}$. In this general case to every operator there can be attached a vector belonging to the vector semispace shell $S(\langle\Theta\rangle)$, or after Minkowski normalization to the unit shell.

4.3. Weighted Mulliken charges as expectation values of a projector

In this manner, an extension of the Mulliken ideas has been set up; producing weighted atomic convex charge distributions and bond orders, which can be attached to the expectation values of some projection operator.

Indeed, if instead of using the projector (22) the following generalized Mulliken operator is employed:

$$\Pi_A[\Theta] = \sum_{\alpha\in A}\Pi_\alpha[\Theta] = \sum_{\alpha\in A}\sum_{\beta} Z_{\alpha\beta}^{-1}\left(\Theta\left|\alpha\right\rangle\left\langle\beta\right|\Theta\right), \tag{28}$$

then it is easy to show that:

$$Q_A[\Theta] = \langle\Pi_A[\Theta][\rho]\rangle \tag{29}$$

and the weighted atomic charges become in this manner expectation values of an Hermitian operator possessing the form (28).

That the projection operators as defined in expression (28) are Hermitian can be easily shown. It is sufficient to show that the matrix expressions of the operators (28) become Hermitian.

Thus, it is just necessary to show that the following equality holds for an arbitrary pair of basis functions,$\{\chi_\mu;\chi_\nu\}$:

$$\langle\mu|\,\Pi_A[\Theta]\,|\nu\rangle = \left(\langle\nu|\,\Pi_A[\Theta]\,|\mu\rangle\right)^*. \tag{30}$$

To prove this, it is adequate to pursue the following argument, where the definition (28) can be explicitly employed, along with the fact that the matrix representation of positive definite operators is Hermitian; so one can write the following sequence of equalities:

$$\begin{aligned}
\langle \mu | \Pi_A [\Theta] | \nu \rangle &= \int_D \chi_\mu^* (\mathbf{r})\, \Pi_A [\Theta]\, \chi_\nu (\mathbf{r})\, d\mathbf{r} \\
&= \sum_{\alpha \in A} \sum_{\beta} \int_D \chi_\mu^* (\mathbf{r})\, Z_{\alpha\beta}^{-1} \left(\Theta | \alpha \rangle \langle \beta | \Theta\right) \chi_\nu (\mathbf{r})\, d\mathbf{r} \\
&= \sum_{\alpha \in A} \sum_{\beta} Z_{\alpha\beta}^{-1} \int_D \chi_\mu^* (\mathbf{r}) \left(\Theta | \alpha \rangle \langle \beta | \Theta\right) \chi_\nu (\mathbf{r})\, d\mathbf{r} \\
&= \sum_{\alpha \in A} \sum_{\beta} Z_{\alpha\beta}^{-1} \langle \mu | \Theta | \alpha \rangle \langle \beta | \Theta | \nu \rangle \\
&= \sum_{\alpha \in A} \sum_{\beta} Z_{\alpha\beta}^{-1} Z_{\mu\alpha} Z_{\beta\nu} = \sum_{\alpha \in A} Z_{\mu\alpha} \delta_{\alpha\nu} = \delta\big(\nu \in A\big) Z_{\mu\nu}.
\end{aligned}$$

This result could be already sufficient to demonstrate the Hermitian nature of the projector as defined in equation (28), because the matrix representation of the positive definite Hermitian weighting operator Θ is necessarily Hermitian. However, in order to complete the proof, then, it can be also written a similar set of equalities for the right hand part of equation (30):

$$\begin{aligned}
\left(\langle \nu | \Pi_A [\Theta] | \mu \rangle\right)^* &= \int_D \chi_\mu^* (\mathbf{r}) \left(\Pi_A [\Theta]\right)^* \chi_\nu (\mathbf{r})\, d\mathbf{r} \\
&= \sum_{\alpha \in A} \sum_{\beta} \left(Z_{\alpha\beta}^{-1}\right)^* \int_D \chi_\mu^* (\mathbf{r}) \left(\Theta | \beta \rangle \langle \alpha | \Theta\right) \chi_\nu (\mathbf{r})\, d\mathbf{r} \\
&= \sum_{\alpha \in A} \sum_{\beta} Z_{\beta\alpha}^{-1} \langle \mu | \Theta | \beta \rangle \langle \alpha | \Theta | \nu \rangle \\
&= \sum_{\alpha \in A} \sum_{\beta} Z_{\beta\alpha}^{-1} Z_{\mu\beta} Z_{\alpha\nu} = \sum_{\alpha \in A} Z_{\alpha\nu} \delta_{\mu\alpha} \\
&= \delta\left(\mu \in A\right) Z_{\mu\nu} = \delta\left(\mu \in A\right) Z_{\nu\mu}.
\end{aligned}$$

Therefore, the elements of the matrix representation of the operator $\Pi_A [\Theta]$ correspond to the same matrix elements in both cases. The matrix elements of the operator are furthermore coincident with the matrix representation of the positive definite weighting operator, so the equalities (30) are fulfilled for every pair of basis functions.

This property is important also for the CMM definition of the projectors, as defined in equation (22), because they are but a particular case of the operator (28) construction, where: $\Theta = I$.

A final noteworthy point shall be taken into account. While the unit operator is not observable, as far as the quantum mechanical lore admits, the new weighted projectors are easily attached to quantum mechanical observables, then the atomic charges and bond orders issued from the WMM can be considered additive partitions of any observable definition. Consequently, in this sense, such weighted molecular parameters may contain more quantum mechanical meaning than the CMM derived ones. In fact, the generalized Mulliken weighted atomic charges, can be considered the atomic contributions within a given molecule to the expectation value of the associated weight operator. An expectation value can thus be considered as a superposition of atomic elements, which in turn can be made by orbital superpositions. These atomic partitions, when normalized in the Minkowski sense, can be easily compared to any of the alternative distributions one can define in a molecule by choosing different weight operators. In the same manner, a molecule can be described by a set of these weighted distributions. Such a possibility will be later on discussed.

4.4. WMM and generalized Mulliken indices

As the basis set functions are centred commonly on atomic sites within a molecule, then one can condense the WMM elements into such atomic centres, producing an array, which can be called a *condensed atomic WMM*:

$$\mathbf{A} = \left\{ A_{PQ} = \sum_{\alpha\in P} \sum_{\beta\in Q} M_{\alpha\beta} \right\}.$$

In this way the Mulliken atomic charge on atom P can be retrieved from the diagonal elements of matrix **A:**

$$|\mathbf{Q}\rangle = \{Q_P = A_{PP}\} = Diag\,(Q_P)\,,$$

and the atomic Mulliken bond orders can be retrieved from the products, forming, along with atomic charges, an atomic Mulliken charge and bond order matrix:

$$\mathbf{R} = \left\{ R_{PQ} = A_{PQ} A_{QP} \wedge R_{PP} = Q_P \right\}.$$

In order to start defining generalized atomic Mulliken bond orders, it is interesting to construct a new matrix set from **A**, by constructing submatrices of **A,** of dimension $(n \times n)$ involving n atoms out of N, the total number of atoms in the studied molecule:

$$\mathbf{A}^{(n)}\,(\mathbf{a}) = \left\{ A_{P_k Q_k};\, (k = 1, n) \right\}, \tag{31}$$

in this definition the matrices $\mathbf{A}^{(n)}(\mathbf{a})$ will depend on the atomic indices collected into the n-dimensional vector $\mathbf{a}$. Then the generalized Mulliken bond order index involving n atoms can be defined as the circulant of the matrices of type (31), as defined in the Appendix 2, where only cyclic permutations are admitted in the implicit nested summation symbol:

$$M^{(n)}(\mathbf{a}) = Cir\left(\mathbf{A}^{(n)}(\mathbf{a})\right).$$

Such a definition corresponds to the computational part of an already described theoretical procedure [4], involving projection, see Appendix 1 for more details, of any arbitrary order density matrix over the atomic centred basis functions, proceeding afterwards to a further condensation of the projected density into generalized Mulliken multiple bond indices.

As a consequence of this projection-condensation over a circulant origin, the generalized atomic Mulliken indices possess a well-defined invariant property. Denoting by $P(\mathbf{a})$ any permutation of the atomic indices contained in the set **a,** it is obvious that the cyclic permutations are the only ones entering the generalized Mulliken index; an invariant computational structure is obtained in this way:

$$M^{(n)}(\mathbf{a}) = M^{(n)}(P(\mathbf{a})).$$

5. Several remarks about the nature of weighting operators entering WMM definition

From now on it will be used the term atomic condensed charges, bond orders, polyatomic bond orders... as to connect WMM deduced parameters with the original CMM definitions. However, the significance of this entire family of new WMM, in fact as many possible as positive definite operators can be described, perhaps cannot be entirely connected with the original charge and bond order definitions simply issued from CMM. The reason is simple: CMM is related to WMM when the chosen weight operator is the unit one, as already discussed. One cannot expect that the weighted atomic charges, when obtained from other positive definite operators than the unit one, behave in the same manner or have the same trends as the classical Mulliken ones. They will be called in this way as they conveniently renormalized can become a collection of numbers attached to every molecular atom which sum up to the number of electrons in a molecule when properly renormalized, but in the same manner, effortlessly can sum up to one when Minkowski normalized. In this later case the signification of these atomic parameters will be the one of a discrete probability distribution, sharing the whole expectation value atomic contributions of the attached positive definite operator. The set of all the weighted atomic charges, when belonging to the unit shell and collected into an array will become a stochastic column or row matrix depending on which form of ordering is employed. In this section follows a sample of the enormous quantity of possible operator choices, of which the idea of WMM can be based.

5.1. Convex combinations of positive definite operators

It is well know that a convex combination of positive definite operators is positive definite and the same apply to their matrix representations. To remind this property to the reader, just consider a set of matrix representations $\{\mathbf{Z}_I\}$ all of them positive definite, then it holds for each member of the matrix set:

$$\forall I \wedge \forall \mathbf{x} \neq \mathbf{0} : \theta_I = \mathbf{x}^+ \mathbf{Z}_I \mathbf{x} \in \mathbf{R}^+,$$

then using a convex set of scalars $\{\lambda_I\}$ such that:

$$\forall I : \lambda_I \in \mathbf{R}^+ \wedge \sum_I \lambda_I = 1,$$

the new matrix

$$\mathbf{Z} = \sum_I \lambda_I \mathbf{Z}_I \rightarrow \forall \mathbf{x} \neq \mathbf{0} : \mathbf{x}^+ \mathbf{Z} \mathbf{x} = \sum_I \lambda_I \mathbf{x}^+ \mathbf{Z}_I \mathbf{x} = \sum_I \lambda_I \theta_I \in \mathbf{R}^+. \tag{32}$$

Thus composite superpositions of weighting positive definite operators can be used in the definition of WMM.

It should be noted that, in fact, this kind of operator combinations can be also done by choosing a set of positive definite scalars, not necessarily summing 1. Property (32) will hold the same.

5.2. Electrostatic molecular potential as weighting operator

Among all positive definite operators one can select to construct a WMM, there is the choice of the electronic part of the electrostatic molecular potential (EMP), with the sign changed as to become positive definite. In this case, due to the nature of the EMP operator it can be written:

$$V(\mathbf{R}) = \int_D \rho(\mathbf{r}) |\mathbf{r} - \mathbf{R}|^{-1} \, d\mathbf{r} = \int_D |\mathbf{r} - \mathbf{R}|^{-1} \rho(\mathbf{r}) \, d\mathbf{r} = \left\langle |\mathbf{r} - \mathbf{R}|^{-1} \right\rangle, \tag{33}$$

then, nothing opposes to define a WMM in this context as:

$$\mathbf{M}(V(\mathbf{R})) = \mathbf{D}\mathbf{V}(\mathbf{R}),$$

where the nature of the EMP matrix representation is:

$$\mathbf{V}(\mathbf{R}) = \left\{ V_{\mu\nu}(\mathbf{R}) = \int_D \chi_\mu^*(\mathbf{r}) |\mathbf{r} - \mathbf{R}|^{-1} \chi_\nu(\mathbf{r}) \, d\mathbf{r} \right\}.$$

The interesting thing to be noted now is such that within this characteristic WMM made from EMP, the corresponding weighted Mulliken charges and bond orders are dependent of the three-dimensional space point considered. This can provide the potential users of WMM with interesting points of view, as the atomic centres can be used in turn as vantage points, defining several charge distributions, every one associated to an atomic centre.

In case this spatial dependence is not needed, it can be arbitrarily chosen the centre of nuclear charges as a reference:

$$\mathbf{R} \rightarrow \mathbf{C} = N^{-1} \sum_I Z_I \mathbf{R}_I .$$

As an alternative space independent possible solution, then just the expression (33) can be considered as an operator and the WMM can be defined now as:

$$\mathbf{M}(V) = \mathbf{DV};$$

but the matrix associated to the integrals has to be computed now as:

$$\mathbf{V} = \left\{ V_{\mu\nu} = \int_D \chi_\mu^* (\mathbf{R})\, V(\mathbf{R})\, \chi_\nu (\mathbf{R})\, \mathrm{d}\mathbf{R} \right\} .$$

Such a matrix above will produce a total expectation value equal to the Coulomb electronic repulsion.

5.3. Coulomb and exchange operators

The sets of Coulomb $\{J_i\}$ and exchange $\{K_i\}$ operators over the MO set, as well as weighted sums of them, can be used too for the purposes of constructing WMM families. In such case, it can be quite interesting to choose among all the MO set, the ones associated to the operators corresponding to frontier orbitals, as they will provide with alternative, albeit complementary, charges to the Fukui definitions. For example,

$$\mathbf{M}(J_i) = \mathbf{DJ}_i$$

with the obvious description:

$$\mathbf{J}_i = \left\{ J_{i;\mu\nu} = \int_V \chi_\mu^* (\mathbf{r})\, J_i (\mathbf{r})\, \chi_\nu (\mathbf{r})\, \mathrm{d}\mathbf{r} = (ii|\,\mu\nu) \right\} .$$

A similar positive definite representation can be described for exchange operators as it can be written:

$$\mathbf{K}_i = \left\{ K_{i;\mu\nu} = \int_V \chi_\mu^* (\mathbf{r})\, K_i (\mathbf{r})\, \chi_\nu (\mathbf{r})\, \mathrm{d}\mathbf{r} = (i\mu|\, i\nu) \right\} .$$

5.4. Kinetic energy density operator

Kinetic energy atomic charges and bond orders can become most interesting to understand or to complement the nature of the chemical bond notion. When using kinetic energy WMM, the operator matrix representation can be considered as an overlap between the gradient of the two involved basis functions, so results may be expected very similar to CMM, but coming from a completely different source.

5.5. Two-electron and many-electron operators

Two-electron or many-electronic operators can be used too, provided that they are previously reduced to one electron structures, like in the cases discussed in sections 5.2. and 5.3. above.

5.6. Density function as a positive definite operator

A possible positive definite operator choice may consist into the density function itself. The use of the density function viewed as a positive definite operator opens the way to connect charges and bond orders with the structure of quantum similarity formalism [21].

Indeed, when the density function becomes an operator itself, one can analyze the so-called overlap self-similarity measure as the source of the density function matrix representation for the purpose of constructing the WMM. Overlap self-similarity can be described by means of the two-electron Dirac delta function:

$$\langle \rho \mid \rho \rangle = \langle \rho\,[\rho] \rangle = \int\!\!\int \rho\,(\mathbf{r}_1)\delta\,(\mathbf{r}_1 - \mathbf{r}_2)\,\rho\,(\mathbf{r}_2)\,\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2 = \int_D |\rho\,(\mathbf{r})|^2\,\mathrm{d}\mathbf{r}, \qquad (34)$$

which can be also written as:

$$\langle \rho \mid \rho \rangle = \sum_\mu \sum_\nu D_{\mu\nu} \left[\sum_\lambda \sum_\sigma \langle \mu\nu : \lambda\sigma \rangle\, D_{\lambda\sigma} \right];$$

so, defining the matrix representation:

$$\mathbf{Z} = \left\{ Z_{\mu\nu} = \sum_\lambda \sum_\sigma \langle \mu\nu : \lambda\sigma \rangle\, D_{\lambda\sigma} \right\}$$

with the four centre overlap integral defined as:

$$\langle \mu\nu : \lambda\sigma \rangle = \int_D \chi_\mu^*\,(\mathbf{r})\chi_\nu\,(\mathbf{r})\,\chi_\lambda^*\,(\mathbf{r})\,\chi_\sigma\,(\mathbf{r})\,\mathrm{d}\mathbf{r}.$$

Instead of the Dirac two-electron delta function, as it is well known in quantum similarity that gives rise to integrals of type (34), other positive definite operators can be used, like the Coulomb operator [22]. Then the self-similarity becomes the Coulomb energy of the studied system and the formalism will be related to the Coulomb operators already discussed in sections 5.2. and 5.3.

Another density function can be also employed as the operator entering the similarity measure, but in order to keep this discussion as simple as possible it will not be further deepened, thus entering in this way within other branching schemes, which surely can be further developed.

5.7. *Spherical Gaussian functions as positive definite operators*

5.7.1. *Spherical Gaussian operators*

A similar operator to the EMP one, as discussed in section 5.2, can be described as a Gauss distribution centred at an arbitrary point in 3D space, that is: a spherical Gaussian operator (SGO), defined by the function

$$\gamma\left(\theta;\mathbf{R}\right)=exp\left(-\theta\left|\mathbf{r}-\mathbf{R}\right|^{2}\right), \tag{35}$$

where the exponent θ is an arbitrary parameter; the operator is presented unnormalized in the present description for the sake of simplification, but can be considered normalized too, adding the normalization constant as a constant multiplicative factor. The positive definite operator matrix representation to be used in WMM will then be:

$$\mathbf{Z}\left(\theta,\mathbf{R}\right)=\left\{Z_{\mu\nu}\left(\theta,\mathbf{R}\right)=\int_{D}\chi_{\mu}^{*}\left(\mathbf{r}\right)\gamma\left(\theta,\mathbf{R}\right)\chi_{\nu}\left(\mathbf{r}\right)\mathrm{d}\mathbf{r}\right\}.$$

It can be seen that the matrix entering WMM will depend of the position in space were the SGO is located. In this case a set of privileged points in 3D space appears to be the one constituted by the atomic centres: $\{\mathbf{A}_I\}$. A similar situation has been encountered when analyzing the EMP in section 5.2.

5.7.2. *Elliptical Gaussian operators*

The exponent parameter θ has been chosen previously in equation (35) as a scalar, but the expression (35) can be more generally defined as a three parameter operator, yielding in this way an elliptical Gaussian operator (EGO), if necessary:

$$\gamma\left(\Theta;\mathbf{R}\right)=exp\left(-\left(\mathbf{r}-\mathbf{R}\right)^{T}\Theta\left(\mathbf{r}-\mathbf{R}\right)\right)\wedge\Theta=Diag\left(\theta_{x};\theta_{y};\theta_{z}\right). \tag{36}$$

Whenever the more general EGO in the form (36), is chosen as a unique parameter operator, as in equation (35), it seems that a choice like: $\theta=f\left(Z_{I}^{-1}\right)$will be interesting for such a SGO, when the operator is also chosen centred at atomic centre $\mathbf{R}=\mathbf{A}_{I}$.

5.7.3. SGO condensed atomic density parameters

WMM charges and bond orders will become a distribution in this way as, for instance:

$$Q_\mu(\theta,\mathbf{R})=\sum_\nu D_{\mu\nu}Z_{\mu\nu}(\theta,\mathbf{R}).$$

However, when considering SGO definition (35) as a two-electron operator, then it can be also obtained:

$$\begin{aligned}q_\mu=\langle Q_\mu\rho\rangle&=\int_D Q_\mu(\theta,\mathbf{R})d\mathbf{R}=\sum_\nu D_{\mu\nu}\int_D Z_{\mu\nu}(\theta,\mathbf{R})\,\rho(\mathbf{R})\,d\mathbf{R}\\&=\sum_\nu D_{\mu\nu}\int_D\int_D\chi_\mu^*(\mathbf{r})\,exp\left(\theta\,|\mathbf{r}-\mathbf{R}|^2\right)\chi_\nu(\mathbf{r})\rho(\mathbf{R})\,d\mathbf{r}d\mathbf{R}.\end{aligned}$$

The results for a given molecule shall be renormalized as to ensure the proper sum equivalent to the total number of electrons or the unity, as in any other case already discussed in the introduction of this paragraph, when considering a positive definite operator choice.

This operator description can be associated to a simplified formalism, attached to the one previously described in section 5.6. above.

5.7.4. Convex combinations of SGO

Moreover, nothing opposes to define as an operator a convex combination of SGO's, centred at particular sites, like:

$$\Gamma=\sum_I\lambda_I\gamma(\theta_I,\mathbf{A}_I).$$

Moreover, any SGO can be taken as an unbounded delimiter of the atomic sites, a situation perhaps more adequate to the quantum mechanical features of LCAO MO theory, than other well-defined finite boundaries found in the literature [23].

5.7.5. Products of SGO

Also, products of two or many SGO's, centred at two or more centres can be used, for instance, to describe bond order boundaries, that is:

$$\Gamma(A,B)=\gamma(\theta_A,\mathbf{A})\,\gamma(\theta_B,\mathbf{B})\,.$$

Quite a large set of applications and variants of SGO may be searched for in the future.

6. How WMM transforms with unitary and other possible transformations

The most important result to be shown now in this context is the fact that in WMM, keeping in mind that this includes also CMM, the operator positive definite matrix representation shall not be further manipulated. For example: using powers of it. Such matrix transformations produce the impossibility to attach the transformed function charge or bond order partition to atomic centres and thus lacking of one of the fundamental properties of Mulliken matrices. The following simple and well-known arguments prove this feature.

6.1. *Unitary transformations*

The operator positive definite matrix representation employed at any WMM level has the advantage to be non-singular in any case, but also Hermitian and thus diagonalizable by means of a unitary transformation, that is:

$$\exists \mathbf{U} \rightarrow \mathbf{U}^{+}\mathbf{U} = \mathbf{U}\mathbf{U}^{+} = \mathbf{I} : \mathbf{U}^{+}\mathbf{Z}\mathbf{U} = \Theta \wedge \Theta$$
$$= Diag\,(\theta_1, \theta_2, \ldots \theta_k, \ldots) \wedge \forall k : \theta_k \in \mathbf{R}^{+}.$$

In this way one can write:

$$\mathbf{M} = \mathbf{D}\mathbf{U}\Theta\mathbf{U}^{+} \rightarrow \mathbf{U}^{+}\mathbf{M}\mathbf{U} = \mathbf{U}^{+}\mathbf{D}\mathbf{U}\Theta \rightarrow \mathbf{M}_U = \mathbf{D}_U\Theta. \tag{37}$$

This last result proves that a diagonal positive definite matrix representation can be used, provided that the charge and bond order matrix is transformed adequately. The original WMM and the transformed one are easily related by the unitary transformation:

$$\mathbf{M} = \mathbf{U}\mathbf{M}_U\mathbf{U}^{+} \leftrightarrow \mathbf{U}^{+}\mathbf{M}\mathbf{U} = \mathbf{M}_U.$$

Moreover, equation (37) permits to define several transforms, producing a WMM, which will be equivalent to the transformed charge and bond order matrix:$\mathbf{D}_U = \mathbf{U}^{+}\mathbf{D}\mathbf{U}$. That is:

$$\mathbf{M}_U = \mathbf{D}_U\Theta \rightarrow \Theta^{-p}\mathbf{M}_U\Theta^{1-p} = \Theta^{-p}\mathbf{D}_U\Theta^{+p}. \tag{38}$$

6.2. *Löwdin transformation*

For example taking: $p = +\frac{1}{2}$, the resulting WMM transform becomes the weighted Löwdin matrix (WLM):

$$\mathbf{M}_L = \Theta^{-\frac{1}{2}}\mathbf{M}_U\Theta^{+\frac{1}{2}} = \Theta^{-\frac{1}{2}}\mathbf{D}_U\Theta^{+\frac{1}{2}} = \mathbf{D}_L, \tag{39}$$

so the WLM and the charge and bond order matrix in the Löwdin orthonormalized basis set are coincident. Transformations of this kind are also equivalent to transform the basis set functions. However, transforms of type (37) or (38), destroy the attachment of the transformed basis set to the original LCAO MO atomic centres.

To grasp this last remark it is just necessary to consider formally the construction of the operator matrix representation, as Löwdin was usually employing, to obtain an orthonormalized basis set:

$$\mathbf{C}^{+}\Omega\mathbf{C} = \mathbf{Z} \rightarrow \left(\Theta^{-\frac{1}{2}}\mathbf{U}^{+}\right)\mathbf{C}^{+}\Omega\mathbf{C}\left(\mathbf{U}\Theta^{-\frac{1}{2}}\right) = \mathbf{I},$$

where the function basis set is collected into a row vector:

$$\langle X| = \left(\chi_1; \chi_2; \ldots \chi_\mu; \ldots\right).$$

The Löwdin basis set functions can then be written as:

$$\langle\lambda| = \langle X|\left(\mathbf{U}\Theta^{-\frac{1}{2}}\right),$$

so it can be also written:

$$|\lambda_i\rangle = \sum_{\mu}\chi_\mu U_{\mu i}\theta_i^{-\frac{1}{2}}.$$

The subindex of the Löwdin basis set function has been chosen as *i-th* to stress its difference with the original basis set functions. The *ordering of the resultant Löwdin functions is arbitrary*, as it depends of the order of the columns of the transformation matrix and this order depends, in turn, on the ordering chosen for the matrix representation eigenvalue spectrum of the operator. Thus, no condensation into atomic centres is possible to be applied for transformed WMM like (38) or (39). To see this more detailed, one can say that the indexing of Löwdin orbitals depends on the indexing of the spectrum of the overlap matrix, so the i-th Löwdin basis function is attached to the i-th overlap eigenvalue, and overlap eigenvalues are not attached at all in general to any initial AO ordering.

6.3. Cholesky transformation

Moreover, other transformations can be envisaged. Taking into account the positive definiteness of the operators accepted as weights and the same property for their matrix representations **Z**, there is also possibility to perform a well-known Cholesky decomposition, as it has been commented when discussing the overlap matrix properties. There always exists an upper triangular, non-singular, matrix **T**, which:

$$\mathbf{Z} = \mathbf{T}^{+}\mathbf{T}.$$

Thus, one can write:

$$\mathbf{M} = \mathbf{DZ} \rightarrow \mathbf{TMT}^{-1} = \mathbf{TDT}^{+} \rightarrow \mathbf{M}_T = \mathbf{D}_T.$$

This is a result similar to the previous Löwdin transformation, because Cholesky decomposition is equivalent to a Gram-Schmidt orthonormalization process over the basis functions [10–12]. In the same way the transformed orthonormalized function set is not attachable to any atomic centre, but is delocalized over the entire molecular atomic sites as in Löwdin transformation.

However, a partial unitary or Cholesky transformation involving just the functions located at every atomic centre, leading to orthonormalized functions belonging to each centre, but not to atoms at other centres in a given molecule, can be employed without destroying the attachment of the functions belonging to a given atom. Then, in this case the transformation matrix is block-diagonal, but this feature has not a greater interest other than to be mentioned for the sake of completeness. It will produce an effect similar to using as basis set an orthogonal AO's set centred on each atom.

A final remark shall be written here. In any case, even if charges and bond orders cannot be attached to any specific atomic centre, they can still be computed just for constructing the transformed functions.

6.4. Unitary transformation leaving the basis functions attached to their centres

Still there is a possibility which transforming the basis set coefficients leaves invariant the association of the basis set functions to the molecular centres. A unitary matrix can be obtained when some one electron operator choice has been adopted.

6.4.1. General procedure involving any one-electron operator

The net result when diagonalizing the matrix representation of some Hermitian operator R under some subset of the MO basis set:

$$\mathbf{Z}_R = \left\{ z_{R;ij} = \langle i | \, R \, | j \rangle \right\}.$$

Is such that in any case, the matrix $\mathbf{Z}_R$ will furnish a unitary transformation $\mathbf{U}$, attached to its eigenvectors, that is:

$$\mathbf{Z}_R \mathbf{U} = \mathbf{U} \Delta \rightarrow \Delta = Diag\,(r_k) \wedge \mathbf{U}^{+}\mathbf{U} = \mathbf{U}\mathbf{U}^{+} = \mathbf{I}.$$

This unitary matrix will act over the MO basis set, transforming them in the way shown below:

$$| R | \, p\rangle = \sum_k u_{kp} \, |k\rangle,$$

and in order to see how the MO coordinates with respect to some atomic orbital basis set are transformed, suppose known a monoelectronic basis set, then MO can be expressed by the linear combinations of the MO coordinate matrix elements and thus it can be written:

$$|R|\,p\rangle = \sum_k u_{kp}\,|k\rangle = \sum_k u_{kp} \sum_\mu c_{\mu k}\,|\mu\rangle = \sum_\mu \sum_k \left(c_{\mu k} u_{kp}\right)|\mu\rangle\,.$$

So, this is the same as to transform the MO coordinates, while preserving the attachment of the basis set functions to some centres, as the new transformed coordinates $\mathbf{C}_L = \left\{c_{L;\mu p}\right\}$ can be defined as:

$$c_{L;\mu p} = \sum_k \left(c_{\mu k} u_{kp}\right) \rightarrow \mathbf{C}_L = \mathbf{CU}.$$

6.4.2. The density function in the new MO basis set

If the first order density function is written in terms of the MO as in equation (10):

$$\rho\,(\mathbf{r}) = \sum_p \omega_p\,|p\rangle\,\langle p|\,,$$

where the set of positive real numbers $\left\{\omega_p\right\}$ represent the MO occupations, then it will be obtained the following relationship between the original and the new transformed MO:

$$\begin{aligned}\rho_R\,(\mathbf{r}) &= \sum_p \omega_p\,|R|\,p\rangle\,\langle p\,|R\,| = \sum_p \omega_p \sum_k \sum_l u_{kp} u^*_{pl}\,|k\rangle\,\langle l| \\ &= \sum_k \sum_l \left(\sum_p \omega_p u_{kp} u^*_{pl}\right)|k\rangle\,\langle l|.\end{aligned}$$

Then, constructing the diagonal matrix:

$$\mathbf{A} = Diag\left(\omega_p\right)$$

a new non-diagonal occupation number matrix can be defined as:

$$\mathbf{B} = \mathbf{UAU}^+ = \{b_{kl}\}\,,$$

and the new density function can be written:

$$\rho_R\,(\mathbf{r}) = \sum_k \sum_l b_{kl}\,|k\rangle\,\langle l|.$$

6.4.3. Monodeterminantal closed shell particular case

In monodeterminantal closed shells, when the transformed MO are the occupied ones, the particular case: $\mathbf{A} = 2\mathbf{I}$ is encountered, so:

$$\mathbf{B} = 2\mathbf{U}\mathbf{U}^{+} = 2\mathbf{I}$$

and thus:

$$\rho_R(\mathbf{r}) = 2\sum_k \sum_l \delta_{kl} |k\rangle \langle l| = 2\sum_k |k\rangle \langle k| = \rho(\mathbf{r}),$$

that is, the well-known result is found stating that the old and the unitary transformed density functions are the same.

7. Classical Mulliken charges and bond orders as a zero-th order approach to molecular populations

7.1. Taylor series expansion of WMM charges

The discussion put forward in the previous sections proves sufficiently that CMM can be easily associated to a WMM, where the corresponding operator is the identity one. In this sense one can write:

$$Q_A \equiv Q_A[I].$$

This formal possibility immediately suggests that, whenever a Taylor series in terms of another operator, Ξ say, can be defined attached to the operator Θ, like:

$$\Theta = \sum_{p=0}^{\infty} \frac{1}{p!}\xi_p \Xi^p = I + \xi_1 \Xi + \frac{1}{2}\xi_2 \Xi^2 + O(3) \tag{40}$$

then, it can also be written, just using the Taylor series (40) into the definitions (27) up to (29), the following Taylor series attached to atomic charges:

$$Q_A[\Theta] = Q_A + \xi_1 Q_A[\Xi] + \frac{1}{2}\xi_2 Q_A\left[\Xi^2\right] + O(3),$$

proving that the constructed charges or Mulliken's atomic populations, computed using CMM, could be considered as the zero-th order terms in this kind of atomic charge definition, when admitting that a weighting operator in the form of a Taylor series with the structure (40) can be described. A previous work of Pipek [2d], associated to another contextual development of population distributions, but containing a series expansion of population operators shall be quoted.

7.2. Parameterized Taylor series

One can also, without loss of generality, consider the operator series in equation (40), associated to a parameter t; then it can be written, for example:

$$\Theta(t) = \sum_{p=0}^{\infty} \tfrac{1}{p!}\xi_p t^p \Xi^p = I + \xi_1 t \Xi + \tfrac{1}{2}\xi_2 t^2 \Xi^2 + O(3); \tag{41}$$

hence, in this way, the weighted Mulliken charges will depend on such a parameter and one can write:

$$Q_A[\Theta(t)] = Q_A + \xi_1 t Q_A[\Xi] + \tfrac{1}{2}\xi_2 t^2 Q_A\left[\Xi^2\right] + O(3), \tag{42}$$

and it is straightforward to see that:

$$\lim_{t\to 0} Q_A[\Theta(t)] = Q_A.$$

It can be said that this results on CMM constructed charges and, obviously, bond orders too, are limiting cases of a much general computational perspective, within a quantum mechanically equally correct definition.

8. WMM constructed charges and quantum similarity measures

Among the collection of Taylor series which can be used for implementing equations (40) or (41), when seeking for a charge expression like (42), for construction of the operator intervening into the weighted Mulliken charge definition, there appear to be two immediate logical choices, among many other possible ones.

A well defined choice, though, for the Taylor series (41) can be adopted in the form of an exponential function, which always constitutes the basic procedure, yielding a positive definite operator formalism as a result, whichever ground operator is chosen and, as such, has been widely used in quantum mechanics [24]. The second direct choice concerns the attached operator, acting as the exponential variable. It appears that these operators can indeed be selected in a quite arbitrary way, even without the restriction to be positive-definite or Hermitian. However, it seems a plausible idea that the density function itself constitutes some kind of natural option for the operator in the variable part. The use of density as operator and its matrix representation in LCAO framework has been recently discussed [21].

The first order density function, using the matrix elements of the CBO matrix as defined in equation (4) can be written as in equation (10):

$$\rho(\mathbf{r}) = \sum_{\mu}\sum_{\nu} D_{\mu\nu}\chi_{\mu}(\mathbf{r})\,\chi_{\nu}^{*}(\mathbf{r}). \tag{43}$$

In that case, one can also construct the following parameterized exponential operator:

$$\Theta(t) = \exp(t\rho) = \sum_{p=0}^{\infty} \tfrac{1}{p!} t^p \rho^p. \tag{44}$$

Thus, the WMM atomic charge definition will finally become:

$$Q_A[\rho; t] = Q_A + tQ_A[\rho] + \tfrac{1}{2} t^2 Q_A\left[\rho^2\right] + O(3). \tag{45}$$

Of course, the zero-th order term in equation (45) is coincident with the CMM atomic charge.

8.1. *First order corrections and self-similarity measures*

Now, the first order correction, in terms of the parameter t, will have the form:

$$Q_A[\rho] = \sum_{\alpha \in A} M_{\alpha\alpha}[\rho] = \sum_{\alpha \in A} \sum_{\beta} D_{\alpha\beta} Z_{\beta\alpha}[\rho] \tag{46}$$

and the set of terms $\left\{Z_{\beta\alpha}[\rho]\right\}$intervening into the WMM definition (24) are nothing else than the *half-contracted similarity measures* [22]:

$$\begin{aligned} Z_{\beta\alpha}[\rho] &= \sum_{\mu} \sum_{\nu} D_{\mu\nu} \int_D \chi_\mu(\mathbf{r}) \chi_\nu^*(\mathbf{r}) \chi_\beta(\mathbf{r}) \chi_\alpha^*(\mathbf{r})\, d\mathbf{r} \\ &= \sum_{\mu} \sum_{\nu} D_{\mu\nu} (\mu\nu\beta\alpha) = \int_D \rho(\mathbf{r}) \chi_\beta(\mathbf{r}) \chi_\alpha^*(\mathbf{r})\, d\mathbf{r}. \end{aligned} \tag{47}$$

Moreover, equation (47) can be considered as well as the definition of the elements of a density function matrix representation, with respect to the chosen atomic basis set. The set of integrals $\{(\mu\nu\beta\alpha)\}$ are quadruple centre overlap integrals, which summed up produce a resultant expectation value as follows:

$$\begin{aligned} \sum_{\alpha} \sum_{\beta} D_{\alpha\beta} Z_{\beta\alpha}[\rho] &= \sum_{\alpha} \sum_{\beta} D_{\alpha\beta} \sum_{\mu} \sum_{\nu} D_{\mu\nu} (\mu\nu\beta\alpha) \\ &= (\rho\,|\rho) = \int_D |\rho(\mathbf{r})|^2 d\mathbf{r} = \left\langle \rho^2 \right\rangle, \end{aligned}$$

a result which, in turn, is nothing else than the so-called *self-similarity measure* [22] of a quantum system, described by the chosen density function Euclidean norm.

The density function (43) can be also defined in terms of the partition over every particular atom in a given molecular system, that is:

$$\rho(\mathbf{r}) = \sum_A \rho_A(\mathbf{r}) = \sum_A \Omega_A[\rho] = \sum_A \left(\sum_{\alpha\in A} \sum_\beta D_{\alpha\beta} \chi_\alpha(\mathbf{r}) \chi_\beta^*(\mathbf{r}) \right), \tag{48}$$

and, thus, the atomic charge expression (46) may be also written as follows:

$$\begin{aligned} Q_A[\rho] &= \sum_{\alpha\in A} \sum_\beta D_{\alpha\beta} Z_{\beta\alpha}[\rho] = \sum_{\alpha\in A} \sum_\beta D_{\alpha\beta} \sum_\mu \sum_\nu D_{\mu\nu}(\mu\nu\beta\alpha) \\ &= (\rho\,|\rho_\mathrm{A}) = \int_D \rho(\mathbf{r})\,\rho_\mathrm{A}(\mathbf{r})\,\mathrm{d}\mathbf{r}. \end{aligned} \tag{49}$$

This result indicates that the first order charge contribution becomes an *overlap-like similarity measure* [22] between the whole density function and the partial density fragment of an atom of the system, as defined in equation (48). Equation (49) may become a quite interesting LCAO feature when, instead of a unique atomic charge, one wants to consider molecular fragment charge definitions, made among molecular subsets containing several atoms. That is, considering some molecular fragment, formally described as: $F = \{A_1, A_2, \ldots, A_{n_F}\}$, formed by n_F atoms, then the fragment charge is defined as:

$$\begin{aligned} Q_F[\rho] &= \sum_{I=1}^{n_F} \sum_{\alpha\in A_I} \sum_\beta D_{\alpha\beta} Z_{\beta\alpha}[\rho] = \sum_{I=1}^{n_F} \sum_{\alpha\in A_I} \sum_\beta D_{\alpha\beta} \sum_\mu \sum_\nu D_{\mu\nu}(\mu\nu\beta\alpha) \\ &= \sum_{I=1}^{n_F} \left(\rho\,\middle|\rho_{A_I}\right) = \int_D \rho(\mathrm{r})\,\rho_F(\mathrm{r})\,\mathrm{dr}. \end{aligned}$$

8.2. Second and higher order corrections

A parallel development to the first order correction can be followed for the second order terms in the parameter t, and the procedure becomes easily extensible to the higher order expression of the charge contributions.

The second order atomic charge contribution can be defined, for instance, as:

$$Q_A\left[\rho^2\right] = \sum_{\alpha\in A} M_{\alpha\alpha}\left[\rho^2\right] = \sum_{\alpha\in A} \sum_\beta D_{\alpha\beta} Z_{\beta\alpha}\left[\rho^2\right]$$

and now only it is need to construct the elements of the second order matrix **Z.** There are quite similar to the first order ones:

$$Z_{\beta\alpha}\left[\rho^2\right]=\sum_\mu\sum_\nu D_{\mu\nu}\sum_\lambda\sum_\sigma D_{\lambda\sigma}\int_D \chi_\mu(\mathbf{r})\,\chi_\nu^*(\mathbf{r})\,\chi_\lambda(\mathbf{r})\,\chi_\sigma^*(\mathbf{r})\,\chi_\beta(\mathbf{r})\,\chi_\alpha^*(\mathbf{r})\,d\mathbf{r}$$
$$=\sum_\mu\sum_\nu D_{\mu\nu}\sum_\lambda\sum_\sigma D_{\lambda\sigma}\,(\mu\nu\lambda\sigma\beta\alpha)=\int_D |\rho(\mathbf{r})|^2\chi_\beta(\mathbf{r})\,\chi_\alpha^*(\mathbf{r})\,d\mathbf{r}; \quad (50)$$

where the associated expectation value defined as:

$$\sum_\alpha\sum_\beta D_{\alpha\beta}Z_{\beta\alpha}\left[\rho^2\right]=\sum_\alpha\sum_\beta D_{\alpha\beta}\sum_\mu\sum_\nu D_{\mu\nu}\sum_\lambda\sum_\sigma D_{\lambda\sigma}\,(\mu\nu\lambda\sigma\beta\alpha)$$
$$=\left(\rho^2\,|\rho\right)=\int_D|\rho(\mathbf{r})|^3 d\mathbf{r}=\left\langle\rho^3\right\rangle,$$

produces a *triple density self-similarity measure* [25].

The second order atomic charge contribution can be easily written as:

$$Q_A\left[\rho^2\right]=\sum_{\alpha\in A}\sum_\beta D_{\alpha\beta}Z_{\beta\alpha}\left[\rho^2\right]=\sum_{\alpha\in A}\sum_\beta D_{\alpha\beta}\sum_\mu\sum_\nu D_{\mu\nu}\sum_\lambda\sum_\sigma D_{\lambda\sigma}\,(\mu\nu\lambda\sigma\beta\alpha)$$
$$=\left(\rho^2\,|\rho_\mathrm{A}\right)=\int_D|\rho(\mathbf{r})|^2\,\rho_\mathrm{A}(\mathbf{r})\,d\mathbf{r}.$$

From this previous experience, it is obvious that the pth order term to the atomic charge contribution can be written by means of a similarity measure like:

$$Q_A\left[\rho^p\right]=\sum_{\alpha\in A}\sum_\beta D_{\alpha\beta}Z_{\beta\alpha}\left[\rho^p\right]=\left(\rho^p\,|\rho_\mathrm{A}\right)=\int_D|\rho(\mathbf{r})|^p\,\rho_\mathrm{A}(\mathbf{r})\,d\mathbf{r}.$$

And the expectation value for the operator (44), could be easily written in terms of p-th order self-similarity measures:

$$\langle\Theta(t)\rangle=\langle\exp(t\rho)\rangle=\int_D\rho(\mathbf{r})\exp(t\rho(\mathbf{r}))\,d\mathbf{r}$$
$$=\sum_{p=0}^{\infty}\tfrac{1}{p!}t^p\int_D\rho(\mathbf{r})\,|\rho(\mathbf{r})|^p\,d\mathbf{r}=\sum_{p=0}^{\infty}\tfrac{1}{p!}t^p\left\langle\rho^p\right\rangle.$$

9. Approximate implementation of the exponential quantum similarity corrections to Mulliken charges and bond orders

Computation of higher order similarity measures and the necessary integrals may become a cumbersome task. To overcome such a problem the Taylor series (45) can be cut at the first order, provided that the parameter t is chosen conveniently small as to make upper terms irrelevant. Another possibility can be envisaged throughout the approximation of the high order similarity measure integrals in terms of the first order elements.

9.1. Approximation of higher order similarity matrices

In order to develop such an idea, the second order integrals can be expressed by means of the first order ones, in such a way that:

$$Z_{\alpha\beta}\left[\rho^2\right] \approx Z^{(2)}_{\alpha\beta}[\rho] = \sum_{\lambda} Z_{\alpha\lambda}[\rho] Z_{\lambda\beta}[\rho],$$

this amounts the same as to express the integrals (50) as:

$$\begin{aligned} Z_{\beta\alpha}\left[\rho^2\right] &= \sum_{\mu}\sum_{\nu} D_{\mu\nu} \sum_{\gamma}\sum_{\eta} D_{\gamma\eta}\,(\mu\nu\gamma\eta\beta\alpha) \\ &\approx \sum_{\lambda}\left(\sum_{\mu}\sum_{\nu} D_{\mu\nu}\,(\mu\nu\alpha\lambda) \sum_{\gamma}\sum_{\eta} D_{\gamma\eta}\,(\gamma\eta\lambda\beta)\right), \end{aligned}$$

and, in turn, this is the same as to simply express the representation matrices as successive powers of the first order one:

$$\mathbf{Z}\left[\rho^2\right] \approx (\mathbf{Z}[\rho])^2 .$$

It is straightforward afterwards to assume for any order that the following approximation holds:

$$\mathbf{Z}\left[\rho^p\right] \approx (\mathbf{Z}[\rho])^p . \tag{51}$$

9.2. An approximate exponential operator matrix representation in WMM

Due to the approximate expression (51), then there appears the possibility to construct the matrix representation of the exponential operator in equation (44) with the form:

$$\mathbf{Z}[\Theta; t] \approx \mathbf{S} + (\exp(t\mathbf{Z}[\rho]) - \mathbf{I}) . \tag{52}$$

With respect to this expression as written in equation (52) above, it is interesting to note that the matrix $Z[\Theta; t]$ is formed employing the matrix representation of the density function instead of the density function itself, as in expression (44) and the sequel. In this sense the approximation in equation (52) is coherent with the structure of the theoretical development as described so far, whenever one accepts the easy approach to use a discrete matrix representation of a continuous operator instead of the operator itself.

In this context, the weighted atomic charges can be now written as:

$$Q_A[\Theta;t] \approx Q_A + \sum_{\alpha \in A} [\mathbf{D}[\exp(t\mathbf{Z}[\rho]) - \mathbf{I}]]_{\alpha\alpha}. \tag{53}$$

9.3. *Matrix representation of the exponential function*

The exponential matrix appearing in equations (52) and (53) can be easily expressed in terms of its eigenvalues and eigenvectors [12]. Indeed, if the secular equation of the first order matrix $\mathbf{Z}[\rho]$ is written by means of the matrix equation:

$$\mathbf{Z}[\rho]\mathbf{U} = \mathbf{U}\Delta,$$

where $\{\mathbf{U}; \Delta\}$ are the unitary matrix of the column eigenvectors:

$$\mathbf{U} = (\mathbf{u}_1; \mathbf{u}_2; \ldots \mathbf{u}_n) \wedge \mathbf{U}^+\mathbf{U} = \mathbf{U}\mathbf{U}^+ = \mathbf{I}$$

and the diagonal matrix containing the corresponding eigenvalues respectively:

$$\Delta = Diag(\Delta_1; \Delta_2; \ldots \Delta_n),$$

then, it can be easily written:

$$[\exp(t\mathbf{Z}[\rho]) - \mathbf{I}] = \mathbf{U}[\exp(t\Delta) - \mathbf{I}]\mathbf{U}^+ \tag{54}$$

as $\mathbf{U}$ is an unitary matrix and the exponential matrix $\exp(t\Delta)$ on the right side of equation (54) has just a diagonal structure, which can be written as a whole, like:

$$\exp(t\Delta) - \mathbf{I} = Diag(\exp(t\Delta_1) - 1; \exp(t\Delta_2) - 1; \ldots \exp(t\Delta_n) - 1).$$

This results permit to set up an easy computational implementation of the theoretical definition of atomic charges originating from a WMM.

10. Using off-diagonal density matrix elements into the exponential operator

10.1. *Density matrix*

So far the density function has been used in order to develop the theoretical set up, for the construction of WMM within a Taylor series expansion. There are alternative possibilities. In fact, the first order density function in equation (43) can be written in terms of the so-called density matrix [26], or:

$$\rho\left(\mathbf{r}_1;\mathbf{r}_2\right)=\sum_{\mu}\sum_{\nu}D_{\mu\nu}\chi_{\mu}\left(\mathbf{r}_1\right)\chi_{\nu}^{*}\left(\mathbf{r}_2\right), \tag{55}$$

and used subsequently into the exponential operator definition (44) instead of the diagonal elements, which constitute the first order density function, as one can formally write:

$$\rho\left(\mathbf{r}\right)\equiv\rho\left(\mathbf{r}_1;\mathbf{r}_1\right)=\rho\left(\mathbf{r}_2;\mathbf{r}_2\right)=\rho\left(\mathbf{r};\mathbf{r}\right).$$

In this off-diagonal case, which will be discussed now, the definition of charges and bond orders in WMM will be formed by different matrix products structures than these obtained formerly using the diagonal terms of the density matrix.

10.2. WMM atomic charges

For the atomic charges definition, instead of the first order correction as in equation (47), it will be obtained now:

$$\begin{aligned}Z_{\beta\alpha}\left[\rho\right]&=\sum_{\mu}\sum_{\nu}D_{\mu\nu}\int_{D}\chi_{\mu}\left(\mathbf{r}_1\right)\chi_{\beta}^{*}\left(\mathbf{r}_1\right)d\mathbf{r}_1\int_{D}\chi_{\alpha}\left(\mathbf{r}_2\right)\chi_{\nu}^{*}\left(\mathbf{r}_2\right)d\mathbf{r}_2\\&=\sum_{\mu}\sum_{\nu}D_{\mu\nu}S_{\mu\beta}S_{\alpha\nu}=\left[\mathbf{SDS}\right]_{\beta\alpha},\end{aligned}$$

thus, the WMM $\mathbf{M}\left[\rho\right]$ it is easily defined in terms of the CMM as:

$$\mathbf{M}\left[\rho\right]=\mathbf{DSDS}=\left(\mathbf{DS}\right)^{2}=\mathbf{M}. \tag{56}$$

10.3. pth order corrections

Furthermore, as it can be seen that the following property will be associated to the p-th order correction to the WMM:

$$\mathbf{M}\left[\rho^{p}\right]=\left(\mathbf{DS}\right)^{p+1}=\mathbf{DS},$$

the general expression for the p-th correction for atomic WMM charges in this context could be simply written as:

$$\forall p>0: Q_A\left[\rho^{p}\right]=\sum_{\alpha\in A}M_{\alpha\alpha}\left[\rho^{p}\right]=\sum_{\alpha\in A}\left[\mathbf{DS}\right]_{\alpha\alpha}=Q_A$$

the atomic charges, within this WMM choice, can now be basically expressed by means of:

$$Q_A[\rho;t] = \exp(t)\,Q_A,$$

suggesting that the WMM charges and bond orders, in this case, will coincide with the CMM ones, except for an arbitrary constant depending of the parameter t.

As a consequence of this result, it appears that for WMM attached charge definition, the density function seems relevant, but the off-diagonal elements of the density matrix do not introduce any new information whatsoever to the parameters deduced via CMM.

11. Using the shape function as an atomic charge and bond order generator

The shape function [15] $\sigma(\mathbf{r})$ can be simply defined as a homothetic transformation of the density function [16] as:

$$\sigma(\mathbf{r}) = N^{-1}\rho(\mathbf{r}) \leftrightarrow \rho(\mathbf{r}) = N\sigma(\mathbf{r})\,; \tag{57}$$

hence, it will be worthwhile to study the role of such a function into the operator series (44) and charge definitions (45). For instance, the operator (44) can be written alternatively in terms of the shape function:

$$\Theta(t) = \exp(tN\sigma) = \sum_{p=0}^{\infty}\tfrac{1}{p!}(tN)^p\sigma^p$$

so, defining a new parameter as:

$$\tau = tN,$$

the charge form (45) will be now expressed as:

$$Q_A[\sigma;\tau] = Q_A + \tau Q_A[\sigma] + \tfrac{1}{2}\tau^2 Q_A\left[\sigma^2\right] + O(3)\,. \tag{58}$$

On the other hand, in expression (27) the charge and bond order matrix can be also referred to the shape function with the appropriate homothetic redefinitions. The charge and bond order matrix (4) can be redefined accordingly as:

$$\mathbf{d} = \sum_i \alpha_i \mathbf{c}_i \mathbf{c}_i^{+} = \left\{d_{\mu\nu}\right\} \wedge \forall i : \alpha_i = N^{-1}\omega_i$$

the two charge and bond order matrices are related in the same way as the density function and the shape function in equation (57) are:

$$\mathbf{d} = N^{-1}\mathbf{D} \leftrightarrow \mathbf{D} = N\mathbf{d},$$

so, with these definitions in mind it can be finally written:

$$\sigma(\mathbf{r}) = \sum_{\mu} \sum_{\nu} d_{\mu\nu} \chi_{\mu}(\mathbf{r}) \chi_{\nu}^{*}(\mathbf{r}) .$$

Therefore, the involved charges using the shape function can be written, for example in the CMM derived expression:

$$Q_A = N \sum_{\alpha} \sum_{\beta} d_{\alpha\beta} S_{\alpha\beta},$$

suggesting that a set of atomic shape function charges can be described as:

$$q_A = N^{-1} Q_A \leftrightarrow Q_A = N q_A,$$

with the general property, already discussed when the normalized WMM was introduced:

$$\sum_{A} q_A = 1.$$

As a result, when employing the shape function, the set $\{q_A\}$ constitutes a discrete probability distribution, as it is a fact that: $\forall A : q_A > 0$. Moreover, collecting the atomic charges into a vector, as already discussed:

$$\mathbf{q} = (q_1; q_2; \ldots q_A \ldots; q_n),$$

then, as such a vector belongs to a vector semispace and being convex [18,19], can be considered without doubt as a unit shell member of such a mathematical structure. Defining a similar vector: $\mathbf{Q} = \{Q_A\}$, containing the atomic charges, then the following homothetic relationship holds:

$$\mathbf{q} = N^{-1}\mathbf{Q} \leftrightarrow \mathbf{Q} = N\mathbf{q}. \tag{59}$$

The same ideas can be made extensible to the atomic charges of any order via a WMM. Owing to the relationships (59), equation (58) can be easily rewritten as:

$$q_A[\sigma; \tau] = q_A + \tau q_A[\sigma] + \tfrac{1}{2}\tau^2 q_A\left[\sigma^2\right] + O(3);$$

accordingly, the same results can be obtained, as commented before in the density function case, this time involving any correction order. For example, the first order correction may be written:

$$\begin{aligned} q_A[\sigma] &= \sum_{\alpha \in A} \sum_{\beta} d_{\alpha\beta} Z_{\beta\alpha}[\sigma] = \sum_{\alpha \in A} \sum_{\beta} d_{\alpha\beta} \sum_{\mu} \sum_{\nu} d_{\mu\nu} (\mu\nu\beta\alpha) \\ &= (\sigma \,|\sigma_{\mathrm{A}}) = \int_D \sigma(\mathbf{r}) \sigma_{\mathrm{A}}(\mathbf{r}) \, d\mathbf{r}. \end{aligned} \tag{60}$$

In equation (60) the function $\sigma_A(\mathbf{r})$ is a generic atomic contribution to the shape function, defined as the density function counterpart in equation (48):

$$\sigma_A(\mathbf{r}) = \sum_{\alpha \in A} \sum_{\beta} d_{\alpha\beta} \chi_\alpha(\mathbf{r}) \chi_\beta^*(\mathbf{r}),$$

in this way:

$$\sigma(\mathbf{r}) = \sum_A \sigma_A(\mathbf{r}).$$

12. Conclusions

A broad survey of the Mulliken original ideas on atomic charges and bond orders has been put forward. It has been shown how the density condensation into atomic, diatomic and polyatomic indices can be extended to any expectation value of a weighting positive definite operator. The same can be said about non-singular Hermitian operators by extension. A general theoretical formalism can be employed in this manner, not only to obtain a partitioning of the expectation values of a weight operator, but to set up a well founded set of discrete molecular parameters, which can be used as descriptors. Whenever the weight operator is positive definite, the atomic condensed density vectors can be associated to a vector semispace element, and therefore, upon a Minkowski normalization procedure, they can be transformed into elements of the unit shell of the corresponding semispace; therefore homogenizing all the possible molecular representations obtained in this way. The normalized condensed density vectors can be used to represent the molecular structure by a set of discrete arrays. Finally, the structure of the weighted condensed density elements allows describing the classical Mulliken atomic charges as a zero-th order approximation and in this way a connection between quantum similarity measures and condensed atomic density distributions can be easily performed.

Appendix A: Classical projection operators

Any projection operator over a basis set function in any MO framework can be naturally defined. In order to define unambiguously such an operator set, suppose that any basis function $|\alpha\rangle$ is chosen and the corresponding projector constructed:

$$\Pi_\alpha = \sum_\lambda S_{\lambda\alpha}^{(-1)} |\alpha\rangle \langle\lambda| , \tag{A.1}$$

where $\mathbf{S}^{-1} = \left\{ S_{\lambda\alpha}^{(-1)} \equiv S_{\alpha\lambda}^{(-1)} \right\}$ are the elements of the symmetric inverse basis set metric or overlap matrix. The above-defined projector permits to write:

$$\Pi_\alpha [|\alpha\rangle] = |\alpha\rangle . \tag{A.2}$$

The projector Π_α can be used on the first order electron density such that:

$$\Pi_\alpha[\rho] = \sum_\nu P_{\nu\alpha} |\alpha\rangle\langle\nu| \tag{A.3}$$

and so the projectors possess the necessary property that:

$$\sum_\alpha \Pi_\alpha[\rho] = \rho. \tag{A.4}$$

The projectors can also be extended to higher order by means of a tensor product, for example like:

$$\Pi^{(2)}_{\alpha\beta} = \Pi_\alpha \otimes \Pi_\beta, \tag{A.5}$$

This allows the definition of multicenter electron occupation numbers when using higher order electron densities. Defining the action of the operator $\Pi^{(2)}_{\alpha\beta}$ over the first order density function as:

$$\Pi^{(2)}_{\alpha\beta}[\rho] = \sum_\mu \sum_\nu P_{\mu\nu} \Pi_\alpha [|\mu\rangle\langle\nu|] \Pi_\beta \tag{A.6}$$

one finds that the action of the projector (A.5) over the first order density function is easily described in terms of the corresponding overlap integrals between basis functions, producing:

$$\Pi^{(2)}_{\alpha\beta}[\rho] = P_{\alpha\beta} |\alpha\rangle\langle\beta| \tag{A.7}$$

Equation (A.7) shows how the projector (A.5) retrieves the $|\alpha\rangle\langle\beta|$ component of the first order density function; the coefficient at the left can be interpreted as the corresponding Mulliken charge and bond order matrix element.

Again, the necessary condition for the projector or a tensor product of such projectors is fulfilled, that is:

$$\sum_\alpha \sum_\beta \Pi^{(2)}_{\alpha\beta}[\rho] = \sum_\alpha \sum_\beta P_{\alpha\beta} |\alpha\rangle\langle\beta| = \rho. \tag{A.8}$$

Appendix B: Permanents, circulants and spinless exchange density functions

B.1. Permanent definition and properties

Not many relevant properties are reported for mathematical constructs called permanents or even for permanent structure and properties, being somehow an idea coming from the determinant form, although it merits an entry in encyclopedias of Mathematics [17] and the references therein can be undoubtedly of some aid. Nested summation symbols [27] can be used, however, in discussion and development of permanent properties. Permanents have already used in quantum chemistry [28] and are in the core of generalized Mulliken bond indices [4], thus having a certain chemical interest. The computational development of permanent follows a simple function procedure when nested summation symbols are translated into nested do loops constructs.

B.2. Permanent definition using nested summation symbols

The *permanent* of a square $(N \times N)$ matrix $\mathbf{A} = \{a_{ij}\}$, $Per\,(\mathbf{A})$, can be constructed as the determinant of A, with the alternative feature consisting into that the signature of any index permutation is always taken as positive. Using a nested summation symbol expression one can write compactly:

$$Per\,(\mathrm{A}) = \sum(\mathbf{i}) F\,(\mathbf{i})\, a\,(\mathbf{i})$$

where the vector $\mathbf{i}$ contains a set of N indices, that is:

$$\mathbf{i} = (i_1, i_2, i_3, \ldots, i_N)\,,$$

the *nested summation symbol* $\sum(\mathbf{i})$ stands for a set of nested sums over this N indices:

$$\sum(\mathbf{i}) = \sum_{i_1}\sum_{i_2}\cdots\sum_{i_N}$$

the *filter function* $F\,(\mathbf{i})$ selects from all the possible index vectors, constructed within the nested summation symbol, those corresponding to a permutation, that is:

$$F\,(\mathbf{i}) = \delta\left(\forall p, q : i_p \neq i_q\right),$$

where a *logical Kronecker delta* is used; and, finally, the symbol $a\,(\mathbf{i})$ is the set of products involving the elements of the associated matrix, expressed in the following way:

$$a\,(\mathbf{i}) = a_{1i_1} a_{2i_2} \ldots a_{Ni_N} = \prod_{p=1}^{N} a_{pi_p}.$$

In this definition above, the index permutations are carried out over the column indices, but the procedure and the following discussions remain equally valid and the same as when permuting the ones corresponding to rows.

B.3. Unity matrix permanent

Some particularly interesting results about permanents may be worth to be presented. For instance, take the *unity matrix*, **1**, the unit multiplicative element for the *inward matrix product*, [13] composed by ones in all the matrix entries, that is: $1 = \left\{\forall ij; 1_{ij} = 1\right\}$, then:

$$Per(\mathbf{1}) = \sum(\mathbf{i})F(\mathbf{i})\,1(\mathbf{i}) = N!$$

as:

$$1(\mathbf{i}) = \prod_{k=1}^{N} 1_{ki_k} = 1,$$

and the nested summation symbol with the permutation filter $F(\mathbf{i})$ has $N!$ number of terms.

B.4. Circulant

Also noteworthy is the *circulant* or $Cir(\mathbf{A})$ of a given matrix, which is defined here as a permanent, but with an additional filter, by means of which only cyclic permutations of the involved indices defining the nested summation symbol are chosen:

$$Cir(\mathbf{A}) = \sum(\mathbf{i})F(\mathbf{i})\,C(\mathbf{i})\,a(\mathbf{i}),$$

where the role of filter $C(\mathbf{i})$ consists of just accepting the cyclic permutations within the nested summation symbol, after all the possible the permutations indices sets are previously chosen. Such new filter can be formally defined for all the pair of indices {row, column} of a given cyclic permanent term index pairs as:

$$C(\mathbf{i}) = \delta\left(\{1, i_1\}; \{i_1, i_2\}; \ldots \left\{i_k, i_{k+1}\right\} \ldots \left\{i_{N-1}, 1\right\}\right).$$

When computing the cyclic permanent of the unity matrix it is obtained:

$$Cir(\mathbf{1}) = \sum(\mathbf{i})F(\mathbf{i})\,C(\mathbf{i})1(\mathbf{i}) = (N-1)!.$$

The unity matrix is used as a computational example for the permanent function applications.

B.5. Exchange density function

When constructing the nth order spinless reduced density function according to Löwdin [26] as the nth order determinant of the first order density matrix, it is easy to obtain a general expression for the nth order pure exchange part in terms of the circulant of terms of the density matrix. If the sign and coefficient of the pure exchange part is obviated, then it can be written:

$$\eta\left(\mathbf{n}\right)=Cir\left(\mathbf{p}\right)=\sum\left(\mathbf{i}\right)F\left(\mathbf{i}\right)C\left(\mathbf{i}\right)p\left(\mathbf{i}\right),$$

where by $\mathbf{n}=(1,2,\ldots n)$ it is represented the electron indices involved in the n-th order pure exchange part, the filters used have already been previously described and $p\left(\mathbf{i}\right)$ is a product of the elements of the density matrix $\mathbf{p}$:

$$p\left(\mathbf{i}\right)=\rho\left(1,i_1\right)\rho\left(2,i_2\right)\ldots\rho\left(n,i_n\right)=\prod_{k=1}^{n}\rho\left(k,i_k\right).$$

In this way, for instance, the third order pure exchange part of the corresponding reduced density function can be written as:

$$\eta\left(1,2,3\right)=\rho\left(1,2\right)\rho\left(2,3\right)\rho\left(3,1\right)+\rho\left(1,3\right)\rho\left(3,2\right)\rho\left(2,1\right).$$

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