LCAO MO first order density functions: Partition in monocentric and bicentric terms, reciprocal MO spaces, invariant transformations and Euclidian atomic populations

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Abstract

Here, the first order density function is analyzed under the LCAO MO theory framework, using a partition in two terms, namely monocentric (monoatomic or atomic) and bicentric (diatomic or bond) contributions. The monoatomic term possess a Minkowski norm positive definite, while for the diatomic term just a Minkowski real pseudonorm can be defined. The atomic Minkowski norm can be proven to be less, equal or greater than the number of electrons, while the diatomic Minkowski pseudonorm in every one of these monoatomic cases appears to be positive, null or negative, respectively. Such a behavior cannot provide both norms with some physical sense. Moreover, the same behavior can be described for every MO density contribution, using the unit MO norms instead of the number of electrons. Thus, shape functions behave in the same way as these individual MO density terms. In this work it is also studied the possibility to transform the LCAO basis set by means of some unitary transformation in such a way that the density function remains invariant, while zeroing the diatomic Minkowski pseudonorm. In this zero bicentric pseudonorm case some gross atomic populations in the Mulliken sense become coincident with the Roby definition, as the transformed basis set produces a null diatomic contribution. The role of reciprocal space is presented from the point of view of density function partition. Invariant transformations of the density functions are studied within a general formalism, where the problems previously commented arise as particular cases. Finally, a way to define Euclidian atomic populations is given, based on the alternative metric matrix, associated to reciprocal space, which can be linked to the MO coefficients matrix.

1. Introduction

Since the widespread use of DFT techniques, see Ref. [1] as a recent example, first order density functions in molecular quantum mechanics have acquired a leading role, which has been even more enhanced with the appearance of applications developed within the so-called conceptual DFT, see Ref. [2] for a comprehensive review. The interest in density function theoretical aspects in our laboratory have been developing steadily [3–16], in parallel with the use of density functions within the theory [25–55] and practice [56–65] of molecular quantum similarity [25], see also Ref. [48] for a modern account. Recently, several connected studies on density function have been published [17–22] and the present paper has to be considered an added contribution to such previous work. Also, some recent work on molecular energy partition [23,24] has triggered in the author’s mind the question of the density partition role in this kind of studies. Therefore, the present work can be associated to the development of the density problems from several points of view.

Beyond the previous considerations, the idea of the present discussion is the search on the possibility to attach some meaning, within the LCAO MO framework, to the natural partition of the density function into a pair of functions, containing the atomic and diatomic parts of the whole density function, respectively. Such a function pair will be termed in several ways in order to ease the literary development of the present work, like: atomic–diatomic, monocentric–bicentric, atom–bond. This natural geometric division brings to the definition of the Minkowski norm of both partitioned functions. The study of the Minkowski norms connects with several interesting problems leading to the definition of atomic populations and the basic underlying theory. Such theoretical concept, essentially chemical, merits some modern discussion, as looking at the present status of classical population analysis, like the one provided by a recent publication [66], the feeling appears that few aspects of the question have changed since the original Mulliken’s definition [67]. On the other hand, the quantum mechanical meaning of atomic populations has been object of
our interest recently. Our point of view has been mainly focused into the Mulliken’s [67] opinion, appearing as one of the atomic population sources, which can be most accurately attached to quantum mechanical expectation value evaluation techniques [68]. This is an idea coincident with the point of view of other authors, who studied the problem later on in a similar way [69]. Moreover, the close relationship of the density function with the LCAO MO framework can be related with the geometrical source of reciprocal spaces [70], although, as far as we know, such connection has never studied in depth. As reciprocal space transformations leave density functions invariant, they have been also included here, in order to complete the present study on atom–bond partition of density functions, because several transformations, leaving invariant the density function as a whole, are also studied in detail, since they can produce a zero diatomic Minkowski pseudonorm, showing, at the same time, the manner on how a general framework density function transformation can be constructed.

Thus, this paper will be structured as follows. First some introductory notation will be given, followed with the atom–bond partitioning of the density function. After these preliminaries, the norms of the atom–bond partition are studied next and the relationships of Minkowski norms with MO atomic populations and the shape function studied. This will be followed by studying the circumstances where the diatomic function part can possess a zero Minkowski pseudonorm. A discussion on reciprocal space and atom–bond partition of the density function followed with a general study of the invariant transformations of the density function, encompassing the previous studied cases. This discussion finally conducts towards an alternative way to define Euclidian atomic populations, based on the definition of the metric matrix, associated to the MO coefficient matrix.

2. Preliminary notation and definitions

The first order density function within any LCAO MO framework can be described in terms of the AO basis functions centered in some point of the space surrounding the molecular frame.

Suppose that \( \rho(\mathbf{r}) \) is the density function. In terms of the MO set \( M = \{ |l \rangle \} \) it can be written, employing the occupation number set: \( \{ n_l \} \), in a general manner [22] as:

\[
\rho(\mathbf{r}) = \sum_l n_l |l \rangle \langle l | = \sum_l c_l^\dagger c_l |l \rangle \langle l | = \rho_l(\mathbf{r}).
\]

The MO set can be described in terms of an AO basis set centered in some point \( P \): \( A = \{ |P; \mu \rangle \} \), where the Greek indices denote linearly independent functions, that is:

\[
|l \rangle = \sum_P \sum_\mu c_{l \mu} |P; \mu \rangle,
\]

therefore the density function can be expressed as:

\[
\rho(\mathbf{r}) = \sum_l c_l \sum_q \sum_\mu \sum_{\nu \mu} c_{l \mu}^\dagger c_{q \nu} |P; \mu \rangle \langle \nu | \langle P; \nu | Q \rangle.
\]

\[
= \sum_P \sum_q \sum_{\mu \nu} \sum_{\nu \mu} D_{PQ}^{\nu \mu} \langle P; \mu | Q \rangle,
\]

where:

\[
D = \left\{ D^{\nu \mu}_{PQ} = \sum_l c_l c_{l \mu}^\dagger c_{P \nu} \right\}
\]

is the charge and bond order matrix. Such a naming is here preferred in front of the density matrix option, as this last can generate confusion, whenever references are made to the also called density matrix, obtained from the first order density function, when considering the possibility to attach two distinct electron coordinates to the bra-ket basis set function products.

3. Atom–bond partition of the density function

In any molecular case, the LCAO MO density function can be expressed as the sum of two functions:

\[
\rho(\mathbf{r}) = \rho_A(\mathbf{r}) + \rho_B(\mathbf{r})
\]

containing monocentric \( A \) and bicentric \( B \) elements, namely:

\[
\rho_A(\mathbf{r}) = \sum_P \sum_q \sum_{\mu \nu} D_{PQ}^{\nu \mu} |P; \mu \rangle \langle P; \nu |,
\]

and

\[
\rho_B(\mathbf{r}) = 2 \sum_P \sum_q \sum_{\mu \nu} \sum_{\nu \mu} D_{PQ}^{\mu \nu} |P; \mu \rangle \langle Q; \nu |.
\]

The Minkowski norm of the density function can be written in terms of the partition above:

\[
(\rho(\mathbf{r})) = (\rho_A(\mathbf{r})) + (\rho_B(\mathbf{r})
\]

where it is used the following symbolic convention:

\[
(f(\mathbf{r})) = \int_D f(\mathbf{r}) d\mathbf{r}.
\]

It is well known that first order density functions have a Minkowski norm equal to the number of electrons \( N \), or \( (\rho(\mathbf{r})) = N \). Thus, in any circumstance:

\[
N = (\rho_A(\mathbf{r})) + (\rho_B(\mathbf{r})).
\]

It can be easily proved that the atomic function part is a positive definite function, that is: \( (\rho_A(\mathbf{r})) \in \mathbb{R}^+ \). So, in case that:

\[
(\rho_A(\mathbf{r})) \leq N \rightarrow (\rho_B(\mathbf{r})) \in \mathbb{R}^+.
\]

However, there cannot be proved that this previous inequality holds for any density function, but perhaps in some circumstances the following property could hold:

\[
(\rho_A(\mathbf{r})) > N \rightarrow (\rho_B(\mathbf{r})) \in \mathbb{R}^-.
\]

Consequently, \( (\rho_B(\mathbf{r})) \) becomes a pseudonorm which can be associated to some kind of integral yielding values in the real field.

4. Properties of the atom–bond partition norms

The properties of the Minkowski norms of the elements of the atom–bond partition of the density function are of fundamental importance in order to assign a possible physical significance to them. Here this issue will be discussed.

4.1. Positive definiteness of the atomic term

First it will be proved that the atomic part of the proposed partition is positive definite in any circumstance. In order to obtain such a result one can just write the following sequence of equalities:

\[
\rho_A(\mathbf{r}) = \sum_P \sum_q \sum_{\mu \nu} D_{PQ}^{\nu \mu} |P; \mu \rangle \langle P; \nu |.
\]

\[
= \sum_P \sum_q \sum_{\mu \nu} \sum_{\nu \mu} D_{PQ}^{\nu \mu} \langle P; \mu | Q \rangle.
\]

\[
D = \left\{ D^{\nu \mu}_{PQ} = \sum_l c_l c_{l \mu}^\dagger c_{P \nu} \right\}
\]

is the charge and bond order matrix. Such a naming is here preferred in front of the density matrix option, as this last can generate
\[ \rho_A (\mathbf{r}) = \sum_{\mu \in \mathcal{P}} \sum_{\nu \in \mathcal{P}} \left( \sum_i c_{\mu i}^* c_{\nu i} \right) |P \rangle \langle \mu| \langle \nu| P \rangle \]
\[ = \sum_i \phi_i \left( \sum_{\mu \in \mathcal{P}} \left( \sum_{\nu \in \mathcal{P}} c_{\mu i}^* |P \rangle \langle \mu| \right) \right) \left( \sum_{\nu \in \mathcal{P}} c_{\nu i}^* \langle P| \right) \]
\[ = \sum_i \phi_i \left( \sum_{\mu \in \mathcal{P}} \left( \sum_{\nu \in \mathcal{P}} c_{\mu i}^* |P \rangle \langle \mu| \right) \right) \left( \sum_{\nu \in \mathcal{P}} c_{\nu i}^* \langle P| \right) \]
\[ = \sum_i \phi_i \sum_{\mu \in \mathcal{P}} \left| c_{\mu i} \right|^2 \]
\[ = \sum_i \sum_{\mu \in \mathcal{P}} \left| c_{\mu i} \right|^2 \]

which corresponds to a sum of products of positive numbers.

4.2. The atomic and diatomic norm ranges

That the Minkowski norm \( \langle \rho_A \rangle \) is positive comes from the previously deduced property as written in the last equality of Eq. (4). However, that the Minkowski norm of the atomic part of the density function splitting can be larger than the number of particles shall be proved with a counterexample.

Suppose now the simple case of the hydrogen molecule described by a 1s type normalized AO function centered at each hydrogen atom. Within this naive basis set, the possible resultant MO's, can be written as:

\[ |1\rangle = \left( \frac{1}{2 + \pi} \right) (|a\rangle + |b\rangle) \quad |2\rangle = \left( \frac{1}{2 - \pi} \right) (|a\rangle - |b\rangle) \]

where \( \pi = \langle a | b \rangle \) is the overlap integral between both AO basis functions and thus will depend on the hydrogen molecule internuclear distance.

So, the density functions can be considered constructed with the basis set:

\[ |1\rangle = \left( \frac{1}{2 + \pi} \right) (|a\rangle + |b\rangle) \quad |2\rangle = \left( \frac{1}{2 - \pi} \right) (|a\rangle - |b\rangle) \]

\[ = \left( \frac{1}{2 - \pi} \right) (|a\rangle + |b\rangle - 2|a\rangle |b\rangle) \]

For example, the first order density for the ground state will be:

\[ \rho_A (\mathbf{r}) = 2 |1\rangle \langle 1| = \left( \frac{1}{1 + \pi} \right) (|a\rangle |a\rangle + |b\rangle |b\rangle + 2|a\rangle |b\rangle) \]

Then, in this case the atomic–diatomic partition will be expressed as:

\[ \rho_{\mu} = \left( \frac{1}{1 + \pi} \right) (|a\rangle |a\rangle + |b\rangle |b\rangle) \quad \rho_{\nu} = \left( \frac{2}{1 + \pi} \right) |a\rangle |b\rangle \]

and thus into account that the AO basis set is normalized:

\[ \langle a | a \rangle = 1 \quad \langle b | b \rangle = 1 \quad \langle a | b \rangle = \pi \]

\[ \langle a | b \rangle = \pi = \langle b | a \rangle = \langle b | a \rangle \]

It is obtained:

\[ \langle \rho_{\mu} \rangle = \left( \frac{2}{1 + \pi} \right) \quad \langle \rho_{\nu} \rangle = \left( \frac{2}{1 + \pi} \right) \]

As \( \pi \in [0,1] \rightarrow \langle \rho_{\mu} \rangle \leq 2 \rightarrow \langle \rho_{\nu} \rangle > 0 \), a property which is also present in the cation density function.

However, for the double excited state it can be written:

\[ \rho_{22} (\mathbf{r}) = 2 |2\rangle \langle 2| = \left( \frac{1}{1 - \pi} \right) (|a\rangle |a\rangle + |b\rangle |b\rangle - 2|a\rangle |b\rangle) \]

so the atom–bond partition yields in this case:

\[ \rho_{22} = \left( \frac{1}{1 - \pi} \right) (|a\rangle |a\rangle + |b\rangle |b\rangle) \quad \rho_{2a} = -\left( \frac{2}{1 - \pi} \right) |a\rangle |b\rangle \]

and the Minkowski norms are written as:

\[ \langle \rho_{2a} \rangle = \left( \frac{2}{1 - \pi} \right) \quad \langle \rho_{2a} \rangle = -\left( \frac{2}{1 - \pi} \right) \]

therefore: \( \langle \rho_{2a} \rangle \geq 2 \rightarrow \langle \rho_{2a} \rangle < 0 \).

A similar behavior is found in the excited singlet and triplet states and in the anion. For instance, in the excited singlet–triplet states:

\[ \rho_1 (\mathbf{r}) = |1\rangle \langle 1| + |2\rangle \langle 2| \]

\[ = \left( \frac{1}{2 + \pi} \right) (|a\rangle |a\rangle + |b\rangle |b\rangle + 2|a\rangle |b\rangle) \]

\[ = \left( \frac{1}{2 - \pi} \right) (|a\rangle |a\rangle + |b\rangle |b\rangle - 2|a\rangle |b\rangle) \]

yielding, for instance:

\[ \rho_{2a} (\mathbf{r}) = \left( \frac{2}{1 - \pi} \right) (|a\rangle |a\rangle + |b\rangle |b\rangle) \]

and thus creating a negative diatomic Minkowski pseudonorm.

4.3. Résumé

When performing an atom–bond partition of the density function: \( \rho = \rho_A + \rho_B \), the Minkowski norm \( \langle \rho_A \rangle \) is positive definite in any case, but can be lesser or greater than the number of electrons, while the Minkowski pseudonorm \( \langle \rho_B \rangle \) is a real number, yielding even negative values in circumstances where \( \langle \rho_A \rangle \) becomes greater than the number of electrons.

5. Minkowski norms, atomic populations, MO norms and shape functions

It is regrettable one cannot expect, within an atom–bond partition of the density function, that the norm of the atomic part will be less than the number of electrons in any circumstance. Because if it could be so, one might interpret the Minkowski norm of the atomic part, as the fraction of atomic bulk electrons remaining in the molecule and the diatomic pseudonorm as the fraction of the former atomic attached electrons, associated to molecular bonding or polarization. But as it has been previously discussed, this is not possible in general: therefore, one can conclude that the Minkowski norms of the atom–bond density function partition parts have just a geometrical or algebraic meaning in general devoid of physical content.

However, when the atomic Minkowski norm is greater than the number of electrons, producing as a consequence a negative Minkowski bond pseudonorm, then this could mean, at the light of the studied hydrogen molecule counterexample, that a contribution of antibonding MO’s into the construction of the density function is relevant, and this will be so with increasing weight, as the atomic Minkowski norm differs more from the number of electrons. This, in turn, can also help to reinterpret the cases, where the atomic Minkowski norm remains below the electron number, as a measure of the bonding MO’s contribution into the molecular formation. However, the bonding–antibonding MO characteristics correspond to more geometrical than physical properties too, even if they have customarily being long time employed in chemical lore in order to interpret the nature of the chemical bonds.

The behavior of the Minkowski norm of the density function atomic part provides the ultimate reason, which confirms why Mulliken [67] gross atomic populations will always yield the number of electrons when summed up, while the definition of Roby [71] can yield a sum of atomic populations lower or greater than this number. This situation will not be changed at all, even when
every part of the atomic basis set is orthonormalized within each atomic center. Mulliken gross atomic populations summing up to the number of electrons is just the consequence that MO densities appear as Minkowski normalized, as discussed next.

5.1. Behavior of the monocentric and bicentric MO components of the density function

Similar trends as the ones discussed so far in density functions can be found for each MO contribution to the density function itself, as one can easily define a set of MO densities \( \{ \rho_i(r) \} \) and write:

\[
\rho(r) = \sum_{\mu} c_{\mu} \rho_\mu(r) = \sum_{\mu} \sum_{\mu'} \sum_{\mu''} \sum_{\mu'''} c_{\mu}^e c_{\mu'}^e c_{\mu''}^e c_{\mu'''e}^e |P; \mu| \langle v; Q| P; \mu'\rangle \langle v'; Q'| P; \mu''\rangle \langle v'''; Q''| P; \mu'''\rangle
\]

So, also for every MO density an atom–bond partition can be also set up:

\[
\rho_i(r) = \rho_{\mu i}(r) + \rho_{\mu i}(r) \wedge (\rho_i(r)) = 1
\]

with:

\[
\forall r: \rho_{\mu i}(r) = \sum_{P} \sum_{\mu} \sum_{v} c_{\mu}^e c_{\mu i}^e |P; \mu| \langle v; Q| P; \mu \rangle \geq 0
\]

and in addition one can imagine an obvious definition for \( \rho_{\mu i}(r) \).

The Minkowski norm of any function \( \rho_{\mu i}(r) \) yields in this way:

\[
(\rho_{\mu i}(r)) \in \mathbb{R}^+, \text{ without ensuring that } (\rho_{\mu i}(r)) \leq 1 \text{ and consequently there can be the possibility that: } (\rho_{\mu i}(r)) < 0 \text{, in order to keep the MO norm unity.}
\]

Therefore, one can conclude that the density function behavior, when the Minkowski norms of the atom–bond partition are considered, is just the consequence of the MO density contributions behavior. Hence, it could be interesting to systematically observe whenever MO bonding or antibonding characters produce a monocentric Minkowski norm less or greater than the unitary. However, the geometric meaning of these MO properties appears quite evidently, when just MO manifolds are studied under the assumption of a completely orthogonalized atomic function basis set, like the one obtained under Löwdin procedure, as described in the Ref. [72]. In this case, the bicentric part pseudonorm will be zero for all the MO set elements. Such an interesting situation will be studied in the next paragraphs.

5.2. Shape function partition and behavior

A similar reasoning as the one performed within MO densities can be associated to the shape function. See, for example, the discussion of Ref. [73] for more details and a better understanding of the mathematical structure of this kind of homothetic density function. Shape functions, because they bear a close relationship with density functions, can be, as a consequence, similarly partitioned into atomic and diatomic shape function terms. Shape functions possess unit Minkowski norms, due to the simple reason consisting into that shape functions can be considered as convex linear combinations of MO densities. Hence, one will face a behavior of shape functions similar to MO’s, and knowing this fact there will not be developed a redundant discussion about such functions.

6. The zero diatomic Minkowski pseudonorm case

In any of the previously studied cases, a particular situation will be obtained whenever the Minkowski pseudonorm contribution of the diatomic term in some global density, MO density or shape function becomes zero. For instance, if this property holds for a given density function, then:

\[
(\rho(r)) = N = (\rho_{\mu i}(r)) = (\rho_{\mu i}(r)) = 0.
\]

In atomic density functions this is always the case, of course. In molecules, such a property can be obtained whenever the molecular density function in question is manipulated in such a way that the resulting transform becomes invariant but possessing such diatomic part with a null pseudonorm property.

6.1. Alternative form of the density function and its atomic–diatomic partition

In fact, one can write the density function in Eq. (2) by means of the complete sum\(^2\) of the inward matrix product\(^3\) (see Ref. [11] for more details on these operations) between the charge and bond order matrix (3) and the tensorial product of the AO basis set components:

\[
(\rho) = (P|\mu) \wedge (|v; Q) \rightarrow (\rho) = (P|\mu) \langle v; Q| P; \mu \rangle \langle v; Q| P; \mu \rangle \langle v; Q| P; \mu \rangle
\]

Also, if the diagonal matrix: \( \Omega = \text{Diag}(c_{\mu i}) \) contains the MO occupation numbers, the charge and bond order matrix can be alternatively written as:

\[
D = C \Omega C^+\]

with the matrix \( C = \{ c_{\mu i}^e \} \) containing the MO coefficients as columns. In that case, the density function Minkowski norm can be rewritten as:

\[
(\rho(r)) = (D \langle |v; Q| P; \mu \rangle) = (D \odot S),
\]

the matrix \( S = \{ S_{\mu i} \} \) being the overlap matrix attached to the chosen AO functional basis set.

In fact, the matrix \( D \) can be decomposed into a hyperdiagonal atomic hypermatrix: \( D_{s a} \) which can be imagined as a direct sum matrix, and another hypermatrix with a null hyperdiagonal: \( D_{s b} \). For example:

\[
D = D_{s a} + D_{s b} \wedge D_{s a} = \text{Diag}(D^{PP}) \odot D^{PP} \wedge D_{s b} = \{ \delta(P \neq Q) D^{PQ} \}
\]

with the monoatomic and diatomic submatrices constructed in general as:

\[
\forall P, Q: D^{PQ} = \{ D_{PQ} | P \in \mathbb{P} \wedge Q \in \mathbb{Q} \}
\]

The same partition can be applied to the overlap matrix, therefore:

\[
(\rho(r)) = (D_{s a} + D_{s b} \ast (S_{s a} + S_{s b})) = (D_{s a} \ast S_{s a}) + (D_{s b} \ast S_{s b})
\]

because:

\[
D_{s a} \ast S_{s b} = D_{s b} \ast S_{s a} = 0 = \{ O_{\mu i} \}
\]

6.2. Unitary transformation of the overlap matrix into an atomic hyperdiagonal matrix

In order to obtain further information, one can look for a unitary transformation \( U \text{U} = U^T \text{U} \equiv I \equiv \text{U}^T = \text{U} \) such that, when applied to the overlap matrix, yields as a result a hyperdiagonal

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matrix:
\[ U^* S U = U^* S_A \wedge U^* S_B = 0. \]  
(7)

So, when the unitary transformation is employed within the Minkowski norm, after noting that from Eq. (7) it can be written:
\[ S = U^* S U^* \]  
(8)

The following equalities hold:
\[
N = \langle \rho (r) \rangle = \langle D * U^* S U^* \rangle = \sum_{p} \sum_{q} \sum_{\mu} \sum_{\nu} D_{pq}^{\mu \nu} \langle U^* S U^* \rangle_{pq}^{\mu \nu}
\]
\[
= \sum_{p} \sum_{q} \sum_{\mu} \sum_{\nu} D_{pq}^{\mu \nu} U_{pq}^{\mu \nu} U_{pq}^{\nu \mu} = \sum_{p} \sum_{q} \sum_{\mu} \sum_{\nu} U_{pq}^{\mu \nu} U_{pq}^{\nu \mu}
\]
\[
= \langle U D U^* \rangle_A = \langle U D U^* \rangle_{A+B} = \langle U^* D_A + U^* S_B \rangle
\]
\[
= \sum_{p} \sum_{q} \sum_{\mu} \sum_{\nu} U_{pq}^{\mu \nu} U_{pq}^{\nu \mu} = \sum_{p} \sum_{q} \sum_{\mu} \sum_{\nu} U_{pq}^{\mu \nu} S_{pq}^{\mu \nu}
\]  
(9)

The interest of this result is twofold. First, the density function Minkowski norm remains invariant, and second, the Minkowski pseudonorm of the diatomic term is null. Therefore, the atomic elements of the last term in the above equalities can be written like:
\[ Q = \sum_{p} \sum_{q} \sum_{\mu} \sum_{\nu} D_{pq}^{\mu \nu} U_{pq}^{\mu \nu} \rightarrow \sum_{p} \sum_{q} Q_{pq} = N \]

and can be interpreted as atomic populations in both the Mulliken or Roby sense, while summing up the total number of electrons in both cases. That is, in such case Mulliken and Roby population definitions are coincident.

This is due to the fact that the whole process is obviously equivalent to transform the AO basis set, with a unitary matrix in a manner like:
\[
\langle U^* z | U \rangle = \langle z | U^* S U \rangle = \langle z | U^* S A \rangle = \text{Diag} \langle U^* S \rangle = U^* S_B,
\]

which can be interpreted, in turn, as a basis set transformation leading to a new diatomic orthogonal basis set, where some monoatomic overlaps are preserved.

6.3. Complete diagonalization of the overlap matrix

Supposing a complete diagonalization of the overlap matrix is found, in terms of another unitary matrix:
\[ \Sigma = X^* S X \rightarrow S = X \Sigma X^*, \]

where the diagonal matrix \( \Sigma = \text{Diag}(\sigma_{ij}) \) contains the spectrum of the overlap matrix, it is obvious that in this case:
\[ S_A = \Sigma \wedge X^* S_B = 0, \]

therefore one can also write:
\[ N = \langle \rho (r) \rangle = \langle D * X \Sigma X^* \rangle = \langle X \Sigma \Sigma X^* \rangle = \langle \text{Diag} (X^* D_A) \Sigma \rangle
\]
\[ = \sum_{p} \sum_{q} \sum_{\mu} \sum_{\nu} D_{pq}^{\mu \nu} \sigma_{\mu} \]

and the Mulliken–Roby atomic populations acquire a simple form:
\[ \forall p : X^* Q_p = \sum_{\mu} D_{pq}^{\mu \nu} \sigma_{\mu}. \]

However, as it happens too with the Löwdin atomic population definition, there is dubious that the above expression subindices will correspond, as the initial ones, to basis set functions attached to a given atomic center.

7. Reciprocal space transformation and atom–bond partition

In one of his last scientific creations, Löwdin [70] described reciprocal representations and reciprocal basis as fundamental tools to understand scalar products in pre-Hilbert spaces.

Given a vector space with a metric or overlap matrix \( S \), say, then the reciprocal space is defined with a basis set transformation leading to the same space but possessing as a metric the inverse \( S^{-1} \) of the former metric matrix. It is straightforward to describe such basis set transformation.

Starting from the basis set definition as described in Eq. (6), then, owing to the linear independence of the AO basis functions, one can write:
\[ \langle |z| |z\rangle = S \rightarrow S^{-1} \]

therefore it can also be written:
\[ S^{-1} \langle |z| |z\rangle S^{-1} = S^{-1} S S^{-1} = S^{-1}. \]

This defines a simple basis set transformation, leading as such to the reciprocal space definition:
\[ \langle \langle j| |j\rangle = S^{-1}. \]

As it can be written the reverse basis set transformation:
\[ \langle \langle j| |j\rangle S = \langle |z| \rangle, \]

thus allowing the density function in expression (5) to be also written as:
\[ \rho (r) = \langle D * | j| |j\rangle = \langle SDS * | j| |j\rangle, \]

(10)

which is the invariant density function but expressed in reciprocal space. The Minkowski norm of the density function written as in expression (10) is now:
\[ N = \langle \rho (r) \rangle = \langle SDS * | j| |j\rangle = \langle SDS * S^{-1} \rangle. \]

The new charge and bond order matrix in the reciprocal space framework, \( ^8D \), can be easily written as:
\[ ^8D = SDS, \]

(11)

implying that the MO coefficient matrix has to be transformed according to the rule:
\[ ^8C = SC. \]

This result is consistent with the well known MO coefficient matrix property:
\[ CC^* = S^{-1} \wedge C^* SC = C \wedge ^8C^* S^{-1}SC = I. \]

Now, employing the unitary matrix which can hyperdiagonalize the direct overlap as in Eq. (7), one can write:
\[ U^* S U = U^* S_A \wedge U^* S_B = 0, \]

and in the same manner as in Eq. (8) there can be employed:
\[ S^{-1} = U^* S_A U^+ \]
as the atomic hyperdiagonal matrix in reciprocal space is coincident with the inverse of the initial counterpart, because from Eq. (8) and the unitary nature of the transformation matrix, one easily obtains:
\[ S^{-1} = \left(U^* S_A U^+ \right)^{-1} = \left(U^* \right)^{-1} S_A^{-1} U^{-1} = U^* S_A^{-1} U. \]

Then, the density function in reciprocal space can be written in a similar manner as in the initial formalism and the condensed Minkowski norm expressed as in Eq. (9). For that reason, obviating the obvious intermediate equalities:
which provides with a new set of Mulliken–Roby atomic populations defined in reciprocal space, whose sum will be the number of electrons:

$$\forall P : \mathbf{Q}_P = \sum_{\mu \in P} \sum_{\nu \in P} \mathbf{D}^\dagger_{\mu \nu} \mathbf{S}_{\nu \mu} \rightarrow \sum_P \mathbf{Q}_P = N,$$

which seems to be coherent with the density function invariance when transformed into reciprocal space.

Perhaps, the most interesting of all the reciprocal space transformation is the invariance of the density function followed by the appearance in Eq. (10) of the reciprocal charge and bond order matrix: \( \mathbf{D}, \) as defined in Eq. (11).

### 8. A general theoretical outlook

Up to now, several details have been given here about particular transformations leaving the density function invariant, while transforming the result of the Minkowski norms applied to the monocentric and bicentric partitions of the density function. However, it can be easily shown that these manipulations obey to a general formalism, which can be constructed once and for all. The main ideas leading to this mathematical development will now be given for completeness sake.

The present discussion has been essentially based on the complete sum of the inward matrix product of two matrices, which can be written alternatively in several ways, for example using the involved \( \mathbf{D} \) and \( \mathbf{S} \) matrices:

$$N = \langle \mathbf{D} \ast \mathbf{S} \rangle = \langle \mathbf{DS} \rangle = \langle \mathbf{Diag(\mathbf{DS})} \rangle = \text{Tr}[\mathbf{DS}],$$

but also one can alternatively write:

$$N = \langle \mathbf{D} \ast \mathbf{S} \rangle = \langle \mathbf{S} \ast \mathbf{D} \rangle = \langle \mathbf{SD} \rangle = \langle \mathbf{Diag(\mathbf{SD})} \rangle = \text{Tr}[\mathbf{SD}].$$

Another possibility of transformation of the above expressions corresponds to use of the Cholesky decomposition of the overlap matrix, see for example Ref. [74] and also for a not so well known recursive Cholesky algorithm and more details see Ref. [75]:

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

where the matrix \( \mathbf{T} \) is upper triangular. Then, it can be written:

$$N = \langle \mathbf{D} \ast \mathbf{S} \rangle = \langle \mathbf{D} \ast \mathbf{T}^\dagger \mathbf{T} \rangle = \sum_{\mu \in P} \sum_{\nu \in P} \mathbf{D}_{\mu \nu} \mathbf{T}_{\nu \mu} \mathbf{T}_{\nu \mu}$$

$$= \sum_{\mu \in P} \sum_{\nu \in P} \mathbf{T}_{\nu \mu} \mathbf{D}_{\mu \nu} \mathbf{T}_{\nu \mu} = \langle \mathbf{T} \mathbf{D} \mathbf{T}^\dagger \rangle = \langle \mathbf{D} \mathbf{T} \mathbf{T}^\dagger \rangle = \langle \mathbf{T} \mathbf{T}^\dagger \mathbf{D} \rangle = \langle \mathbf{T} \mathbf{D} \mathbf{T}^\dagger \rangle$$

this last property of the complete sum can be seen as similar to the use of unitary transformations of the overlap matrix as previously studied.

In a general way, whenever one is looking at the complete sum of the result of the inward matrix product of the density matrix by a product of three matrices, one can write a sequence of equalities like:

$$\mathbf{S} = \mathbf{T}^\dagger \mathbf{T}, \quad \mathbf{D} = \mathbf{T} \mathbf{T}^\dagger \mathbf{D} \mathbf{T}^\dagger \mathbf{T},$$

$$\mathbf{N} = \langle \mathbf{D} \ast \mathbf{S} \rangle = \langle \mathbf{D} \ast \mathbf{T}^\dagger \mathbf{T} \rangle$$

where the symmetric nature of the charge and bond order matrix \( \mathbf{D} \) has been used. From these equalities sequence one can obtain all the previous discussed results.

### 9. Direct metric matrix of the MO coefficients and orthogonal atomic populations

To end the present study there will be discussed the problem of the direct MO coefficient metric matrix. As such the problem is related with the previous analysis and it is closely connected with the reciprocal space concept. It has been included here as such a metric matrix can be the source of a novel atomic population definition, which does not possess diatomic crossed contributions.

#### 9.1. MO direct metric matrix

Although the relationship of the eigensystems of the matrix products \( \mathbf{AB} \ast \mathbf{BA} \) has been studied in general from old times [80], there will be discussed the more elementary relationship between: \( \mathbf{C} \mathbf{C}^\dagger \ast \mathbf{CC}^\dagger \), because there appears an interesting add on relationship with atomic charge description.

Nothing opposes to the fact that from the matrix of the MO coefficients one can construct a positive definite metric matrix, in the following way:

$$\mathbf{Z} = \mathbf{C} \mathbf{C}^\dagger \ast \mathbf{I}, \quad j = \mathbf{C}^\dagger \mathbf{C} = \mathbf{A} = \sum_{\mu} \sum_{\nu} \mathbf{C}_{\mu \nu} \mathbf{C}_{\nu \mu},$$

so the subindices of matrix \( \mathbf{Z} \) are attached to MO’s indices. Moreover, the inverse of the AO metric is related to the MO coefficients product matrix in reverse order:

$$\mathbf{S}^{-1} = \mathbf{CC}^\dagger \ast \mathbf{I}, \quad j = e_{\mu \nu}^{-1} = \sum_{\mu \nu} \mathbf{C}_{\mu \nu} \mathbf{C}_{\nu \mu},$$

also, a similar unitary matrix \( \mathbf{V} \) fulfills:

$$\mathbf{Z} = \mathbf{V} \mathbf{\Theta},$$

One can write the sequence:

$$\mathbf{CC}^\dagger \mathbf{U} = \mathbf{U} \mathbf{S}^{-1} \mathbf{C} \mathbf{C}^\dagger \mathbf{U} = \mathbf{C}^\dagger \mathbf{U} \mathbf{S}^{-1} \mathbf{C} \mathbf{C}^\dagger \mathbf{U} = (\mathbf{C}^\dagger \mathbf{U}) \mathbf{S}^{-1} \mathbf{C} \mathbf{C}^\dagger \mathbf{U} = \mathbf{C} \mathbf{C}^\dagger \mathbf{U} = \mathbf{X} \mathbf{\Theta},$$

as well as the sequence:

$$\mathbf{C} \mathbf{C}^\dagger \mathbf{V} = \mathbf{V} \mathbf{\Theta} \mathbf{C} \mathbf{C}^\dagger \mathbf{V} = \mathbf{C} \mathbf{C}^\dagger \mathbf{V} \mathbf{\Theta} = \mathbf{CC}^\dagger \mathbf{V} = (\mathbf{C} \mathbf{C}^\dagger) \mathbf{\Theta} = \mathbf{CC}^\dagger \mathbf{Y} = \mathbf{Y} \mathbf{\Theta},$$

which proves that:

$$\mathbf{S}^{-1} = \mathbf{\Theta},$$

while the eigenvectors of both metric matrices are related by another unitary matrix \( \mathbf{K} \) such that, for example:

$$\mathbf{V} = \mathbf{UK} \rightarrow \mathbf{K} = \mathbf{VU}^\dagger.$$
These matrix relationships induce the MO coefficient transformation:
\[ \mathbf{C}_\nu = \mathbf{CV} \mathbf{\Sigma}^\dagger \rightarrow \mathbf{C}_\nu^I \mathbf{C}_\nu = \mathbf{I}, \]
which turns out to yield an orthonormalized set of vectors. The density matrix can be expressed from the point of view of the orthogonal vector coefficients, as:
\[ \mathbf{C} = \mathbf{C}_\nu \mathbf{V}^\dagger \mathbf{D} = \mathbf{CC}_\nu^I = \mathbf{C}_\nu \mathbf{V}^\dagger \mathbf{D} \mathbf{V} \mathbf{\Sigma}^\dagger \mathbf{C}_\nu = \mathbf{C}_\nu \mathbf{LC}_\nu^I, \]
which proves that the charge and bond order matrix can be written in terms of the orthonormalized MO coefficient matrix as:
\[ \forall \mu, \nu : D_{\mu\nu} = \sum_{l} Q_{l\mu} \mathbf{C}_{l\nu} \mathbf{C}_{\nu l}. \]

9.2. Euclidian atomic populations

This result may suggest in turn that there exists some approximate way to express the matrix \( \mathbf{D} \) in terms of the orthogonal MO coefficients \( \mathbf{C}_\nu \) and a diagonal matrix \( \mathbf{A} \), like:
\[ \mathbf{D}_\nu = \mathbf{C}_\nu \mathbf{A} \mathbf{C}_\nu^I \wedge \langle \mathbf{A} \rangle = N \]
such that:
\[ \langle \mathbf{D}_\nu \times \mathbf{I} \rangle = N \Rightarrow \sum_{\mu, \nu} D_{\nu\mu} = N \]
therefore permitting to define a new set of atomic populations, the Euclidian populations, by means of the expression:
\[ \forall \mathbf{A} : Q_{\mathbf{A}} = \sum_{\mu, \nu} D_{\nu\mu} = \sum_{\mu, \nu} A_{l\mu} \sum_{l} |\mathbf{C}_{l\nu}|^2 = \sum_{l} A_{l\mu} \left( \sum_{\mu, \nu} |\mathbf{C}_{l\nu}|^2 \right). \]

The problem now appears in the evaluation of the elements of the MO occupation numbers matrix \( \mathbf{A} \).

9.3. Evaluation of the Euclidian populations and the role of the occupation numbers

In fact, whenever \( \langle \mathbf{A} \rangle = N \) holds, then one can write:
\[ \sum_{\mathbf{A}} Q_{\mathbf{A}} = \sum_{\mathbf{A}} \sum_{l} A_{l\mu} \sum_{l} |\mathbf{C}_{l\nu}|^2 = \sum_{l} A_{l\mu} = N, \]
thus the quantities \( Q_{\mathbf{A}} \) behave as atomic populations and in their expression no crossing AO basis set terms is present. But on the other hand, the need to know how to compute a proper set \( \{ A_{l\mu} \} \) of MO occupations appears. To guess how this can be done, one can start defining the set of MO atomic contributions to a specific Euclidian atomic population as:
\[ \forall \mathbf{A} : I : q_{\mathbf{A}}^N = \left( \sum_{\mu, \nu} |\mathbf{C}_{l\nu}|^2 \right)^{-1} \rightarrow \langle q_{\mathbf{A}}^N \rangle = \langle q_{\mathbf{A}} \rangle = \langle | \mathbf{A} | \rangle. \]
and transforming afterwards the diagonal MO occupation into an isomorphic column vector: \( \mathbf{A} \equiv \langle | \mathbf{A} | \rangle = \langle A_{\mu\nu} \rangle \), then it is easier to write the Euclidian atomic populations as the scalar products:
\[ \forall \mathbf{A} : Q_{\mathbf{A}} = \langle | \mathbf{A} | | \mathbf{q}^I \rangle = \langle \mathbf{q}_{\nu}^I | \mathbf{A} | \rangle. \]

9.4. A simple example

In order to assess the interest of the presented Euclidian atomic populations, one can remember the simplified molecular hydrogen treatment, previously used as a counterexample of the condensed atomic–diatomic partition of the density function.

In this case, there the coefficient set is composed by two, already orthogonal, two-dimensional MO, which produce in turn a direct diagonal metric matrix: \( \mathbf{Z} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \). Such a metric matrix can provide a diagonal transformation: \( \Sigma^2 \), the square of it can be expressed as: \( \Sigma = \sqrt{2} \begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix} \). Consequently, there is no need here of any complicated computation, as it is easily obtained the MO orthogonal coefficient basis as:
\[ \mathbf{C}_\nu = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix} \]
and one can write for both atoms \( \mathbf{Q} \), the Euclidian population expression, in terms of the occupation numbers in the form: \( \mathbf{Q} = \begin{pmatrix} A_1 + A_2 \\ A_1 - A_2 \end{pmatrix} \). Furthermore, the occupation numbers can be expressed in this case in terms of some positive number in the unit interval: \( \alpha \in [0,1] \), such that: \( A_1 + A_2 = 2 \alpha \), which is the same as to impose the constraints: \( A_1 + A_2 = 2.6 \). Hence, one can also write for both hydrogen atoms: \( \mathbf{Q} = 1 \).

9.5. A quadratic error function

A possible way to determine the vector \( | \mathbf{A} \rangle \) in practical realistic cases could be based into finding the optimal value for the sum of atomic charges squared, which is the same as to find out some optimal value of the squared distance between bare nuclei charges and Euclidian atomic populations, that is:
\[ \begin{aligned} & v^{(2)} = \sum_{\mathbf{A}} (Z_{\mathbf{A}} - Q_{\mathbf{A}})^2 = \sum_{\mathbf{A}} (Z_{\mathbf{A}} - \langle | \mathbf{A} | \rangle)^2 \\ & = \sum_{\mathbf{A}} Z_{\mathbf{A}}^2 - 2 \sum_{\mathbf{A}} Z_{\mathbf{A}} \langle | \mathbf{A} | \rangle + \sum_{\mathbf{A}} \langle | \mathbf{A} | \rangle^2. \end{aligned} \]

This is the same as to consider that the molecular polarization, submitted to some constraints, which will be defined below, has to be not far away from the bare nuclei atomic charges in equilibrium. Such optimization problem needs to be correctly solved under the constraints:
\[ \langle | \mathbf{A} | \rangle = N \wedge \forall \mathbf{A} : A_{\mathbf{A}} \geq 0. \]

This can be easily done, after simplifying the quadratic error function in three steps. First, expressing the sum of squared nuclear charges as the constant:
\[ \theta = \sum_{\mathbf{A}} Z_{\mathbf{A}}^2, \]
then using the vector definition as a linear combination of the atomic vectors, with coefficients made of the nuclear charges:
\[ \mathbf{q} = \sum_{\mathbf{A}} Z_{\mathbf{A}} | \mathbf{q}_{\mathbf{A}} \rangle, \]
and afterwards, defining a square symmetrical matrix made by summing up the atomic vector set \( \{ | \mathbf{q}_{\mathbf{A}} \rangle \} \) tensorial products:
\[ \mathbf{Q} = \sum_{\mathbf{A}} | \mathbf{q}_{\mathbf{A}} \rangle \langle \mathbf{q}_{\mathbf{A}} |. \]

By means of these notational simplifications, one can finally rewrite the quadratic error as the equivalent quadratic function in the vector \( | \mathbf{A} \rangle \):
\[ v^{(2)} = \theta - 2 \langle | \mathbf{A} | \rangle \langle | \mathbf{A} | \rangle + \langle | \mathbf{A} | \rangle^2. \]

In addition, the matrix \( \mathbf{Q} \) can be diagonalized, that is:
\[ \mathbf{W}^T \mathbf{Q} \mathbf{W} = \mathbf{Z} = \text{Diag}(\zeta_{A}) \wedge \mathbf{W}^T \mathbf{W} = \mathbf{I}. \]
and the eigenvector matrix \( \mathbf{W} \) defines at the same time an orthogonal transformation of the occupation number vector.
\[ \begin{align*}
\mu^{(2)} &= \theta - 2\langle q | W^\dagger W | \Delta \rangle + \langle \Delta | W^\dagger \Xi W | \Delta \rangle, \\
\text{so calling:} & \quad |A_W\rangle = W|\Delta\rangle \land |q_{\mu}\rangle = W|q\rangle,
\end{align*} \]

then, if \( n \) is the number of MO, the quadratic error can be simplified to a sum of second order polynomials in the \( |A_W\rangle \) components like:

\[ \mu^{(2)} = \theta - 2\langle q_{\mu} | A_W | \Delta \rangle + \langle A_W | \Xi | A_W \rangle = \sum_i \left( \frac{1}{n-1} \theta - 2q_{\mu,i}A_{W,i} + \xi_{\mu,i}|A_{W,i}|^2 \right). \]

9.6. Unconstrained solution

Thus, the quadratic error function written as above, provides an unconstrained optimal solution for every MO like:

\[ \forall \xi_{\mu} > 0 : A_{W,\mu} = (\xi_{\mu})^{-1} q_{\mu,i} \]

while for the null \( \Xi \) eigenvalues a null occupation can be supposed; that is, one can use the convention:

\[ \forall \xi_{\mu} = 0 : A_{W,\mu} = 0 \land (\xi_{\mu})^{-1} = 0, \]

and defining the diagonal matrix:

\[ \Sigma^{-1}_0 = \text{Diag}\left( (\xi_{\mu})^{-1} \mid \delta(\xi_{\mu} > 0) \right) \]

one can also define \( Q^{-1}_0 \), the pseudoinverse of the matrix \( Q \) as:

\[ Q^{-1}_0 = W\Sigma^{-1}_0 W^\dagger = \sum_i \delta(\xi_{\mu} > 0) (\xi_{\mu})^{-1} [w_i] [w_i^\dagger] \]

whenever the column set \( \{[w_i]\} \) of the matrix \( W \) is employed. Consequently, it can be written:

\[ |A_W\rangle = \Sigma^{-1}_0 [q_{\mu}] \rightarrow |A\rangle = |W^\dagger A_W\rangle = |W^\dagger \Sigma^{-1}_0 [q_{\mu}]\rangle = |W^\dagger \Sigma^{-1}_0 W|q\rangle = Q^{-1}_0 |q\rangle = \sum_i \delta(\xi_{\mu} > 0) (\xi_{\mu})^{-1} [w_i] [q_j] [w_i^\dagger] \]

providing a first guess of the occupation vector, which maybe will not fulfill the necessary constraints as it corresponds to an unconstrained solution of the problem.

The quadratic error at these unconstrained optimal values of the occupation vector will be:

\[ \mu^{(2)}_{\text{opt}} = \theta - \sum_i \delta(\xi_{\mu} > 0) (\xi_{\mu})^{-1} [w_i] [q_{\mu}]^2. \]

9.7. MO occupation complete sum constrained solution

However, in order to take into account the constraint, which forces the complete sum of the occupation number to yield the number of electrons, one can also use a Lagrange undetermined coefficient constructing the augmented function:

\[ L = \epsilon^{(2)} - \lambda \left( N - \sum_i A_i \right) \]

with a null gradient condition written as:

\[ \forall P : \frac{\partial L}{\partial A_i} = 2 \sum_j (Q_{ij} A_j) - 2q_{\mu} - \lambda = 0 \]

implying a non-trivial optimal solution of the kind:

\[ \forall P : \sum_i (Q_{ij} A_j) = \frac{1}{2} \lambda + q_{\mu} \]

which can be transformed into the matrix equation:

\[ Q |\Delta\rangle = \frac{1}{2} |1\rangle + |q\rangle. \]

Now, using \( Q^{-1}_0 \), the pseudoinverse of the matrix \( Q \) as defined before, there appears that such constrained solution is expressible as follows:

\[ |\Delta\rangle = Q^{-1}_0 \left( \frac{1}{2} |1\rangle + |q\rangle \right). \]

where the unity vector \( |1\rangle = |1\rangle = |v_P\rangle \), is a column vector with ones as elements. Finally, the Lagrange multiplier can be obtained using the complete sum of the involved vectors in the above equation, taking into account that:

\[ \langle Q^{-1}_0 |1\rangle = \langle Q^{-1}_0 \rangle, \]

then one can write:

\[ \langle |\Delta\rangle | = N = \frac{1}{2} \langle Q^{-1}_0 |1\rangle + \langle Q^{-1}_0 |q\rangle \rightarrow \lambda = 2 \left( N - \langle Q^{-1}_0 |q\rangle \right) \langle Q^{-1}_0 \rangle^{-1}, \]

with the final result:

\[ |\Delta\rangle = Q^{-1}_0 (\mu |1\rangle + |q\rangle) - \mu = \frac{N - \langle Q^{-1}_0 |q\rangle}{\langle Q^{-1}_0 \rangle}. \]

9.8. Complete constrained solution

However, although the constrained solution above in most cases will be sufficient, there is no guarantee that every non-zero MO occupation number will be, generally speaking, positive definite. In order to take into account the complete sum constraint as in the above subsection, plus making explicitly use of the positive definite nature of the vector \( |\Delta\rangle \) components, one can write:

\[ |\Delta\rangle = |X| \rightarrow \forall |I : A_{W,\mu} = X_\mu^2, \]

using afterwards:

\[ \langle |\Delta\rangle | = N = \sum_i A_{W,\mu} = \sum_i X_\mu^2 = \langle X | X \rangle, \]

therefore, the quadratic error can be rewritten in terms of the vector \( |X\rangle \) components as:

\[ \epsilon^{(2)} = \theta - 2 \sum_i q_{\mu} X_\mu^2 + \sum_i Q_{\mu \nu} X_\mu^2 X_\nu^2. \]

Starting with an adequate vector \( |X\rangle \), that is: a vector with an Euclidian norm equal to the number of electrons, one can transform it by means of orthogonal matrices leaving the norm invariant. The complete sum constrained vector as obtained in the subsection above, can be a good starting point, whenever the absolute values of the possible negative elements, if any, are used prior the elementary Jacobi transformations \[76\] algorithm starts. Elementary Jacobi orthogonal transformations have been already employed in the search of approximate atomic density (ASA) functions \[5,7,9,10\] and are appropriate tools leading to a simple, albeit lengthy, computational algorithm. The ASA algorithm was designed with a similar purpose as the present one and so the complete details, because they are in fact the same, will not be repeated here.

9.9. Significance of the semi-occupation numbers

The previous completely constrained procedure can be associated to a more general context connecting a possible refinement of density functions with the MO density set and quantum similarity theory.
When studying the density function as defined in Eq. (1) the occupation numbers \( \langle \omega \rangle = \{ \omega_i \} \) can be decomposed as squares of a sequence of real numbers, constructing the semi-occupation numbers vector \( x = \{ x_i \} \), obviously related with the previously proposed vector \( X \), and defined as follows:

\[
\langle \omega \rangle = \{ x \} = \{ x \} \rightarrow V : \omega_i = x_i^2;
\]

(12)

then, the density function can be written in terms of such occupation pattern:

\[
\rho(\mathbf{r}) = \sum_i \omega_i \rho_i(\mathbf{r}) = \sum_i x_i^2 \rho_i(\mathbf{r}) \land \sum_i \omega_i = \sum_i x_i^2 = N.
\]

(13)

Taking into account the corresponding constraint as in the last part of Eq. (13), affecting the occupation numbers, the former equalities expressing the density function in the first part of Eq. (13) can be also rewritten as:

\[
\rho(\mathbf{r}) = \langle \omega \rangle |p| = \langle x | p | x \rangle = \langle x | x \rangle = N,
\]

provided that the corresponding isomorphic column vector: \( |p| = \langle \rho(\mathbf{r}) \rangle \) and the diagonal matrix: \( P = \text{Diag}(\rho(\mathbf{r})) \) are properly defined.

In previous papers have been discussed several facets of this real number decomposition of the MO occupation problem \([26,77,78]\), so the present reflection can be taken as an extension of this initial work. In fact, the density function can be also taken as a linear functional of the occupation numbers \( \{ \omega_i \} \); for that reason, when a gradient derivative with respect to these numbers is performed, it is easily obtained:

\[
\frac{\partial \rho(\mathbf{r})}{\partial \omega_i} = |p| - \frac{\partial \rho(\mathbf{r})}{\partial \omega_i} = \rho_i(\mathbf{r});
\]

accordingly to this result, the set of MO densities can be associated to molecular Fukui functions \([77]\) in good accord with the original Fukui definitions. The gradient with respect the real decomposition, giving the semi-occupation numbers vector, provides instead:

\[
\frac{\partial \rho(\mathbf{r})}{\partial x} = 2P|x| - \frac{\partial \rho(\mathbf{r})}{\partial x} = 2x_i \rho_i(\mathbf{r}),
\]

and the Hessian can be also easily computed within the semi-occupation number expression, as it can be written:

\[
\frac{\partial^2 \rho(\mathbf{r})}{\partial x_i \partial x_j} = D_{ij} - \frac{\partial^2 \rho(\mathbf{r})}{\partial x_i \partial x_j} = 2g_{ij} \rho_i(\mathbf{r}),
\]

therefore, the Hessian becomes positive definite as their elements are positive definite functions.

Besides, one can look for an optimization problem with a constraint, providing a Lagrange extended function like:

\[
L(\mathbf{r}) = \rho(\mathbf{r}) - a \{ (x | x) - N \} = \langle x | P | x \rangle - a \{ (x | x) - N \}
\]

then, the extremum condition gives:

\[
\frac{\partial}{\partial x} L(\mathbf{r}) = 2P|x| - 2a|x| = 0
\]

implying a minimum situation, in accordance to the positive definiteness of the Hessian:

\[
(\mathbf{P} - a \mathbf{I})|x| = 0 \rightarrow |x| = 0.
\]

(14)

Every semi-occupation number molecular situation is consequently a constrained result, far from the minimal site.

Whenever \( n \) MO are involved in the construction of the density function, the constraint associated to the semi-occupation numbers corresponds to the surface of a \( n \)-dimensional sphere of radius \( r \) = \( N \), as the constraint can be written like:

\[
v^2 = \sum x_i^2.\]

As a result, the semi-occupation numbers can be seen as the coordinates of \( n \)-dimensional vectors directed from the center of coordinates to the surface of a \( n \)-dimensional sphere of radius \( v \).

Eq. (14) can be transformed into a information bearing eigen-system, just left tensor multiplying it by the diagonal matrix \( \mathbf{P} \):

\[
\mathbf{P} \otimes (\mathbf{P} - a \mathbf{I})|x| = 0.
\]

(15)

Taking into account that diagonal matrices are isomorphic to vectors of the same dimension:

\[
\mathbf{P} \otimes \mathbf{P} = \{ \rho_i(\mathbf{r}) \rho_j(\mathbf{r}) \} = \Theta \land \mathbf{P} \otimes \mathbf{I} = \mathbf{P},
\]

so Eq. (15) can be written as:

\[
\Theta|x| = a \mathbf{P}|x|,
\]

which upon inward integration of the matrices appearing on both sides, yields:

\[
Z|x| = a \mathbf{I}|x|
\]

(16)

taking into account that:

\[
Z = \int \mathbf{P} \mathbf{d}r = \int \rho_i(\mathbf{r}) \rho_j(\mathbf{r}) \mathbf{d}r = \mathbf{P}
\]

is the overlap similarity matrix of the MO density set \( \{ \rho_i \} \), which is coincident with the metric matrix of the same set, and also that the inward integration of the diagonal matrix \( \mathbf{P} \) yields the unit matrix, the implied integrals being the Minkowski norms of the MO densities:

\[
\int \rho_i(\mathbf{r}) \mathbf{d}r = 1 = \mathbf{I}
\]

Eq. (16) yields a positive definite spectrum with the eigenvector corresponding to the highest eigenvalues having all elements positive definite, according to Frobenius theorem \([79]\). Such a property of the MO similarity matrix was already noticed in the earliest development of quantum similarity theory \([26]\) when similarity it was applied to MO ordering independently of symmetry and MO energy considerations.

The eigenvector set provided by the solution of Eq. (16) constitutes an optimal set of semi-occupation numbers, which can be employed to construct a set of optimal density functions in a MO context like Hartree–Fock or Kohn–Sham theories.

10. Conclusions

The search of a possible physical meaning about the norms of the atom–bond partition of the density function, leads to the conclusion that such a partition, being essentially of geometrical nature, do not provide some Minkowski norms, which can be attached to the physics of molecular structures. Even with this negative result, the discussion of atomic-bond density function partition conduces within a natural pathway to the analysis of a wide set of problems, involving invariant transformations of the density matrix, reciprocal spaces and a novel definition of Euclidian atomic populations.

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