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ORIGINAL PAPER

Symmetrical overlap transformations of function basis sets: the LCAO MO and quantum similarity practical cases

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Abstract Quantum chemical computational procedures, like LCAO MO theory and quantum similarity, use non orthogonal function basis sets, which define finite dimensional subspaces of a Hilbert space. Based on the original overlap metric matrices, generated by the chosen finite non orthogonal basis sets, there are several symmetrical overlap and basis set transformations possible. This study tries to find out the general point of view, from where all these procedures can be studied in a clear generalized perspective.

Keywords Quantum chemistry · LCAO MO theory · Quantum similarity · Function basis sets · Metric overlap matrices · Symmetric overlap transformations · Löwdin transformation · Reciprocal spaces · Projected spaces

1 Introduction

In a previous paper, related to study the first order density function [1], has been put forward some partial aspects of the non-orthogonal basis set transformation problem. Concretely, the issues of the role of reciprocal space and the Löwdin transformation as well were discussed. In the present paper it is intended to study in a deepest general framework this kind of basis set transformations based on the associated metric matrix.

Also, some quantum similarity (QS) aspects related to the tensorial representation of molecular sets have been recently studied [2] too. This must be taken as an extension

Dedicated to the memory of Professor P. O. Löwdin.

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of the old QS issue of considering the columns of the quantum similarity matrix as a source of molecular descriptors. A general extensive possibility has been put forward and discussed constituting the background of a problem which here, in the present study, will appear as a particular case of function basis set symmetrical transformation procedures.

Thinking about the many aspects of the quantum chemical theoretical formalism, related on how function basis set transformations can be studied, has aroused the interest of the present author and focused it into the subject of function basis set symmetrical transformations in general. Such previous consideration has led to the idea that one must also focus about the, even more important, relationship of the practical computational finite subspaces with the ideal infinite dimensional Hilbert space, where the first ones belong.

Many aspects studied in this paper have not been, as far as the author knows, studied in deep as a complete theoretical structure, from where many particular facets can be deduced. Thus, the present work will be organized studying first the basic principles, which will be also employed to put forward a convenient notation. Then, the general framework will be developed, which will be used to deduce quite well-known basis set transformations, like Löwdin's [3], which will appear in turn as one possible algorithm among many other choices. In addition, the present paper will also study the applicability which can have the general symmetric transformation definitions, when employed in both LCAO MO and QS theories.

2 Function basis sets and overlap metric matrices

The real, practical birth of modern quantum chemistry has to be traced first to the work of Mulliken [4] on the algebraic framework now known as LCAO MO theory. Afterwards, such quantum chemical origins can be also associated to the first paper of Boys [5], where the use of GTO basis sets was initially promoted. In any case, the main idea was to construct MO's as linear combinations of a finite number of basis set functions, usually centered in the molecular atomic sites or elsewhere in the surrounding tridimensional molecular space.

Independently of the nature of the primitive functions computationally employed to form the basis sets, which will be later used to build the MO's up, one can study imposed by such a choice the basic algebraic problem from a simple abstract point of view. In doing such program primarily, one can also try to secondarily deduce any emerging interesting properties and algorithmic procedures as well.

On the other hand, a similar algebraic situation was presented since the first paper on QS related to molecular sets [6] and the posterior elaboration of a general theory of the problem, see for example references [7,8]. The definition of quantum object set (QOS) concept, see for a recent résumé [9], connects by means of a Cartesian product a set made of an arbitrary finite number of molecular structures with a one-to-one related set of density functions. The QOS density functions tags also can be considered acting as a basis set which generates a finite dimensional subspace, belonging in turn to an infinite dimensional Hilbert space.

Therefore, in an equivalent way the QS framework basic structure is obviously connected with the LCAO MO framework. This is so, as a consequence, in both quantum chemical theoretical cases, that it is known an initial well defined basis set, made of linearly independent real valued functions of homogeneous real variables:[1] $X = \{\chi_\mu \big| \mu = 1, M\}$.

The dependence of the function elements of the basis set X from a coordinate variable set has to be considered homogeneous for all the elements of the set. For instance, all functions will depend in the same manner of the coordinates of one electron, both in the usual LCAO MO basis set case or in the first order density functions, currently employed in QS theory framework.[2] Accordingly, the proposed problem in order to be properly stated and solved has to possess a necessary property consisting into that *all* the elements of X have to bear the same kind of variable types, submitted to a common dimension. It is in this sense that one can say the basis set X is compulsively made of homogeneous functions.

Moreover, the elements of X can be ordered into a row (or column) vector: $\langle\chi| = (\chi_1; \chi_2; \ldots \chi_\mu; \ldots \chi_M)$. Such a vector can be employed to construct a tensor product, which can be expressed indistinctly by means of two equivalent symbolic ways, resulting in the same set of matrix or tensor elements:

$$X = |\chi\rangle \otimes |\chi\rangle = |\chi\rangle\langle\chi| = \left\{x_{\mu\nu} = \chi_\mu \chi_\nu \,|\mu, \nu = 1, M\right\}, \tag{1}$$

the first product is made by means of a tensorial convention, while the second product in Eq. (1) is written employing the well-known Dirac's notation for vectors in a row $\langle u|$ and the transposed column $|u\rangle = (\langle u|)^T$ notation.

The elements of the tensor definition (1) can be integrated submitted to the following convention:

$$\begin{aligned} \mathbf{S} = \langle X\rangle &= \langle |\chi\rangle\langle\chi| \rangle \\ &= \left\{ s_{\mu\nu} = \int_D x_{\mu\nu}(\mathbf{r}) d\mathbf{r} = \int_D \chi_\mu(\mathbf{r})\chi_\nu(\mathbf{r}) d\mathbf{r} \,\middle|\, \mu, \nu = 1, M \right\}, \end{aligned} \tag{2}$$

where the homogeneous variable vectors of the basis set functions have been given explicitly here, in order to easily show the integration structure of every element of the tensor (1).

The resultant matrix $\mathbf{S}$ constructed in Eq. (2) is named the *overlap* (or metric) matrix, see for example [10], which is a common term employed since the initial Mulliken definition in quantum chemistry, see for example [11,12].

[1] From now on it will be supposed that the functions are real valued and defined over real variables. Adapting the present study to the more general framework of complex valued functions, poses no more problems than the ones specified here, but needs some additional notation burden, which it is avoided here in this way.

[2] In both cases though, functions bearing several one electron coordinates can be employed, for instance: geminals in LCAO MO or higher order DF in QS.

In QS theory on the other hand, the basis set functions are electronic density functions and the resultant metric matrix is usually called the (*overlap*) *similarity matrix* associated to the elements of the QOS, see for example references [9–13].

In the following discussion the columns of the overlap matrix (2) will be used; they can be written as follows:

$$\mathbf{S} = \left(|\mathbf{s}_1\rangle\,;\,|\mathbf{s}_2\rangle\,;\ldots\left|\mathbf{s}_\mu\right\rangle;\ldots|\mathbf{s}_M\rangle\right). \tag{3}$$

3 Overlap properties and functions

The overlap matrix (2) obtained from LCAO MO theory, *a priori* corresponds by construction to a positive definite matrix. That is, a symmetric matrix whose eigenvalues are positive definite:

$$\forall I = 1, M : \mathbf{S}\,|\mathbf{u}_I\rangle = \sigma_I\,|\mathbf{u}_I\rangle \rightarrow \sigma_I \in \mathbf{R}^+ \wedge \forall I, J : \langle \mathbf{u}_I|\mathbf{u}_J\rangle = \delta_{IJ}. \tag{4}$$

If the overlap matrix has a null (or a computationally obtained value which is equal or less than the machine precision) eigenvalue, this indicates that there is a function in X which is linearly dependent of the rest, and thus that X is no longer an algebraic correct basis set. In this case, some correction procedure must be followed to construct a suitable basis set.

In QS framework, the overlap similarity matrix is symmetric and non-singular, usually positive definite. However, in some cases, due to the need of optimal molecular superposition in order to obtain the elements of the similarity matrix it can become non definite. This has to be interpreted in the sense that one or more eigenvalues of the similarity matrix can be negative, see for example [14,15]. If the QOS elements are essentially distinct, because all the implied density functions are linearly independent, then the similarity matrix determinant will be always non-null.

In both cases the overlap or metric matrix has to correspond to a symmetric non-singular matrix. The overlap eigensystem as shown in Eq. (4) can be easily computed in any case. It can be also expressed in a compact form like:

$$\mathbf{SU} = \mathbf{U}\Sigma \leftrightarrow \mathbf{U}^T\mathbf{SU} = \Sigma \leftrightarrow \mathbf{S} = \mathbf{U}\Sigma\mathbf{U}^T,$$

where $\mathbf{U} = (|\mathbf{u}_1\rangle; |\mathbf{u}_2\rangle; \ldots |\mathbf{u}_I\rangle; \ldots |\mathbf{u}_M\rangle)$ is an orthogonal matrix: $\mathbf{U}\mathbf{U}^T = \mathbf{U}^T\mathbf{U} = \mathbf{I}$, which has as columns the eigenvectors of $\mathbf{S}$ and $\Sigma = Diag(\sigma_1; \sigma_2; \ldots \sigma_I; \ldots \sigma_M)$ is a diagonal matrix collecting the corresponding eigenvalues in the same order as the eigenvectors are stored.

Any smooth function of the overlap matrix $f(\mathbf{S})$, which is also a symmetric matrix: $f(\mathbf{S}) = (f(\mathbf{S}))^T$, can be easily written by using the fact that for any diagonal matrix, like Σ, one can write:

$$f(\Sigma) = Diag(f(\sigma_1); f(\sigma_2); \ldots f(\sigma_I); \ldots f(\sigma_M)),$$

then it can be also deduced that one can obtain the desired function of the overlap matrix as:

$$f(\mathbf{S}) = \mathbf{U} f(\Sigma) \mathbf{U}^T. \tag{5}$$

4 Equivalent basis set and overlap symmetric transformations

Using an overlap function, from Eq. (5) one can put easily forward a general transformation of the overlap itself, which can be observed as such, or alternatively as a consequence of a transformation performed on the originating function basis set (1). Taking into account that $f(\mathbf{S})$ is a symmetric matrix, one can write:

$$\mathbf{T} = f(\mathbf{S})\mathbf{S}f(\mathbf{S}) = f(\mathbf{S}) \langle |\chi\rangle \langle \chi| \rangle f(\mathbf{S}) = \langle f(\mathbf{S}) |\chi\rangle \langle \chi| f(\mathbf{S})\rangle, \tag{6}$$

a result which can be also easily obtained by means of the basis set transformation:

$$\langle \xi| = \langle \chi| f(\mathbf{S}), \tag{7}$$

which is a transformed basis set providing a new metric matrix, which can be written as:

$$\langle |\xi\rangle \langle \xi| \rangle = \langle f(\mathbf{S}) |\chi\rangle \langle \chi| f(\mathbf{S})\rangle = f(\mathbf{S}) \langle |\chi\rangle \langle \chi| \rangle f(\mathbf{S}) = f(\mathbf{S})\mathbf{S}f(\mathbf{S}) = \mathbf{T}. \tag{8}$$

Thus, Eqs. (6) or (8) correspond to the general form of a particular symmetric non-singular transformation either of the basis set as in Eq. (7) or of the overlap matrix like in Eq. (6). From any of both points of view, the result is a new transformed overlap matrix $\mathbf{T}$.

5 Particular cases of the symmetric transformations of the overlap

Several particular cases can be obtained from the transformations (6) or (8). The most obvious among the plausible ones can be described as follows:

1. $f(\mathbf{S}) = \mathbf{S}$. This will result in the following transformed overlap:

$$\mathbf{T} = \mathbf{S}^3. \tag{9}$$

Such an overlap is equivalent to obtain a new basis set defined as:

$$\langle \xi| = \langle \chi| \mathbf{S},$$

which in turn can be associated to express the initial basis set functions as linear combinations of the initial overlap columns:

$$\forall \nu : \xi_\nu = \langle \chi | \mathbf{s}_\nu \rangle = \sum_\mu s_{\mu\nu} \chi_\mu = \sum_\mu |\chi_\mu\rangle\langle\chi_\mu|\chi_\nu\rangle = \left(\sum_\mu |\chi_\mu\rangle\langle\chi_\mu|\right)|\chi_\nu\rangle$$
$$= P_X(\chi_\nu)$$

That is: every transformed function can be seen as the result to project every initial basis set function, belonging to the infinite dimensional Hilbert space, into the subspace generated by the initial basis set X by means of a projector defined as:

$$P_X = \sum_{\mu} |\chi_\mu\rangle\langle\chi_\mu|.$$

Because of this result, the transformed overlap matrix (9) can be named projected transformation metric matrix.
Also, it is interesting to note that the new overlap metric matrix (9), obtained in the way explained in this paragraph above, can be considered too a metric matrix constructed as follows:

$$\mathbf{T} = \mathbf{SSS} = \mathbf{S}^T\mathbf{SS} \rightarrow \mathbf{T} = \left\{t_{\mu\nu} = \langle \mathbf{s}_\mu | \, \mathbf{S} \, | \mathbf{s}_\nu \rangle \, | \mu, \nu = 1, M \right\}. \tag{10}$$

This is so, because when one considers the columns of the initial overlap matrix as shown in Eq. (3), then the result above in Eq. (10) becomes the same as to consider the metric matrix (9) like the metric of the columns of the original overlap (2), computed within the original metric matrix (2).

2. From another possible form, the choice: $f(\mathbf{S}) = \mathbf{S}^{-1}$, produces a reciprocal space transformed overlap, as one can write:

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

This is equivalent to transform the basis set functions by means of the inverse overlap matrix:

$$\langle \xi | = \langle \chi | \, \mathbf{S}^{-1}.$$

Because of these properties one can call reciprocal transformation to this resultant overlap choice.

3. The oldest of this kind of transformations, the Löwdin transformation, as described in reference [3], uses the inverse square root of the overlap matrix: $f(\mathbf{S}) = \mathbf{S}^{-\frac{1}{2}}$, resulting into a unit metric matrix:

$$\mathbf{T} = \mathbf{S}^{-\frac{1}{2}}\mathbf{S}\mathbf{S}^{-\frac{1}{2}} = \mathbf{I},$$

which is the same as to obtain a new transformed basis set:

$$\langle \xi | = \langle \chi | \, \mathbf{S}^{-\frac{1}{2}},$$

with the additional property of being orthonormalized:

$$\forall \mu, \nu : \langle \xi_\mu | \xi_\nu \rangle = \delta_{\mu\nu}.$$

This new basis set is evidently known as Löwdin orthonormalized basis set.

4. The inverse of the Löwdin transformation, that is: the square root of the original overlap (2), also constitutes an interesting overlap transformation:

$$f(\mathbf{S}) = \mathbf{S}^{+\frac{1}{2}}, \tag{11}$$

as it produces a new kind of transformed overlap, which can be written as:

$$\mathbf{T} = \mathbf{S}^{+\frac{1}{2}}\mathbf{S}\mathbf{S}^{+\frac{1}{2}} = \mathbf{S}^2 = \mathbf{S}\mathbf{S} = \mathbf{S}^T\mathbf{S}, \tag{12}$$

which is the same as to consider that the transformed overlap elements (12) are the result of the scalar products involving the initial overlap column (or row) vectors under an orthonormalized metric. This situation constitutes an alternative to the already discussed transformed form, as shown in Eq. (10) of paragraph 1). This is so, because when one considers the columns of the initial overlap matrix as written in Eq. (3), then the overlap matrix (12) can be easily constructed as the set of the original overlap columns scalar products:

$$\mathbf{T} = \left\{ t_{\mu\nu} = \left\langle \mathbf{s}_\mu | \mathbf{s}_\nu \right\rangle | \mu, \nu = 1, M \right\}. \tag{13}$$

Thus, the new overlap matrix (12), obtained from the square root transformation (11), can be interpreted as the metric matrix of the finite dimensional space, generated by the discrete vector basis set, made in turn by the set of columns of the initial metric matrix $\mathbf{S}$:

$$S = \left\{ \left| \mathbf{s}_\mu \right\rangle | \mu = 1, M \right\}.$$

That is, the metric (12) results when, instead of considering as a basis set the function set X per se, one considers the coordinates set S of the representation of the functions of X with respect themselves. Such a transformation can be called a self-metric transform. It can be of use in QS QOS ordering procedures see for example [15–17].

5. A great deal of other transformation kinds, based in the general framework developed here, can be easily imagined. For instance, given a real parameter α, one can design the exponential transformation:

$$f(\mathbf{S}) = \exp(\alpha\mathbf{S}),$$

which for sufficiently small values of the parameter can be written approximately as:

$$f(\mathbf{S}) = \mathbf{I} + \alpha\mathbf{S} + O(\alpha^2),$$

therefore providing an approximate transformed overlap, which can be written like:

$$\mathbf{T} = (\mathbf{I} + \alpha\mathbf{S})\mathbf{S}(\mathbf{I} + \alpha\mathbf{S}) = \mathbf{S} + 2\alpha\mathbf{S}^2 + O(\alpha^2),$$

which adds (or substracts) a term to the original overlap matrix, originated in the framework of the previous self-metric transformation of paragraph 4).

6 Invariant properties of the symmetric transformations

So far, the symmetric transformations setup developed here possess several invariant properties, when studied involving the diverse mathematical objects, appearing in the current practice of quantum chemistry. For instance, if one constructs linear combinations of the functions from the basis set X, it can be written:

$$\forall I = 1, M : |\phi_I\rangle = \langle \chi | \mathbf{c}_I \rangle \,, \tag{14}$$

where the set $\Phi = \{|\phi_I\rangle \,|I = 1, M\}$ can be associated to some MO set. Then, the column coefficient set ordered in the form of a matrix:

$$\mathbf{C} = (|\mathbf{c}_1\rangle \,; |\mathbf{c}_2\rangle \,; \ldots |\mathbf{c}_I\rangle \,; \ldots |\mathbf{c}_M\rangle) \,,$$

corresponds to the coordinates of each MO expressed with respect to the basis set functions X. The linear combinations (14) remain invariant whenever the basis set is submitted to a symmetric transformation like the ones studied before, while the coefficient columns of $\mathbf{C}$ are transformed by the inverse of the chosen transformation matrix, that is:

$$\begin{aligned} \forall I = 1, M : |\phi_I\rangle &= \langle \chi | \, f\,(\mathbf{S}) \, [f\,(\mathbf{S})]^{-1} \, |\mathbf{c}_I\rangle \\ &= \langle \xi | \, [f\,(\mathbf{S})]^{-1} \, |\mathbf{c}_I\rangle = \langle \xi | \mathbf{d}_I \rangle \,, \end{aligned} \tag{15}$$

where the transformed coefficients can be written now by means of:

$$\forall I = 1, M : |\mathbf{d}_I\rangle = [f\,(\mathbf{S})]^{-1} \, |\mathbf{c}_I\rangle$$

and the symmetric transformation inverse is easily constructed taking into account equation (5):

$$[f\,(\mathbf{S})]^{-1} = \mathbf{U} \, [f\,(\Sigma)]^{-1} \, \mathbf{U}^T$$

and complementarily using the straightforward inverse of a diagonal matrix form:

$$[f\,(\Sigma)]^{-1} = Diag \left(f(\sigma_1)^{-1}; f(\sigma_2)^{-1}; \ldots f(\sigma_I)^{-1}; \ldots f(\sigma_M)^{-1} \right) .$$

Thus, if this double transformation leaves the MO structure invariant, everything else depending of MO's becomes invariant. Within LCAO MO theory everything, from many electron wave functions up to expectation values, depends on MO coefficients and basis sets, consequently the whole tree made of LCAO MO theoretical branches

become invariant. For example, the invariant first order density function can be expressed in any symmetrically transformed basis set, provided that the MO coordinates are transformed by the symmetrical inverse:

$$\rho(\mathbf{r}) = \sum_I \omega_I \left|\phi_I\right\rangle \left\langle\phi_I\right| = \sum_I \omega_I \left\langle \mathbf{c}_I|\chi\right\rangle \left\langle\chi|\mathbf{c}_I\right\rangle = \sum_I \omega_I \left\langle \mathbf{d}_I|\xi\right\rangle \left\langle\xi|\mathbf{d}_I\right\rangle .$$

Therefore, the one electron expectation values observables associated to the MO theoretical evaluation remain invariant, whenever the double symmetric transformation of type (15) is employed.

7 Some QS considerations

The discussion on the possible metric matrix symmetric transformations can be of use in QS calculation of similarity and dissimilarity indices. In fact, once any of the discussed non-orthogonal metric matrices $\mathbf{T} = \left\{t_{\mu\nu}\right\}$ is known, then its elements can be employed to obtain two kinds of complementary indices.

The first one can be connected with the cosines of the angles subtended by two vectors, it is customarily known in QS lore as Carbó similarity index [18,19] (CSI), which in general can be obtained as:

$$\forall \mu, \nu = 1, M : r_{\mu\nu} = t_{\mu\nu} \left(t_{\mu\mu} t_{\nu\nu}\right)^{-\frac{1}{2}} . \tag{16}$$

The second QS index possibility has been recently described [20]. It can be associated to a normalized Euclidian distance index. It has been proposed to name it as Carbó-Hodgkin-Richards dissimilarity index (CHRDI) and can be defined as:

$$\forall \mu, \nu = 1, M : d_{\mu\nu} = \left(1 - 2t_{\mu\nu} \left(t_{\mu\mu} + t_{\nu\nu}\right)^{-1}\right)^{\frac{1}{2}} . \tag{17}$$

Both CSI and CHRDI indices vary in the interval: [0, 1]. However, while the maximal value of the CSI corresponds to a maximal similarity, the maximal value of the CHRDI corresponds to a minimal similarity. Conversely, a minimal CSI value corresponds to a minimal similarity, while a minimal CHRDI value corresponds to a maximal similarity. It is in this sense, as both indices are varying within the same unit interval the two indices can be considered complementary.

Thus, computation of QS indices can benefit of the collection of transformed overlap similarity matrices, which can be obtained using the algebraic framework developed here. QS indices, like the ones in expressions (16) and (17) proposed above, can be employed to order the elements of QOS, for instance using Kruskal trees, see for instance references [15,16] or any other ordering numerical device, see for example [21].

In this sense, the construction and interpretation of the varied symmetric overlap transformations can be of great help in obtaining diverse points of view, pointing towards the implementation of accurate and many faceted molecular qualitative structure-properties relationships associated to a quantum origin.

8 Final remarks

One must be aware of the fact that, when performing a symmetrical transformation of the original overlap metric matrix **S**, implicitly performs a symmetrical transformation of the original function basis set X. Therefore, the new transformed overlap matrix can be thought as made by transformed functions, which have to be considered linear combinations of the original ones.

As a consequence of the symmetrical transformations, the transformed functions in both studied frameworks, LCAO MO or QS, no longer possess some of the fundamental attributes of the original functions.

In molecular LCAO MO theory the new transformed functions are nevermore attached to a given unique center, but become multicenter functions.

In QS framework, the original density functions, which are uniquely attached and define the nature of every quantum object (QO) in a QOS, once submitted to a symmetrical overlap transformation cannot be considered uniquely associated to a specific QO, but become a linear combination of the whole set of density functions considered as a basis set. However, in any symmetrical transformation case, every transformed function can be supposed that it continues representing the associated QO, now characterized within the ensemble of the whole QOS elements, including itself.

As a final résumé one can say that a multiple point of view has to be considered, when studying the problem posed by the mathematical and computational use of finite dimensional functional basis sets. One must be aware that the finite function set X is a subset of an infinite dimensional Hilbert space. As the elements of this set X must be linearly independent by construction, they generate a finite dimensional subspace within the Hilbert space where they belong.

The direct overlap matrix **S**, obtained from the elements of X, corresponds to the Gram matrix of X too, but must be considered as a mathematical object belonging to Hilbert space.

On the other hand, the columns of the overlap matrix can be viewed as the coordinates of the functions of X, when expressed as linear combinations of themselves. That is, when observed from the point of view of the finite dimensional space generated by X. Thus, the columns (or rows) of the overlap matrix can be considered as a discrete representation of a basis set within some column (or row) vector space.

The metric matrix of this finite dimensional vector space can be subject of diverse symmetrical transformations, based on the original overlap matrix, which are equivalent to perform similar transformations on the basis set X. Löwdin's transformation is just one of them, transforming the original basis set into an orthonormalized one.

9 Conclusions

Based on the original overlap metric matrix associated to a basis set constructed by a finite number of functions, symmetrical transformations of overlap matrices constitute a large family of basis set transformations, which can be employed for various purposes both in usual LCAO MO and in QS theories. Such transformations leave

the MO's invariant and thus atomic and molecular quantum mechanical expectation values too.

A specific particular case of the family of symmetrical transformations of the overlap metric matrix can be used to obtain orthonormalized function basis sets via Löwdin's procedure.

Symmetrical overlap transformations can have a computational valuable potential use in QS, permitting to obtain a collection of similarity indices and thus a multifaceted point of view in the ordering of molecular QOS, enhancing the qualitative assessment of molecular structure-properties relationships.

Written in the way presented in this paper, overlap symmetrical transformations can also have a valuable pedagogical potential to understand the nature and properties of function basis sets in LCAO MO theory.

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