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Diagonal coefficient representation of density functions and quantum similarity measures

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Abstract Quantum similarity measures within a new theoretical point of view are described for arbitrary order density functions, with the aid of attached pseudo-wave functions, in a vector semispace structure associated with a Minkowski metric.

1 Introduction

1.1 p-th order density functions

In the MO framework any density function up to an arbitrary order p can be written in the following way, see for example [1]:

$$
\begin{aligned}
&\rho^{(p)}\left(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_p\right) \\
&= \sum_{i_1} \sum_{i_2} \cdots \sum_{i_p} \sum_{j_1} \sum_{j_2} \cdots \sum_{j_p} P_{i_1 i_2 \ldots i_p; j_1 j_2 \ldots j_p} \left|i_1 i_2 \ldots i_p\right\rangle\left\langle j_1 j_2 \ldots j_p\right|
\end{aligned}
\tag{1}
$$

where: $\{\mathbf{r}_I \ (I = 1, p)\}$ are the position coordinates of the particles; the indices of the summation symbols run over the number of involved MO set: $\{\varphi_i \ (i = 1, m)\}$ used

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to construct the wave function; the coefficients $\mathbf{P} = \left\{ P_{i_1 i_2 \ldots i_p; \, j_1 j_2 \ldots j_p} = P\left([\mathbf{i}]\,;\,[\mathbf{j}]\right) \right\}$ form a m^{2p} -dimensional hypermatrix; and finally by the symbol: $\left| i_1 i_2 \ldots i_p \right) = |[\mathbf{i}]\rangle$ it is represented the p-th order tensor product of the same number of MO's, that is:

$$\left| i_1 i_2 \ldots i_p \right) = \varphi_{i_1}\left(\mathbf{r}_1\right) \otimes \varphi_{i_2}\left(\mathbf{r}_2\right) \otimes \ldots \varphi_{i_p}\left(\mathbf{r}_p\right) = |[\mathbf{i}]\rangle . \tag{2}$$

To allow an easy description, the set of p subindices are collected into a p-tuple, or: $\mathbf{i} = \left\{ i_1, i_2, \ldots i_p \right\}$, while preserving the p-tuple symbol $\mathbf{p} = \{1, 2, \ldots p\}$ for the canonically ordered set of p integers, permitting in this way to rewrite the expression (1) in quite a compact form:

$$\rho^{(p)}\left(\mathbf{r}\left[\mathbf{p}\right]\right) = \sum [\mathbf{i}] \sum [\mathbf{j}] P\left([\mathbf{i}]\,;\,[\mathbf{j}]\right) |[\mathbf{i}]\rangle \langle [\mathbf{j}]| , \tag{3}$$

the symbols $\sum [\mathbf{i}] \wedge \sum [\mathbf{j}]$ are nested summation symbols [2–5].

The coefficient hypermatrix $\mathbf{P}$ is a Hermitian one, depending on the structure of the wave function employed when constructing the density function. Being the coefficient hypermatrix Hermitian in the sense:

$$P\left([\mathbf{i}]\,;\,[\mathbf{j}]\right) = P\left([\mathbf{j}]\,;\,[\mathbf{i}]\right)^* .$$

Equation 3 can be written as the complete sum of an inward hypermatrix product [6], provided it is previously defined the hypervector: $|\varphi\rangle = \{|[\mathbf{i}]\rangle\}$, whose elements are the MO tensor products defined in Eq.2, then:

$$\rho^{(p)}\left(\mathbf{r}\left[\mathbf{p}\right]\right) = \langle \mathbf{P}* |\varphi\rangle \langle \varphi| . \tag{4}$$

1.2 Invariant unitary transformations of p-th order density functions

Thus, for the collection of all the pairs of possible p-tuples, there shall exist a unitary hypermatrix: $\mathbf{U} = \{U\left([\mathbf{i}]\,;\,[\mathbf{j}]\right)\}$, which diagonalizes the coefficient hypermatrix in the sense:

$$\mathbf{U}^+\mathbf{P}\mathbf{U} = \Omega \wedge \Omega = Diag\left(\omega\left[\mathbf{i}\right]\right) \rightarrow \mathbf{P} = \mathbf{U}\Omega\mathbf{U}^+ . \tag{5}$$

The structure of the unitary hypermatrix acting over the MO tensor product can be also thought as a tensor product of unitary matrices. Indeed, suppose known a set of unitary matrices: $\{\mathbf{U}_I\}$ of the same dimension, then: $\forall I : \mathbf{U}_I^+\mathbf{U}_I = \mathbf{U}_I\mathbf{U}_I^+ = \mathbf{I}$. Defining the hypermatrix:

$$\mathbf{U} = \overset{p}{\underset{I=1}{\otimes}} \mathbf{U}_I = \left\{ U_{1;i_1 j_1} U_{2;i_2 j_2} \ldots U_{p;i_p j_p} \right\} = \{U\left([\mathbf{i}]\,;\,[\mathbf{j}]\right)\},$$

then the hypermatrix product can be written by means of nested summation symbols and a logical Kronecker delta [2–5]:

$$\mathbf{U}^+\mathbf{U} = \mathbf{U}^+\mathbf{U} = \mathbf{I} \rightarrow \sum [\mathbf{k}] U^*\left([\mathbf{k}]\,;\,[\mathbf{i}]\right) U\left([\mathbf{k}]\,;\,[\mathbf{j}]\right) = \delta\left(\mathbf{i} = \mathbf{j}\right).$$

When using the coefficient description (5) into the density expression (3), this becomes the same as to substitute every element of the coefficient hypermatrix by a hyperbilinear form, depending of the real eigenvalue elements and the unitary hypermatrix ones:

$$\rho^{(p)}\left(\mathbf{r}\left[\mathbf{p}\right]\right) = \sum [\mathbf{i}] \sum [\mathbf{j}] \left(\sum [\mathbf{k}]\omega\left([\mathbf{k}]\right) U\left([\mathbf{i}]\,;[\mathbf{k}]\right) U^*\left([\mathbf{j}]\,;[\mathbf{k}]\right)\right) |[\mathbf{i}]\rangle\,\langle[\mathbf{j}]|$$

$$= \sum [\mathbf{k}]\omega\left([\mathbf{k}]\right)\left(\sum [\mathbf{i}] \sum [\mathbf{j}] U\left([\mathbf{i}]\,;[\mathbf{k}]\right) |[\mathbf{i}]\rangle\,\langle[\mathbf{j}]|\,U^*\left([\mathbf{j}]\,;[\mathbf{k}]\right)\right)$$

but now renaming the unitary transformed tensor MO products as:

$$|U\,|[\mathbf{i}]\rangle\,\rangle = \sum [\mathbf{i}]\,U\left([\mathbf{i}]\,;[\mathbf{k}]\right)|[\mathbf{i}]\rangle,$$

then the density may be associated to a diagonal coefficient hypermatrix form:

$$\rho^{(p)}\left(\mathbf{r}\left[\mathbf{p}\right]\right) = \sum [\mathbf{i}]\omega\left([\mathbf{i}]\right)|U\,|[\mathbf{i}]\rangle\,\langle\,[\mathbf{i}]|\,U| \tag{6}$$

while remaining invariant.

In the same manner as Eq. 4 represents in a compact form Eqs. 3, 6 can be written in the same way:

$$\rho^{(p)}\left(\mathbf{r}\left[\mathbf{p}\right]\right) = \langle\Omega Diag\left(|U\,|\varphi\rangle\,\langle\varphi|\,U|\right)\rangle, \tag{7}$$

using for the transformed MO's tensor product a symbol like: $|U\,|\varphi\rangle = \mathbf{U}\,|\varphi\rangle$ and the diagonal part of its direct product, coinciding with the trace of the involved hyperdiagonal matrices.

Therefore, the density function up to an arbitrary order can be formally associated to a diagonal coefficient representation, where the non-negative diagonal elements acquire the form of occupation numbers when dealing with first order. In second and superior orders, the diagonal coefficient hypermatrix remains real, but some of their elements can be negative, as occurs in the expression of the second order density function for a unique determinant in closed shells, where the Coulomb part has a coefficient structure which is twice the unity matrix and the exchange part can bear negative coefficients and has already a diagonal form.

It is easy to find out too that, in any case and order, the expressions (6) or (7) can be separated into three parts corresponding to pure Coulomb terms, mixed Coulomb-exchange and pure exchange terms. Coulomb terms will correspond to the set of possible indices $[\mathbf{i}] \rightarrow i_1 = i_2 = \dots i_p$ and the pure exchange to the contrary situation, where no index is coincident with the rest. This is important at the moment to obtain projected-condensed forms from the p-th order density and in this way generalized bond orders involving several molecular centers [7].

1.3 Pseudo-wave functions

In the same manner as it has been already discussed within the study of first order density functions [8–10], now for each p-th order density function there can be defined a pseudo-wave function:

$$\Psi^{(p)}\left(\mathbf{r}\left[\mathbf{p}\right]\right) = \sum \left[\mathbf{i}\right]\left(\omega\left(\left[\mathbf{i}\right]\right)\right)^{\frac{1}{2}}\left|U\right|\left[\mathbf{i}\right]\rangle, \tag{8}$$

which can also be written in compact form as a total sum:

$$\Psi^{(p)}\left(\mathbf{r}\left[\mathbf{p}\right]\right) = \left\langle \Omega^{\frac{1}{2}}\left|U\right|\varphi\right\rangle$$

Accepting that there is always a unitary transformation which permits the simplification of Eq. 3 into Eq. 6, this transformation can always be supposedly performed. This fact allows thus simplifying the notation and permits thus writing: $\left|\left[\mathbf{i}\right]\right\rangle \equiv \left|U\right|\left[\mathbf{i}\right]\rangle$, in order to ease the notation. The inward matrix product [6] of the pseudo-wave function (8) is able to reconstruct the parent density function:

$$\rho^{(p)}\left(\mathbf{r}\left[\mathbf{p}\right]\right) = \Psi^{(p)}\left(\mathbf{r}\left[\mathbf{p}\right]\right) * \left(\Psi^{(p)}\left(\mathbf{r}\left[\mathbf{p}\right]\right)\right)^{*}. \tag{9}$$

It can be said then that the p-th order pseudo-wave functions defined in this way generate the corresponding density function and one can formally write:

$$R\left(\Psi^{(p)}\left(\mathbf{r}\left[\mathbf{p}\right]\right) \rightarrow \rho^{(p)}\left(\mathbf{r}\left[\mathbf{p}\right]\right)\right).$$

It can be easily seen when the order coincides with the total number of particles of the system, N say, that then the pseudo-wave function (8) shall be coincident with the original wave function and the density (9) becomes the usual quantum mechanical definition of the squared module of the wave function:

$$\Psi^{(N)}\left(\mathbf{r}\left[\mathbf{N}\right]\right) = \Psi\left(\mathbf{r}\left[\mathbf{N}\right]\right) \wedge \rho^{(N)}\left(\mathbf{r}\left[\mathbf{N}\right]\right) = \left|\Psi\left(\mathbf{r}\left[\mathbf{N}\right]\right)\right|^{2} = \rho\left(\mathbf{r}\left[\mathbf{N}\right]\right).$$

1.4 Minkowski metric

Up to any order one can be interested not only in the density functions written as Eqs. (6) or (9), which have a well-defined Minkowski norm:

$$\int_{D} \rho^{(p)}\left(\mathbf{r}\left[\mathbf{p}\right]\right) dV^{(p)} = N^{(p)}$$

but into Minkowski normalized densities, belonging to the corresponding vector semi-space unit shell. They can be related one to another by a simple homothecy, a scale factor. When studying the first order densities Minkowski normalized on the number

of particles in order to distinguish them from their homothetic unit shell counterparts, these last ones are the called shape functions. Moreover, the Minkowski norm of the total particle density function coincides with the Euclidian norm of the wave function, as it is usually written in textbooks:

$$\int_D \rho\left(\mathbf{r}\left[\mathbf{N}\right]\right)dV = \int_D |\Psi\left(\mathbf{r}\left[\mathbf{N}\right]\right)|^2 dV = 1 \tag{10}$$

For this reason, from now on it will be supposed that the densities used are such that: $N^{(p)} = 1$, except when the contrary is needed and the function scaled to the proper Minkowski norm different from unity.

In the case of using the p-th order density form (9), the well-known property holds the same for Minkowski normalized densities and one can write:

$$\int_D \rho^{(p)}\left(\mathbf{r}\left[\mathbf{p}\right]\right)dV^{(p)} = \int_D \left|\Psi^{(p)}\left(\mathbf{r}\left[\mathbf{p}\right]\right)\right|^2 dV^{(p)} = 1,$$

an equality which indicates that the complete particle property (10) is extensible to any density order.

It is time too to indicate now that the density definition (9) generates a density hypermatrix as it is sufficient to consider the described form as the hyperdiagonal element of a density hypermatrix element:

$$\rho^{(p)}\left(\mathbf{r}\left[\mathbf{p}\right];\mathbf{s}\left[\mathbf{p}\right]\right) = \Psi^{(p)}\left(\mathbf{r}\left[\mathbf{p}\right]\right) * \left(\Psi^{(p)}\left(\mathbf{s}\left[\mathbf{p}\right]\right)\right)^*, \tag{11}$$

as it is customary for lower order density functions, see [1] for example. Where the new set of variables $\mathbf{s}\left[\mathbf{p}\right] = \{\mathbf{s}_I\left(I = 1, p\right)\}$ are equivalent to the particle coordinates, when dealing with diagonal terms, then: $\mathbf{r}\left[\mathbf{p}\right] = \mathbf{s}\left[\mathbf{p}\right]$, and the expression (11) becomes Eq. (9).

2 Quantum similarity measures

After establishing the previous formalism it is easy to define a weighted overlap similarity measure between two density functions, belonging to a pair of quantum systems A and B. For this purpose, one can suppose known a positive definite weighting operator, depending of two sets of particle coordinates, that is: $\Xi\left(\mathbf{r}\left[\mathbf{p}\right];\mathbf{s}\left[\mathbf{p}\right]\right)$, say. As the chosen operator is positive definite, it can be expressed as the module of another non-singular operator, for example:

$$\Xi\left(\mathbf{r}\left[\mathbf{p}\right];\mathbf{s}\left[\mathbf{p}\right]\right) = \left|\Theta\left(\mathbf{r}\left[\mathbf{p}\right];\mathbf{s}\left[\mathbf{p}\right]\right)\right|,$$

then the weighted quantum similarity measure in a Minkowski metric vector semispace can be formally expressed as the integral:

$$\left\langle \rho_A^{(p)} \middle| \Xi \middle| \rho_B^{(p)} \right\rangle$$
$$= \int_D \int_{D'} \left[\rho_A^{(p)} \left(\mathbf{r}\left[\mathbf{p}\right] \middle| \Xi \left(\mathbf{r}\left[\mathbf{p}\right]; \mathbf{s}\left[\mathbf{p}\right] \right) \right)^2 \rho_B^{(p)} \left(\mathbf{s}\left[\mathbf{p}\right] \right) \right]^{\frac{1}{2}} dV^{(p)} dV'^{(p)}.$$

The representation of a weighted Minkowski scalar product [9,10], which taking into account the expression of the pseudo-wave functions (8), associated to any density matrix order by means of Eq. (9), allows that the quantum similarity measure can be made equivalent to a weighted Euclidian product of pseudo-wave functions:

$$\left\langle \rho_A^{(p)} \middle| \Xi \middle| \rho_B^{(p)} \right\rangle = \left(\Psi_A^{(p)} \middle| \Xi \middle| \Psi_B^{(p)} \right)$$
$$= \int_D \int_{D'} \left[\Psi_A^{(p)} \left(\mathbf{r}\left[\mathbf{p}\right] \right) \right]^* \middle| \Theta \left(\mathbf{r}\left[\mathbf{p}\right]; \mathbf{s}\left[\mathbf{p}\right] \right) \middle| \Psi_B^{(p)} \left(\mathbf{s}\left[\mathbf{p}\right] \right) dV^{(p)} dV^{(p)}.$$

Using now expression (8) the quantum similarity measure can be written as:

$$\left\langle \rho_A^{(p)} \middle| \Xi \middle| \rho_B^{(p)} \right\rangle = \left(\Psi_A^{(p)} \middle| \Xi \middle| \Psi_B^{(p)} \right)$$
$$= \sum_{[\mathbf{i}]} \sum_{[\mathbf{j}]} \left[(\omega_A\left([\mathbf{i}]\right))^{\frac{1}{2}} \right]^* (\omega_B\left([\mathbf{j}]\right))^{\frac{1}{2}} \langle [\mathbf{i}]; A | \Xi | B; [\mathbf{j}] \rangle \qquad (12)$$

where the signs of the square roots of the density coefficient hyperdiagonal matrix are taken to be positive, a situation which is chosen to simplify the pseudo-wave function definition and make it easily reproducible for any case. The problem reduces to the evaluation of a hypermatrix representation of the weight operator in the basis sets of MO's of systems A and B: $\mathbf{X}_{AB} = \{ \langle [\mathbf{i}]; A | \Xi | B; [\mathbf{j}] \rangle \}$. When both systems coincide, $A = B$, then the corresponding hypermatrix $\mathbf{X}_{AA}$ is positive definite and the integral leads to a quantum self-similarity measure. If the square roots of the diagonal density coefficients are collected into the hypervectors $\mathbf{w}_A \wedge \mathbf{w}_B$ respectively, then the quantum similarity measure (12) can be expressed as a complete sum of inward matrix products like:

$$\left\langle \rho_A^{(p)} \middle| \Xi \middle| \rho_B^{(p)} \right\rangle = \langle \mathbf{w}_A^* * \mathbf{X}_{AB} * \mathbf{w}_B \rangle = \langle (\mathbf{w}_A^* \otimes \mathbf{w}_B) * \mathbf{X}_{AB} \rangle.$$

3 Conclusions

Under a complete general framework, where nested summation symbols are the basic tools employed, density functions can possess a simplified form in terms of a diagonal coefficient matrix. This serves to set up a general pseudo-wave function scheme attached to any p-th order density function. Finally, both developments allow defining in a new way a set of weighted similarity measures within Minkowski metric semispace formalism.

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