

On the definition of the effectively unpaired electron density matrix: A similarity measure approach

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Abstract

The mathematical concepts of similarity and distance in metric spaces are used to relate Takatsuka et al. and Head-Gordon definitions of the effectively unpaired electron density matrix. This approach opens the possibility of new suitable definitions of this quantity to given purposes.

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The effectively unpaired electron density matrix, or odd electron density matrix, was proposed a long time ago as an appropriate tool to describe the occupancy of different portions of space by spin-up and spin-down electrons [1,2]. Subsequently, this matrix also was used in studies of statistical population analyses to determine the distribution of holes in many-electron systems [3,4]. More recently, the effectively unpaired electron density matrix has aroused the interest of several authors which have studied the mathematical features of this device and its relationships with other quantities [5–8]. From a practical point of view, this matrix presents the interest of being a suitable tool to measure the extent of the radical and diradical character in molecular species [9], to calculate electronic densities in molecules [10] as well as to perform other applications related with the determination of bond orders in molecular structure [11–13].

The definition of the effectively unpaired electron density matrix u , or simply u matrix, is not unique. Two different approaches have been reported; that originally proposed by Takatsuka et al. [1,2] and that more recently reformulated by Head-Gordon [7]. Although both approaches and

their corresponding results have already been discussed [14,15], in this letter we show that the two definitions can be derived from the mathematical concepts *similarity* and *distance* in metric spaces. The procedure allows us to achieve a better relationship between the two definitions, pointing out that each of them arises from a determined metric of a space. For that goal, we show that the u matrix is a similarity measure [16,17], that is, a function of a particular distance metric [18].

Let us begin by considering the mathematical concepts of *distance* and *similarity* measures. As is well-known, a real valued function d is defined as a *distance* measure between two elements x and y in a metric space M if the following properties are fulfilled: $d(x,y) \geq 0$; $d(x,x) = 0$; $d(x,y) = d(y,x)$ (symmetry) and $d(x,z) \leq d(x,y) + d(y,z)$ (triangle inequality) [18]. Complementary to the idea of distance is the concept of *similarity* [16,17]. Its measure is estimated by means of a real valued function s fulfilling the properties: $0 \leq s(x,y) \leq 1$; $s(x,x) = 1$ and $s(x,y) = s(y,x)$ [16,17], which quantifies the number of matches between some qualitative or quantitative features of two given objects, whereas the distance measures the ‘difference’ between them. The use of similarities instead of distances requires to consider some specific functional relationships between s and d [16,17]. According to these ideas, we will show the relationships between the two above mentioned

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formulations for the effectively unpaired electron density matrix.

The original definition of the effectively unpaired electron density matrix expresses the deviation from the idempotency of the spin-free one-particle reduced density matrix 1D (1-RDM) [1] of a given state function, and thus is formulated as

$$u = 2{}^1D - {}^1D^2. \quad (1)$$

Because the spin-free one-hole reduced density matrix ${}^1\bar{D}$ (1-HRDM) is related to the 1-RDM by means of the averaged fermionic anticommutation relation [4]

$${}^1D + {}^1\bar{D} = 2I, \quad (2)$$

where I stands for the identity matrix, this u matrix may be written in an alternative form as the product of 1-RDM and the 1-HRDM [4] matrices, given by

$$u = {}^1D{}^1\bar{D}. \quad (3)$$

For a more detailed analysis of the properties and applications of the u matrix defined by Eq. (1) see Refs. [5,6]. To make simpler the comparison between the two definitions of the u matrix, we will use the natural orbital basis set in which all these matrices are diagonal. Thus, Eqs. (1) and (3) are written as

$$u_i = n_i\bar{n}_i = 2n_i - n_i^2 \quad (4)$$

or in a more adequate expression to our aims

$$u_i = 1 - (n_i - 1)^2 = 1 - \frac{(n_i - \bar{n}_i)^2}{(n_i + \bar{n}_i)^2}, \quad (5)$$

where n_i and \bar{n}_i stands for the i th eigenvalue (population) of the 1D and ${}^1\bar{D}$ matrices, respectively, and the relation $n_i + \bar{n}_i = 2$ is fulfilled by all orbitals (cf. Eq. (2)). The values of u_i range from $u_i = 0$ (for $n_i = 0$ and $n_i = 2$, closed shell character) to $u_i = 1$ (for $n_i = 1$, radical character), revealing its physical meaning [4,14]. The term $\frac{(n_i - \bar{n}_i)^2}{(n_i + \bar{n}_i)^2}$ may be regarded as a *normalized* partial distance d_i between the particle population n_i and the hole population \bar{n}_i (cf. the properties required for such quantities as mentioned at the beginning of this Letter). Hence, Eq. (5) expresses partial similarities s_i [16], where the specific functional relationship between s_i and d_i is given by $s_i = 1 - d_i$. Consequently, the elements of the u matrix are partial similarities between particle and hole populations, and may be equated as $u_i = s_i$.

In the Head-Gordon formulation [7], the effectively unpaired electron density matrix is defined as

$$u_i = \min(n_i, 2 - n_i), \quad (6)$$

which is a linear interpolation between the above mentioned points $n_i = 0$, $n_i = 1$ and $n_i = 2$. This equation can be reformulated as

$$u_i = 1 - |n_i - 1| = 1 - \frac{|n_i - \bar{n}_i|}{|n_i + \bar{n}_i|}. \quad (7)$$

The term $\frac{|n_i - \bar{n}_i|}{|n_i + \bar{n}_i|}$ may be regarded again as a *normalized* partial distance between the particle population n_i and the hole

population \bar{n}_i although, in this case, a different criterion to define the *distance* has been used. Therefore, both definitions proposed for the u matrix only differ in the metric used to describe them. In the case of the u matrix expressed by Eq. (5), the metric may be recognized as of *divergence type* whereas the definition of Head-Gordon (Eq. (7)) corresponds to one of *Bray/Curtis type* [16,17]. Hence, it may be concluded that both representations of the u matrix are coming from different similarity measures associated with different metrics of distance. These partial similarities that correspond to each natural orbital indicate how similar, in the population sense, are both particle and hole distributions. Analogously, the total similarity between particle and hole population distributions, which is defined by the trace of the u matrix

$$s = \text{tr}(u) = \sum_i u_i \quad (8)$$

may be interpreted as a global measure of the ‘overlap’ between the particles and holes clouds, revealing their physical separability/non-separability. Thus, for non-correlated closed shell state functions each term of Eq. (8) is zero and so is s , which indicates the perfect separability of the clouds.

Finally, it is worthwhile to note that the above described relationship between both definitions for the u matrix, which only differ in how the distance between the particle and hole distributions is measured, suggests that other mathematical definitions retaining the physical meaning of this quantity are possible for specific purposes choosing different distance metrics. Thus, for example, it may be suggested to formulate the u matrix as $u_i = \Delta(n_i)\Delta(\bar{n}_i)$, with $\Delta(x)$ defined as a ‘step’ function with $\Delta(x) = 1$ for $x > 0$ and 0 otherwise. This new definition which also emphasizes closed shell character around $n_i = 0$ and $n_i = 2$ and radical character around $n_i = 1$, might also be derived from a distance metric defined by $d(x, y) = 1 - \Delta(|x|)\Delta(|y|)$, where $|\cdot|$ means absolute value. In this case, u_i is uniformly distributed with value $u_i = 1$ for $0 < n_i < 2$ and consequently the radical character may not be properly appreciated. Hence, in practice the distance metrics must only be regarded as feasible if they predict reasonable chemical results.

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