

## On density function coordinate matrix

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Received: 20 November 2012 / Accepted: 26 April 2013 / Published online: 7 May 2013  
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**Abstract** The present letter presents a short discussion about the misleading name associated to a matrix, connected to (first order) density functions defined in turn within the LCAO-MO framework, which is widespread in quantum chemistry. The author proposes to call such a matrix form with the logical name of: *density function coordinate matrix*.

**Keywords** Density function · Density matrix · Density function coordinates · Density function coordinate matrix · LCAO-MO · Basis sets · Charge and bond order matrix

Sir,

When constructing the first order density functions in LCAO-MO theory, a basis set is previously defined:  $B = \{\chi_\mu(\mathbf{r}) \mid \mu = 1, N\}$ , which could be formed by AO or optimized functions, usually Gaussian type orbitals. The usual involved basis set elements are functions of the vector  $\mathbf{r}$ , the one electron coordinates. The tensor product of this initial basis set:

$$B \otimes B = \{\chi_\mu(\mathbf{r}) \chi_\nu^*(\mathbf{r}) \mid \mu, \nu = 1, N\}$$

it is also needed, because its elements can now be considered the basis set to build the first order density function in this way:

$$\rho(\mathbf{r}) = \sum_\mu \sum_\nu D_{\mu\nu} \chi_\mu(\mathbf{r}) \chi_\nu^*(\mathbf{r}). \quad (1)$$

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The matrix elements  $\{D_{\mu\nu}\}$ , can be calculated by using the matrices:  $\mathbf{D}_I = \mathbf{c}_I \mathbf{c}_I^\dagger = \{D_{I;\mu\nu} = c_{\mu;I} c_{\nu;I}^*\}$  which are calculated from the tensor product of the column vectors:  $\{\mathbf{c}_I = [c_{\mu I} | \mu = 1, N]\}$ , acting in turn as the coordinates of each MO  $\psi_I(\mathbf{r})$ , when it is expressed with respect to the basis set B:

$$\psi_I(\mathbf{r}) = \sum_{\mu} c_{\mu;I} \chi_{\mu}(\mathbf{r}); \quad (2)$$

Then, the density function can be alternatively expressed as:

$$\rho(\mathbf{r}) = \sum_I \omega_I \psi_I(\mathbf{r}) \psi_I^*(\mathbf{r}), \quad (3)$$

where  $\{\omega_I | I = 1, M\}$  is a set of scalars symbolizing the MO occupation numbers. Equations (1) to (3) lead to the definition of the matrix:

$$\mathbf{D} = \sum_I \omega_I \mathbf{D}_I. \quad (4)$$

The matrix (4) is currently called in the literature *density matrix*. Such naming of the matrix in Eq. (4) is quite misleading. This is so because, after the first description of Löwdin in a well-known paper [1], the so-called **density matrix** corresponds to the density function, expressed as (1) or (3) but assigning two different variables to each of the tensor function pairs, that is:

$$\rho(\mathbf{r}, \mathbf{r}') = \sum_{\mu} \sum_{\nu} D_{\mu\nu} \chi_{\mu}(\mathbf{r}) \chi_{\nu}^*(\mathbf{r}'). \quad (5)$$

The density function (1) can be associated to the diagonal elements of the density matrix (5) or might be alternatively considered also constructed by means of an integral involving a Dirac delta function, as follows:

$$\rho(\mathbf{r}) = \int_D \delta(\mathbf{r} - \mathbf{r}') \rho(\mathbf{r}, \mathbf{r}') d\mathbf{r}'.$$

The obvious fact which appears when calling both mathematical objects: the two electron function  $\rho(\mathbf{r}, \mathbf{r}')$  and the  $(N \times N)$  matrix  $\mathbf{D}$  as “density matrices” appears quite confusing to the present author and no wonder if both to students and researchers in the field too.

In several works where density functions have been discussed, see for example references [2–5], the term “charge and bond order matrices” has been employed in order to avoid the confusion. However, some referees didn’t agree on calling in this way the matrix  $\mathbf{D}$ . They reasonably argued that this name was appropriate in old quantum chemical papers, dealing with primitive LCAO-MO theoretical procedures, where the number of atoms and the dimension of the basis set B were coincident.

Certainly, although the name of old procedures was kept in order to differentiate and preserve the diverse nature of the two mathematical objects defined in Eqs. (4) and (5), the present author feels that some better and logical terminology might be applied to this elementary but important question.

Such nomenclature prospect can be easily developed observing again Eq. (1). There, one can easily admit that the density function defined in this way can be considered as a vector of some Hilbert space, constructed using a linear combination of the elements of tensor basis set:  $B \otimes B$ , and whose coefficients are given in turn by the elements of the matrix  $\mathbf{D}$ .

Therefore, one can easily realize the elements of the matrix  $\mathbf{D}$  act as *coordinates* of the density function when it is expressed as a vector with respect to the tensor basis set:  $B \otimes B$ .

Thus, it seems natural to propose renaming matrix  $\mathbf{D}$  as: *density function coordinates matrix*<sup>1</sup>. Such brand new name will obviously eliminate the ambiguous density matrix terminology.

## References

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<sup>1</sup> They can be also associated to a second rank *tensor*, but the term matrix might be more appropriate.