J Math Chem (2011) 49:836–842
DOI 10.1007/s10910-010-9780-5

ORIGINAL PAPER

Mathematical aspects of the LCAO MO first order density function (4): a discussion on the connection of Taylor series expansion of electronic density (TSED) function with the holographic electron density theorem (HEDT) and the Hohenberg-Kohn theorem (HKT)

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Received: 15 October 2010 / Accepted: 18 November 2010 / Published online: 3 December 2010

Abstract Taylor series expansion of electronic density (TSED) functions are set up in order to propose them as an alternative description of the holographic electron density theorem (HEDT) functions. The manipulation of the obtained TSED general formulation leads to a connection between TSED, HEDT and Hohenberg-Kohn theorem (HKT).

Keywords Taylor series of electronic density (TSED) · Holographic electron density theorem (HEDT) · Hohenberg-Kohn theorem (HKT)

1 Introduction

In a series of works related to electronic density functions (DF) [1–21] it has been analyzed during the last decade several aspects of such functions in our laboratory. More recently, the development of several studies related with modern aspects of quantum similarity [22–33], has put forward the possibility to connect HEDT [34–37] with the Taylor series of electronic density (TSED) functions [20]. A recent paper has also put forward the holographic nature of Gaussian functions [21] as an extra appealing aspect of the problem connecting HEDT and TSED. As GTO are the usual basis functions employed as basis set functions in modern LCAO MO theory, it seems worth to further study the role of TSED and his connection with HEDT. In this paper TSED will be essentially set up as the background theory to construct the DF variation at any point of space. As a consequence of this analysis, one can easily establish the connection between TSED, HEDT and Hohenberg-Kohn theorem (HKT) [38].

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2 General notation and definitions

Suppose any electronic density function (DF): $\rho(\mathbf{r}|\mathbf{R}) \equiv \rho(\mathbf{r})$, where $\mathbf{R}$ in the usual Born-Oppenheimer approach are parameterized atomic coordinates in a given configuration for a known molecule, and $\mathbf{r}$ the electron coordinates.

In modern times within LCAO MO theory, whatever the theoretical framework which is used to arrive to a DF computational form, a general DF expression can be employed:

$$\rho(\mathbf{r}) = \sum_{\mu}\sum_{\nu} D_{\mu\nu} |\mu\rangle \langle\nu| \tag{1}$$

where: $\{|\mu\rangle\}$ is a set of *smooth* basis functions, usually GTO. In this context, smooth functions also refer to the so-called *entire* functions. Entire functions are those which are equivalent to its Taylor series expansion in the whole space. Such function kind, like GTOs are, possesses a convergent series and inherits good properties related to differentiability, derivability and integrability. In Eq. (1), $\mathbf{D} = \left\{D_{\mu\nu}\right\}$ is the charge and bond order matrix, defined by means of the MO occupations: $\{\omega_I\}$ and the MO set itself: $\{|I\rangle\}$, constructed in turn, as linear combinations of the basis set functions and the MO coefficients $\mathbf{C} = \left\{c_{\mu I}\right\}$ matrix:

$$|I\rangle = \sum_{\mu} c_{\mu I} |\mu\rangle .$$

Then the DF can be also written in terms of the MO set:

$$\rho(\mathbf{r}) = \sum_{I} \omega_I |I\rangle \langle I|;$$

moreover, when constructing the LCAO coefficient matrix: $\mathbf{C} = (|\mathbf{c}_1\rangle, |\mathbf{c}_2\rangle, \ldots |\mathbf{c}_I\rangle, \ldots)$, in terms of the column set: $\{|\mathbf{c}_I\rangle\}$, then one can construct the charge and bond order matrix in terms of these columns:

$$\mathbf{D} = \sum_{I} \omega_I |\mathbf{c}_I\rangle \langle\mathbf{c}_I| .$$

3 Auxiliary definitions and Taylor series

In general, here it is considered the Taylor series expansion of an exact non relativistic DF. In this case, an exact non relativistic DF can be expressed as a unique function, that is: being by itself a basis function. Equation (1) can be considered either an infinite LCAO expansion which can be considered equivalent to the exact DF case, or one can also deal with approximate DFs, which can be expressed in the same way but with finite summations, as it is the case in modern practical atomic and molecular calculations.

In any case, in order to construct the corresponding Taylor series, there is handy to define two simple mathematical elements. First, the tensorial p-th order product of any vector $\mathbf{r}$ say, using the notation:

$$\bigotimes_{k=1}^{p} [\mathbf{r}] = \mathbf{r} \otimes \mathbf{r} \otimes \mathbf{r} \cdots \otimes \mathbf{r}$$

Second, one must define somehow a p-th rank tensor containing as elements the p-th order derivatives of the DF computed at some specific point $\mathbf{t}$; which will be noted by: $\partial^p \rho\,(\mathbf{t})$. Such p-th derivative tensors become well-defined at any point, because of the smoothness of the basis set functions one can choose, which can be employed in turn within the DF definition according to Eq. (1).

With these definitions in mind, then the DF Taylor series at a point $\mathbf{t}$ can be given by an elegant and compact expression, which has some similar structure to the well-known monovariate expansion:

$$\rho\,(\mathbf{r}) = \rho\,(\mathbf{t}) + \sum_{p=1}^{\infty} \frac{1}{p!} \left\langle \bigotimes_{k=1}^{p} [\mathbf{r} - \mathbf{t}] * \partial^p \rho\,(\mathbf{t}) \right\rangle. \tag{2}$$

In the Eq. (2) above, the whole bracket symbol stands for the complete sum of the inward product of both tensors.

An inward tensor product of two tensors of the same rank, followed with a complete sum of the resultant tensor elements, may be alternatively written using Einstein convention as the scalar: $\gamma = a^{ijk\cdots p} b_{ijk\ldots p}$.

Another notation has been employed here in order to obtain a general TSED expression, which can be easily related with the usual Taylor series for univariate functions. In fact, every term in the TSED in Eq. (2) can be also seen as a scalar product between two mathematical objects considered as vectors belonging to vector spaces of the same dimension, schematically:

$$\forall \mathbf{a} = \{a_I\} \wedge \mathbf{b} = \{b_I\} \in V_p : \langle \mathbf{a} * \mathbf{b} \rangle \equiv \langle \mathbf{a} | \mathbf{b} \rangle = \sum_I a_I b_I.$$

4 The TSED series in the neighborhood of a point and the variation of a DF

When Eq. (2) is developed around a point and nearby the point $\mathbf{r}$ itself; that is, whenever one can write: $\mathbf{t} = \mathbf{r} - \delta\mathbf{r}$, being $\delta\mathbf{r}$ a neighborhood of $\mathbf{r}$, then one can also rewrite Eq. (2) as:

$$\rho\,(\mathbf{r}) = \rho\,(\mathbf{r} - \delta\mathbf{r}) + \sum_{p=1}^{\infty} \frac{1}{p!} \left\langle \bigotimes_{k=1}^{p} [\delta\mathbf{r}] * \partial^p \rho\,(\mathbf{r} - \delta\mathbf{r}) \right\rangle,$$

which one can rearrange to produce the variation of the DF at this point as follows:

$$\delta\rho\left(\mathbf{r}\right)=\rho\left(\mathbf{r}\right)-\rho\left(\mathbf{r}-\delta\mathbf{r}\right)=\sum_{p=1}^{\infty}\frac{1}{p!}\left\langle\bigotimes_{k=1}^{p}\left[\delta\mathbf{r}\right]*\partial^{p}\rho\left(\mathbf{r}-\delta\mathbf{r}\right)\right\rangle. \tag{3}$$

In order to obtain a more elegant and simpler expression, deducible from Eq. (3), without excessive error one can suppose:

$$\partial^{p}\rho\left(\mathbf{r}-\delta\mathbf{r}\right)\cong\partial^{p}\rho\left(\mathbf{r}\right),$$

thus, in this manner it can be also written a general compact form for the DF variation in the neighborhood of a point $\mathbf{r}$:

$$\delta\rho\left(\mathbf{r}\right)\cong\sum_{p=1}^{\infty}\frac{1}{p!}\left\langle\bigotimes_{k=1}^{p}\left[\delta\mathbf{r}\right]*\partial^{p}\rho\left(\mathbf{r}\right)\right\rangle. \tag{4}$$

However, the terms of higher order, that is with: $p\geq 3$, will become irrelevant in Eq. (4), because of the infinitesimal nature of $\delta\mathbf{r}$, then one can also reasonably and safely write:

$$\delta\rho\left(\mathbf{r}\right)\cong\left\langle\delta\mathbf{r}\right|\partial\rho\left(\mathbf{r}\right)\left\rangle+\frac{1}{2}\left\langle\delta\mathbf{r}\right|\partial^{2}\rho\left(\mathbf{r}\right)\left|\delta\mathbf{r}\right\rangle+O\left(3\right). \tag{5}$$

In Eq. (5) no position coordinate vector is preferent, thus the DF variation expression above becomes valid for *any* vector $\mathbf{r}$ in position space. Moreover, the previous equation shows that in a neighborhood of any point, the DF variation becomes known with sufficient accuracy, whenever first (gradient vector) and second order (Hessian matrix) derivatives are well defined at this point.

Extremum points $\mathbf{r}^{(*)}$ possess a null gradient, therefore Eq. (5) simplifies in this case to just a second order expression involving the Hessian matrix only, therefore Eq. (5) can be written:

$$\delta\rho\left(\mathbf{r}^{(*)}\right)\cong\frac{1}{2}\left\langle\delta\mathbf{r}^{(*)}\right|\partial^{2}\rho\left(\mathbf{r}^{(*)}\right)\left|\delta\mathbf{r}^{(*)}\right\rangle+O\left(3\right).$$

It can be concluded that the present TSED result becomes equivalent to the HEDT: it is also expressed in a general way and possesses a well-defined simple equation attached to every point in position space.

As a consequence, it can be said: *TSED is an alternative definition of HEDT consisting into the fact that, at the neighborhood of any point* $\mathbf{r}$, *the DF variation can be known with sufficient accuracy, provided the DF gradient vector and Hessian matrix at* $\mathbf{r}$.

In fact, taking into consideration the complete expression (2), TSED constitutes a *recipe* to obtain or reproduce the whole DF from the knowledge of the information in a neighborhood of an analytical point $\mathbf{t}$. This property goes beyond the HEDT in

the sense that less information is needed than in HEDT, as this theorem requires the complete knowledge of a finite region around the point **t**, and that no practical formula to reproduce the entire DF is provided. HEDT is a theorem of existence, but provides no rule in order to re-construct the DF from the primary information available, as appears to be the case in the TSED context.

Compared to HEDT, TSED approach has the advantage to explicitly provide a mathematical recipe which permits to express the whole DF. It has to be recognized in practice that the implemented expansion must be finite to become feasible. So, the density function will not be reproduced exactly in many points, especially at the singularities. At best, and upon conditions of convergence, the series will give the same accuracy as the machine precision which implements it, as it is customary in such numerical computational framework. In any case, the proposed point of view permits to compute, within some accuracy, which will depend on many circumstances, DF values at points which are far away from the expansion point.

5 Some remarks

The TSED result, as stated above in Eq. (5), appears in good agreement with Bader's basic ideas about the role of first and second derivatives of the DF, which he has been proposing in order to put in evidence atoms in molecules and the topology of chemical bonds [39]; furthermore, see also reference [40] for a recent review of Bader's theoretical insight. Although some controversy has issued from the general interpretation of Bader's point of view [41–44], the basic background of his original theoretical description still can be related to the present findings.

Also, the present results are consistent with the previously studied fact of considering the DF gradient as a source of curved Riemannian coordinates in molecular spaces, while the Hessian matrix could be associated to the so-called Jacobi curvature [13,26].

On the other hand, more than a decade ago, Sen and the present authors [3] have analyzed HKT from several perspectives, among them a perturbation theory point of view. As a consequence of such a discussion within the framework of perturbation theory, these authors found that, an equivalent matrix representation was connecting the first order density variation with the first order Hamiltonian variation. They proposed that this fact could be considered as an alternative formulation of HKT. Such a result is also consistent with a theorem involving non-commuting Hermitian matrices [45], which constitutes the finite dimensional formulation, equivalent to HKT.

In the present discussion it has been shown that DF variation can be obtained at every point of space, just considering known the DF gradient and Hessian, constituting such a DF property an alternative complement and an ancillary reformulation of HEDT. Therefore, one can conclude that HEDT and HKT are facets of the some intrinsic mathematical structure properties, which can be attached to any electronic DF.

Finally, the authors want to make explicit that the present TSED outlined approach covers two aspects. The first one can be associated to an alternative demonstration of a HEDT-like theorem, dealing with the exact non relativistic DF. In general, such a DF

has not to be made explicit, in the same manner as in the HEDT original formulation [34]. The second aspect which one can stress deals with the possibility to explicitly construct the DF from available reduced information with the help of the TSED recipe. Despite this approach may present restrictions on accuracy in practical computational applications, in HEDT this possibility do not explicitly appears. Thus, in some manner TSED complements the HETD formulation.

6 Conclusion

TSED, HEDT and HKT can somehow be considered corollaries of the metrical, analytical and topological structure of the electronic DF.

Acknowledgments This work has been partially sponsored by the Spanish Ministry of Educación y Ciencia under the grant reference: CTQ2009-09370. The authors are sincerely grateful to the referees because their comments improved many aspects of the initial manuscript.

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