

# Stereographic Projection of Density Functions (DF) and the Holographic Electronic Density Theorem (HEDT)

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**ABSTRACT:** Mezey's holographic electronic density theorem is discussed from the point of view of stereographic projection techniques. Such a mathematical procedure is analyzed in depth from the point of view of first-order density functions; the procedure is then extended to any relevant quantum chemical function. This endeavor provides the background to construct a Holographic General Function Theorem (HGFT) for multivariate well-behaved functions. Stereographic projections, applied first as a way to obtain pictures of molecular quantum chemical functions, are shown to provide a flexible and original vantage point for visualizing, from any location and any chosen perspective, the form of any well-behaved function, irrespective of the number of variables involved. The pictographic possibilities of the HGFT are explored and exploited in several examples.

## INTRODUCTION

Since the publication of the Holographic Electronic Density Theorem (HEDT) by Mezey,<sup>1</sup> a large amount of interest has been developed on the imaginable applications of such a remarkable feature of electronic density functions (DF). However, as far as the authors know, there have been no published clues about the practical application of the HEDT as a way to represent DF, except in a few cases related to molecular quantum similarity stereoisomer studies<sup>2–5</sup> or other fields.<sup>6</sup> On the other hand, the present authors have tried to develop different points of view about the nature and alternatives of HEDT by emphasizing (a) the role of Gaussian functions as carriers of holographic properties,<sup>7</sup> (b) the HEDT relationship with quantum similarity measures,<sup>8</sup> and (c) the connection of HEDT with both DF Taylor series and the Hohenberg–Kohn theorem,<sup>9</sup> a problem that was earlier studied by Mezey.<sup>10</sup> Moreover, when describing a modern résumé of the mathematical background developed for quantum similarity purposes, the holographic nature of the unit shell in vector semispaces has been put into evidence.<sup>11</sup>

When analyzing the extensive literature generated by the HEDT in order to build up these previous studies, it was apparent that algorithmic applications of HEDT have been elusive. One exception is the related holographic principle, which Mezey<sup>12</sup> has associated with latent molecular properties. Nevertheless, many types of structures of the observable universe can be studied with holographic frameworks,<sup>13–17</sup> and therefore holographic features must be somehow employed as a viewing platform to understand and represent observable properties like DF and other quantum chemical functions.

Similar holographic features have been found in other physical domains, for example, condensed matter,<sup>18</sup> superfluidity and superconductivity,<sup>19</sup> and many body physics.<sup>20</sup> Also, it has been recently established that the phenomenological inclusion of particle size reveals the existence of nanoparticle holographic properties. This last outcome has been described within another line of work of the present authors, also related with quantum similarity: quantum quantitative structure–property relationships (QSPR). When QSPR models are properly

adapted to nanotechnology results and data, thus transforming into *nano-QSPR*, the compulsory inclusion of a model term including particle size suggests the holographic nature of nanoparticle behavior.<sup>21</sup>

Studying carefully the HEDT formulation, which was originally intended for the treatment of possible local nonanalyticities (cf. Mezey's paper), it is immediately obvious that the main HEDT proof argument is essentially based on a schematic stereographic projection of the DF. (See Figure 1 of ref 1 to visualize this HEDT aspect.) Although for properties other than electronic density, a similar treatment may require additional steps, the present authors wondered if a representation based on the holographic theorem could provide an easily implemented graphical tool. We also wondered whether HEDT might be extended to provide a new way to view not only such important quantum chemical objects as DF but also electrostatic molecular potentials (EMP)<sup>22</sup> or any other quantum chemical function of interest.<sup>23–27</sup> The present paper explores this possibility.

Following the previously mentioned research paths and Mezey's HEDT original ideas, in the present study it is proposed to set up a *holographic general function theorem* (HGFT) which encompasses HEDT and relates well-behaved functions to holograms, which then become the basic logical structure. HGFT frames in a broad manner the holographic nature of functions, which can be associated with observables from any domain of physical sciences, although we emphasize quantum chemistry functions.

In this paper, first, DF and shape functions (ShF) originally defined by Parr and Bartolotti<sup>28</sup> will be briefly defined to set up the symbols and mathematical background. Afterward, the concept of extended DF and ShF spaces will be settled. Next, the general structure of function extended spaces will be described for any dimension. Stereographic projections in function extended spaces will be described afterward, and the HGFT will be stated. Remarks on practical questions follow. Examples

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involving a spherical GTO and the simplest form of a hydrogen DF are used to elucidate the main ideas, followed by practical illustrations of the stereographic representation for DF pictures from a number of selected molecular structures within the so-called ASA framework.<sup>29–31</sup> Additional illustrative examples are available on a dedicated Web site.<sup>32</sup>

## ■ DENSITY FUNCTIONS (DF) AND SHAPE FUNCTIONS (ShF)

ShF,<sup>28</sup>  $\sigma(\mathbf{r})$ , can be simply defined from any arbitrary one-electron DF,  $\rho(\mathbf{r})$ , in any of the following ways:

$$\forall \rho(\mathbf{r}): \langle \rho \rangle = \int_D \rho(\mathbf{r}) d\mathbf{r} = N \rightarrow \sigma(\mathbf{r}) = N^{-1} \rho(\mathbf{r}) = \langle \rho \rangle^{-1} \rho(\mathbf{r}) \quad (1)$$

where  $N$  is the number of electrons and the integral represented by the symbol  $\langle \rho \rangle$  is the Minkowski norm of the DF  $\rho(\mathbf{r})$ . Because of the definition contained in eq 1, a ShF like  $\sigma(\mathbf{r})$  behaves as a probability distribution:

$$\forall \sigma(\mathbf{r}): \langle \sigma \rangle = \int_D \sigma(\mathbf{r}) d\mathbf{r} = 1 \wedge \int_{d \subseteq D} \sigma(\mathbf{r}) d\mathbf{r} \in [0, 1]$$

Thus, the ShF can be interpreted as the probability for an electron to be located in three-dimensional position space within a given volume element  $d$ .

ShF can be generalized into volume functions within the scope of quantum similarity measures;<sup>33</sup> also they can be straightforwardly extended in connection with higher order DF.

## ■ DF AND SHF EXTENDED SPACES

The ordered pair made by a three-dimensional Euclidean space position vector  $\mathbf{r} \in E_3(\mathbf{R})$  and the value of a known DF or ShF at this point:

$$\mathbf{p} = (\mathbf{r}, \rho(\mathbf{r})) \vee \mathbf{s} = (\mathbf{r}, \sigma(\mathbf{r})) \in C_4(\mathbf{R}) \quad (2)$$

can be considered as an extended point associated within some four dimensional real space  $C_4(\mathbf{R})$ , where the fourth coordinate corresponds to the function value at the considered position provided by the first vector part. Such a construct can be seen as a kind of special hybrid Cartesian product of the Euclidean space with a functional space  $F_\infty(\mathbf{R})$ :

$$C_4(\mathbf{R}) = E_3(\mathbf{R}) \times F_\infty(\mathbf{R})$$

possessing in addition the structure of a vector space, as one can sum and multiply by a scalar the elements of  $C_4(\mathbf{R})$  in the customary way, but under some new axiomatic rules, proving in this manner that its elements comply with the associated usual properties of these operations in vector spaces. We will call such hybrid vector spaces *function extended spaces*.

## ■ GENERAL FUNCTION EXTENDED SPACES OF ANY DIMENSION

Four-dimensional function extended spaces like the previously described ones can also be constructed when considering any well-behaved function of the three-dimensional Euclidean position coordinates,  $\gamma(\mathbf{r})$ . Then, in general, the function extended vector space  $C_4(\mathbf{R})$  can be made of vectors like

$$\mathbf{w} = (\mathbf{r}, \gamma(\mathbf{r})) \in C_4(\mathbf{R})$$

Furthermore, the non-negative nature of the DF and the associated ShF makes the fourth vector coordinate non-negative. However, this restriction is not generally required for

function extended spaces. It is only necessary that the function values that define the fourth coordinate be continuous.

## ■ STEREOGRAPHIC PROJECTIONS IN FUNCTION EXTENDED SPACES

The restriction to three-dimensional position spaces and consequently four dimensional function extended spaces is justified as a result of our primary aim to describe stereographic projections on first order DF and the attached ShF. However, this is not a limiting property of these spaces but a particular feature arising from our interest in electronic DF.

However, the position coordinates of function extended spaces do not need to be restricted to three-dimensional Euclidean spaces. For well-behaved functions of  $n$  variables, the function extended space can be defined as being made of extended vectors with  $n + 1$  dimensions.

Because of this, function extended spaces like  $C_4(\mathbf{R})$  can be considered as a particular form of a general  $C_{n+1}(\mathbf{R})$  vectorial structure, which can be constructed as the hybrid Cartesian product of an Euclidian  $n$ -dimensional space with a function space containing vectors, constructed in turn by functions of  $n$ -dimensional variables.

Thus, it is elementary to generalize stereographic projections from a function extended space of  $(n + 1)$  dimensions, using the same symbols as the ones used in the equations of the above sections, but now taking into account that the original position vectors belong to some Euclidean  $n$ -dimensional space, that is,  $\mathbf{r} \in E_n(\mathbf{R})$ .

It is well-known<sup>34–36</sup> that the stereographic projection of a point vector, defined into the function extended space and written as  $\mathbf{p} = (\mathbf{r}, \rho(\mathbf{r})) \in C_{n+1}(\mathbf{R})$ , can be associated with a new scaled vector:

$$P_S(\mathbf{p}) = \mathbf{P} = (R - \rho(\mathbf{r}))^{-1} \mathbf{r} \in E_n \quad (3)$$

of the position space, where  $R$  is a parameter, which usually is chosen as the unit and can be defined as the radius of the sphere:

$$|\mathbf{r}|^2 + |\rho(\mathbf{r})|^2 = R^2 \quad (4)$$

Therefore, the stereographic projection can be written as

$$\mathbf{P} = (R - \rho(\mathbf{r}))^{-1} \mathbf{r} = \lambda^{-1} \mathbf{r} = \{\lambda^{-1} r_I | I = 1, n\} = \{P_I | I = 1, n\} \quad (5)$$

and it can be reversed; that is, one can try to obtain the original coordinates from the stereographic ones by using eq 4 and the inverse relationship of eq 5, which can be written as

$$\mathbf{r} = \lambda \mathbf{P} = (R - \rho(\mathbf{r})) \mathbf{P} \quad (6)$$

Therefore, from the stereographic projected coordinates, one can recover the initial coordinates following the simple general algorithm:

$$\forall I = 1, n: r_I = \frac{2RP_I}{|\mathbf{P}|^2 + 1} \wedge \rho(\mathbf{r}) = \frac{R(|\mathbf{P}|^2 - 1)}{|\mathbf{P}|^2 + 1} \quad (7)$$

where the Euclidean norm of the projected position vector, written in the usual way as

$$|\mathbf{P}|^2 = \langle \mathbf{P}^* \mathbf{P} \rangle = \sum_{I=1}^n P_I^2$$

has an obvious fundamental role.

Equations 5, 6, and 7 constitute a quite general framework, which together with the structure proposed by Mezey as a means to demonstrate the HEDT, permits us to state that: "every well behaved function of an arbitrary number of variables  $n$  can be subject to a reversible stereographic projection into the surface of an  $n$ -dimensional sphere of arbitrary radius."

The previous sentence is the *holographic general function theorem* (HGFT), which holds for well-behaved functions of any number of variables, including DF and ShF of first and higher arbitrary orders.<sup>37</sup>

## ■ EMP AND INFINITE VALUES IN STEREOGRAPHIC PROJECTIONS

A possible problem, which can be encountered when applying eq 5, is associated with the factor  $\lambda^{-1} = (R - \rho(\mathbf{r}))^{-1}$ , which can sometimes introduce the presence of an infinite value into the stereographic transformation grid. However, theoretically, one can invoke the Alexandrov one-point compactification, as Mezey<sup>1</sup> did when establishing the HEDT. In fact, in the present case, one can avoid the possible infinite values by choosing an appropriate radius  $R$  of the sphere (4), which can provide the following property fulfillment:  $\forall \mathbf{r}: R - \rho(\mathbf{r}) \neq 0$ . This becomes a sensitive procedure when full EMPS are considered as the functions to be represented, because they become infinite at atomic positions. The EMPS first described by Bonnacorsi et al.<sup>22</sup> are functions of one-electron position coordinates like the DF. A recent study on ASA EMP behavior has been performed,<sup>38</sup> which is relevant for the present paper. In any case, stereographic projections are quite interesting in the graphical representation of EMP. One can see such interest when interpreting the physical structure of this class of quantum chemical fields as the interaction energy of a proton with a given arbitrary molecular structure. The stereographical representation of the proton–molecule interaction values obtained on the surface of a sphere or spheroid, will give information over all the space directions, while the usual map representations provide EMP isopotential contours.

## ■ SPHEROIDAL STEREOGRAPHIC REPRESENTATIONS

Equation 4 defining a sphere in  $C_{n+1}$  can be easily transformed into a unit radius structure, as one can also write:

$$|R^{-1}\mathbf{r}|^2 + |R^{-1}\rho(\mathbf{r})|^2 = 1 \quad (8)$$

This result allows one to take into account the feasibility of stereographic projection into a spheroid, whose principal axis can be gathered into a vector of  $C_{n+1}$ , with a constant in the function position, like

$$\mathbf{A} = \{a_I, \alpha|I = 1, n\} = (\mathbf{a}, \alpha) \quad (9)$$

and possessing an inward inverse, which can be defined at once as

$$\mathbf{A}^{[-1]} = \{a_I^{-1}, \alpha^{-1}|I = 1, n+1\} = (\mathbf{a}^{[-1]}, \alpha^{-1})$$

and which can be used over the function extended vector  $\mathbf{p}$  in order to define the general spheroidal structure:

$$\mathbf{q} = \mathbf{A}^{[-1]}\mathbf{p} = (\mathbf{a}^{[-1]}\mathbf{r}, \alpha^{-1}\rho(\mathbf{r})) \rightarrow |\mathbf{q}|^2 = \sum_{I=1}^n \left( \frac{r_I}{a_I} \right)^2 + \left( \frac{\rho(\mathbf{r})}{\alpha} \right)^2 = 1$$

The unit spherical form in eq 8 corresponds to the definition of the vector:  $\mathbf{A} = R(\mathbf{1}_n \mathbf{1}) = R\mathbf{1}_{n+1}$ .

Additionally, in all of the previously proposed formulations, the DF can be substituted by the corresponding ShF without a loss of generality.

## ■ SCHEMATIC EXAMPLES

**Spherical GTO.** Consider the GTO function

$$\gamma(\alpha|\mathbf{r}) = \left( \frac{\alpha}{\pi} \right)^{3/2} \exp(-\alpha|\mathbf{r}|^2)$$

where  $\mathbf{r} = (x, y, z) = (x_1, x_2, x_3)$ . The stereographic projection associated with this problem can be written as

$$I = 1, 3: X_I = \frac{x_I}{R - \gamma(\alpha|\mathbf{r})} \rightarrow \mathbf{X} = (X_1, X_2, X_3): |\mathbf{X}|^2 = \sum_{I=1}^3 X_I^2 \quad (10)$$

and the reverse formulation has the following arrangement:

$$I = 1, 3: x_I = \frac{2RX_I}{|\mathbf{X}|^2 + 1} \wedge \gamma(\alpha|\mathbf{r}) = \frac{R(|\mathbf{X}|^2 - 1)}{|\mathbf{X}|^2 + 1}$$

Elementary considerations permit us to extend this algorithm to  $n$  dimensions instead of three. In the same manner, one can quote the recent discussion led by the present authors<sup>7,8</sup> about the hologram properties that can be associated with Gaussian functions. From the Gaussian hologram property, it is easy to express an  $n$ -variable Gaussian function as a one-dimensional Gaussian in spherical coordinates and write

$$|\mathbf{r}|^2 = R^2 \in \mathbb{R}^+ \rightarrow \gamma(\alpha|\mathbf{r}) \equiv \gamma(\alpha|R) = \left( \frac{\alpha}{\pi} \right)^{n/2} \exp(-\alpha R^2)$$

Except for the normalization factor and the latent angular variables, this expression appears equivalent to the multivariate Gaussian function

$$\gamma(\alpha|x) = \sqrt{\frac{\alpha}{\pi}} \exp(-\alpha x^2) \rightarrow \langle \gamma(\alpha|x) \rangle = 1$$

This possibility provides the spherical Gaussian functions of an arbitrary number of variables with the property that, over a sphere of radius  $R$ , the value of the function will be the same multivariate Gaussian exponential, scaled by a normalization factor, but taking into account the exponent and the number of variables.

**The Simplest Approximate Density for a Hydrogen Molecule.** As another example, we demonstrate the stereographic projection for an approximate DF, specifically that of the hydrogen molecule or molecular ion. One can construct such a MO with a linear combination of two spherical Euclidian normalized GTO functions, symmetrically centered at a distance  $D_{AB}$  along the  $z$  axis. Such a simplified MO can be written as

$$\psi_{\pm}(\mathbf{r}) = C(\gamma(\alpha|\mathbf{r} - \mathbf{A}) \pm \gamma(\alpha|\mathbf{r} - \mathbf{B})) = C(\gamma_A \pm \gamma_B) \quad (11)$$

where one can consider  $C$  as a normalization factor and also the fact that the following integral values are fulfilled:

$$\langle |\gamma_A|^2 \rangle = \langle |\gamma_B|^2 \rangle = 1 \wedge \langle \gamma_A \gamma_B \rangle = \langle \gamma_B \gamma_A \rangle = S(D_{AB}) = S$$

$S$  being the overlap between both GTOs; then the normalization factor can be written as  $C = (2 \pm 2S)^{-1/2}$ .

One can easily write the DF for the hydrogen ground state as

$$\rho(\mathbf{r}) = (1 + S)^{-1} (\rho_{AA}(\mathbf{r}) + \rho_{BB}(\mathbf{r}) + 2\rho_{AB}(\mathbf{r})) \quad (12)$$

where  $\forall I, J = A, B$ :  $\rho_{IJ} = \gamma_I \gamma_J$ . Owing to the Gaussian structure of the two involved basis functions, it can be written

$$\begin{aligned} \rho_{AA} &= \nu^2 \exp(-2\alpha |\mathbf{r} - \mathbf{A}|^2) \wedge \\ \rho_{BB} &= \nu^2 \exp(-2\alpha |\mathbf{r} - \mathbf{B}|^2) \end{aligned}$$

where  $\nu$  is the original Euclidean normalization factor of a spherical Gaussian, thus  $\nu^2 = (2\alpha/\pi)^{3/2}$ . Also, as one can consider in any case without a loss of generality that  $\mathbf{A} = -\mathbf{B}$ , then the cross-term can be easily written as a spherical Gaussian centered at the origin:<sup>33</sup>

$$\rho_{AB} = \nu^2 \exp\left(-\frac{\alpha D_{AB}^2}{2}\right) \exp(-2\alpha |\mathbf{r}|^2)$$

Consequently, eq 12 can be finally written:

$$\rho(\mathbf{r}) = K(\gamma_{AA}(2\alpha|\mathbf{A}|) + \gamma_{BB}(2\alpha|\mathbf{B}|) + 2L\gamma_{AB}(2\alpha|\mathbf{0}|)) \quad (13)$$

where the functions involved in eq 13 correspond to the generic un-normalized spherical Gaussian:

$$\gamma_{IJ}(2\alpha|\mathbf{Z}|) = \exp(-2\alpha |\mathbf{r} - \mathbf{Z}|^2)$$

with the auxiliary definitions:

$$K = \left(\frac{2\alpha}{\pi}\right)^{3/2} (1 + S)^{-1} \wedge L = \exp\left(-\frac{\alpha D_{AB}^2}{2}\right)$$

and finally with the overlap value defined by

$$S = \langle \gamma_A \gamma_B \rangle = \exp\left(-\frac{\alpha D_{AB}^2}{2}\right)$$

One can see, even considering this slightly complicated example, that eq 13 provides an easy way to study the stereographic projection of a density function once a DF form can be well established. The stereographic formulas in this case can be obtained from eq 10 upon the substitution:  $\gamma(\alpha|\mathbf{r}|) \rightarrow \rho(\mathbf{r})$ .

Also, the use of the square root of the density function can be easily set in this simple case, as the analytical form available as the simplified MO in eq 11 gives such a DF transformation:

$$\sqrt{\rho(\mathbf{r})} = \sqrt{2} \psi_+(\mathbf{r}) = \sqrt{2} C(\gamma_A + \gamma_B)$$

and now it is a matter of using the substitution:  $\gamma(\alpha|\mathbf{r}|) \rightarrow \sqrt{2}\psi_+(\mathbf{r})$ .

Using the DF as written in eq 13 with the subsequently defined parameters, a sequence of stereographic representations has been constructed. They are presented in Figure 1. The sequence of surfaces in Figure 1 presents the projection of the DF with the Gaussian exponent chosen as unity on the surface of a sphere of radius 0.7. The auxiliary stereographic sphere is first centered at the bond center, which was earlier proposed as the origin of the molecular coordinate system. Then, the sphere is moved along the bond axis in the negative  $z$  direction, providing the picture sequence depicted in Figure 1. Even with this

simple model, the density appears not only around both nuclei but also significantly in the bond region.

Figure 1 has to be discussed in depth because the significance of the peaks appearing and disappearing in the four slides is not immediately apparent. First, the two peaks of the upper surface correspond to both density maxima on the H atoms. However, as the sphere center is moving and approaching the atom located at position  $\mathbf{A}$ , the remaining peak of the second stereographic surface corresponds to the bond density, associated with the Gaussian  $\gamma_{AB}(2\alpha|\mathbf{0}|)$  centered at the origin. In the two lower figures, only the peak of the bond density appears. An alternative computation using a DF constructed with ASA densities<sup>29–31,39,40</sup> centered at both H atoms has been performed. The results show a similar behavior, and because of this they are not shown.

Note also that the  $X_1$  and  $X_2$  transformed coordinates represented in the numeric scales of Figure 1 are dimensionless. See Figure 2 for more details.

The stereographic pictures, even in this simple example furnished by Figure 1, provide a completely new point of view on electronic DF distributions. The following examples will try to present this original way to examine DF in more complex molecular environments.

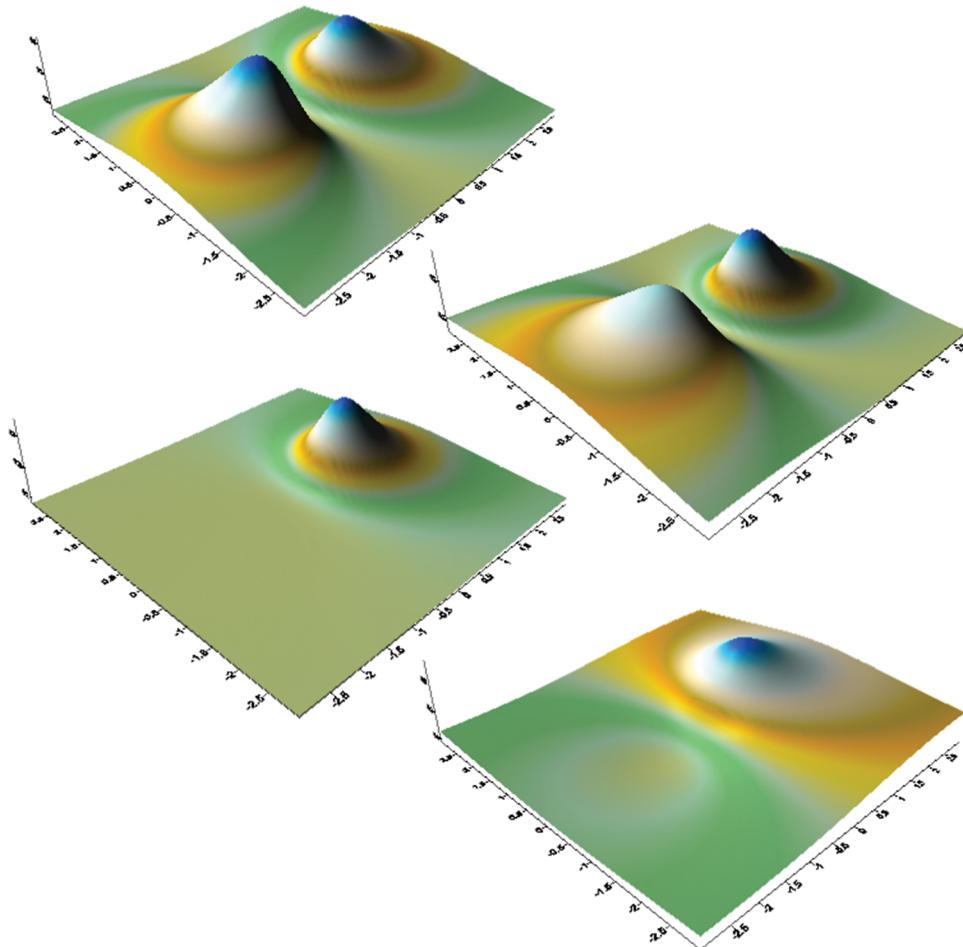
Except in the methodology to represent isodensity surfaces proposed by Mezey several years ago,<sup>41–44</sup> it is difficult to visualize the electronic density in the chemical bonding areas using the conventional maps of DF that are commonly provided in the literature. Figure 1 as in Mezey's representation permits this visualization of the DF bonding structure. The following examples will reveal more details about this possibility.

## ■ STEREOGRAPHIC PROJECTIONS PRACTICAL PROPERTIES AND CHARACTERISTICS

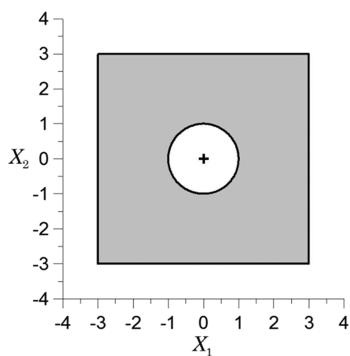
**Preliminary Considerations.** Although the possibility to use stereographic projections to obtain drawings of quantum chemical functions has been described in the Introduction, the present work cannot be considered complete without some applications to polyatomic molecules. The pictures, in and of themselves, demonstrate nothing,<sup>45</sup> but in the present case they truly complement the previous mathematical exposition and provide a novel way to represent molecular environments and interactions.

Any DF source computed at any theoretical level admits a stereographic projection, but for practical reasons, mainly related to the development of quantum similarity<sup>46</sup> and also in order to ease the implementation, only quantum chemical DFs in the ASA framework are considered here. Polarized ASA DF has been chosen on various molecular structures as a stereographic projection example. It has been recently proved that ASA DF generated EMPs are everywhere positive without exception, unless some fitting to an *ab initio* model is provided<sup>31</sup> or an ASA polarized version is employed.<sup>38</sup> The pictures of ASA EMP, conveniently scaled and investigated here, were found to behave with the same shape features as in the ASA DF examples provided below. Consequently, it was decided to not show them. ASA DFs were employed several years ago to visualize large molecular structures,<sup>47–49</sup> in the same way that Mezey had previously done<sup>42–44</sup> within other approximate kinds of DF, with similar results.

Molecular polarized ASA DFs have been constructed with atomic populations as a way to refine promolecular models using a bulk atomic number of electrons only. Molecular atomic populations and optimized geometries have been obtained by



**Figure 1.**  $\text{H}_2$  molecule DF stereographic pictures according to the analytic form generated with two Gaussian functions used as the LCAO MO basis set. See the text for more information on how to interpret the surfaces. Both H GTO exponents have been taken as 1. The H atoms have been centered at  $A = (-0.7, 0, 0)$  and  $B = (+0.7, 0, 0)$  respectively (coordinate units are in au). A sphere of radius  $R = 0.7$  au, centered at the bond coordinate sequence  $x = \{0, -0.35, -0.70, -1.05\}$  and  $y = z = 0$  has been employed and corresponds to the figures from the top to the bottom of the figure.

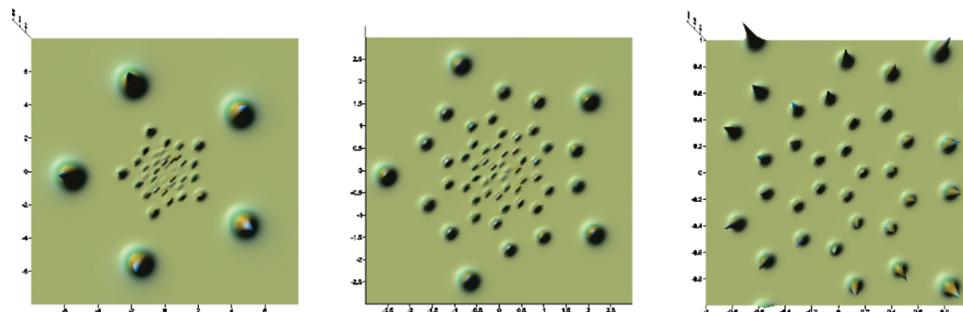


**Figure 2.** Schematic topology of the stereographic projection plane of a function computed at the points within the surface of a sphere of radius  $R$ , as used in this paper. In the plane of the present figure, the location of the circle origin, [the point  $(0,0)$  in the map signaled by a cross] is coincident with the chosen tridimensional sphere center. Stereographic projection points belonging to the surface of the southern hemisphere lie within the white circle of radius  $R$ , coincident with the chosen sphere radius. The unbounded gray zone located outside the white circle (but bounded for practical reasons into a square) corresponds to the stereographic projection of the northern hemisphere function points.

means of Spartan 10,<sup>50</sup> mainly within a 3-21G basis set and under HF theory. In this manner, the pictures of this work can be associated with the recently published computational studies about quantum similarity<sup>8,45,51</sup> mainly based on ASA DF. Thus, the basic program used to obtain the present paper graphical examples can complement the recently published molecular quantum similarity program suite (MQSPS).<sup>45</sup>

Also, the elegance but implementation difficulty of function extended spaces has been quite simplified in order to obtain a simpler but practical stereographic projection version, with an applied procedure like the one offered in Figure 1, where the desired DF is computed on the surface of some sphere, constructed according to the number of function variables with a chosen origin and fixed radius.

**Stereographic Pictures Flexibility.** In any case, as in the simple molecular hydrogen DF of Figure 1, the stereographic representation of DF corresponds to a quite flexible new point of view, which reveals the molecular three-dimensional environment. Stereographic vision flexibility of interesting functions is associated with the fact that the spherical (or spheroidal) surface can be centered anywhere around the molecular structure, even over an atom, and the stereographic



**Figure 3.** ASA DF projection associated with the  $C_{60}$  molecule and shown along three snapshots of a traveling zoom toward the stereographic projection plane origin. The projection sphere origin has been kept still and placed at the molecular center of inversion.

surface of the sphere radius can be shrunk and enlarged at will, until a simpler or more complex picture appears.

Besides the Figure 1 sequence of pictures, another set of molecular sequences is shown below, and several others are kept as supplementary material at a Web site.<sup>52</sup> In this way, the interested readers can be able to freely download and peruse more examples of stereographic representations of DFs.

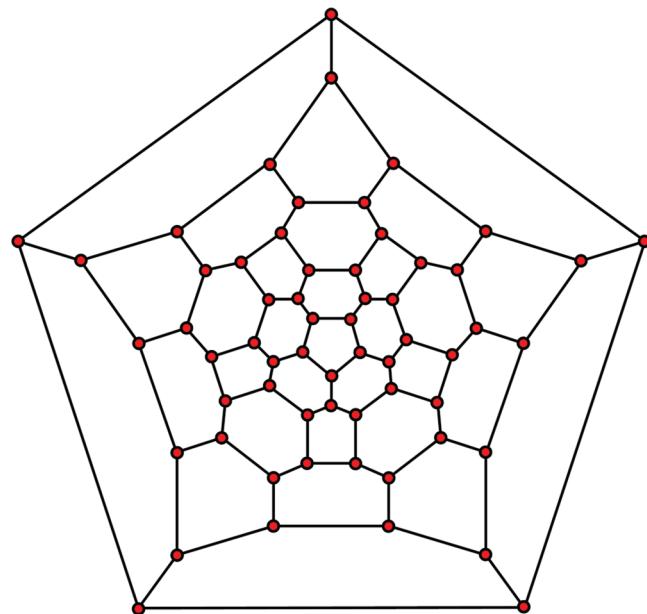
From the usual static pictures of the DF, one can acquire the impression that electronic density around the molecular bonds is almost nonexistent. However, with the aid of the adequate stereographic picture point of view, the existence of the electronic density around the chemical bonds can be fully represented, even at the approximate ASA DF level, as is shown in the provided molecular simple hydrogen initial representation and in the pictures supplied on the Web.<sup>52</sup>

#### ■ PROGRAM CODE, STEREOGRAPHIC PROJECTION PICTURES CHARACTERISTICS, AND A PICTOGRAPHIC EXAMPLE

**The Stereographic Projection Program Code.** The program STEREOP computes several quantum chemical functions in the ASA framework, and forms part of the MQSPL<sup>53</sup> Web site collection. The Fortran 95 source code can be downloaded from a public Web site.<sup>32</sup> The input can be constructed automatically from the Program 1 prepared data output of the MQSPL. The program output results are presented in the form of a text file, which is processed afterward with a standard graphics code.<sup>54</sup>

**Contents and Structure of the Stereographic Projection Planes.** All of the following and Web-placed figures have been obtained with the stereographic projection of the DF values computed on the surface of a sphere of a given origin  $R$  and chosen radius  $R$ . Every figure referred to in this paper contains the function values on the points of the sphere's surface stereographic projection of both the sphere's northern and southern hemispheres. Within the stereographic projection plane, its central point or origin is coincident with  $R$ , the sphere's center in three-dimensional space. The southern hemisphere is projected within the surface of a circle of radius  $R$  centered at the plane origin; the northern hemisphere surface becomes projected into the surrounding region of the previously mentioned southern hemisphere circle. Figure 2 presents a scheme of both southern and northern regions along its location in the stereographic projection plane.

**A Complex Stereographic Picture Example: Buckminsterfullerene.** Due to its peculiar three-dimensional structure, the buckminsterfullerene ( $C_{60}$ ) molecule constitutes a difficult

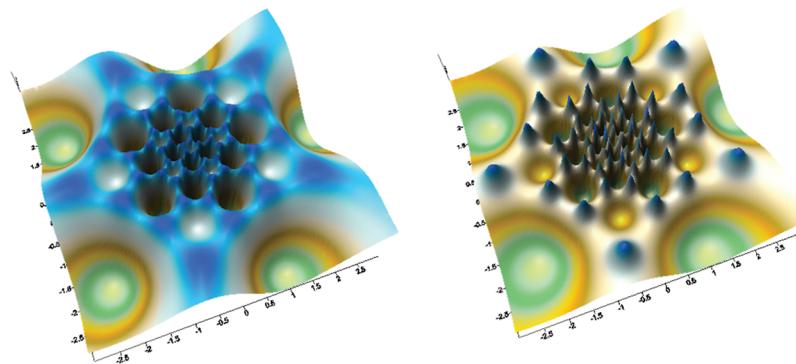


**Figure 4.** Usual topological representation of the  $C_{60}$  molecule as a planar graph, displaying a pentagonal structure, which is faithfully reproduced in the stereographic projections of Figure 3.

case when its DF structure has to be described and depicted in full. Because of this, it has been chosen as an example of stereographic projection. Figure 3 presents the  $C_{60}$  map obtained placing the projection sphere origin at the molecular center of inversion. The stereographic sphere projection radius has been chosen as  $R = 6.6$  au, in order to place the 60 carbon atoms on the projection sphere surface. Figure 3 constitutes a three-step zooming sequence toward the origin of the projection plane.

In Figure 3, the leftmost picture reveals that all 60 carbon atom peaks are found symmetrically distributed along the projection plane. The stereographic projection produces a distortion of the molecular topology, leading to the configuration of the corresponding isomorphic planar graph shown in Figure 4.

Figure 5 corresponds to two views similar to the central projection part of Figure 3, but reducing (left) and increasing (right) the projection sphere diameter. The respective stereographic sphere radii are  $R = 5$  (left) and  $R = 7.5$  (right). In both cases, the carbon atoms are located far away from the projection sphere surface and produce smoother density variations, preserving the molecular symmetry.



**Figure 5.** Two stereographic projections of the  $C_{60}$  molecule obtained in a similar way as the surface shown at the center of Figure 3, but setting the stereographic sphere radius at  $R = 5$  au (left) and  $R = 7.5$  au (right). In the left figure case, the projection sphere lies inside the  $C_{60}$  surface, whereas the right drawing shows the molecular structure ASA DF of  $C_{60}$  when contained within the stereographic sphere.

## CONCLUSIONS

A general way to represent multivariate well-behaved functions has been described. It is based on the description of the new concept of function extended spaces and leads to the formulation of a general holographic theorem for well-behaved functions. From this mathematical background, one can design simple algorithms to represent multivariate functions of interest. Thus, the present methodology arises from a general description allowing the treatment of well-behaved functions of many variables and connecting it with general holographic features, providing finally an algorithm to obtain new representations of the DF.

This technique was exemplified by studying the first-order DF structure (under a polarized ASA framework) using the stereographic projection algorithm. The method opens multiple ways to represent molecules and other quantum objects. The obtained pictures on first-order ASA DF easily reveal the molecular bond densities and the positions of the atoms. Usually, the atoms of the studied molecular structures located in the three-dimensional space do not have to be coincident with the projection sphere surface. When this occurs though, the DF peak corresponding to an atom located in such a position greatly increases in intensity and at the same time acquires a pronounced sharp structure.

The described stereographic projection procedure opens a new panorama directed not only to represent DF and other function structures in a static fashion but also by means of dynamic or interactive facilities.

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### Notes

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