ORIGINAL PAPER

Riemannian three dimensional molecular spaces

Ramon Carbó-Dorca

Abstract   A simple manipulation of the first order density function permits to define a curved 3D Riemannian coordinate set, which can substitute the usual flat 3D Cartesian space, where atoms and molecules are supposed to exist. Several simple models are discussed. Gaussian type orbitals generate a space division with positive and negative curvatures, the later one being near the centre of the functions; contrarily Slater type orbitals provide a positive curvature everywhere.

Keywords   Density function · Riemann spaces · Gaussian curvature · GTO · STO · Atomic shell approximation · LCAO MO

1 Introduction

In a recent article [1] was put forward the possibility that Riemannian 3D spaces [2, 3] can be constructed from first order density functions attached to quantum objects. In such a preliminary study, the description of the possible Riemann spaces was associated to three linearly independent functions, like for instance: ground state, anion and cation densities, when atoms or molecules were involved. This has not to be necessarily so. In fact, a unique density function could be sufficient to structure such a Riemann curved space, substituting the flat Cartesian 3D space, where quantum objects are embedded. This article deals with this new option. First, a naïve description of the procedure to construct a 3D Riemann space out of a first order density function will be

R. Carbó-Dorca
Department of Inorganic and Physical Chemistry, Ghent University, Krijgslaan 281, 9000 Gent, Belgium

R. Carbó-Dorca (✉)
Institut de Química Computacional, Universitat de Girona, Girona, 17071 Catalonia, Spain
e-mail: quantumqsar@hotmail.com

given. Then, will be studied simple examples, based essentially on GTO, STO, atomic shell approximations (ASA) for atoms and a plain density function for the hydrogen molecule. The results obtained in this latter case will be analyzed as deep as possible and to finalize the present study, a general formulation of the procedure set within the LCAO MO framework will be given.

2 Alternative formulation of the Riemannian molecular frame and space curvature

When atoms and molecules are described as quantum objects, that is: if considered as submicroscopic objects having a density function tag associated to the structure information forming the object, see reference [5] for an update of this concept, then a Riemannian coordinate system framework can be easily formulated on these objects. This can be done just employing a unique molecular density function, calling it for instance: $\rho(\mathbf{r}|\mathbf{R})$; where $\mathbf{r}$ are the 3D electron position coordinates and in $\mathbf{R}$ are collected, as columns or rows, the 3D nuclear position coordinates of the molecular atoms.

Indeed, one can use the three gradient components of the density function as a curvilinear coordinate system. That is:

$$(k=1,3): x_k = \frac{\partial\rho(\mathbf{r}|\mathbf{R})}{\partial r_k} \rightarrow \mathbf{x} = (x_1; x_2; x_3)^T = \frac{\partial\rho(\mathbf{r}|\mathbf{R})}{\partial\mathbf{r}} = |\mathbf{g}(\mathbf{r}|\mathbf{R})\rangle. \quad (1)$$

Therefore, the Jacobian connected with the coordinate system (1) has to be constructed in this scenario by means of the Hessian of the density function $\rho(\mathbf{r}|\mathbf{R})$ or:

$$(k=1,3): |\gamma_k\rangle = \frac{\partial}{\partial\mathbf{r}}\left(\frac{\partial\rho(\mathbf{r}|\mathbf{R})}{\partial r_k}\right) = \frac{\partial x_k}{\partial\mathbf{r}} = \left(\frac{\partial x_k}{\partial r_1}; \frac{\partial x_k}{\partial r_2}; \frac{\partial x_k}{\partial r_3}\right)^T.$$

Then, the gradient vectors ordered as columns form now the columns of the Hessian matrix acting as a Jacobian source. One can write, for example:

$$\mathbf{\Gamma}(\mathbf{r}|\mathbf{R}) = (|\gamma_1\rangle; |\gamma_2\rangle; |\gamma_3\rangle) = \left\{\Gamma_{lk} = \frac{\partial^2\rho(\mathbf{r}|\mathbf{R})}{\partial r_l \partial r_k}\right\} = \frac{\partial}{\partial\mathbf{r}} \otimes \frac{\partial}{\partial\mathbf{r}}[\rho(\mathbf{r}|\mathbf{R})].$$

So, the condition of linear independence of the curvilinear coordinate system can now be written formally as:

$$K = Det|\mathbf{\Gamma}(\mathbf{r}|\mathbf{R})| \neq 0. \quad (2)$$

Such a usual definition to test the linear independence of the columns or rows of a matrix, which is computed using a given unique background 3D surface, also constitutes the so-called Gaussian curvature [4], K, which here basically consists in the value of the Hessian matrix determinant (2) of the chosen density function computed at each surface point. In this case the Gaussian curvature is coincident with the Jacobian of the Riemannian coordinate system (1).

3 The fundamental metric tensor

Furthermore, Eq. (1) define a transformation of coordinates for the 3D molecular space. In consequence, with the Jacobian–Gaussian condition (2), the 3D Cartesian coordinates have to be expressible in terms of a set of three functions of the chosen curvilinear coordinates, or what is the same: a new triplet of functions exists, permitting to write:

$$(k = 1, 3) : r_k = p_k \left(\mathbf{x} \left| \mathbf{R} \right. \right) \to \mathbf{r} = \left| \mathbf{p} \left(\mathbf{x} \left| \mathbf{R} \right. \right) \right\rangle = \left(p_1 \left(\mathbf{x} \left| \mathbf{R} \right. \right) ; p_2 \left(\mathbf{x} \left| \mathbf{R} \right. \right) ; p_3 \left(\mathbf{x} \left| \mathbf{R} \right. \right) \right)^T,$$

where the notation $\left| \mathbf{p} \left(\mathbf{x} \left| \mathbf{R} \right. \right) \right\rangle$ is used to stress the vector structure of the coordinate functions.

The gradients and the Hessian matrix can be easily defined now for this new coordinate system as:

$$\mathbf{G} \left(\mathbf{x} \left| \mathbf{R} \right. \right) = \left(\left| g_1 \right\rangle ; \left| g_2 \right\rangle ; \left| g_3 \right\rangle \right) = \left\{ G_{lk} = \frac{\partial \ p_k \left(\mathbf{x} \left| \mathbf{R} \right. \right)}{\partial \ x_l} \right\}.$$

Admitting that the independence of every two pairs of coordinates will hold, this allows to write, for example:

$$\forall k, l : \frac{\partial r_k}{\partial r_l} = \sum_j \frac{\partial r_k}{\partial x_j} \frac{\partial x_j}{\partial r_l} = \delta_{kl}$$

and a similar equation can be set for the coordinates (1). Then, it can be found the following relationships for the two matrices constructed with the gradient vectors:

$$\mathbf{\Gamma G} = \mathbf{G \Gamma} = \mathbf{I} \to \mathbf{G} = \mathbf{\Gamma}^{-1} \wedge \mathbf{\Gamma} = \mathbf{G}^{-1}, \tag{3}$$

being $\mathbf{I}$ the corresponding (3×3) unit matrix. Equation (3) prove that the two Hessian matrices are inverse one from the other.

Any direction at a point of 3D space is defined by the vector differentials:

$$\left| d\mathbf{x} \right\rangle = \mathbf{\Gamma} \left| d\mathbf{r} \right\rangle, \tag{4}$$

where a column vector symbol has been employed, for example:

$$\left| d\mathbf{x} \right\rangle = \left(dx_1; dx_2; dx_3 \right)^T$$

A differential line element of the curved 3D-space, constructed as explained before, can be related to the squared module of the differential vector, that is:

$$
\begin{aligned}
\left| \left| d\mathbf{x} \right\rangle \right|^2 &= \left\langle d\mathbf{x} | d\mathbf{x} \right\rangle = \left\langle d\mathbf{r} \left| \mathbf{\Gamma}^T \mathbf{\Gamma} \right| d\mathbf{r} \right\rangle \\
&= \sum_k \sum_l \left(\sum_t \Gamma_{tk} \Gamma_{tl} \right) dr_k dr_l = \sum_k \sum_l T_{kl} dr_k dr_l,
\end{aligned}
\tag{5}
$$

constituting an expression, which in this case defines a positive definite quadratic form, associated in turn to the symmetric positive definite fundamental metric tensor:

$$\mathbf{T} = \left\{ T_{kl} = \sum_t \Gamma_{tk}\Gamma_{tl} \right\} = \mathbf{\Gamma}^T\mathbf{\Gamma} \rightarrow \mathbf{T} > 0 \wedge Det\,|\mathbf{T}| = |Det\,|\mathbf{\Gamma}||^2 > 0.$$

In the present case the following symmetrical property of the Hessian matrix will also hold:

$$\forall k, l : \Gamma_{lk} = \frac{\partial^2\rho\,(\mathbf{r}\,|\mathbf{R})}{\partial r_l \partial r_k} = \frac{\partial^2\rho\,(\mathbf{r}\,|\mathbf{R})}{\partial r_k \partial r_l} = \Gamma_{kl} \rightarrow \mathbf{\Gamma}^T = \mathbf{\Gamma};$$

therefore, in this situation the fundamental metric tensor is just the square of the Hessian matrix:

$$\mathbf{T} = \mathbf{\Gamma}^2.$$

Moreover, the fundamental metric tensor can be employed to obtain an approximation of the 3D Riemannian surface at any point, as using the Taylor series:

$$\rho\,(\mathbf{r}) \approx \rho\,(\mathbf{r}_0) + (\mathbf{r} - \mathbf{r}_0)^T \frac{\partial\rho\,(\mathbf{r}_0\,|\mathbf{R})}{\partial\mathbf{r}}$$
$$+ \frac{1}{2}(\mathbf{r} - \mathbf{r}_0)^T \left[\frac{\partial}{\partial\mathbf{r}} \otimes \frac{\partial}{\partial\mathbf{r}} [\rho\,(\mathbf{r}_0\,|\mathbf{R})] \right] (\mathbf{r} - \mathbf{r}_0) + O\,(3)$$

or simply:

$$\rho\,(\mathbf{r}) - \rho\,(\mathbf{r}_0) \approx \langle\mathbf{r} - \mathbf{r}_0|\mathbf{g}\,(\mathbf{r}_0\,|\mathbf{R})\rangle + \frac{1}{2}\langle\mathbf{r} - \mathbf{r}_0|\,\mathbf{\Gamma}\,(\mathbf{r}_0\,|\mathbf{R})\,|\mathbf{r} - \mathbf{r}_0\rangle + O\,(3)$$

$$\rightarrow \rho\,(\mathbf{r}) - \rho\,(\mathbf{r}_0) \approx \langle\mathbf{x} - \mathbf{x}_0|\,\mathbf{G}\,|\mathbf{x}_0\rangle + \frac{1}{2}\langle\mathbf{x} - \mathbf{x}_0|\,\mathbf{G}\,|\mathbf{x} - \mathbf{x}_0\rangle + O\,(3)$$

$$= \frac{1}{2}(\langle\mathbf{x}|\,\mathbf{G}\,|\mathbf{x}\rangle - \langle\mathbf{x}_0|\,\mathbf{G}\,|\mathbf{x}_0\rangle) + O\,(3) \tag{6}$$

So, the final expression (6) can be further employed to obtain the density function in Riemannian coordinates in the neighborhood of any point $\mathbf{r}_0$ up to second order. Thus, when choosing: $\mathbf{r}_0 = \mathbf{0}$, the interesting result is:

$$\mathbf{x}_0 = \mathbf{\Gamma}\mathbf{r}_0 \rightarrow \mathbf{x}_0 = \mathbf{\Gamma}\mathbf{0} = \mathbf{0},$$

which permit to write Eq. (6) in the form:

$$\rho\,(\mathbf{r}) \approx \rho\,(\mathbf{0}) + \frac{1}{2}\langle\mathbf{x}|\,\mathbf{G}\,|\mathbf{x}\rangle + O\,(3).$$

4 Two simple examples involving one function

4.1 Gaussian type orbital

Atoms possess spherical symmetry, thus a good but naïve model to illustrate first of all the previous theoretical discussion in the simplest way, could be found in a unique unnormalized[1] Gaussian type orbital (GTO) of 1s symmetry:

$$|g\,(\mathbf{r}\,|\alpha\,)\rangle = \exp\left(-\alpha\,|\mathbf{r}|^2\right) \wedge \alpha \in \mathbf{R}^+. \tag{7}$$

The gradient of GTO function (7), which will construct the Riemannian coordinate system according with the present discussion, it is easily found to be:

$$\frac{\partial}{\partial \mathbf{r}}\,|g\,(\mathbf{r}\,|\alpha\,)\rangle = -2\alpha\mathbf{r}\,|g\,(\mathbf{r}\,|\alpha\,)\rangle\,, \tag{8}$$

which possess a Hessian also easily written as:

$$\boldsymbol{\Gamma}\,(\mathbf{r}\,|\alpha\,) = \frac{\partial}{\partial \mathbf{r}} \otimes \frac{\partial}{\partial \mathbf{r}}\,[g\,(\mathbf{r}\,|\alpha\,)] = -2\alpha\frac{\partial}{\partial \mathbf{r}} \otimes [\mathbf{r}g\,(\mathbf{r}\,|\alpha\,)]$$
$$= 2\alpha\,(2\alpha\,(\mathbf{r} \otimes \mathbf{r}) - \mathbf{I})\,g\,(\mathbf{r}\,|\alpha\,)\,. \tag{9}$$

In order to obtain the Gaussian curvature of this simple model it is sufficient to study the eigensystem of the following matrix:

$$\mathbf{M} = 2\alpha\,(\mathbf{r} \otimes \mathbf{r}) - \mathbf{I}, \tag{10}$$

which can be also written, after rearranging terms as:

$$\mathbf{M}\,|\mathbf{v}\rangle = \mu\,|\mathbf{v}\rangle \rightarrow (\mathbf{r} \otimes \mathbf{r})\,|\mathbf{v}\rangle = \left(\frac{\mu+1}{2\alpha}\right)\,|\mathbf{v}\rangle = \lambda\,|\mathbf{v}\rangle$$

Then, writing the tensor product alternatively as: $\mathbf{r} \otimes \mathbf{r} = |\mathbf{r}\rangle\,\langle\mathbf{r}|$: one can see that choosing: $|\mathbf{v}\rangle = |\mathbf{r}\rangle$:

$$|\mathbf{r}\rangle\,\langle\mathbf{r}|\,|\mathbf{v}\rangle = |\mathbf{r}\rangle\,\langle\mathbf{r}|\mathbf{v}\rangle = |\mathbf{r}\rangle\,\langle\mathbf{r}|\mathbf{r}\rangle = \langle\mathbf{r}|\mathbf{r}\rangle\,|\mathbf{r}\rangle \rightarrow \lambda = \langle\mathbf{r}|\mathbf{r}\rangle\,.$$

This result shows simply that $|\mathbf{r}\rangle$ is an eigenvector of $|\mathbf{r}\rangle\,\langle\mathbf{r}|$ with eigenvalue: $\langle\mathbf{r}|\mathbf{r}\rangle = r_1^2 + r_2^2 + r_3^2 = |\mathbf{r}|^2 = r^2$. As the matrix $|\mathbf{r}\rangle\,\langle\mathbf{r}|$ is Hermitian, the other two eigenvectors $\{|\mathbf{a}\rangle\,;\,|\mathbf{b}\rangle\}$ have to be orthogonal to the already known eigenvector$|\mathbf{r}\rangle$, that is the same as:

$$\langle\mathbf{r}|\mathbf{a}\rangle = \langle\mathbf{r}|\mathbf{b}\rangle = 0 \rightarrow |\mathbf{r}\rangle\,\langle\mathbf{r}|\,|\mathbf{a}\rangle = 0\,|\mathbf{r}\rangle \wedge |\mathbf{r}\rangle\,\langle\mathbf{r}|\,|\mathbf{b}\rangle = 0\,|\mathbf{r}\rangle\,. \tag{11}$$

---

[1] The GTO has been chosen not normalized in order to ease the notation. Normalized 1s GTO will just scale by a positive definite constant the deduced formulae.

Thus, the remnant eigenvectors, being orthogonal to $|\mathbf{r}\rangle$, both possess a degenerate eigenvalue 0. These two degenerate eigenvectors, besides the fact they shall fulfill the orthogonality conditions (11), being degenerate they can be arbitrarily chosen as linear combinations of any pair of linearly independent orthogonal vectors to $|\mathbf{r}\rangle$. More important is the fact that the eigenvalues of the Hessian matrix $\mathbf{M}$ can be calculated now to be:

$$\mu_1 = 2\alpha \langle \mathbf{r}|\mathbf{r}\rangle - 1 \wedge \mu_2 = \mu_3 = -1$$

and the Gaussian curvature becomes easily computable as:

$$\begin{aligned}
K = Det\,|\mathbf{\Gamma}| &= (2\alpha g\,(\mathbf{r}\,|\alpha))^3\, Det\,|2\alpha\,(\mathbf{r}\otimes\mathbf{r}) - \mathbf{I}| \\
&= (2\alpha g\,(\mathbf{r}\,|\alpha))^3\,\mu_1\mu_2\mu_3 = (2\alpha)^3\, g\,(\mathbf{r}\,|3\alpha)\,(2\alpha\,\langle\mathbf{r}|\mathbf{r}\rangle - 1) \\
&= (2\alpha)^3\, g\,(\mathbf{r}\,|3\alpha)\left(2\alpha r^2 - 1\right)
\end{aligned} \tag{12}$$

This last result is interesting as the power of the exponent, the Gaussian function itself and the scalar product of the position vector, that is: the square of the vector radius: $\langle\mathbf{r}|\mathbf{r}\rangle = r^2$, are positive definite; except the vector radius value at the point $|\mathbf{r}\rangle = |\mathbf{0}\rangle$. Thus the GTO Gaussian curvature can be considered:

(a) Positive : $2\alpha r^2 > 1$

(b) Zero : $2\alpha r^2 = 1 \rightarrow r_0 = \sqrt{\dfrac{1}{2\alpha}}$

(c) Negative : $2\alpha r^2 < 1$.   (13)

Then, it seems that in the unique GTO case, a zero curvature radius r_0 exists. Outside the sphere of radius:r_0, the space possess a positive curvature and inside a negative one. The radius of zero curvature for a simple GTO is inversely proportional to the square root of twice the GTO exponent. This means that as sharper becomes the GTO, shorter the zero curvature radius will be. More diffuse the GTO a larger radius bear. These facts seem to constitute a coherent picture with what one has in mind about GTO's form and behavior.

The fundamental tensor in this single GTO case it is easily computed as:

$$\begin{aligned}
\mathbf{T} = \mathbf{\Gamma}^2 &= (2\alpha g\,(\mathbf{r}\,|\alpha))^2\,(2\alpha\,|\mathbf{r}\rangle\,\langle\mathbf{r}| - \mathbf{I})^2 \\
&= 4\alpha^2 g\,(\mathbf{r}\,|2\alpha)\,(\mathbf{I} + \beta\,(\mathbf{r}\,|\alpha)\,|\mathbf{r}\rangle\,\langle\mathbf{r}|)
\end{aligned}$$

with the function $\beta\,(\mathbf{r}\,|\alpha)$ defined as:

$$\beta\,(\mathbf{r}\,|\alpha) = 4\alpha\,(\alpha\,\langle\mathbf{r}|\mathbf{r}\rangle - 1) = 4\alpha\left(\alpha r^2 - 1\right).$$

In molecular cases it will be also interesting to see how the Hessian is modified when the GTO is displaced towards a centre **R**:

$$g\left(\mathbf{r} - \mathbf{R} \,|\, \alpha\right) = \exp\left(-\alpha\left|\mathbf{r} - \mathbf{R}\right|^2\right)$$

then, the gradient is simply:

$$\frac{\partial}{\partial \mathbf{r}} g\left(\mathbf{r} - \mathbf{R} \,|\, \alpha\right) = -2\alpha\left(\mathbf{r} - \mathbf{R}\right) g\left(\mathbf{r} - \mathbf{R} \,|\, \alpha\right)$$

and the Hessian can be written as:

$$\frac{\partial}{\partial \mathbf{r}} \otimes \frac{\partial}{\partial \mathbf{r}} g\left(\mathbf{r} - \mathbf{R} \,|\, \alpha\right) = -2\alpha\left[2\alpha\left(\mathbf{r} - \mathbf{R}\right) \otimes \left(\mathbf{r} - \mathbf{R}\right) - \mathbf{I}\right] g\left(\mathbf{r} - \mathbf{R} \,|\, \alpha\right);$$

that is, the result appears to be like the formulae (8) and (9) respectively, employing the substitution $\mathbf{r} \rightarrow \mathbf{r} - \mathbf{R}$. A translation will not change the Riemannian coordinate structure a fact which is also in accordance to the GTO behavior.

4.2 Slater type orbital

A much less popular but effortless model can be constituted by a single Slater type orbital (STO) of 1s symmetry. Analogously to the former GTO example one can write an unnormalized 1s STO as[2]:

$$|s\left(\mathbf{r} \,|\, \alpha\right)\rangle = \exp\left(-\alpha\left|\mathbf{r}\right|\right) \wedge \alpha \in \mathbf{R}^+ \wedge \left|\mathbf{r}\right| = r = \sqrt{x^2 + y^2 + z^2}$$

the Riemannian coordinate system will be given by:

$$\frac{\partial}{\partial \mathbf{r}} |s\left(\mathbf{r} \,|\, \alpha\right)\rangle = -\alpha \frac{\partial\left|\mathbf{r}\right|}{\partial \mathbf{r}} |s\left(\mathbf{r} \,|\, \alpha\right)\rangle = -\alpha \frac{\mathbf{r}}{\left|\mathbf{r}\right|} |s\left(\mathbf{r} \,|\, \alpha\right)\rangle \equiv -\alpha r^{-1} \mathbf{r} |s\left(\mathbf{r} \,|\, \alpha\right)\rangle$$

and the Hessian matrix can be written as:

$$\mathbf{\Gamma} = \alpha r^{-1} \left[a\left(r \,|\, \alpha\right)\left(\mathbf{r} \otimes \mathbf{r}\right) - \mathbf{I}\right] |s\left(\mathbf{r} \,|\, \alpha\right)\rangle \wedge a\left(r \,|\, \alpha\right) = r^{-1}\left(r^{-1} + \alpha\right)$$

so, the Gaussian curvature will be associated to the product of the three eigenvalues of the matrix:

$$\mathbf{M} = a\left(r \,|\, \alpha\right)\left(\mathbf{r} \otimes \mathbf{r}\right) - \mathbf{I},$$

which are easily computed, in a similar way as in the GTO case, to be like:

$$\mu_1 = a\left(r \,|\, \alpha\right)\langle\mathbf{r}|\mathbf{r}\rangle - 1 \wedge \mu_2 = \mu_3 = -1$$

---

[2] A Cartesian formalism is used, instead of the usual spherical coordinate expressions, in order to have a match, as far as possible, with the Cartesian GTO treatment.

and thus, the STO Gaussian curvature, can be simplified in such a way that the positive definite factor: $\alpha^3 \, |s \, (\mathbf{r} \, |3\alpha \,)\rangle$ is not taken into account, as its inclusion will not add new information. The Gaussian curvature can be computed as the triple product:

$$K = \mu_1 \mu_2 \mu_3 = a \, (r \, |\alpha \,) \, \langle \mathbf{r} | \mathbf{r} \rangle - 1 = r^{-1} \left(r^{-1} + \alpha \right) r^2 - 1 = \alpha r > 0.$$

Therefore, contrarily to the GTO case, the STO Riemannian space is everywhere positively curved, except at $r = 0$.

   This fact is coherent with the well-know fulfillment of the cusp conditions [6] by STO's, a property which is lacking in the GTO function family.

5 The atomic ASA model as another example

The previous simplified one GTO function model can be upgraded to a slightly more sophisticated ground, by using atomic densities of ASA type [7]–[11]. In this atomic model it is used a convex linear combination of 1s GTO's fitted to any *ab initio* atomic density function:

$$\rho \, (\mathbf{r}) = \sum_I \omega_I g \, (\mathbf{r} \, |\alpha_I \,),$$

in order to obtain the optimal positive definite coefficients $\{\omega_I\}$ and the GTO exponents $\{\alpha_I\}$.

   The Hessian matrix becomes in the ASA framework:

$$\boldsymbol{\Gamma} \, (\mathbf{r}) = 2 \sum_I \omega_I \alpha_I \, (2\alpha_I \, (\mathbf{r} \otimes \mathbf{r}) - \mathbf{I}) \, g \, (\mathbf{r} \, |\alpha_I \,)$$

$$= \left(4 \sum_I \omega_I \alpha_I^2 g \, (\mathbf{r} \, |\alpha_I \,) \right) (\mathbf{r} \otimes \mathbf{r}) - \left(2 \sum_I \omega_I \alpha_I g \, (\mathbf{r} \, |\alpha_I \,) \right) \mathbf{I}$$

which presents the same structure as the formerly defined $\mathbf{M}$ matrix in Eq. (10), as one can write:

$$\boldsymbol{\Gamma} \, (\mathbf{r}) = \eta \, (\mathbf{r} \otimes \mathbf{r}) - \theta \mathbf{I} \leftarrow \eta = \left(4 \sum_I \omega_I \alpha_I^2 g \, (\mathbf{r} \, |\alpha_I \,) \right) \wedge \theta$$

$$= \left(2 \sum_I \omega_I \alpha_I g \, (\mathbf{r} \, |\alpha_I \,) \right)$$

keeping in mind that, as the coefficients in the ASA framework are positive definite by construction, then: $\eta, \theta \in \mathbf{R}^+$; therefore, the Hessian eigensystem can be rewritten as:

$$|\mathbf{r}\rangle \, \langle \mathbf{r}| \, |\mathbf{v}\rangle = \left(\frac{\mu + \theta}{\eta} \right) |\mathbf{v}\rangle \rightarrow \mu_1 = \eta \, \langle \mathbf{r} | \mathbf{r} \rangle - \theta; \, \mu_2 = \mu_3 = -\theta$$

and the Gaussian curvature of the ASA atom everywhere in space is simply expressed as:

$$Det\,|\mathbf{\Gamma}\,(\mathbf{r})| = \theta^2\,(\eta\,\langle\mathbf{r}|\mathbf{r}\rangle - \theta)\,,$$

thus, the sign of the Gaussian curvature will depend uniquely on the difference:

$$\Delta = \eta\,\langle\mathbf{r}|\mathbf{r}\rangle - \theta = \eta r^2 - \theta.$$

At large distances one can assume a positive curvature, while a flat surface will occur when: $r = \sqrt{\frac{\theta}{\eta}}$ and negative curvature is to be expected at distances less than this one. However, one must take into account that both parameters $\{\eta, \theta\}$ are functions of the electron position too.

In fact, using the column vector definitions:

$$|\alpha\rangle = \{\alpha_I\} \wedge |1\rangle = \{1\} \wedge |w\rangle = \{\omega_I \alpha_I g\,(\mathbf{r}\,|\alpha_I)\}$$

the parameters $\{\eta, \theta\}$ and the difference Δ can be rewritten as:

$$\eta = \langle\alpha|w\rangle \wedge \theta = \langle 1|w\rangle \rightarrow \Delta = 2\,\langle w|\left(2r^2\,|\alpha\rangle - |1\rangle\right) = 2\left(2r^2\eta - \theta\right).$$

As all the elements of the difference Δ are positive definite, the curvature only will become certainly negative when:

$$\forall I : 2r^2\alpha_I < 1,$$

most surely at distances not far from the nuclear centre.

However, resuming all the previous results and using: $\theta = \langle|w\rangle\rangle = \sum_I w_I$, also one can see that:

$$\Delta > 0 \leftarrow 2r^2\,\langle w|\alpha\rangle > \langle|w\rangle\rangle$$
$$\Delta = 0 \leftarrow 2r^2\,\langle w|\alpha\rangle = \langle|w\rangle\rangle$$
$$\Delta < 0 \leftarrow 2r^2\,\langle w|\alpha\rangle < \langle|w\rangle\rangle$$

Thus, it seems that in every ASA atom there is a surface of zero Gaussian curvature, inside this surface the space curvature is negative and outside positive, in perfect accord with the one GTO case. May be this feature may constitute the measure of some kind of atomic radius at zero curvature:

$$r_0 = \sqrt{\frac{\langle|w\,(r_0)\rangle\rangle}{2\,\langle w\,(r_0)|\alpha\rangle}}.$$

Also, the definitions of the $\{\eta, \theta\}$ parameter pair may be interpreted quite approximately as follows:

$$\theta \approx \langle \alpha \rangle \wedge \eta \approx \left\langle \alpha^2 \right\rangle \approx \langle \alpha \rangle^2 \to r_0 \approx \sqrt{\frac{1}{2 \langle \alpha \rangle}}$$

which resembles the one GTO result. It is only necessary to take into account that θ can be interpreted as an average exponent of the ASA atomic shells. However, this quite rough approach usually provides a highly negative curvature, when numerically tested, but can be employed as starting point to compute the zero curvature radii by means of an iterative procedure. The exact radius of zero curvature is quite small for different ASA fitted basis sets and atoms; it belongs approximately to the interval between 0.1 and 0.01, becoming smaller as the atomic number increases. Small variations of the vector radius produce considerable curvature changes for all ASA atoms.

6 Bader theory and molecular Riemann spaces

Besides, the present Riemannian description of the 3D space surrounding any quantum object has to be directly related to Bader's theory [12] of atoms in molecules (AIM). The reason is simple: Bader analyzes and relies on the gradient and the Hessian of the first order density function, as tools for characterizing atoms and bonds within a molecular structure.

The connection, if possible, shall be found in the fact that Riemann spaces can be described in a molecule when a first order density function is known. To handle a straightforward example as in the atomic case, the first best move is to analyze the simplest homonuclear diatomic molecule. The best candidate for this purpose is the hydrogen molecule, described with a minimal GTO basis set: using a 1s function on each Hydrogen atom: $\{s_a; s_b\}$. The first order density function for the system ground state can be defined in this very approximate way as:

$$\rho(\mathbf{r}) = N^2 \left(|s_a|^2 + |s_b|^2 + 2s_a s_b \right) \wedge N^2 = \frac{1}{\sqrt{2(1+S)}} \wedge S = \langle s_a | s_b \rangle$$

However, the expression can be further simplified, not taking into account the normalization factors and written as:

$$\rho(\mathbf{r}) = g(\mathbf{r} - \mathbf{R}_a | 2\alpha) + 2g(\mathbf{r} - \mathbf{R}_a | \alpha) g(\mathbf{r} - \mathbf{R}_b | \alpha) + g(\mathbf{r} - \mathbf{R}_b | 2\alpha). \quad (14)$$

Knowing that the product of two GTO is another GTO, centered in this case at the origin, due to the hydrogen molecule symmetry, and multiplied by a positive definite constant: $\Theta(R_{ab}; \alpha) \equiv \Theta$, depending of the interatomic distance and the exponent. The density (14) can be written now:

$$\rho(\mathbf{r}) = g(\mathbf{r} - \mathbf{R}_a | 2\alpha) + 2\Theta(R_{ab}; \alpha) g(\mathbf{r} | 2\alpha) + g(\mathbf{r} - \mathbf{R}_b | 2\alpha)$$

Then, the gradient of the molecular hydrogen density function, not taking into account the implied function norms, can be written as:

$$
\begin{aligned}
\frac{\partial}{\partial \mathbf{r}} \rho\left(\mathbf{r}\right) &= \frac{\partial}{\partial \mathbf{r}} \left(|s_a|^2 + |s_b|^2 + 2 s_a s_b\right) \\
&= \left(\frac{\partial}{\partial \mathbf{r}} g\left(\mathbf{r} - \mathbf{R}_a \,|2\alpha\right) + \frac{\partial}{\partial \mathbf{r}} g\left(\mathbf{r} - \mathbf{R}_b \,|2\alpha\right) + 2\Theta \frac{\partial}{\partial \mathbf{r}} g\left(\mathbf{r} \,|2\alpha\right)\right) \\
&= -4\alpha \left((\mathbf{r} - \mathbf{R}_a)\, g\left(\mathbf{r} - \mathbf{R}_a \,|2\alpha\right) + (\mathbf{r} - \mathbf{R}_b)\, g\left(\mathbf{r} - \mathbf{R}_b \,|2\alpha\right) + 2\mathbf{r}\Theta g\left(\mathbf{r} \,|2\alpha\right)\right)
\end{aligned}
$$

and from there one can obtain the Hessian matrix:

$$
\frac{\partial}{\partial \mathbf{r}} \otimes \frac{\partial}{\partial \mathbf{r}} \rho\left(\mathbf{r}\right) = 4\alpha \begin{pmatrix} (2\alpha\,(\mathbf{r} - \mathbf{R}) \otimes (\mathbf{r} - \mathbf{R}) - \mathbf{I})\, g\left(\mathbf{r} - \mathbf{R} \,|2\alpha\right) \\ + 2\Theta\,[2\alpha\,(\mathbf{r} \otimes \mathbf{r}) - \mathbf{I}]\, g\left(\mathbf{r} \,|2\alpha\right) \\ + (2\alpha\,(\mathbf{r} + \mathbf{R}) \otimes (\mathbf{r} + \mathbf{R}) - \mathbf{I})\, g\left(\mathbf{r} + \mathbf{R} \,|2\alpha\right) \end{pmatrix} \qquad (15)
$$

taking into account that it can be written: $\mathbf{R} = \mathbf{R}_a = -\mathbf{R}_b$.

To find analytically the eigenvalues or the determinant of the complete Hessian (15) will be obviously difficult. However, there is possible to separately analyze two contributions types, say. One of them, corresponding to one of the pair of atomic locations is:

$$
\frac{\partial}{\partial \mathbf{r}} \otimes \frac{\partial}{\partial \mathbf{r}} \rho_{aa}\left(\mathbf{r}\right) = 4\alpha\,(2\alpha\,(\mathbf{r} - \mathbf{R}) \otimes (\mathbf{r} - \mathbf{R}) - \mathbf{I})\, g\left(\mathbf{r} - \mathbf{R} \,|2\alpha\right)
$$

the alternative symmetrical contribution can be constructed just changing the subindices: $a \leftrightarrow b$, which is equivalent to change the sign of the vector $\mathbf{R}$. In this case a similar situation as in Eq. (12) appears, when the determinant has to be computed, essentially with the vector $\mathbf{r}$ substituted by: $\mathbf{r} - \mathbf{R}$.

The other distinct contribution is located at the origin and can be written as:

$$
\frac{\partial}{\partial \mathbf{r}} \otimes \frac{\partial}{\partial \mathbf{r}} \rho_{ab}\left(\mathbf{r}\right) = 8\alpha\Theta\,[2\alpha\,(\mathbf{r} \otimes \mathbf{r}) - \mathbf{I}]\, g\left(\mathbf{r} \,|2\alpha\right).
$$

The Hessian second part as above written, when taken separately from the rest of atomic centered contributions still is more similar to the one GTO case. However, this doesn't mean that the resultant Hessian behaves as a superposition of such separate moieties, but shall be treated as a whole.

Such an analysis cannot go beyond the two equivalent atomic contributions in case STO's are used. As the product of two STO's centered at different sites, cannot be expressed easily by another STO centered midway of the two nuclei, as in the GTO studied case.

Resuming this picture: it seems one can expect a similar behavior of this simple hydrogen molecular case as in the atomic case: a positive Gaussian curvature far from the nuclei, but with a possible region of negative curvature near the nuclei and perhaps at the midpoint of the interatomic distance.

To gain some insight over the function form, the molecular axis can be considered to be the vector: $\mathbf{r} = (r, 0, 0)$. Thus, along this direction the Hessian becomes:

$$\mathbf{J} = \frac{\partial}{\partial \mathbf{r}} \otimes \frac{\partial}{\partial \mathbf{r}} \rho(\mathbf{r}) = 4\alpha \begin{pmatrix} Diag\left[(2\alpha |r - R|^2 - 1), -1, -1\right] \gamma(r - R |2\alpha) \\ +2Z Diag\left[(2\alpha r^2 - 1), -1, -1\right] \gamma(r |2\alpha) \\ +Diag\left[(2\alpha |r + R|^2 - 1), -1, -1\right] \gamma(r + R |2\alpha) \end{pmatrix}$$

where it is employed the symbol: $\gamma(x |a) = \exp(-ax^2)$; so, it can be written:

$$K = Det |\mathbf{J}| = 4\alpha \left\{ \begin{array}{l} (2\alpha |r - R|^2 - 1) \gamma(r - R |2\alpha) + (2\alpha r^2 - 1) \gamma(r |2\alpha) \\ + (2\alpha |r + R|^2 - 1) \gamma(r + R |2\alpha) \end{array} \right\}$$
$$* \{\gamma(r - R |2\alpha) + \gamma(r |2\alpha) + \gamma(r + R |2\alpha)\}^2$$

which proves that the curvature along the bond axis will depend on the sign of the combination:

$$K(r) \equiv \left\{ \begin{array}{l} (2\alpha |r - R|^2 - 1) \gamma(r - R |2\alpha) + (2\alpha r^2 - 1) \gamma(r |2\alpha) \\ + (2\alpha |r + R|^2 - 1) \gamma(r + R |2\alpha) \end{array} \right\}$$

Obviously enough, the position in the positive or negative axis will provide the same curvature sign in symmetrical points, except at the origin where one will have:

$$K(0) \equiv 2\left(2\alpha R^2 - 1\right) \gamma(R |2\alpha) - 1,$$

in order to find some clues about the sign of $K(0)$, it can be assumed as an example: $R = 1 \wedge \alpha = 1$, therefore: $K(0) \equiv 2e^{-2} - 1 < 0$, for instance.

Also, in order to obtain more information, the curvature at the origin can be rearranged up to second order as:

$$K(0) \equiv 2\frac{2\alpha R^2 - 1}{e^{2\alpha R^2}} - 1 \approx 2\frac{2\alpha R^2 - 1}{2\alpha R^2 + 1} - 1 \tag{16}$$

then, calling: $\beta = 2\alpha R^2$, one can write Eq. (16) as:

$$K(0) \approx 2\frac{\beta - 1}{\beta + 1} - 1.$$

Taking into account that β will be always positive, one can deduce that whenever: $\beta < 3$, then the curvature at the origin will be negative. Thus, it seems that in this simple model of the hydrogen molecule ground state (and by straightforward extension to the hydrogen molecular ion) a negative curvature can be present at the centre (and possibly its neighborhood) of the molecular bond, whenever the following relationship holds:

$$2\alpha R^2 < 3 \rightarrow R < \sqrt{\frac{3}{2\alpha}},$$

which is reminiscent of the Eq. (13) for one GTO; however, now the involved distance is half the interatomic distance.

It will be also interesting too, to look at the first excited state density function of this simple hydrogen molecular model. In fact, there will be present exactly the same Hessian structure (15) with the mixed centre contribution changed of sign. Thus, the curvature at the origin for the first excited state can be now written as:

$$K^* (0) \equiv 2 \left(2\alpha R^2 - 1 \right) \gamma \left(R \left| 2\alpha \right. \right) + 1,$$

so the $K^* (0)$ sign will be only depending of the sign and magnitude of the first term, but there continues to be plausible the existence of a negative curvature at the origin as in the ground state. However, whenever: $2\alpha R^2 > 1$, the curvature will always be positive in this case.

6.1 Some questions

How this characteristic behavior, attributable to the GTO 3D form, can influence the issue of discussions about the characterization of bonds in complex molecules, when carried on throughout the analysis of the density function? Perhaps this is one of these good questions demanding further analysis. More than this: as STO's generate a positive curved 3D Riemann molecular space, perhaps this characteristic GTO negative curvature will not be present in molecular densities constructed with this kind of exponential functions. And this fact can carry the previous question further on: if the Riemannian 3D space characteristics depending on the density function, also depend so heavily on the basis set employed: it is advisable to rely on the first order density function gradient and Hessian to characterize chemical bonds?

7 The general LCAO density function

In the LCAO formalism [13], the first order density function can be made by employing the so-called charge and bond order matrix: $\mathbf{D} = \left\{ D_{\mu\nu} \right\}$ and the tensor product $|\boldsymbol{\chi}\rangle \langle \boldsymbol{\chi}| = \{|\mu\rangle \langle \nu|\}$ of the basis functions vector: $\langle \boldsymbol{\chi}| = (\langle 1|; \langle 2|; \ldots \langle \nu|; \ldots)$. Every basis function can be, as it is usual, associated to some GTO:

$$|\mu\rangle = g \left(\mathbf{r} - \mathbf{R}_\mu \left| \alpha_\mu \left| \mathbf{n}_\mu \right. \right. \right)$$

centered at $\mathbf{R}_\mu$, with exponent α_μ and pseudo quantum numbers $\mathbf{n}_\mu$. Then, employing the inward matrix product formalism it can be written:

$$\rho (\mathbf{r}) = \langle \mathbf{D} * |\boldsymbol{\chi}\rangle \langle \boldsymbol{\chi}| \rangle = \sum_\mu \sum_\nu D_{\mu\nu} |\mu\rangle \langle \nu|. \tag{17}$$

The basis set functions products can be considered as another GTO $\langle \mu\nu \rangle$, say, multiplied by a constant $K_{\mu\nu}$, which in turn will depend on the distance between the GTO

centers and their exponents, as well as the pseudo quantum numbers. Taking this into account, it can be written:

$$\rho(\mathbf{r}) = \sum_{\mu}\sum_{\nu} D_{\mu\nu} K_{\mu\nu} \langle\mu\nu\rangle = \sum_{\mu}\sum_{\nu} L_{\mu\nu} \langle\mu\nu\rangle$$

where as in expression (17), the matrix $\mathbf{L} = \{L_{\mu\nu}\} = \mathbf{D} * \mathbf{K}$, is defined as the inward matrix product [14] of the charge and bond order matrix by the coefficient matrix: $\mathbf{K} = \{K_{\mu\nu}\}$. Thus, the gradient leading to the 3D Riemannian coordinate framework and the Hessian providing the Gaussian curvature of the generated 3D Riemannian space, can be easily computed by the gradient and Hessian of every element of the reduced basis set: $\{\langle\mu\nu\rangle\}$.

In practice every GTO can be written as a triple product of the one dimensional functions:

$$(k = 1, 3): \gamma_k(r_k|\alpha|n_k) = r_k^{n_k}\exp\left(-\alpha r_k^2\right) \rightarrow g(\mathbf{r}|\alpha|\mathbf{n}) = \prod_k \gamma_k(r_k|\alpha|n_k),$$

therefore, employing the derivatives:

$$(k = 1, 3): \eta_k = \frac{d}{dr_k}\gamma_k(r_k|\alpha|n_k) \wedge \lambda_k = \frac{d^2}{dr_k^2}\gamma_k(r_k|\alpha|n_k) \quad (18)$$

the gradient and Hessian of any GTO can be written as he products of the one dimensional derivatives (18) and 1D Gaussian functions as:

$$\frac{\partial}{\partial\mathbf{r}}g(\mathbf{r}|\alpha|\mathbf{n}) = \mathbf{\Gamma} = \{\Gamma_k\} \rightarrow \Gamma_k = \eta_k\gamma_p\gamma_q$$

and

$$\frac{\partial}{\partial\mathbf{r}} \otimes \frac{\partial}{\partial\mathbf{r}}g(\mathbf{r}|\alpha|\mathbf{n}) = \mathbf{H} = \{H_{kl}\} \rightarrow H_{kk} = \lambda_k\gamma_p\gamma_q \wedge H_{kl} = \eta_k\eta_l\gamma_p$$

with the indices p, q different from k, l.

As the curvature is invariant upon translations, the position vector $\mathbf{r}$ shall be transformed into $\mathbf{r} - \mathbf{R}$ whenever the corresponding GTO are centered at the 3D Cartesian space position $\mathbf{R}$.

8 Conclusions

It is trivial to transform the 3D Cartesian space, where quantum objects as atoms or molecules are embedded, into a Riemannian 3D curved space. For this purpose there is only need to know a one particle quantum mechanical density function attached to the quantum object. In atoms described with a GTO basis set, there seems to appear, separated by a zero curvature surface, in 3D Riemannian space two well-defined zones,

with positive and negative Gaussian curvature, lying respectively outside and inside of this surface.

A zero surface atomic radius can be easily defined from this picture for simple atomic GTO descriptions. Such a picture will certainly disappear when STO are employed. It is difficult to grasp analytically in general what will be and which form will present the curvature variation picture in molecular structures and more interesting: which kind of chemical or physical information can be obtained from it. In GTO basis sets one can be confident that at not so large distances from the nuclei and interatomic midpoints, the Gaussian curvature of the associated 3D Riemann molecular spaces will be positive. However one shall be aware that at short distances from nuclei and somewhere in the middle of interatomic distances it may become negative. In the STO framework the curvature will be everywhere positive.

References

1. R. Carbó-Dorca, S. Van Damme, *Riemann spaces, molecular density function semispaces, quantum similarity measures and quantum quantitative structure-properties relationships (QQSPR)* Hommage to Prof. J. J. Bonet (Invited contribution) *Afinidad;* (in press)
2. L.P. Eisenhart, *Riemannian Geometry* (Princeton University Press, Princeton, 1997)
3. P.A.M. Dirac, *General Theory of Relativity* (Princeton University Press, Princeton, 1996)
4. R. Carbó-Dorca, SAR QSAR Environ. Res. **18**, 265–284 (2007)
5. W.P. Thurston, *Three-Dimensional Geometry and Topology* (Princeton University Press, Princeton, 1997)
6. R.T. Pack, W. Byers Brown, J. Chem. Phys. **45**, 556–559 (1966)
7. P. Constans, R. Carbó-Dorca, J. Chem. Inf. Comp. Sci. **35**, 1046–1053 (1995)
8. P. Constans, X. Fradera, Ll. Amat, R. Carbó-Dorca, *Quantum Molecular Similarity Measures (QMSM) and the Atomic Shell Approximation (ASA)*, Proceedings of the 2nd. Girona Seminar on Molecular Similarity. July 1995. Advances in Molecular Similarity, vol. 1 (JAI PRESS INC., Greenwich, (Conn.), 1996), pp. 187–211
9. Ll. Amat, R. Carbó-Dorca, J. Comput. Chem. **18**, 2023–2029 (1997)
10. Ll. Amat, R. Carbó-Dorca, J. Comput. Chem. **20**, 911–920 (1999)
11. Ll. Amat, R. Carbó-Dorca, J. Chem. Inf. Comput. Sci. **40**, 1188–1198 (2000)
12. R.F.W. Bader, *Atoms in molecules* (Oxford Science Publications, Clarendon Press Oxford, 1990)
13. R. Carbó-Dorca, J. Mol. Struct. (Teochem) **537**, 41–54 (2001)
14. P.O. Löwdin, Phys. Rev. **97**, 1474–1489 (1955)