Intrinsic Curvatures of Atomic Orbitals for Hydrogen-Like Atoms

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Abstract: *Within the quantum model for the hydrogen-like atom and taking into account the concepts of differential geometry, we calculate the intrinsic curvature of several types of atomic orbitals. Based on this concept of intrinsic curvature, a classification of atomic orbitals (AO) is given. We conclude by discussing the advantages of characterizing atomic quantum states by intrinsic curves for the AO of the hydrogen-like atom.*

Key Words: *differential geometry, quantum mechanics, quantum chemistry, intrinsic curvature, guiding curve, atomic orbitals, hydrogen-like atoms*

1. INTRODUCTION

In our analysis of atomic orbitals, we start from the known fact in Quantum Mechanics and Atomic Physics, that there are no less than n^2 quantum states for an excited hydrogen atom (H-like atom) with a specified principal quantum number n [1-3].

Thus, a classification of these quantum states is necessary. We add that in Quantum Chemistry quantum states are also called orbitals [3-5], which is why we also use this name throughout the paper.

In this paper, we aim to analyze and find some intrinsic properties of atomic orbitals. For this reason, we consider the guidance curves [6] for several types of orbitals and then calculate their corresponding curvatures [7].

In this regard, in Section 2, the basic model equations, several types of orbitals and general curvature formulas are presented.

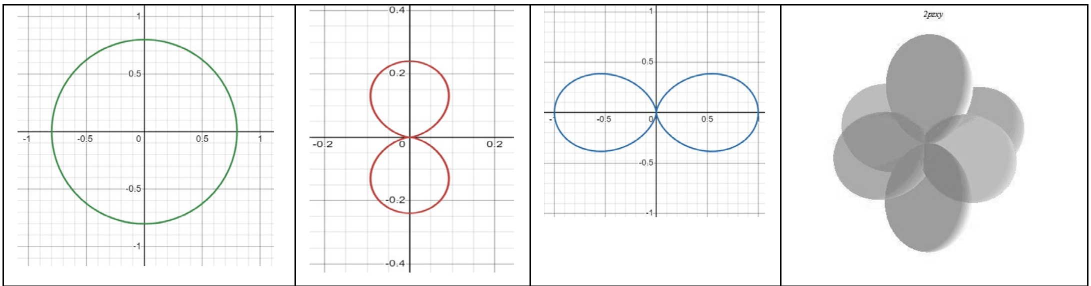
In Section 3, using orbital intrinsic curvatures, we analyze orbital guidance curves to obtain a classification of atomic quantum states.

Finally, we conclude the paper by discussing the advantages of characterizing atomic quantum states by intrinsic curvatures for several types of orbitals.

2. CURVATURES FOR ORBITALS FROM GUIDING CURVES

In the framework of quantum model of H-like atom, we obtain the expressions of the wave functions characterized by the set of quantum numbers such as the principal quantum number $n=1, 2...$, the orbital quantum number $l=0, ..., n-1$, and the magnetic orbital quantum number $m=-l..l$ [3].

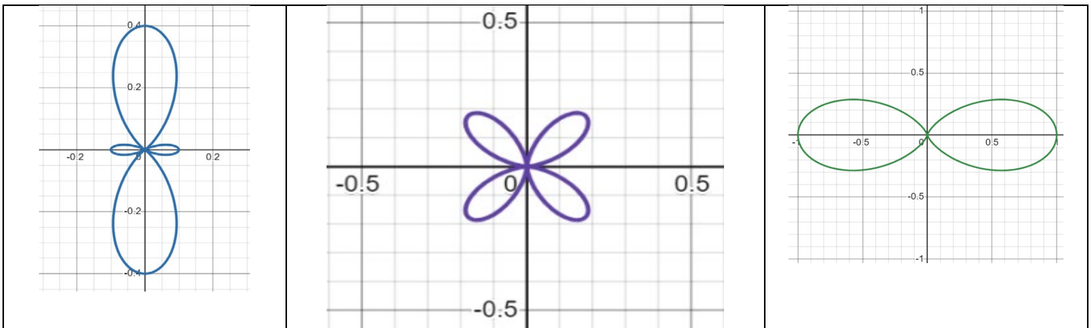
After obtaining the atomic orbitals, we calculate their normal curvatures. We note that the orbitals have an axial symmetry, see Fig. 1.



(1 0 0)	(2 1 0)	(2 1 1)	$2p_z$ $2p_x$ $2p_y$

Fig. 1: The guiding curves in coordinates *(u, v)* for hydrogen-like orbital types 1s, 2p and a superposition of orbitals $2p_x$, $2p_y$, $2p_z$

Thus, when considering a meridian plane for a conveniently fixed azimuth angle, it is sufficient to make a cross section through that orbital which leads to obtaining a guiding curve corresponding to it, see Figs. 1-2.



(3 2 0)	(3 2 1)	(3 2 2)

Fig. 2: The guiding curves in coordinates *(u, v)* for hydrogen-like orbital type 3d

Working in the spherical coordinates on the unit sphere, hence with radius r=1, co-latitude θ *in* $(0, \pi)$ and azimuth ϕ *in* $[0, 2\pi)$, we exemplify the analysis of the intrinsic curvatures of the orbitals for the excited hydrogen atom with $n=3$ [8, 3].

Then, using analytical expressions of wave-functions [3, 1] that correspond of the quantum states $(n = 1, ..., 3,\ l = 0, ..., n-1,\ m = 0, ..., l)$, we compute the normal curvatures corresponding to the guiding curves of these states.

For a quantum state $(n\ l\ m)$, having the corresponded harmonic $Y_{lm} = C_{lm} \cdot f_{lm}(\theta)$, we have the guiding curve in a parametrised form described by the vector of position (see Figs. 1-2), thus:

$$\boldsymbol{r}_{lm} = |Y_{lm}|^2 \cdot (\sin\theta, \cos\theta) = C_{lm}^2 \cdot f_{lm}(\theta)^2 \cdot (\sin\theta, \cos\theta) = (u, v),\ \theta \in (0, \pi/2]$$

The guiding curve is a plane curve, so, the formula for its normal curvature is as follows: [6]

$$k=\frac{|r'\times r"|}{|r'|^3}=\frac{|v"u'-u"v'|}{|u'^2+v'^2|^{3/2}},r=(u,v),r'=\frac{dr}{d\theta},r"=\frac{d^2r}{d\theta^2} \tag{1}$$

Based on this general formula, we obtain the intrinsic curvatures corresponding to orbitals, as follows:

$$k_{lm}(f)=\frac{\left|2ff"-6f'^2-f^2\right|}{C_{lm}{}^2|f|\left(4f'^2+f^2\right)^{3/2}} \tag{2}$$

and

$$\frac{ds_{lm}}{d\theta}(f)=s_{lm}'(f)=C_{lm}{}^2\cdot|f_{lm}|\cdot\sqrt{4f_{lm}{}'^2+f_{lm}{}^2} \tag{3}$$

where θ is a free parameter in the interval [0,π/2].

In the next section, after first highlighting the guiding curve of the corresponded orbital, we show how the formulas (2)-(3) help us to compute the curvature for each type of orbitals.

3. ATOMIC ORBITALS CLASSIFICATION BY THEIR CURVATURES

Below, we make a classification of the atomic quantum states based on normal curvature concept (see Tab.1)

We start from the spherical harmonic expressions for the types of orbitals *1s, 2p, 3d*:

$Y_{00}(\theta) = 1/2 \quad sqrt(1/\pi)$

$Y_{10}(\theta) = 1/2 \quad sqrt(3/\pi)\cos\theta$

$Y_{11}(\theta,\phi) = -1/2\, sqrt(3/\pi)\sin\theta \exp(i\cdot\phi)$

$Y_{20}(\theta) = 1/4 \quad sqrt(5/\pi)(3\cos^2\theta-1)$

$Y_{21}(\theta,\phi) = -1/2\, sqrt(15/2\pi)\sin\theta\cos\theta \exp(i\cdot\phi)$

$Y_{22}(\theta,\phi) = 1/4\, sqrt(15/2\pi)\sin^2\theta \quad \exp(2i\cdot\phi)$

Thus, the guidance curves in parametric form for the types of *1s, 2p, 3d* orbitals are as follows:

$r_{1s} = C_{00}{}^2\cdot(\sin\theta, \cos\theta)$

$r_{pz} = C_{10}{}^2\cdot\cos^2\theta\cdot(\sin\theta, \cos\theta)$

$r_{px} = C_{11}{}^2\cdot\sin^2\theta\cdot(\sin\theta, \cos\theta)$

$r_{dz} = C_{20}{}^2\cdot(3\cos^2\theta-1)^2\cdot(\sin\theta, \cos\theta)$

$r_{21} = C_{21}{}^2\cdot\cos^2\theta\sin^2\theta\cdot(\sin\theta, \cos\theta)$

$r_{22} = C_{22}{}^2\cdot\sin^4\theta\cdot(\sin\theta, \cos\theta)$

We obtain the normal curvatures of these curves which generate by rotation the orbitals of the types 1s, 2p, 3d, as follows:

$$\begin{aligned} k_{00}(\theta) &= \frac{1}{C_{00}{}^2} \\ ds_{00} &= C_{00}{}^2 d\theta \end{aligned} \tag{4}$$

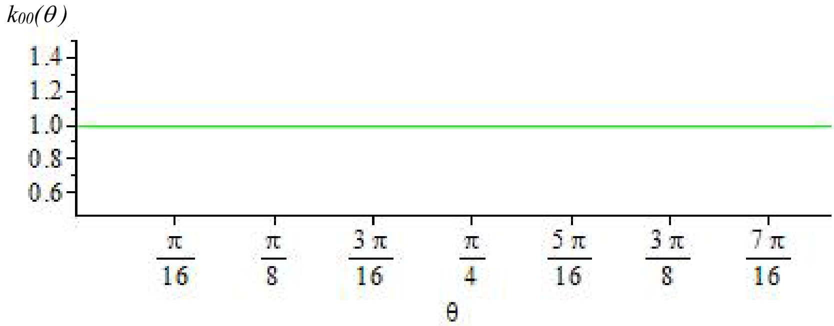


Fig. 3: Graphical curvature of state (3 0 0) with $\theta \in [0,\pi/2]$

$$k_{10}(\theta) = \left|\frac{3(cos^2\theta - 2)}{{C_{10}}^2 \cos\theta \sqrt{|(3\cos^2\theta - 4)|^3}}\right|$$

$$ds_{10} = {C_{10}}^2 |\cos\theta| \sqrt{3\sin^2\theta + 1} d\theta \tag{5}$$

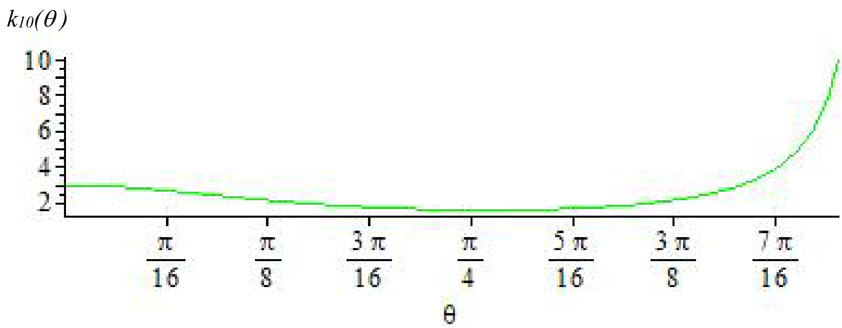


Fig. 4: Graphical curvature of state (3 1 0) with $\theta \in [0,\pi/2)$

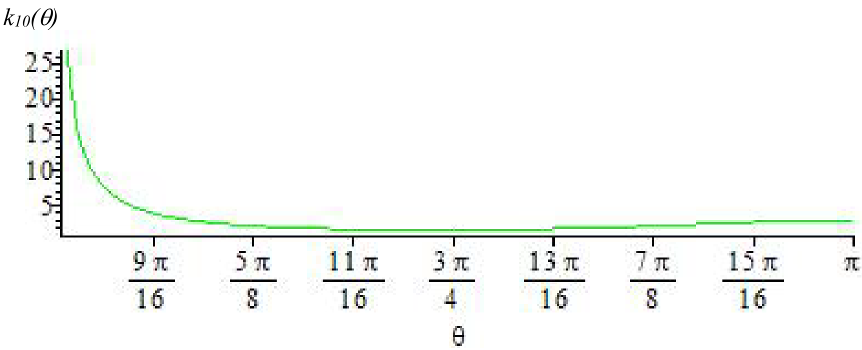


Fig. 5: Graphical curvature of state (3 1 0) with $\theta \in (\pi/2, \pi]$

$$k_{11}(\theta) = \left|\frac{3(1 + cos^2\theta)}{{C_{11}}^2 \sin\theta \sqrt{(3\cos^2\theta + 1)^3}}\right|$$

$$ds_{11} = {C_{11}}^2 |\sin\theta| \sqrt{3\cos^2\theta + 1} d\theta \tag{6}$$

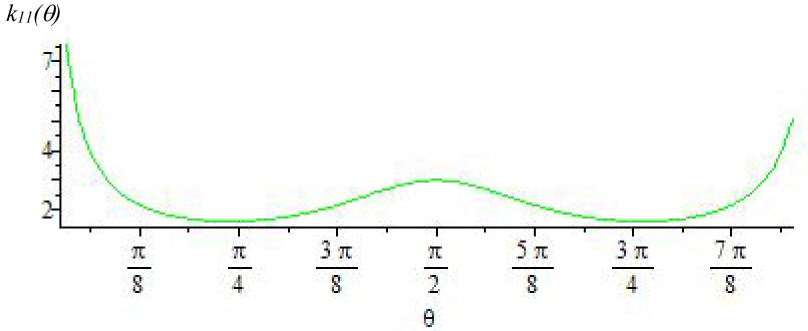


Fig. 6: Graphical curvature of state (3 1 1) with $\theta \in (0,\pi)$

$$k_{20}(\theta) = \frac{|135\,cos^4\,\theta - 150\,cos^2\,\theta - 13|}{{C_{20}}^2|3\,cos^2\,\theta - 1|\sqrt{(-135\,cos^4\,\theta + 138\,cos^2\,\theta + 1)^3}}, arccos(1/\sqrt{3})\sim 55°$$
$$ds_{20} = {C_{20}}^2|3\,cos^2\,\theta - 1|\sqrt{|135\,cos^4\,\theta - 138\,cos^2\,\theta - 1|}d\theta \tag{7}$$

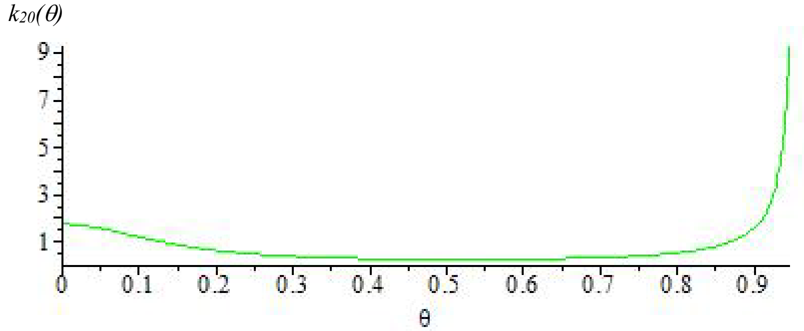


Fig. 7: Graphical curvature of state (3 2 0) with $\theta \in [0,$ *arccos* $(1/\sqrt{3}))$

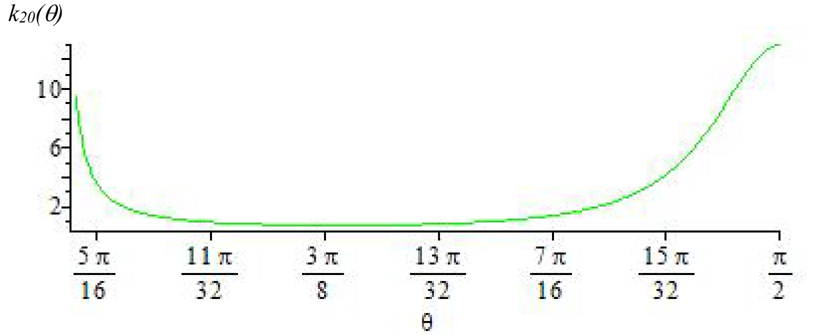


Fig. 8: Graphical curvature of state (3 2 0) with $\theta \in ($*arccos* $(1/\sqrt{3}), \pi/2]$

$$k_{21}(\theta) = \frac{|3(2 - 5\,cos^2\,\theta + 5\,cos^4\,\theta)|}{{C_{21}}^2|\,sin\,\theta\,cos\,\theta\,|\sqrt{(4 - 15\,sin^2\,\theta\,cos^2\,\theta)^3}}$$
$$ds_{21} = {C_{21}}^2|\,sin\,\theta\,cos\,\theta\,|\sqrt{4 - 15\,sin^2\,\theta\,cos^2\,\theta}\,d\theta \tag{8}$$

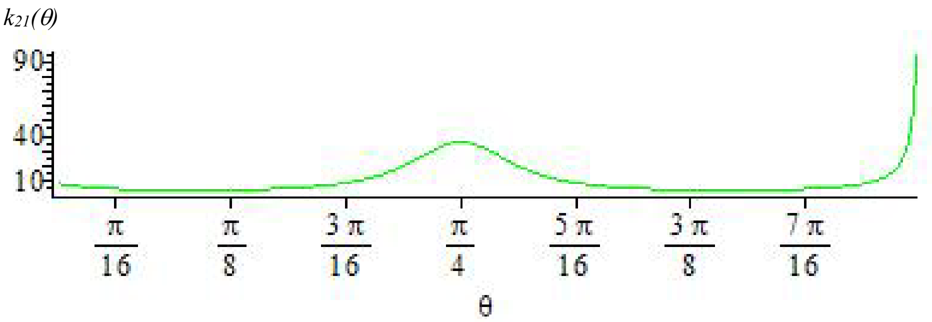


Fig. 9: Graphical curvature of state (3 2 1) with $\theta \in [0,\pi/2)$

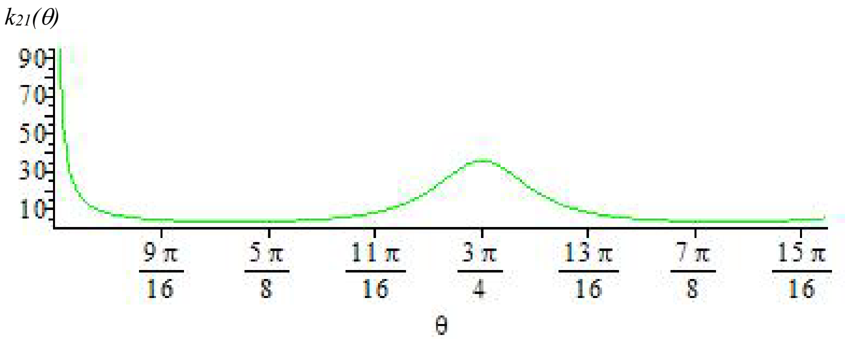


Fig. 10: Graphical curvature of state (3 2 1) with $\theta \in (\pi/2, \pi]$

$$k_{22}(\theta) = \frac{5(1+3\cos^2\theta)}{C_{22}{}^2|\sin^3\theta|\sqrt{(15\cos^2\theta+1)^3}}$$
$$ds_{22} = C_{22}{}^2|\sin^3\theta|\sqrt{15\cos^2\theta+1}d\theta \tag{9}$$

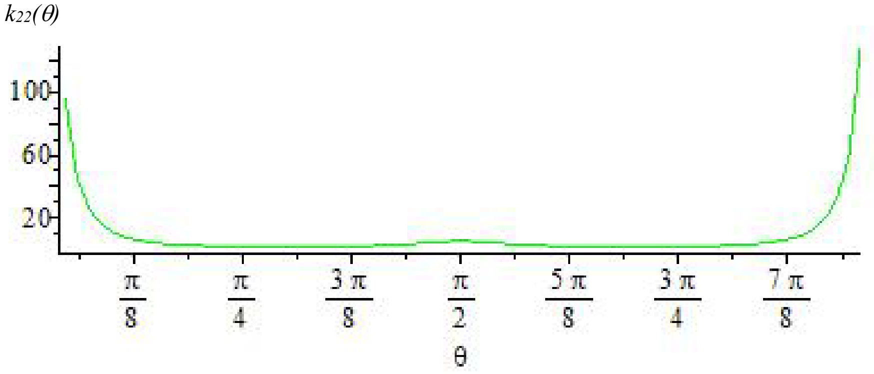


Fig. 11: Graphical curvature of state (3 2 2) with $\theta \in (0,\pi)$

We mention that for the simplicity of our exposition on graphs of normal curvatures in Figs. 3-11, we consider C≡1.

In the table below of intrinsic curves $k(\theta)$ with $\theta \in (0,\pi/2]$ and taking in the account Equations (4)-(9) and Figs. 3-11, we obtain the θ - nodal values for the guiding curves of orbital types *1s, 2p, 3d*.

Tab. 1: The nodal angular values for co-latitude corresponding of orbital types *1s, 2p, 3d*.

(l m) for n up to 3	θ *values such as* $k(\theta)\rightarrow\infty$	θ *values such as* $s'(\theta) = 0$
(0 0)	-	-
(1 0)	$\pi/2$	$\pi/2$
(1 1)	0	0
(2 0)	$arccos(1/\sqrt{3})$~55°	$arccos(1/\sqrt{3})$
(2 1)	0, $\pi/2$	0, $\pi/2$
(2 2)	0	0

From Tab.1, we observe that $k(\theta)\rightarrow\infty <=> s'(\theta) = 0$ this fact happening because these relationships occur for the same θ values.

In addition, in Fig. 12, we recall the classification of atomic quantum states according to spherical harmonics. [8]

Furthermore, in the same Figure 12, we give the 3D shape for the atomic orbitals. We note that Y_{l0} harmonics are always real-valued. In addition, to represent Y_{lm} harmonics with m>0, we use the expressions $|ReY|^2$ in these cases [9].

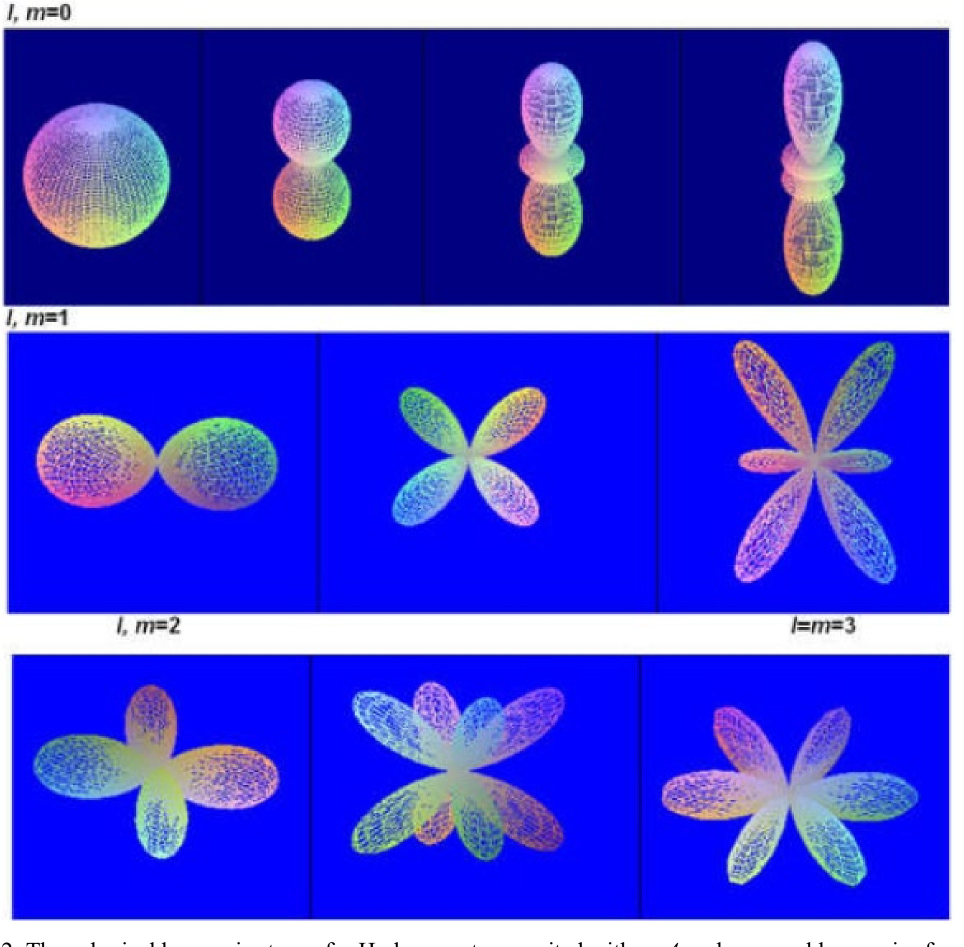


Fig. 12: The spherical harmonics types for Hydrogen atom excited with $n=4$ such as zonal harmonics for $m=0$, sectoral harmonics for $l=m$ and tesseral harmonics for rest values of m

Finally, comparing both classifications, namely the one based on curvature and the one based on harmonics, we notice that the first classification, being an intrinsic method, does not depend on coordinates and represents another way of classifying the quantum states associated with an excited Hydrogen atom with a certain main quantum number n.

4. CONCLUSIONS

We have obtained the intrinsic curves for several types of orbitals and given a classification for them using the concept of intrinsic curvature. This result is in good agreement with the classification for orbitals by spherical harmonics [8].
An advantage of using the curvature classification is that it better characterizes the nodal values for co-latitude than in the case of harmonics one, so, it is more relevant being an intrinsic property of orbitals, because it is dependent only on a free parameter on the curve.
Curvature classification is also useful as a new way to characterize atomic quantum states.

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REFERENCES

[1] B. H. Bransden, Ch. Joachain, *Physics of Atoms and Molecules*, 2003.
[2] D. Constantin, L. Preda, M. Rushton, *U.P.B Sci. Bulletin*, Series A, **85**, 1, 2023.
[3] D. Constantin et al., *The orbitals of Rydberg atom., Rom. Astron. J.* **30**, 1, pp 35-41, 2020.
[4] D. Constantin et al., *Quasi-harmonic potential in Schrödinger equation and Laplace Transform*, 2018. Available at https://arxiv.org/abs/1804.02455
[5] D. Constantin et al., *The Hydrogen-like atom: geometric representation of its orbital types, BSG Proceedings* **27**, 17-21, 2020.
[6] C. Udriste, *Diff. Geom. - lecture notes*, Ed. Politehnica Buc, 2015.
[7] S. Radnef, *Cartesian coordinates of an intrinsically defined curve, INCAS BULLETIN*, Volume **15**, Issue 4, pp. 211 – 219, https://doi.org/10.13111/2066-8201.2023.15.4.18, 2023.
[8] D. Constantin et al., *The quantum states for Hydrogen atom : spherical harmonics, INCAS BULLETIN*, Volume **16**, Issue 1 pp. 25 – 31, https://doi.org/10.13111/2066-8201.2024.16.1.3, 2024.
[9] S. Brandt, H. D. Dahmen, *The picture book of Quantum Mechanics*, 3rd Edition, 2001.