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ARTICLE *in* INTERNATIONAL JOURNAL OF QUANTUM CHEMISTRY · MARCH 2003

Impact Factor: 1.43 · DOI: 10.1002/qua.10508

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Hydrogenic Orbitals in Momentum Space and Hyperspherical Harmonics: Elliptic Sturmian Basis Sets

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Received 15 January 2002; accepted 10 March 2002

DOI 10.1002/qua.10508

ABSTRACT: Momentum space hydrogenic orbitals can be regarded as orthonormal and complete Sturmian basis sets and explicitly given in terms of (hyper)-spherical harmonics on the 4-D hypersphere S^3. Among the alternative coordinate systems that allow separation of variables, the usual ones involving parameterizations of the sphere S^3 by circular functions correspond to canonical subgroup reduction chains; we also investigate harmonic "elliptic" sets (as, e.g., obtained by parameterizations in terms of Jacobi elliptic functions). In this article we list the canonical hydrogenic Sturmian sets and the orthogonal transformations connecting them. The latter enjoy useful three-term recurrence relationships that allow their efficient calculations even for large strings. We also consider modifications needed when the conservation of the symmetry of Sturmians with respect to parity. Finally, we discuss some properties of elliptic hydrogenic Sturmians and their relations with canonical Sturmians. Because elliptic Sturmians cannot be expressed in closed form, it is important to find expansions in a suitable basis set and calculate the transformation coefficients. We derive three-term recursion relationships fulfilled by the coefficients of the transformation between elliptic Sturmians and canonical Sturmians. A concluding discussion on the connections between configuration space and momentum space hydrogenic Sturmians completes this article. Int J Quantum Chem 92: 212–228, 2003

Key words: elliptic orbitals; momentum space; hyperspherical harmonics; recoupling coefficients; separation of variables

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1. Introduction

The investigation of the nonrelativistic Schrödinger equation for hydrogenic atoms in momentum space has great relevance not only for the obvious importance of the physical problem but also because it allows the construction of basis sets enjoying different symmetry properties useful in atomic and molecular structure calculations and for the description of atoms in fields.

Hydrogenic orbitals in momentum space, first obtained by Podolski and Pauling [1] by direct Fourier transform, can indeed be identified, within a normalization factor, with hyperspherical harmonics of a 4-D sphere, as shown by Fock [2] through his famous stereographic projection. Modernly they can be referred to as momentum space Sturmians [3–7], being the counterpart of the so-called "natural spin" [8] or configuration space Sturmian orbitals [9, 10], which are finding increasing applications in atomic and molecular quantum chemistry. For recent reviews, see Refs. [11] and [12]. The reciprocity existing between configuration and momentum space has to be applied with care when trying to extend all the symmetry properties that can be found in momentum space to the corresponding configuration space Sturmians. The symmetry and completeness properties of these sets make them in fact adapt to solve quantum mechanical problems where the hyperspherical symmetry of the kinetic energy operator is broken by the interaction potential, but the corresponding perturbation matrix elements can be worked out explicitly, as in the case of Coulomb interactions.

In the present work, after explaining the connection between the hydrogen atom and the 4-D hypersphere (Section 2), we review and update the classification of hydrogenic Sturmians in momentum space given in Ref. [13] (Section 3), requesting the conservation of parity (Section 4). In addition, elliptic Sturmians in momentum space are introduced (Section V), in which the modulus of Jacobi elliptic functions can be seen as an additional "degree of freedom," making them more flexible with respect to the canonical Sturmians. As also stressed in the concluding Section 6, the aim of this work has been to show that they are less "intractable" than previously believed [14].

2. Background

In 1935 Fock obtained the wave functions of hydrogen atom $\Psi(\mathbf{p})$ in momentum space by solving the Schrödinger equation related by Fourier transform to the one in configuration space:

$$(p^2 + p_0^2)\Psi(\mathbf{p}) = \frac{1}{\pi^2}\int \frac{\Psi(\mathbf{p}')}{|\mathbf{p} - p'|^2}\, d\mathbf{p}', \qquad (1)$$

where p_0 corresponds to the energy $E_0 = -p_0^2/2$ (a.u. will be used throughout this article). The wave functions $\Psi(\mathbf{p})$ can be related to 4-D spherical harmonics, i.e., eigenfunctions of the Laplace operator on S^3. The momentum $\mathbf{p}$ with Cartesian coordinates

$$\begin{aligned} p_x &= p\ \sin\vartheta \cos\varphi \\ p_y &= p\ \sin\vartheta \sin\varphi \\ p_z &= p\ \cos\vartheta, \end{aligned} \qquad (2)$$

where p is the modulus of $\mathbf{p}$ and ϑ and φ its polar angles, is projected onto a 4-D hypersphere of unit radius:

$$\begin{aligned} x &= \frac{2p_0p_x}{p_0^2 + p^2} = \sin\chi \sin\vartheta \cos\varphi \\ y &= \frac{2p_0p_y}{p_0^2 + p^2} = \sin\chi \sin\vartheta \sin\varphi \\ z &= \frac{2p_0p_z}{p_0^2 + p^2} = \sin\chi \cos\vartheta \\ w &= \frac{p_0^2 - p^2}{p_0^2 + p^2} = \cos\chi, \end{aligned} \qquad (3)$$

where $0 \le \chi \le \pi$. Equation (3) exhibits the relationship between the Euclidean space (p_x, p_y, p_z) and the S^3 surface $(x^2 + y^2 + z^2 + w^2 = 1)$, and also gives an explicit parameterization in polar coordinates $(\chi, \vartheta, \varphi)$ of the S^3 hypersphere. Figure 1 illustrates Fock's stereographic projection, but to make it readable we have drawn it considering one dimension lower, i.e., projecting a 2-D plane on the 3-D sphere S^2, instead of the 3-D space on the 4-D hypersphere S^3.

The eigenfunction for the hydrogen atom in momentum space is [6, 7, 12]

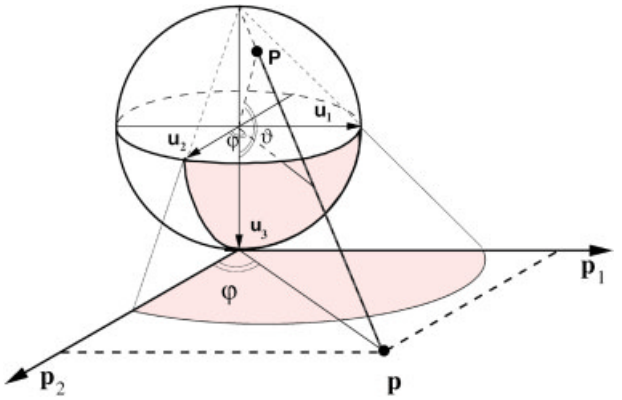

FIGURE 1. Stereographic projection establishes a relationship between points on a sphere S^{d-1} and a Euclidean space R^d. The case $d = 3$ is the one used by Fock for the hydrogen atom (see Section 2). The familiar "geographic" case $d = 2$ is shown here for illustration: stereographic projection of a point **p** in a plane with coordinates $p_1 = p \sin \varphi$ and $p_2 = p \cos \varphi$ onto the surface of a sphere having unitary radius with coordinates $u_1 = \sin \vartheta \sin \varphi$, $u_2 = \sin \vartheta \cos \varphi$, $u_3 = \cos \vartheta$, where $\cos \vartheta = (p_0^2 - p^2)/(p_0^2 + p^2)$. The shaded zone represents the projection of the points of the plane onto the part of spherical bowl comprised between the equator and the axes u_1 and u_2. The points fulfilling the condition $p = p_0$ are projected onto the equator. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

$$\Psi_{n,l,m}(\mathbf{p}) = \frac{4p_0^{5/2}}{(p_0^2 + p^2)^2} \cdot Y_{n,l,m}(\chi, \vartheta, \varphi), \qquad (4)$$

where $Y_{n,l,m}(\chi, \vartheta, \varphi)$ is a 4-D hyperspherical harmonic, the wave function for the free motion of a particle on the S^3 surface. Thus, the principal quantum number n (which labels the energy spectrum) can appropriately be interpreted as a hyperangular momentum quantum number, manifesting that the hidden symmetry giving rise to the accidental degeneracy emerging in the 3-D configuration space treatment is actually a 4-D symmetry, which has been analyzed and discussed in various articles [15], reviews [16], and books [17]. The invariance group for the Hamiltonian of the hydrogen atom is thus $O(4)$, the continuous group of rotations in the 4-D Euclidean space. The actual symmetry of the hydrogen atom Schrödinger equation has therefore become apparent only in the momentum space approach: The degeneracy existing for a given n gives rise to n^2 Sturmians that belong to the same irreducible representation of $O(4)$.

The hydrogenic Hamiltonian can be expressed as a function of the orbital angular momentum $\hat{\mathbf{l}}$ and of the Runge–Lenz vector $\hat{\mathbf{A}}$ in its reduced form $\hat{\mathbf{K}}$ [15, 18]:

$$\hat{H} = -\frac{1}{2}(\hat{\mathbf{l}}^2 + \hat{\mathbf{K}}^2 + 1)^{-1}, \qquad (5)$$

where

$$\hat{\mathbf{K}} = \hat{\mathbf{A}}/p_0 = \left[\frac{1}{2}(\hat{\mathbf{l}} \times \hat{\mathbf{p}} - \hat{\mathbf{p}} \times \hat{\mathbf{l}}) + \frac{np_0\mathbf{r}}{r}\right]\Big/ p_0. \qquad (6)$$

The Cartesian components of $\hat{\mathbf{l}}$ and $\hat{\mathbf{K}}$ can be identified with the generators of 4-D rotations, in virtue of the isomorphism of the hydrogen atom with the sphere S^3. Let us consider the Euclidean 4-D space: There are six possible distinct bidimensional planes identified by the various couples of Cartesian axes; by indicating one of those planes as ef, a rotation of an angle α upon it is performed by the operator $e^{i\alpha\hat{J}_{ef}}$, where $\hat{J}_{ef}$ is one of the six generators of $O(4)$ [17, 19]:

$$\hat{J}_{ef} = \frac{1}{i}\left(u_e \frac{\partial}{\partial u_f} - u_f \frac{\partial}{\partial u_e}\right). \qquad (7)$$

Their commutation relations are

$$[\hat{J}_{ef}, \hat{J}_{gh}] = i(\delta_{fh}\hat{J}_{eg} - \delta_{fg}\hat{J}_{eh} - \delta_{eh}\hat{J}_{fg} + \delta_{eg}\hat{J}_{fh}). \qquad (8)$$

Equation (8) enables us to associate the generators of $O(4)$ with the components of $\hat{\mathbf{l}}$ and $\hat{\mathbf{K}}$ on the basis of their commutation relations [19]:

$$\hat{l}_x = \hat{J}_{23} \quad \hat{l}_y = \hat{J}_{31} \quad \hat{l}_z = \hat{J}_{12}$$

$$\hat{K}_x = \hat{J}_{14} \quad \hat{K}_y = \hat{J}_{24} \quad \hat{K}_z = \hat{J}_{34}. \qquad (9)$$

The generalized Beltrami–Laplace operator for the motion in d dimensions can be written as [19]

$$\sum_e \frac{\partial^2}{\partial u_e^2} = \frac{1}{r^{d-1}}\frac{\partial}{\partial r}\left(r^{d-1}\frac{\partial}{\partial r}\right) - \frac{1}{r^2}\sum_{f>e}\hat{J}_{ef}^2. \qquad (10)$$

A d-dimensional hyperspherical harmonic solves the eigenvalue equation on the d-dimensional sphere S^{d-1} parameterized by the set of angles Ω_{d-1}:

$$\sum_{b>a}\hat{J}_{ab}^2 Y_{j,\alpha}(\Omega_{d-1}) = j(j + d - 2)Y_{j,\alpha}(\Omega_{d-1}), \qquad (11)$$

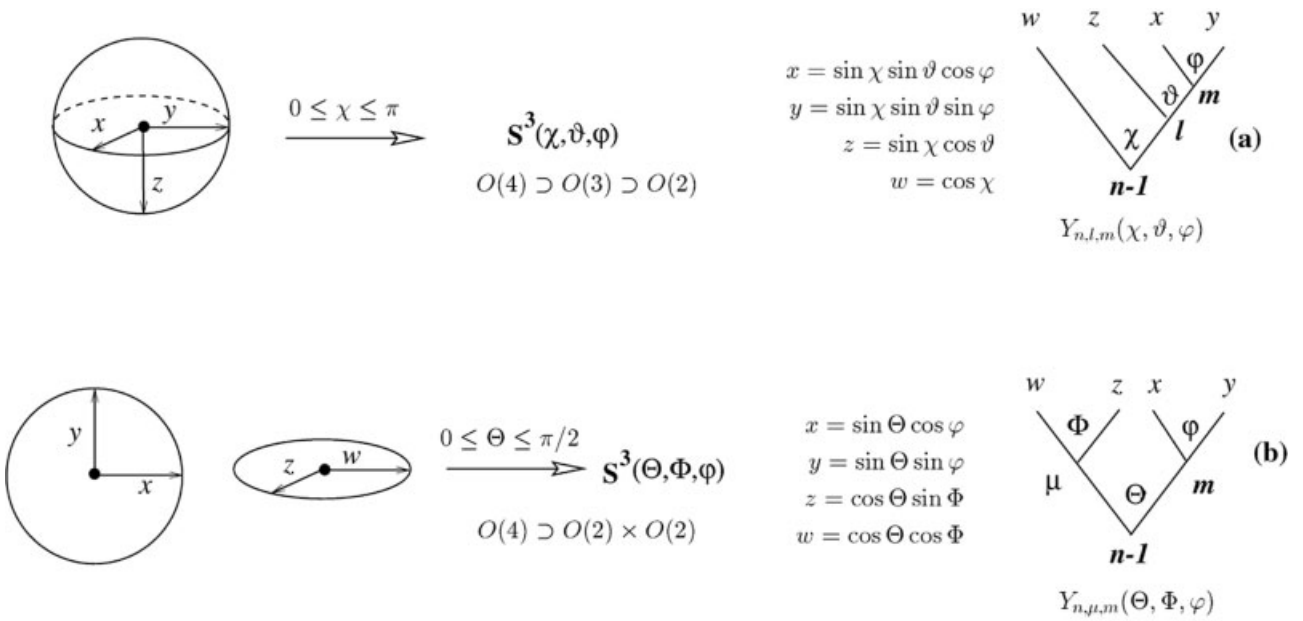

FIGURE 2. Two different constructions of S^3 sphere corresponding to the (a) asymmetrical and (b) symmetrical parameterization. The relationship of Cartesian coordinates with spherical coordinates is obtained by labeling with angular variables the intersections (nodes) between two tree "branches" and considering that the branch converging to the node from the left (right) represents the cosine (sine) of the involved angle. Thus, starting from a leaf and going down to the root of the tree, through the various nodes, we establish a relation between Cartesian coordinates and angles. Each of these angles is related to rotations in a space whose dimension is equal to the number of the upper free ends (or leaves), and thus to the corresponding rotation operator, so that every node can also be labeled by its eigenvalue (quantum number). Thus, in both types of parameterizations according to the particular subspaces involved in the construction of S^3 we will have alternative basis sets of the canonical type, i.e., corresponding to different subgroup reduction chains (see also Ref. [44]).

where α is a set of $d - 2$ labels (quantum numbers). For the case $d = 4$ one has a six-term sum:

$$\sum_{b>a} \hat{J}_{ab}^2 Y_{j,\alpha}(\Omega_3) = j(j+2) Y_{j,\alpha}(\Omega_3), \qquad (12)$$

where α denotes two quantum numbers. Use of Eq. (9) shows that the operator in Eq. (12) coincides with $\hat{\mathbf{I}} + \hat{\mathbf{K}}^2$, and therefore momentum space Sturmians (which, as we have seen, essentially coincide with 4-D harmonics) can be identified with basis sets for irreducible representations of the rotational group $O(4)$, as suggested by Eq. (4). The hyperangular momentum quantum number $j = n - 1$ labels the energy levels.

That of Eq. (3) is only one of the possible parameterizations separating the Hamiltonian for the motion on S^3 (for it, $\alpha = l, m$): Starting from other suitable parameterizations alternative momentum space orbitals can be worked out. A complete classification of the bases of $O(4)$, including symmetry properties and connections among them, will be given in the following sections.

3. Canonical Bases of $O(4)$

As mentioned in the previous section, the hyperspherical harmonics in Eq. (4) are not the only possible choice for 4-D harmonics. Such a variety of choices is illustrated by the alternative ways of building the 4-D S^3 hypersphere starting from lower dimension (hyper)-spheres. In particular, there exist two basically distinct ways that have been depicted in Figure 2: The first [Fig. 2(a)] consists of starting from the S^2 sphere (i.e., the physical 3-D sphere) and adding a rotation in the fourth dimension. The "inverse" of this construction in group theory corresponds to the following chain reduction of $O(4)$ into its subgroups: $O(4) \supset O(3) \supset O(2)$.

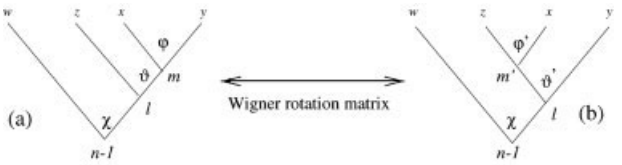

FIGURE 3. Representation of the change of quantization axis for the spherical basis sets from m (z axis) to m' (y axis), corresponding to Eq. (15).

An alternative approach [Fig. 2(b)] starts from two S^1 circles, each described by an angle, belonging to orthogonal R^2 spaces and then forms their product $R^2 \times R^2 = R^4$; a third angle is needed to cover S^3. In group theory this corresponds to the subgroup reduction chain $O(4) \supset O(2) \times O(2)$. The related parameterizations will be given the nicknames of *asymmetrical* and *symmetrical* for the first and second cases, respectively. Figure 2 illustrates graphically the two schemes for the construction of S^3 and shows connections between Cartesian and hyperspherical coordinates and the representation of the corresponding hyperspherical harmonics according to the tree method. This graphical method, a full account of which can be found in Refs. [20–23], permits a visualization not only for the connection between coordinates but also for the rotation operators for which the harmonics are eigenfunctions.

The following paragraphs will deal with the classification and description of the various sets corresponding to the different parameterizations. Obviously the choice of a particular basis set is completely pointless when the symmetry of the problem is the original S^3 one (as in the case of hydrogenoid atoms), but it becomes crucial when such a symmetry is broken, and yet the perturbation Hamiltonian can still be written in terms of the generators of the 4-D rotation group, as in the case for instance for hydrogenoid atoms in electric and/or magnetic fields. Important in quantum chemistry are molecular orbitals, which describe symmetry breakings occurring when atoms join to form molecules.

3.1. ASYMMETRICAL PARAMETERIZATIONS: SPHERICAL AND ZEEMAN SETS

The harmonics in Figure 2(a) correspond, as sketched before, to a subgroup reduction chain $O(4) \supset O(3) \supset O(2)$, where a fourth dimension is added to the Euclidean tridimensional space $[x, y, z]$ whose generators are $\hat{l}_x$, $\hat{l}_y$, and $\hat{l}_z$, or, according to the previous identification, $\hat{J}_{12}$, $\hat{J}_{23}$, and $\hat{J}_{13}$ [see Eq. (9)]. Explicitly these harmonics can be written as the product between the usual tridimensional spherical harmonic $Y_{l,m}(\vartheta, \varphi)$, eigenfunctions of the quadratic "orbital angular momentum" operator $\hat{\mathbf{l}}^2 = \hat{l}_x^2 + \hat{l}_y^2 + \hat{l}_z^2$ with eigenvalues $l(l+1)$, and a properly normalized Gegenbauer polynomial [24] of the additional variable $\cos\chi$ [Eq. (3)]:

$$Y_{n,l,m}(\chi, \vartheta, \varphi) = B_{n,l} \sin^l\chi C_{n-1-l}^{l+1}(\cos\chi) Y_{l,m}(\vartheta, \varphi), \tag{13}$$

where the normalization of factor $B_{n,l}$ is defined as follows:

$$B_{n,l} = \frac{\Gamma(2l+2)}{2^{l+1}\Gamma(l+3/2)} \left[\frac{2n(n-1-l)!}{\Gamma(n+l+1)}\right]^{1/2}. \tag{14}$$

The harmonics $Y_{n,l,m}(\chi, \vartheta, \varphi)$ are also eigenfunctions of $\hat{l}_z$ with eigenvalue m; this corresponds to the choice of the (xy) plane where the rotation subgroup $O(2)$ acts and thus of z as the polar axis. Continuing to identify $O(3)$ as acting on the tridimensional space $[x, y, z]$—the fourth dimension being not involved yet—when the (yz) or (xz) planes are chosen for the $O(2)$ subspaces one has the harmonics $Y_{n,l,m'}(\chi, \vartheta, \varphi')$ and $Y_{n,l,m''}(\chi, \vartheta, \varphi'')$, eigenfunctions of $\hat{l}_y$ (y polar axis) and $\hat{l}_x$ (x polar axis), respectively. Interchanges among the polar axes, illustrated for example in Figure 3, can be performed by means of a Wigner rotation matrix:

$$Y_{n,l,m'}(\chi, \vartheta', \varphi') = \sum_{m'} D^l_{m,m'}(0, \pi/2, \pi/2) Y_{n,l,m}(\chi, \vartheta, \varphi). \tag{15}$$

Let us now consider a 3-D subspace where the rotation group $O(3)$ acts, and let w be one of the axes: Two of the generators involved in the tridimensional rotation operator are now components of the vector $\hat{\mathbf{K}}$ according to Eq. (9). For example, the basis $[(xy)w]z$ described by tree (b) in Figure 4 is diagonal with respect to the operators $\hat{K}_x^2 +$

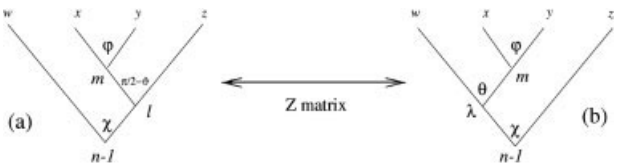

FIGURE 4. Transformation from the spherical to the Zeeman basis set, which implies the change of the tridimensional quantum number from l to λ.

$\hat{K}_y^2 + \hat{l}_z^2$ and $\hat{l}_z$. Let the eigenvalue corresponding to the first operator be now denoted as $\lambda(\lambda + 1)$, Labarthe's quantum number λ having the same range as l. This basis set, which we call a Zeeman basis, has been recently introduced [25–27]. It is useful for the treatment of the diamagnetism in hydrogen atom and for the description of the behavior of Rydberg atoms in magnetic fields. Note that, analogously to what has been just shown for the spherical basis, one can choose $\hat{K}_y$ or $\hat{K}_x$ as diagonal operators, thus leading to $Y_{n,\lambda,\mu'}(\chi', \theta', \phi')$ and $Y_{n,\lambda,\mu''}(\chi', \theta'', \phi'')$ harmonics, where μ' and μ'' denote the corresponding eigenvalues. The connection between these bases and the Zeeman basis (compare with the illustration in Fig. 3 of the case of the spherical basis) is given by a Wigner rotation matrix, similar to Eq. (15). Beside the Zeeman basis set [and those basis sets with a different projection axis, i.e., $Y_{n,\lambda,\mu'}(\chi', \theta', \phi')$ and $Y_{n,\lambda,\mu''}(\chi', \theta'', \phi'')$], there are six other bases of the same kind that can be identified: Three of them are eigenfunctions of the quadratic operator $\hat{K}_x^2 + \hat{l}_y^2 + \hat{K}_z^2$ [with eigenvalue $\lambda'(\lambda' + 1)$] and of $\hat{K}_x$, $\hat{l}_y$, and $\hat{K}_z$, respectively (with eigenvalues μ'', m' and μ), while the last three bases are diagonalized by the quadratic operator $\hat{l}_x^2 + \hat{K}_y^2 + \hat{K}_z^2$ and by the operator $\hat{l}_x$, $\hat{K}_y$, and $\hat{K}_z$, respectively (with eigenvalues m'', μ', and μ). A summary of the 12 bases of $O(4)$ corresponding to asymmetrical parameterizations in given in Table I.

Orthogonal transformations that lead to a change in the tridimensional angular momentum quantum number (transformations among l, λ, λ', λ'') can be performed by means of the Z matrices introduced in [13] (see also [28]). For example, the orthogonal transformation between the spherical [Eq. (4)] and the Zeeman basis sets [$Y_{n,l,m}(\chi, \vartheta, \varphi) = \Sigma_\lambda Z_{l,\lambda}^{n,m} Y_{n,\lambda,m}(\chi', \theta, \varphi)$] is depicted in Figure 4. In Ref. [13] it was shown that the harmonic superposition between the two bases, which had previously been defined indirectly through the steps spherical basis → Stark basis → Zeeman basis and calculated as a sum on two vector coupling coefficients [25, 29] [see Eq. (22)], can be written as a single sum of the Racah type:

TABLE I

Twelve bases corresponding to the reduction of the group $O(4)$ to the subgroup chain $O(4) \supset [O(3)]_{i,j,k} \supset [O(2)]_{i,j}$.

d = 3-subspace	d = 2-subspace	Basis set
$[x, y, z]$: $\hat{l}_x^2 + \hat{l}_y^2 + \hat{l}_z^2$		
(spherical sets)	(x, y) $\hat{l}_z$	$\|n, l, m\rangle$
	(y, z) $\hat{l}_x$	$\|n, l, m''\rangle$
	(z, x) $\hat{l}_y$	$\|n, l, m'\rangle$
$[x, y, w]$: $\hat{K}_x^2 + \hat{K}_y^2 + \hat{l}_z^2$		
(Zeeman sets)	(x, y) $\hat{l}_z$	$\|n, \lambda, m\rangle$
	$(y,w)\hat{K}_y$	$\|n, \lambda, \mu'\rangle$
	$(x,w)\hat{K}_x$	$\|n, \lambda, \mu''\rangle$
$[x, z, w]$: $\hat{K}_x^2 + \hat{K}_z^2 + \hat{l}_y^2$	(z, x) $\hat{l}_y$	$\|n, \lambda', m'\rangle$
	$(z,w)\hat{K}_z$	$\|n, \lambda', \mu\rangle$
	$(x,w)\hat{K}_x$	$\|n, \lambda', \mu''\rangle$
$[y, z, w]$: $\hat{K}_y^2 + \hat{K}_x^2 + \hat{l}_x^2$	(y, z) $\hat{l}_x$	$\|n, \lambda'', m''\rangle$
	$(y,w)\hat{K}_z$	$\|n, \lambda'', \mu\rangle$
	$(y,w)\hat{K}_y$	$\|n, \lambda'', \mu'\rangle$

The bases are classified according to the diagonal operator acting on the hyperplane $[i, j, k]$ and to that acting on the plane (i, j).

$$Z_{l,\lambda}^{n,m} = (-)^{l+\lambda}[C(l)C(\lambda)]^{1/2} \sum_r \frac{(-)^r \Gamma\left(\frac{m+l+p(l)+1}{2}+r\right)\left(\frac{n-m-p(l)-p(\lambda)-1}{2}-r\right)!\,\Gamma\left(\frac{m+\lambda+p(\lambda)+1}{2}+r\right)}{r!\left(\frac{l-m-p(l)}{2}-r\right)!\left(\frac{\lambda-m-p(\lambda)}{2}-r\right)!\left(\frac{n+m+p(l)+p(\lambda)+1}{2}+r\right)!(m+r)!}, \tag{16}$$

where

$$C(k) = \frac{\left(\frac{n+k-1}{2}+p(k)\right)!\left(\frac{k+m}{2}-q(k)\right)!\left(\frac{k-m}{2}-q(k)\right)!\,\Gamma\left(\frac{n-k}{2}+p(k)\right)}{\Gamma\left(\frac{n+k+2}{2}+p(k)\right)\Gamma\left(\frac{m+k+1}{2}+q(k)\right)\Gamma\left(\frac{k-m+1}{2}+q(k)\right)\left(\frac{n-k-1}{2}-p(k)\right)!},$$

$p(k) = -1 + (-1)^{k-n}/4$, and $q(k) = (-1)^{k-m} - 1/4$. Note that $Z^{n,m}_{l,\lambda}$ is zero when $n + l + \lambda + m$ is even and shows the symmetries $Z^{n,m}_{l,\lambda} = Z^{n,-m}_{l,\lambda}$ and $Z^{n,m}_{l,\lambda} = Z^{n,m}_{\lambda,l}$. The sum in 16 [28] is a hypergeometric function ${}_4F_3$ of unit argument and can be connected with Racah polynomials [30, 31], although it cannot be reduced to the ordinary Racah's or 6-j coefficient, which performs angular momentum recoupling. Indeed, like a Racah's recoupling coefficient it is orthogonal with respect to summation on two angular momentum quantum numbers (l and λ), but contains a projection quantum number. As shown in Ref. [13], the $Z^{n,m}_{\lambda,l}$ coefficient can be compactly written as a 6-j symbol extended to allow not only multiples of 1/2, as ordinary vector recoupling coefficients, but also multiples of 1/4:

$$Z^{n,m}_{l,\lambda} = (-)^{(l+\lambda)/2+1+p(l)+p(\lambda)} \sqrt{\left(l+\frac{1}{2}\right)\left(\lambda+\frac{1}{2}\right)} \times \begin{Bmatrix} p(\lambda) - \frac{1}{4} & \frac{n-1}{2} & \frac{\lambda}{2} - \frac{1}{4} \\ p(l) - \frac{1}{4} & \frac{m-1}{2} & \frac{l}{2} - \frac{1}{4} \end{Bmatrix}. \quad (17)$$

The symbol $\{\vdots\}i$ enjoys most properties of ordinary 6-j symbols such as several recurrence relationships, but some symmetries fail, so caution is needed in its use. Additional properties and relations involving the Z matrix will be given in Section 3.3.

3.2. SYMMETRICAL PARAMETERIZATIONS

We will deal now with the symmetrical parameterizations, corresponding to the subgroup reduction chain $O(4) \supset O(2) \times O(2)$. The best known of these basis sets is that corresponding through a Fourier transform to the Sturmian orbitals written in *parabolic* coordinates in configuration space (see our previous article [32]). Due to its importance in the treatment of the hydrogen atom in an electric field, we call the corresponding harmonic set the *Stark* basis. For its use for building molecular orbitals and multidimensional expansions, see [3, 4, 12, 33]. This parameterization is illustrated in Figure 2(b) and can be written as

$$z = \sin\Theta\cos\varphi \quad y = \sin\Theta\sin\varphi$$

$$z = \cos\Theta\sin\Phi \quad w = \cos\Theta\cos\Phi \quad (18)$$

This coordinate set is referred to as cylindrical in Ref. [15]. The corresponding hyperspherical harmonics

TABLE II

Three bases corresponding to the reduction of the group $O(4)$ to the subgroup chain $O(4) \supset [O(2)]_{i,j} \times [O(2)]_{k,l}$.

d = 2-subspace	d = 2-subspace	Basis set
$(y, z)\ \hat{l}_x$	$(x, w)\ \hat{K}_x$	$\lvert n, \mu'', m\rangle$
$(z, x)\ \hat{l}_y$	$(y, w)\ \hat{K}_y$	$\lvert n, \mu', m\rangle$
$(x, y)\ \hat{l}_z$	$(z, w)\ \hat{K}_z$	$\lvert n, \mu, m\rangle$

The bases are classified according to the diagonal operator acting on the planes (i, j) and (k, l).

$$\Psi_{n,\mu,m}(\mathbf{p}) = \frac{4p_0^{5/2}}{(p^2+p_0^2)^2}(-)^{n-1}(i)^m \left(\frac{n}{2\pi^2}\right)^{1/2} \times D^{[(1/2)(n-1)]}_{(\mu+m)/2,(\mu-m)/2}(-\Phi-\varphi, 2\Theta, \varphi-\Phi) \quad (19)$$

simultaneously diagonalize $\hat{l}_z$ and $\hat{K}_z$ (with eigenvalues m and μ), where we give to the z axis the role of a privileged direction in physical space. This explains why the Hamiltonian for a hydrogen atom in a weak electric field directed along the z axis is still diagonal in this basis. Similarly, two other basis sets of this kind can be constructed when the x and y axes are taken as quantization axes (see Table II). Thus, we can have a basis diagonalizing $\hat{l}_x$ and $\hat{K}_z$, and another diagonalizing $\hat{l}_y$ and $\hat{K}_y$, leading to a total of three different basis sets corresponding to symmetrical parameterizations.

The orthogonal transformation between spherical [Fig. 2(a)] and Stark basis [Fig. 2(b)], analogously to what is found in configuration space [32], is given by a Clebsch–Gordan coefficient [34]:

$$\Psi_{n,\mu,m}(\mathbf{p}) = \sum_l (-)^{(n-1+m-\mu)/2} c^{n,m}_{l,\mu} \cdot \Psi_{n,l,m}(\mathbf{p}) \quad (20)$$

$$c^{n,m}_{l,\mu} = \left\langle \frac{1}{2}(n-1), \frac{m-\mu}{2}; \frac{1}{2}(n-1), \frac{m+\mu}{2} \middle| l, m \right\rangle. \quad (21)$$

From this formula, by interchange of the quantum number l with λ we also have the connection between Zeeman and Stark basis sets. Similarly to the treatment in configuration space, also in this case it will be of importance to explicitly introduce parity conservation. This will be done in Section 4.

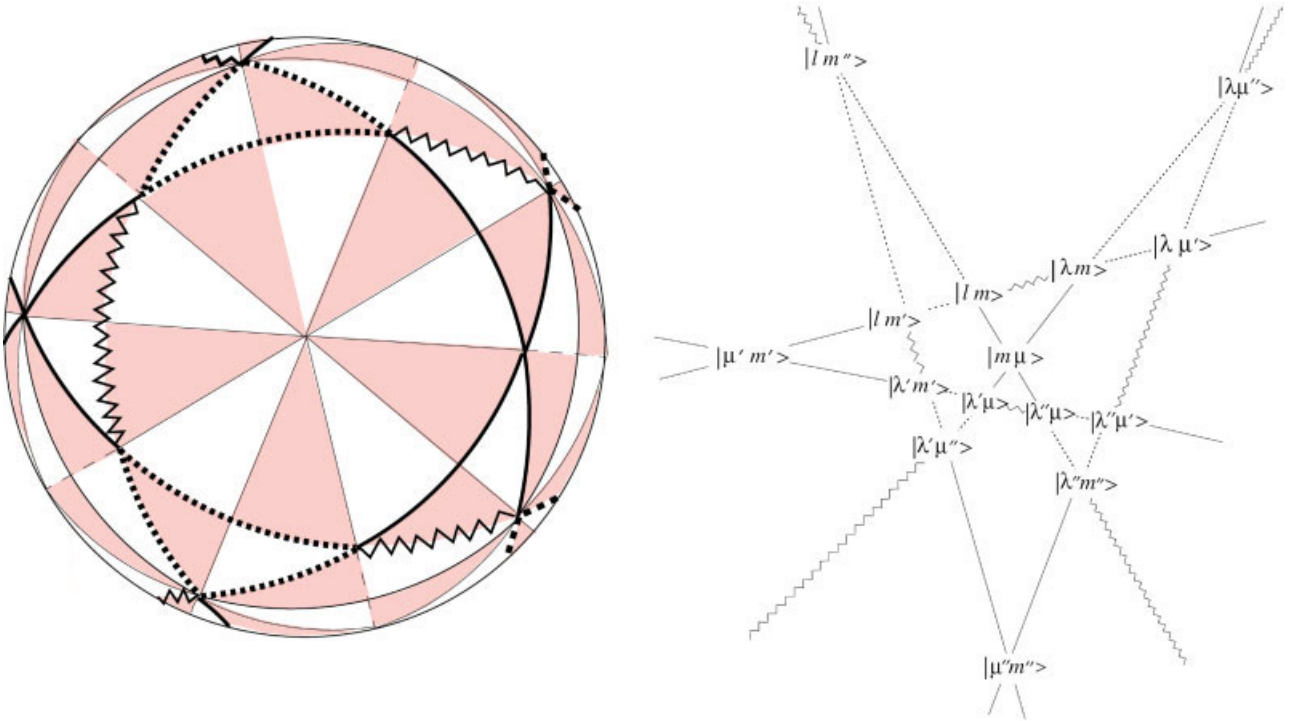

FIGURE 5. Orthogonal transformations among orthogonal bases of $O(4)$. Each basis is labeled by two quantum numbers in the graph, while the quantum number n has not been inserted explicitly because it labels all the bases. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

3.3. SCHEME OF THE ORTHOGONAL TRANSFORMATIONS AMONG THE CANONICAL BASES OF $O(4)$

We have just shown that the number of distinct canonical basis sets for S^3 amounts to 15. Actually, the total number of solutions to the Laplace equation on S^3 (harmonics) is 120; however, due to the fact that for the identification of a plane or of a 3-D space it is only necessary to specify the involved axes and not their sequence, to different systems of hyperspherical coordinates, identifying the same plane, there correspond the same harmonics (or harmonics differing for a phase factor only, i.e., still eigenfunctions of the same rotation operator), so the number of different bases reduces to 15. Refs. [13, 35] provides a discussion on the classification of the 120 coordinate systems and how this reduction is achieved. The 15 basis sets can be depicted together with their connections by the graph in Figure 5. This is a projective plane RP^2 representation, which in turn can be obtained from a graph, associated to the icosahedral group, illustrating the 120 coordinate systems (see Ref. [13]). The connections between different basis sets, which are placed at the vertices of 10 triangles and 6 pentagons, are identified by various types of segments: (1) Vector coupling coefficients [Eq. (20)] are drawn by solid lines, (2) rotation matrix elements [Eq. (15)] by dotted lines, and (3) Z coefficients [Eq. (17)] by zig-zag lines. Figure 5 is also an "abacus" to obtain relationships among ordinary elements of angular momentum algebra, augmented by the Z coefficients: Following the sides of the plane figures one can write interesting sum rules. For example, following the side of the triangle where m is conserved $Z_{l,\lambda}^{n,m}$ can be written as a sum involving two Clebsch–Gordan coefficients:

$$Z_{l,\lambda}^{n,m} = \sum_{\mu} (-)^{\alpha} \left\langle \frac{n-1+m}{2}, -\frac{\mu}{2}; \frac{n-1-m}{2}, \frac{\mu}{2} \middle| l, 0 \right\rangle \times \left\langle \frac{n-1+m}{2}, -\frac{\mu}{2}; \frac{n-1-m}{2}, \frac{\mu}{2} \middle| \lambda, 0 \right\rangle \quad (22)$$

(the phase $\alpha = (n - 1 - m - \mu)/2 + l + \lambda$ is an integer: If it were omitted, the sum would be $\delta_{l\lambda}$). We recognize on the right side the transformation coefficient used for the definition of the Zeeman basis [25]. An alternative sum rule can be ob-

tained from Figure 5, following the sides of a pentagon:

$$d^{l}_{m,m'}\left(\frac{\pi}{2}\right) Z^{n,m}_{l,\lambda} = \sum_{\mu'} (-1)^{m+\mu'} d^{\lambda}_{m,\mu'}\left(\frac{\pi}{2}\right) \times \left\langle \frac{n-1+m'}{2}, -\frac{\mu'}{2}, \frac{n-1-m'}{2}, \frac{\mu'}{2}; l, 0 \right\rangle \times \left\langle \frac{n-1+\mu'}{2}, -\frac{m'}{2}, \frac{n-1-\mu'}{2}, \frac{m'}{2}; \lambda, 0 \right\rangle \tag{23}$$

belongs to the family of well-known "pentagonal" relationships of angular momentum theory [36], such as the Biedenharn and Elliott identity (but also the Clebsch–Gordan series itself). Other sum rules can be derived from Figure 5 (some are well known, as the addition formula for rotation matrices, obtained following the sides of the triangle where l is conserved). Besides those obtained by the graph in Figure 5 the Z coefficient enjoys other interesting relations; here, three-term recurrence relationships will be given where only one of the quantum numbers is varied. Explicitly, we have a three-term recurrence relationship involving n:

$$\frac{n+1}{2}\sqrt{[(n-1)^2-l^2][(n-1)^2-\lambda^2][(n-1)^2-(l+1)^2][(n-1)^2-(\lambda+1)^2]}\, Z^{n-2,m}_{l,\lambda} + n[-\lambda-\lambda^2-l+l\lambda+\lambda^2 l-l^2+\lambda l^2+\lambda^2 l^2+n^2(1+\lambda+\lambda^2+l+l^2-2m^2-n^2)+2m^2] Z^{n,m}_{l,\lambda} + \frac{n-1}{2}\sqrt{[(n+1)^2-l^2][(n+1)^2-\lambda^2][(n+1)^2-(l+1)^2][(n+1)^2-(\lambda+1)^2]}\, Z^{n+2,m}_{l,\lambda} = 0 \tag{24}$$

or involving l (which is completely symmetrical to the relation involving λ):

$$\frac{2l+3}{2}\sqrt{\frac{(l^2-m^2)[(l-1)^2-m^2](n^2-l^2)[n^2-(l-1)^2]}{(2l-3)}}\, Z^{n,m}_{l-2,\lambda} - \frac{n+\frac{1}{2}}{\sqrt{2l+1}}[2-l-3l^3-4l^3-2l^4 + 3\lambda-4\lambda l-4\lambda l^2+3\lambda^2-4l\lambda^2-4l^2\lambda^2+2m^2(l^2+l-1)+2n^2(l^2+l-1+2m^2)] \times Z^{n,m}_{l-2,\lambda} + \frac{2l-1}{2}\sqrt{\frac{[(l+1)^2-m^2][(l+2)^2-m^2][n^2-(l+1)^2][n^2-(l+2)^2]}{2l+5}}\, Z^{n,m}_{l+2,\lambda} = 0 \tag{25}$$

or m:

$$\frac{m+1}{2}\sqrt{(\lambda-m+2)(l-m+2)[(m-1)^2-\lambda^2](l+m)(\lambda+m)(l+m)[(m-1)^2-l^2]}\, Z^{n,m-2}_{l,\lambda} + m[-\lambda-\lambda^2-l+l\lambda+l\lambda^2-l^2+\lambda l^2+l^2\lambda^2+m^2(1+\lambda+\lambda^2+l+l^2-m^2-2n^2)+2n^2] \times Z^{n,m}_{l,\lambda}\frac{m-1}{2}\sqrt{(\lambda-m)(l-m)[(m+1)^2-\lambda^2][(m+1)^2-l^2](\lambda+m+2)(l+m+2)}\, Z^{n,m+2}_{l,\lambda} = 0. \tag{26}$$

Note that these relations are extremely useful for calculation of full strings of coefficients.

4. Conservation of Parity in the Transformations Among Momentum Space Sturmians

An issue of great relevance is the conservation of the parity with respect to the inversion of electronic coordinates in the transformations among $O(4)$ bases: Such a symmetry is present in many physical systems and thus it is important to have Sturmian bases with definite parity.

4.1. SPHERICAL AND STARK BASIS SETS

Here, we exploit the correspondence with the polar and parabolic Sturmian orbitals in configuration space (see our previous article [32]). Because

the momentum space Sturmian in Eq. (4) is the Fourier transform of polar orbitals in the configuration space, it must have the same symmetry properties: Thus, for the inversion one has

$$\hat{P}\Psi_{n,l,m}(\mathbf{p}) = (-1)^l \Psi_{n,l,m}(\mathbf{p}), \tag{27}$$

where the operator $\hat{P}$ performs the inversion of the vector $\mathbf{p} = (p_x, p_y, p_z)$. As in our previous article for the parabolic basis in configuration space, because of the complete reciprocity between the two spaces, Stark Sturmians with the correct parity $\Psi^{\epsilon}_{n,|\mu|,m}(\mathbf{p})$ can be built by the formula ($\epsilon = \pm 1$ is the parity with respect to inversion)

$$\begin{aligned}\Psi^{\epsilon}_{n,|\mu|,m}(\mathbf{p}) &= |n, \mu, m, \epsilon\rangle \\ &= \frac{1}{\sqrt{2}}[\Psi_{n,\mu,m}(\mathbf{p}) \pm (-)^m \Psi_{n,-\mu,m}(\mathbf{p})]\end{aligned} \tag{28}$$

and the conservation of parity in the passage to the set $\Psi_{n,l,m}(\mathbf{p})$ involves the *parity-conserving Clebsch–Gordan* coefficients (pCG):

$$\begin{aligned}\langle n, l, m|n, \mu, m, \epsilon\rangle &= (-)^{(n-1+m-\mu)/2} C^{n,m,\epsilon}_{l,|\mu|} \\ &= (-)^{(n-1+m-\mu)/2} \frac{1 + \epsilon(-)^l}{\sqrt{2(1+\delta_{\mu,0})}} c^{n,m}_{l,|\mu|},\end{aligned} \tag{29}$$

which have been defined in our previous article [Ref. [32], Eq. (31), Section 3].

4.2. ZEEMAN BASIS SETS

As we have seen in the previous sections, there exist nine different Zeeman sets. They do not correspond to any Sturmian orbitals in configuration space. To study their behavior with respect to the inversion, let us consider the tree in Figure 4(b); the corresponding parameterization is

$$\begin{aligned} x &= \frac{2p_0 p_x}{p_0^2 + p^2} = \cos\chi' \sin\theta \cos\varphi \\ y &= \frac{2p_0 p_y}{p_0^2 + p^2} = \cos\chi' \sin\theta \sin\varphi \\ z &= \frac{2p_0 p_y}{p_0^2 + p^2} = \sin\chi' \\ w &= \frac{p_0^2 - p^2}{p_0^2 + p^2} = \cos\chi' \cos\theta. \end{aligned} \tag{30}$$

As a consequence one has the following relationships among the coordinates (p_x, p_y, p_z) in momentum space and the angles (χ', θ, φ) of the Zeeman parameterization of the 4-D sphere S^3 on which the 3-D momentum space has been projected:

$$\begin{aligned} p_x &= \frac{p_0^2 + p^2}{2p_0} \cos\chi' \sin\theta \cos\varphi \\ p_y &= \frac{p_0^2 + p^2}{2p_0} \cos\chi' \sin\theta \sin\varphi \\ p_z &= \frac{p_0^2 + p^2}{2p_0} \sin\chi'. \end{aligned} \tag{31}$$

The corresponding momentum space Sturmian can be expressed as [see Eq. (13)]

$$\begin{aligned}\Psi_{n,\lambda,m}(\mathbf{p}) &= (-)^{n-1-|m|}(i)^{\lambda+m-|m|} \frac{4p_0^{5/2}}{(p_0^2 + p^2)^2} \\ &\times B_{n,\lambda} \cos^{\lambda}\chi' C^{\lambda+1}_{n-1-\lambda}(\sin\chi') Y_{\lambda,m}(\theta, \varphi),\end{aligned} \tag{32}$$

where $B_{n,\lambda}$ had been defined in Eq. (14). Taking into account that inversion changes the sign of $\mathbf{p} = (p_x, p_y, p_z)$ but leaves p^2 unchanged, from Eqs. (30) and (31) one sees that such an operation corresponds to the transformation of angles (χ', θ, φ) into $(-\chi', \theta, \varphi + \pi)$. Considering that

$$\begin{aligned} C^{\lambda+1}_{n-1-\lambda}(\sin(-\chi')) &= C^{\lambda+1}_{n-1-\lambda}(-\sin\chi') \\ &= (-)^{n-\lambda-1} C^{\lambda+1}_{n-1-\lambda}(\sin\chi') \end{aligned}$$

and that

$$e^{im(\varphi+\pi)} = (-)^m e_{im\varphi},$$

one has

$$\hat{P}\Psi_{n,\lambda,m}(\mathbf{p}) = (-)^{n-\lambda-1+m}\Psi_{n,\lambda,m}(\mathbf{p}). \tag{33}$$

Thus, we have shown that the basis $\Psi_{n,\lambda,m}(\mathbf{p})$ is the set of eigenfunctions of the operator that performs the inversion of $\mathbf{p}$, and the same proof applies to the bases $\Psi_{n,\lambda',m'}(\mathbf{p})$ and $\Psi_{n,\lambda'',m''}(\mathbf{p})$; thus, the three matrices $\mathbf{Z}$, which—as in Figure 4—perform the transformation to the functions $\Psi_{n,l,m}(\mathbf{p})$, $\Psi_{n,l,m'}(\mathbf{p})$, and $\Psi_{n,l,m''}(\mathbf{p})$, should be factorized in two blocks to conserve the parity. These conclusions are consistent with the observation that the matrix elements $Z^{n,m}_{l,\lambda}$ are zero when $n + l + \lambda + m$ is even [13, 37].

The transformation between Stark and Zeeman basis sets [Eq. (20) with λ instead of l] involves the pCG coefficients, which have been amended by requesting the conservation of parity [compare with Eq. (29)]. One has to consider that the Zeeman basis set has parity $(-)^{n-\lambda-1+m}$:

$$\Psi^{\epsilon}_{n,|\mu|,m}(\mathbf{p}) = \sum_{|\mu|=0 \text{ or } 1}^{n-|m|-1} (-)^{(n-1+m-\mu)/2} C^{n,m,\epsilon}_{\lambda,|\mu|} \Psi_{n,\lambda,m}(\mathbf{p})$$

$$C^{n,m,\epsilon}_{\lambda,|\mu|} = \frac{1 + \epsilon(-)^{n-\lambda-1+m}}{\sqrt{2(1+\delta_{\mu,0})}}\, c^{n,m}_{\lambda,\mu}. \tag{34}$$

We will now consider the transformations that involve rotation matrices. In Figure 5 there are four triangles whose three sides are represented by dotted segments. In one of these, l remains a good quantum number and so does parity, which is $(-1)^l$ for spherical bases. For the other three triangles, the situation differs because of those vertices that correspond to Zeeman Sturmians that diagonalize one of the Cartesian components of $\hat{\mathbf{K}}$. Because $\hat{\mathbf{K}}$ and $\hat{P}$ do not commute, those functions cannot be simultaneously eigenfunctions of $\hat{P}$. For definiteness, let us consider the Sturmian $\Psi_{n,\lambda,\mu''}(\mathbf{p})$; the corresponding parameterization is

$$x = \frac{2p_0 p_x}{p_0^2 + p^2} = \cos\chi' \sin\theta' \cos\varphi''$$

$$y = \frac{2p_0 p_y}{p_0^2 + p^2} = \cos\chi' \cos\theta'$$

$$z = \frac{2p_0 p_z}{p_0^2 + p^2} = \sin\chi'$$

$$w = \frac{p_0^2 - p^2}{p_0^2 + p^2} = \cos\chi' \sin\theta' \sin\varphi''; \tag{35}$$

thus, one can write

$$p_x = \frac{p_0^2 + p^2}{2p_0} \cos\chi' \sin\theta \cos\varphi''$$

$$p_y = \frac{p_0^2 + p^2}{2p_0} \cos\chi' \cos\theta$$

$$p_z = \frac{p_0^2 + p^2}{2p_0} \sin\chi'. \tag{36}$$

Therefore, the inversion of $\mathbf{p}$ in the tridimensional space corresponds to the transformation of angles $(\chi', \theta, \varphi'') \rightarrow (-\chi', \pi - \theta, \pi - \varphi'')$. The expression of the Sturmian is, apart from a normalization factor that is not needed for symmetry considerations,

$$\Psi_{n,\lambda,\mu''}(\mathbf{p}) = \frac{p_0^{5/2}}{(p_0^2 + p^2)^2} \cdot \cos^{\lambda}\chi' C^{\lambda+1}_{n-1-\lambda} \times (\sin\chi')\, P^{|\mu''|}_{\lambda}(\cos\theta) e^{i\mu''\varphi''}. \tag{37}$$

Because of the change in the sign of the argument of the exponential function as a consequence of the inversion, it is evident that the Sturmian in Eq. (37) cannot be an eigenfunction of $\hat{P}$. Applying the projection procedure $\Psi^{\epsilon}(\mathbf{p}) = 1/\sqrt{2}\ [\Psi_{n,\lambda,\mu''}(\mathbf{p}) \pm \Psi_{n,\lambda,\mu''}(-\mathbf{p})]$ one can work out

$$\Psi^{\epsilon}_{n,\lambda,|\mu''|}(\mathbf{p}) = \frac{1}{\sqrt{2}} [\Psi_{n,\lambda,\mu''}(\mathbf{p}) \pm (-)^{n-\mu''-1} \Psi_{n,\lambda,-\mu''}(\mathbf{p})]. \tag{38}$$

$\epsilon = \pm 1$, according to the sign of the linear combination. This result is completely analogous to the one we had in the construction of definite parity Stark Sturmians [Eq. (28)]: To obtain the parity components of a Sturmian that was originally an eigenfunction for one of the $\mathbf{K}$'s Cartesian components, one has to combine two Sturmians having opposite values of μ (or μ' or μ''). Thus, the orthogonal transformation

$$\Psi_{n,\lambda,m}(\mathbf{p}) = \sum_{\mu''} D^{\lambda}_{m,\mu''}(0, \pi/2, \pi/2) \Psi_{n,\lambda,\mu''}(\mathbf{p})$$

becomes, requesting the conservation of the inversion symmetry,

$$\Psi_{n,\lambda,m}(\mathbf{p}) = \sum_{\mu''} D^{\lambda,\epsilon}_{m,|\mu''|}(0, \pi/2, \pi/2) \Psi^{\epsilon}_{n,\lambda,\mu''}(\mathbf{p}),$$

where

$$D^{\lambda,\epsilon}_{m,|\mu''|}(0, \pi/2, \pi/2) = \frac{1 + \epsilon(-)^{n-\lambda-1+m}}{\sqrt{2(1+\delta_{\mu'',0})}} D^{\lambda}_{m,\mu''}(0, \pi/2, \pi/2). \tag{39}$$

The form of Eq. (39) is due to the fact that matrix elements $D^{\lambda}_{m,\mu''}(0, \pi/2, \pi/2)$ differing only in the sign of μ'' can only have equal or opposite values.

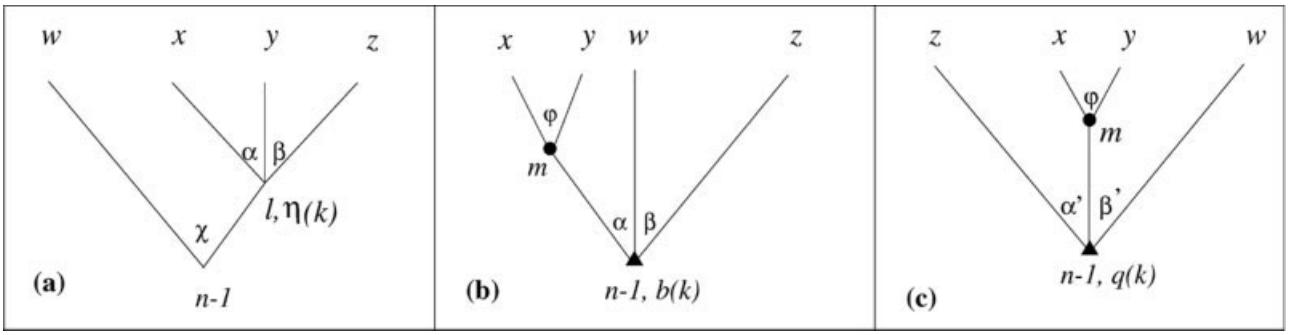

FIGURE 6. Ternary forks for setting up *elliptic* coordinate systems for S^3 [(a) spheroelliptic, (b) elliptic cylindrical of type I, (c) elliptic cylindrical of type II]. Although several alternatives are possible, we found it useful [39], exploiting results from Ref. [38] for S^2 and Ref. [15] for S^3, to adopt the following conventions: In the definitions of coordinates, a left branch corresponds to sn(α, k)dn(β, k'), a middle branch corresponds to cn(α, k)cn(β, k'), and a right branch corresponds to dn(α, k)sn(β, k'). The arguments α and β of the elliptic functions are the variables; the modulus parameter k [and $k' = (1 - k^2)^{1/2}$, with $0 \leq k, k' \leq 1$] adds a degree of freedom to these coordinate systems. The labels b, q, η are separation constants depending on k and in general are to be determined as eigenvalues of secular equations. For S^3, the most general separable coordinates (the ellipsoidal [15]) would accordingly be put into correspondence with "quaternary" forks (they depend essentially on two independent parameters that span the projective plane of Fig. 5). The procedure can be extended to S^{d-1} for which trees involving forks of up to the dth order can be defined (using results from Ref. [45], where different but equivalent graphs were introduced).

In summary, the basis sets that have μ (or μ' or μ'') as a quantum number can be turned into "parity Sturmians" performing a linear combination with the Sturmians labeled by $-\mu$ (or $-\mu'$ or $-\mu''$). These parity Sturmians will no longer be labeled by μ (or μ' or μ'') but by $|\mu|$ (or $|\mu'|$ or $|\mu''|$) plus ϵ, the eigenvalue of the inversion operator $\hat{P}$. As a consequence, matrix elements of orthogonal transformations where $|\mu|$ (or $|\mu'|$ or $|\mu''|$) is conserved as a quantum number have to be premultiplied by the suitable parity factor, which appears in Eqs. (29), (34), and (39).

5. Elliptic Bases of $O(4)$

Besides the canonical bases described in previous sections—deriving from parameterizations of the hypersphere S^3 in terms of the well-known circular function sin and cos—there exist, as described in Refs. [15, 38], bases of $O(4)$ resulting from elliptic parameterizations of S^3. Such parameterizations can be set up by Jacobi elliptic functions sn(a, k), cn(a, k), and dn(a, k) [24] and represented by ternary forks (see Fig. 6) [39]. Trigonometric alternatives are also useful, but a crucial fact is that the value one gets for such functions depends also on a number, k, called *modulus*, that can have any value in the range [0, 1]. Thus, it is understood that the Sturmians coming from elliptic parameterizations will have an additional "degree of freedom" (the modulus) with respect to the canonical Sturmians: The former are more "flexible," but their manipulation is more complicated—for example, they cannot be expressed in a closed form—and in fact, as far as we know, they have never been used for the calculation of properties of atomic and molecular systems other than the hydrogen atom. In the following, we will analyze the symmetry properties of elliptic Sturmians to clarify their relation with canonical Sturmians and insert them in the overall scheme of the alternative hydrogenic Sturmians. Because elliptic Sturmians cannot be expressed in closed form, one has to expand them in some suitable basis set and calculate the coefficients of the expansion: The three-term recursion relationships fulfilled by the transformation coefficients among canonical and elliptic Sturmians will be given.

5.1. SPHEROELLIPTIC COORDINATES AND BASIS SETS

The simplest kind of elliptic Sturmians can be derived from the parameterization of the hypersphere S^3 in spheroelliptic coordinates [see Fig. 6(a)]:

$$x = \sin\chi \,\mathrm{sn}(\alpha, k)\,\mathrm{dn}(\beta, k')$$

$$y = \sin\chi \,\mathrm{cn}(\alpha, k)\,\mathrm{cn}(\beta, k')$$

$$z = \sin\chi\ \mathrm{dn}(\alpha, k)\ \mathrm{sn}(\beta, k')$$

$$w = \cos\chi. \tag{40}$$

The relationship between the modulus k and k' is $k^2 + k'^2 = 1$. The constants of motion for the corresponding harmonics are $\hat{\mathbf{I}}^2 + \hat{\mathbf{K}}^2$, $\hat{\mathbf{I}}^2$, and $\hat{l}_x^2 + k'^2\hat{l}_y^2$ [15, 38]. The momentum space Sturmian set resulting from the parameterization (40) is the Fourier transform of the corresponding counterpart in configuration space, introduced in Ref. [38] and analyzed in the accompanying article [32], as can be seen by comparing operators and coordinates of the two reciprocal spaces.

We will now deal with elliptic parameterizations, deriving from elliptic cylindrical coordinates of Types I and II, which do not have a counterpart in configuration space (the answer to the intriguing question of why some elliptic Sturmians in momentum space do not have counterparts in configuration space will be given in Section 6).

5.2. ELLIPTIC CYLINDRICAL COORDINATES OF TYPES I AND II

Elliptic cylindrical coordinates of type I parameterize S^3 as [see Fig. 6(b)]

$$x = \mathrm{sn}(\alpha, k)\ \mathrm{dn}(\beta, k')\cos\varphi$$

$$y = \mathrm{sn}(\alpha, k)\ \mathrm{dn}(\beta, k')\sin\varphi$$

$$z = \mathrm{sn}(\beta, k)\ \mathrm{dn}(\alpha, k')$$

$$w = \mathrm{cn}(\alpha, k)\ \mathrm{cn}(\beta, k'). \tag{41}$$

The corresponding hyperharmonics are given as $\mathscr{L}(\alpha)\mathscr{L}'(\beta)\{^{\cos m\varphi}_{\sin m\varphi}\}$, where $\mathscr{L}(\alpha)$ and $\mathscr{L}'(\beta)$ are solutions of equations related to the so-called associated Lamé equation [15]: These solutions are not available in closed form, but information on a certain basis set and on its connections with the others can be obtained by studying the corresponding commuting operators.

By setting $\hat{F}_j = -(i/2)\ (\hat{\mathrm{l}}_\mathrm{j} + \hat{\mathrm{K}}_\mathrm{j})$ and $\hat{G}_j = -(i/2)\ (\hat{\mathrm{l}}_\mathrm{j} - \hat{\mathrm{K}}_\mathrm{j})$ (j = x, y, z) such operators are [15]

$$\hat{C} = -2(\hat{\mathbf{F}}^2 + \hat{\mathbf{G}}^2) \tag{42}$$

$$\hat{B} = \hat{F}_x\hat{G}_x + \hat{F}_y\hat{G}_y + \left(\frac{k^2+1}{k^2-1}\right)\hat{F}_z\hat{G}_z \tag{43}$$

$$\hat{R} = (\hat{F}_z + \hat{G}_z)^2. \tag{44}$$

These expressions do not give much information in this form, but we will obtain equivalent commuting operators that can be more readily interpreted. Considering that $\mathbf{l}\cdot\mathbf{K} = 0$, one has $\hat{\mathbf{F}}^2 = \hat{\mathbf{G}}^2 = -(1/4)\ (\hat{\mathbf{I}}^2 + \hat{\mathbf{K}}^2)$. From Eq. (44) it follows that $\hat{R} = (-i\hat{l}_z)^2 = -\hat{l}_z^2$. So, the meaning of $\hat{C}$ and $\hat{R}$ is clear: They are absolutely equivalent to the familiar operators $\hat{\mathbf{I}}^2 + \hat{\mathbf{K}}^2$ and $\hat{l}_z^2$. Now, we have to explain the meaning of the operator $\hat{B}$. Equation (43) can be rewritten as

$$\hat{B} = \hat{F}_x\hat{G}_x + \hat{F}_y\hat{G}_y + \hat{F}_z\hat{G}_z + \left(\frac{2}{k^2-1}\right)\hat{F}_z\hat{G}_z$$
$$= \hat{\mathbf{F}}\cdot\hat{\mathbf{G}} - \left(\frac{1}{k^2-1}\right)\frac{(\hat{l}_z + \hat{K}_z)(\hat{l}_z - \hat{K}_z)}{2}.$$

The product $\hat{\mathbf{F}}\cdot\hat{\mathbf{G}}$ can be expressed as

$$\hat{\mathbf{F}}\cdot\hat{\mathbf{G}} = \frac{1}{2}(\hat{\mathbf{F}} + \hat{\mathbf{G}})^2 - \frac{1}{2}(\hat{\mathbf{F}}^2 + \hat{\mathbf{G}}^2) = -\frac{\hat{\mathbf{I}}^2}{2} + \frac{\hat{C}}{4}.$$

Therefore, the elliptic cylindrical harmonics of type I diagonalize the operator

$$-\frac{\hat{\mathbf{I}}^2}{2} + \frac{\hat{C}}{4} - \left(\frac{1}{k^2-1}\right)\frac{(\hat{l}_z + \hat{K}_z)(\hat{l}_z - \hat{K}_z)}{2}.$$

Multiplying by -2 and expanding, the latter is found to be equivalent to

$$\hat{\mathbf{I}}^2 + \frac{1}{1-k^2}\hat{K}_z^2 + \frac{1}{k^2-1}\hat{l}_z^2 - \frac{\hat{C}}{2}. \tag{45}$$

Consequently, the basis can be characterized by the set of operators $\hat{\mathbf{I}}^2 + \hat{\mathbf{K}}^2$, $\hat{\mathbf{I}}^2 + (1/1 - k^2)\ \hat{\mathrm{K}}_z^2$, and $\hat{l}_z^2$. In the limit $k \to 0$, the second one tends to $\hat{l}_x^2 + \hat{l}_y^2 + \hat{l}_z^2 + \hat{K}_z^2$, which by an appropriate linear combination with $\hat{C}$ and $\hat{l}_z^2$ gives $\hat{K}_x^2 + \hat{K}_y^2 + \hat{l}_z^2$: This is tantamount to say that the elliptic cylindrical harmonics of type I tend, in this limit, to the Zeeman set $Y_{n,\lambda,m}$. In the opposite limit, the operator tends to $\hat{K}_z^2$; thus, the set tends to that of definite parity Stark harmonics $Y^{\epsilon}_{n,|\mu|,m}$.

The elliptic cylindrical coordinates of type II are [see Fig. 6(c)]

$$x = \mathrm{cn}(\alpha, k)\ \mathrm{cn}(\beta, k')\cos\varphi;$$

$$y = \mathrm{cn}(\alpha, k)\mathrm{cn}(\beta, k')\sin\varphi \tag{46}$$

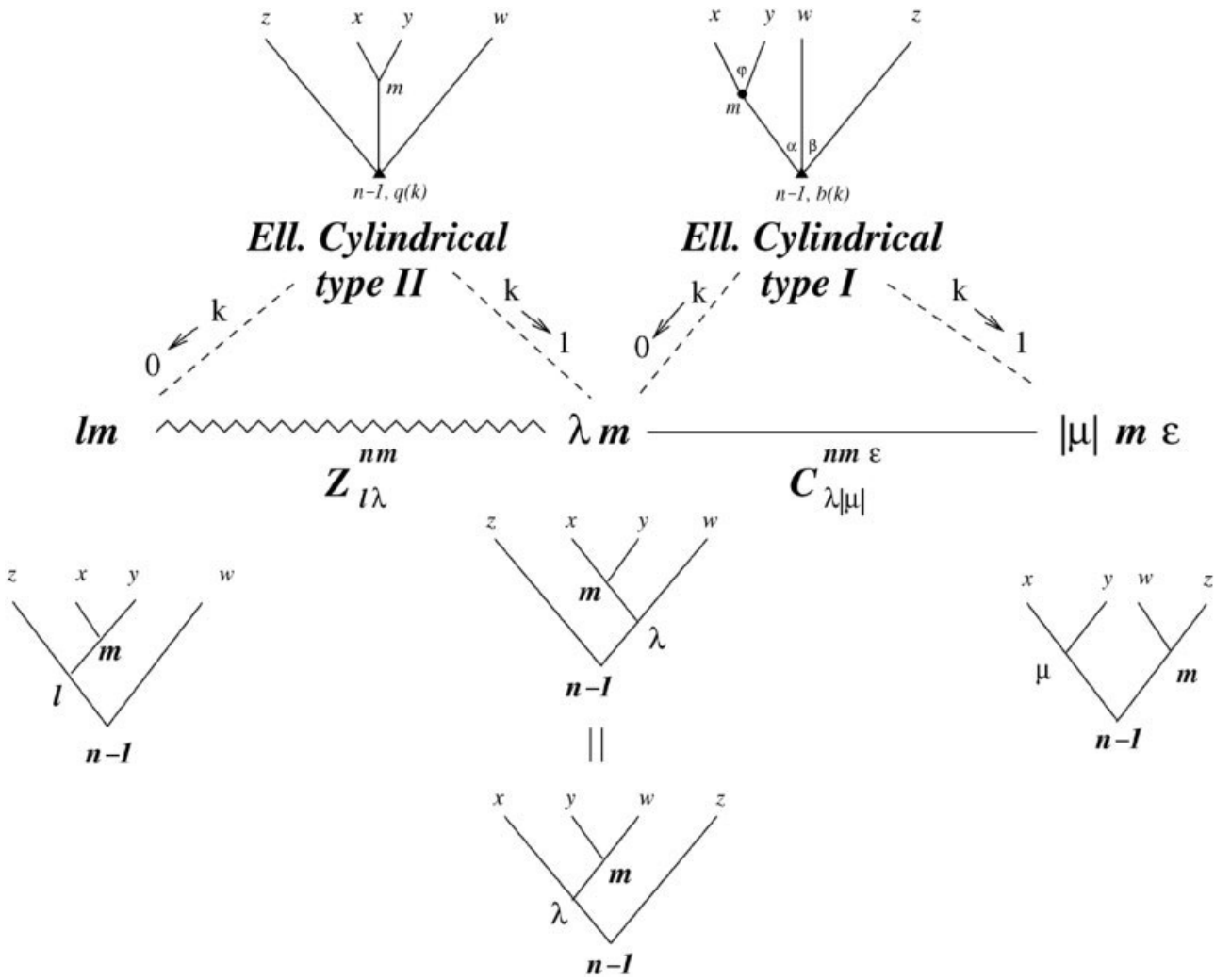

FIGURE 7. Relationships among elliptic and canonical Sturmians. For limiting values of the modulus k, the elliptic Sturmians coincide with the canonical ones, i.e., those corresponding to binary trees.

$$z = \mathrm{sn}(\alpha, k)\,\mathrm{dn}(\beta, k');$$
$$w = \mathrm{dn}(\alpha, k)\,\mathrm{sn}(\beta, k'). \tag{47}$$

The operators that characterize the corresponding set of hyperharmonics are the ones in Eqs. (42) and (44), plus [15]

$$\hat{Q} = \hat{F}_x\hat{G}_x + \hat{F}_y\hat{G}_y + (1 - 2k^2)\hat{F}_z\hat{G}_z. \tag{48}$$

By some passages similar to the ones we made for the elliptic base of type I, $\hat{Q}$ can be written as

$$\hat{Q} = -\frac{\hat{\mathbf{l}}^2}{2} + \frac{k^2}{2}(\hat{l}_z + \hat{K}_z)(\hat{l}_z - \hat{K}_z) + \frac{\hat{C}}{4}.$$

A more perspective equivalent expression for this operator is

$$\hat{\mathbf{l}}^2 + k^2\hat{K}_z^2 - k^2\hat{l}_z^2 - \frac{\hat{C}}{2}. \tag{49}$$

Therefore, this basis can be characterized by the set of operators $\hat{\mathbf{l}}^2 + \hat{\mathbf{K}}^2$, $\hat{\mathbf{l}}^2 + k^2\hat{K}_z^2$, and $\hat{l}_z^2$. As $k \to 0$ it goes into the spherical basis because $\hat{\mathbf{l}} + k^2\hat{K}_z^2 \to \hat{\mathbf{l}}^2$, while as $k \to 1$ one has the operator $\hat{\mathbf{l}}^2 + \hat{K}_z^2$, which by linear combination with $\hat{C}$ and $\hat{R}$ is seen to correspond to the operator that characterizes the Zeeman basis.

Now we can insert the elliptic cylindrical bases of types I and II in a scheme (Fig. 7) where their relationships with the other bases are shown. The basis I, as the modulus k varies, changes continuously from $Y_{n,\lambda,m}$ to $Y^{\epsilon}_{n,|\mu|,m}$, and the basis II from $Y_{n,l,m}$ to $Y_{n,\lambda,m}$.

It is possible to get the unknown elliptic cylindrical eigenfunctions by calculating the coefficients of their expansion in suitable basis sets. As we diagonalize the matrix of $\hat{\mathbf{l}}^2 + k^2\hat{K}_z^2$ on the basis $Y_{n,l,m}$, the eigenvectors diagonalize also $\hat{\mathbf{l}}^2 + \hat{\mathbf{K}}^2$ and $\hat{l}_z^2$; therefore, they are elliptic cylindrical functions of type II. By calculating the matrix of the operator $\hat{\mathbf{l}}^2 + k^2\hat{K}_z^2$ on the basis $Y_{n,l,m}$ we can prove that the coefficients in $Y^{\epsilon}_{n,q,m} = \sum_l b^{n,m,\epsilon}_{q,l} Y_{n,l,m}$—where $Y^{\epsilon}_{n,q,m}$ is the elliptic cylindrical basis set of type II and q is the eigenvalue of $\hat{\mathbf{l}}^2 + k^2\hat{K}_z^2$—are related by the three-term recursion relationship

$$k^2\sqrt{\frac{[n^2-(l-1)^2][(l-1)^2-m^2][n^2-l^2][l^2-m^2]}{(2l-3)(2l-1)^2(2l+1)}}\,b^{n,m,\epsilon}_{q,l-2} + \left\{l(l+1) + k^2\frac{[(l+1)^2-m^2][n^2-(l+1)^2]}{(2l+1)(2l+3)} + k^2\frac{[l^2-m^2][n^2-l^2]}{(2l-1)(2l+1)} - q\right\}b^{n,m,\epsilon}_{q,l} + k^2\sqrt{\frac{[n^2-(l+2)^2][(l+2)^2-m^2][n^2-(l+1)^2][(l+1)^2-m^2]}{(2l+1)(2l+3)^2(2l+5)}}\,b^{n,m,\epsilon}_{q,l+2} = 0. \tag{50}$$

The step of the recurrence is two because $[\hat{\mathbf{l}}^2 + a\hat{K}_z^2, \hat{P}] = 0$ (a can be any number); thus, matrix elements $\langle Y_{n,l,m}|\hat{\mathbf{l}}^2 + a\hat{K}_z^2|Y_{n,l',m}\rangle$ are always zero if l and l' have different parity, and elliptic cylindrical functions have definite inversion symmetry, indicated by $\epsilon = \pm 1$. As $k \to 0$, Eq. (50) is diagonal, while as $k \to 1$ it becomes a recursion in l for the coefficients $Z^{n,m}_{l,\lambda}$ [see Eq. (24)], where the eigenvalue q corresponds to $(n^2 - 1) - \lambda(\lambda + 1) + m^2$ because the operator tends to $\hat{\mathbf{l}}^2 + \hat{K}_z^2$, which can be written as $-4\hat{C} - (\hat{K}_x^2 + \hat{K}_y^2 + \hat{l}_z^2) + \hat{l}_z^2$.

As another example of application of this method, let us calculate the overlaps, i.e., the transformation coefficients, between $Y^{\epsilon}_{n,b,m}$ [the elliptic cylindrical basis set of type I, where b is the eigenvalue of the operator $\hat{\mathbf{l}}^2 + (1/1 - k^2)\hat{K}_z$] and $Y^{\epsilon}_{n,|\mu|,m}$. Putting $Y_{n,b,m} = \sum_{|\mu|} a^{n,m,\epsilon}_{b,|\mu|} Y^{\epsilon}_{n,|\mu|,m}$ one has, by calculating the matrix of $\hat{\mathbf{l}}^2 + (1/1 - k^2)\hat{K}_z^2$ on the basis $Y^{\epsilon}_{n,|\mu|,m}$,

$$\frac{1}{4}\sqrt{[n^2-(m+\mu-1)^2][n^2-(m-\mu+1)^2}\,a^{n,m,\epsilon}_{b,|\mu-2|} + \left[\frac{1}{2}(n^2-1) + \frac{1}{2}(m^2-\mu^2) + \left(\frac{1}{1-k^2}\right)\mu^2 - b\right]a^{n,m,\epsilon}_{b,|\mu|} + \frac{1}{4}\sqrt{[n^2-(m+\mu+1)^2][n^2-(m-\mu-1)^2]}\,a^{n,m,\epsilon}_{b,|\mu+2|} = 0. \tag{51}$$

According to the scheme of Figure 7, the latter recurrence relationship is diagonal as $k \to 1$, while $k \to 0$ [Eq. (51)] it coincides with the recursion in λ for the coefficients $C^{n,m,\epsilon}_{\lambda,|\mu|}$ and the eigenvalue b becomes $(n^2 - 1) - \lambda(\lambda + 1) + m^2$. In Figure 8 we show the correlation diagrams for the separation constants b and q of the elliptic cylindrical orbitals of types I and II in the case $n = 3$, $m = 0$.

6. Summary and Conclusions

The scope of this article has been to offer a complete view of hydrogenic orbitals in momentum space, which essentially coincide with harmonics on the hypersphere S^3. From the alternative sets of coordinates for which the Laplace equation on the hypersphere separates, different sets of orbitals originate: We have classified them and studied some of their properties, in particular investigating the connections between them. Within the framework of information already available in the literature [4, 13] we introduced explicitly the requirement of the conservation of parity with respect to inversion and obtained three-term recurrence relationships for the transformation coefficients, including the Z-matrix elements recently defined [25, 26, 40]. Our detailed investigation has lead to three-term recurrence relationships, which provide a simple calculation scheme for the development of cy-

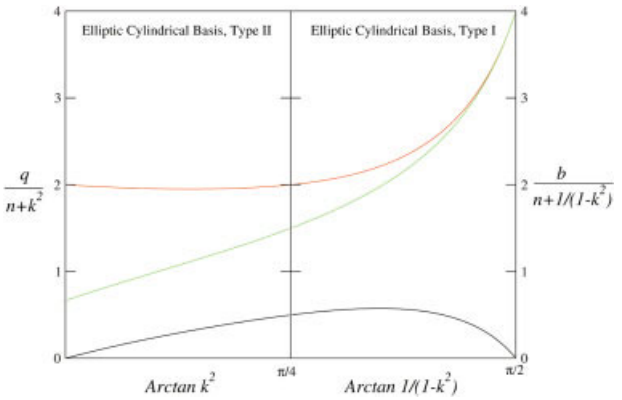

FIGURE 8. Correlation diagram showing the variation of the quantum numbers b and q as a function of k^2 for the case $n = 3$, $m = 0$. Left: Case of elliptic cylindrical basis set of type II. Right: Case of elliptic cylindrical basis set of type I. On the left extreme, q coincides with $l(l + 1)$; at the opposite side, b coincides with μ^2. In the middle of the diagram, both of them coincide with $(n^2 - 1) - \lambda(\lambda - 1) + m^2$ (Zeeman basis set). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

lindrical elliptic orbitals of first and second types both in the familiar spherical and the Stark orbitals. This also has allowed us to elucidate the relationships with respect to the "canonical" bases.

Finally, amplifying the results of our previous article [32], which focused on orbitals in configuration space, we can discuss analogies and differences of the obtained basis sets in the two reciprocal spaces. Of the four types of orbitals in configuration space, three of them (polar, parabolic, spheroelliptic) have a counterpart in momentum space (spherical, Stark, spheroelliptic), respectively. The fourth type of orbital (spheroidal), characterized by being an eigenfunction of the operator $\hat{\mathbf{l}}^2 + 2\alpha\hat{K}_z$, has no counterpart in momentum space. On the other hand, three types of orbitals among those available in momentum space (Zeeman, elliptic cylindrical of type I, elliptic cylindrical of type II) characterized, respectively, by being eigenfunctions of the operators $\hat{K}_x^2 + \hat{K}_y^2 + \hat{l}_z^2$, $\hat{\mathbf{l}}^2 + 1/(1 - k^2)\hat{K}_z^2$, and $\hat{\mathbf{l}}^2 + k^2\hat{K}_z^2$ have no counterpart in configuration space. The reason for this "missing correspondence" (one manifestation being the intractability of spheroidal orbitals according to Coulson [14]) can be attributed to the different role of the $\hat{\mathbf{K}}$ operator: According to its definition [Eq. (6)], it can be seen that it is a second-order differential operator in configuration space, while it acts as a first-order differential operator on eigenfunctions in momentum space. This is at variance with the role of $\hat{\mathbf{l}}$, which is of the first order in both spaces. Because the configuration space Schrödinger equation is of the second order, as it is its counterpart describing motion on S^3, separability of variables implies the action of second-order operators [15, 41]. On the other hand, in configuration space there are no diagonal operators that contain $\hat{\mathbf{K}}^2$ (or any of its Cartesian components).

The fact that each alternative type of orbital in momentum space provides eigenfunctions of Cartesian components of $\hat{\mathbf{l}}^2$ and $\hat{\mathbf{K}}^2$ or of their linear combinations also implies that these orbital sets induce irreducible representations in the group D_{2h} [15]: The correspondence holds for the reciprocal configuration space only in the case of polar, parabolic, and spheroelliptic orbitals, which also induce irreducible representations in D_{2h}, while the spheroidal orbitals do not.

A detailed description of Sturmian basis sets and of their counterpart in momentum space is extremely important for the implementation of the remarkable plane wave expansion:

$$\exp(i\mathbf{p}\cdot\mathbf{r}) = (2\pi)^{3/2} \sum_{n,l,m} u^*_{n,l,m}(\mathbf{r}) \cdot \frac{p_0^2 + p^2}{2p_0^2} \Psi_{n,l,m}(\mathbf{p}), \tag{52}$$

which is seen to be essentially an expansion in 4-D spherical harmonics and Sturmian polar orbitals (their explicit expression can be found in the previous article [32]). Equation (52) is a key formula in momentum space quantum chemistry and was introduced by Shibuya and Wulfman [42] in 1965, who used it to expand one-electron molecular orbitals and obtain secular equations for multicenter problems. A detailed mathematical analysis for such an expansion can be found in Ref. [43].

Previously, we introduced an extension of such a formulation to Stark Sturmians [3], which has proved to have competitive convergence properties when applied to the calculation of the ground state energy of the hydrogen molecular ion. This research emphasized the importance of exploiting the diverse alternative separable coordinate systems. The extension of such expansions to the different types of orbitals treated in this article seems extremely promising and stimulating not only in the 3-D case but also in the d-dimensional wave expansion, as already done [4] for spherical and Stark Sturmians. The solution of many-body Coulomb

problems would in fact require multidimensional plane wave expansions [12].

ACKNOWLEDGMENTS

This research was supported by the Italian National Research Council (CNR), the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST), the Ente Nazionale per l'Energia Alternativa (ENEA), the Agenzia Spaziale Italiana (ASI), and European Contract Theoretical Studies on Electronic and Dynamical Processes in Molecules and Clusters (Contract 1-1999-00005) and COST Actions D9 and D23.

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