## Hyperspherical Symmetry of Hydrogenic Orbitals and Recoupling Coefficients among Alternative Bases

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Fock's representation of momentum space hydrogenic orbitals in terms of harmonics on the hypersphere  $S^3$  of a four-dimensional space is extended to classify alternative bases. These orbitals are of interest for Sturmian expansions of use in atomic and molecular structure calculations and for the description of atoms in fields. Because of the correspondence between the  $S^3$  manifold and the SU(2) group, new sum rules are established which are of relevance for the connection, not only among hydrogen atom orbitals in different bases, but also among the usual vector coupling coefficients and rotation matrix elements. [S0031-9007(98)05785-8]

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The motivation of the classification reported in this study of hyperspherical harmonics of the four dimensional rotation group O(4) is in the spirit of investigations (presented, e.g., in preceding papers [1,2]), where the possibility is considered of exploiting different parametrizations of the  $S^n$  hypersphere to build up alternative "natural" [3] or Sturmian [4] basis sets. Their symmetry and completeness properties 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.

Traditional hydrogenic orbitals used in atomic and molecular physics as expansion bases belong to the  $|nlm\rangle$ representation, which in configuration space corresponds to separation in polar coordinates, and in momentum space to a separation in spherical coordinates on the (Fock's) hypersphere  $S^3$  [5]. The  $|nlm\rangle$  basis will be called *spherical* in the following. *Stark* states  $|n\mu m\rangle$ have also been used for atoms in fields and correspond to separation in parabolic coordinates on ordinary space and in cylindrical coordinates on  $S^3$  (for their use for expanding molecular orbitals, see Ref. [1]). A third basis, to be termed *Zeeman* states and denoted  $|n\lambda m\rangle$ , has been introduced more recently by Labarthe [6] and has found increasing applications [7].

In the following, we classify the different bases and pay special attention to the connections among them. Since in momentum space the orbitals are simply related to hyperspherical harmonics, these connections are given by orthogonal matrix elements similar (when not identical) to the familiar elements of angular momentum algebra, such as Wigner's rotation matrices and vector coupling coefficients. Here we display connecting coefficients in a symmetric graph and as a bonus we can express the overlap between spherical and Zeeman states, originally derived as a sum of the product of two vector coupling coefficients [6], as a single sum. This coefficient  $Z_{I\lambda}^{nm}$ , introduced in

Eq. (3) below, looks like an interesting "hybrid" addition to the "zoo" of angular momentum theory: It involves both angular momentum quantities as well as their projections (as in a vector coupling coefficient or 3-j symbol), and is orthonormal with respect to summations over two angular momentum such as quantum numbers (as in a recoupling Racah's coefficient or 6-j symbol).

In 1935, Fock [8] discovered that the wave function of a hydrogen atom  $|nlm\rangle$  in momentum space, as can be obtained by Fourier transform from configuration space, can be related to four-dimensional spherical harmonics, i.e., eigenfunctions of the Laplace operator on  $S^3$ . 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 three-dimensional configuration space treatment is actually a four-dimensional symmetry, which has been analyzed and discussed in various papers [9], reviews [10], and books [11]. The properly normalized hyperspherical harmonics, here appearing as Fourier transforms of hydrogenic Sturmians [1,12], find their role as atomic orbitals and expansion basis sets in an increasing number of applications [13].

Let us now consider the overlap between the *spherical* and the *Stark basis*. For the latter, the momentum space eigenfunctions, which in configuration space correspond to variable separation in parabolic coordinates, are similarly related to alternative hyperspherical harmonics [1]. The connecting coefficient between *spherical* and *Stark* basis is formally identical to a usual vector coupling coefficient, as was first shown by Park [14] in configuration space (from now on n is omitted from the notation):

$$\langle lm|\mu m\rangle = (-1)^{(n-1+m-\mu)/2}$$

$$\times \left\langle \frac{n-1+m}{2}, -\frac{\mu}{2}; \frac{n-1-m}{2}, \frac{\mu}{2} \middle| l0 \right\rangle$$
(1)

for any allowed  $n, n \ge l + 1$  and  $n \ge |m| + |\mu| + 1$ [15]. The relationship between the two bases is most clearly understood in the four-dimensional momentum space. Such a space involves four orthogonal axes (x, y, z, w), and three (hyper)angles are needed to parametrize the unit hypersphere  $S^3$ . Therefore one can define planes by coupling the axes according to two basically different sequences, say, with an obvious meaning of symbology, [(xy)z]w (leading by permutations to 96 possible different choices of this type) and (xy)(zw)(24 possibilities) [16]. For all of the 120 distinct systems of spherical coordinates, harmonics (i.e., solutions to Laplace equation on  $S^3$ ) can be written explicitly in terms of Jacobi polynomials or their particular cases (see, e.g., Ref. [17]). The  $|lm\rangle$  and  $|\mu m\rangle$  bases are seen to belong to the first and second class, respectively [18].

In the four-dimensional sphere  $S^3$ , to rotations on the six planes xy, xz, yz, wx, wy, wz, there correspond six rotation operators, three of which are conveniently identified with the angular momentum components in physical space  $L_z, L_y, L_x$  and the others with the reduced Runge-Lenz vector components  $K_x, K_y, K_z$  [for any bound state of energy E in atomic units, one has  $\mathbf{K} = (-2E)^{1/2}\mathbf{A}$ , where  $\mathbf{A}$  is the Runge-Lenz vector [9]]. The corresponding eigenvalues will be indicated with  $m, m', m'', \mu'', \mu$ .

The eigenvalue of the quadratic operator  $(L_z^2 + L_x^2 + L_y^2 + K_x^2 + K_y^2 + K_z^2)$  is  $n^2 - 1$  and gives the energy spectrum of the hydrogen atom. Four quadratic operators arise from rotations in the four-tridimensional subspaces, xyz, xyw, xzw, and yzw. One of them,  $L^2 = L_x^2 + L_y^2 + L_z^2$ , is obviously the orbital angular momentum operator with eigenvalues l(l + 1) and the integer l ranging from 0 to n - 1. The other three operators, where the axis w comes into play, are the squared angular momenta  $K_x^2 + K_y^2 + L_z^2$ ,  $K_x^2 + L_y^2 + K_z^2$ , and  $L_x^2 + K_y^2 + K_z^2$ , with eigenvalues here denoted  $\lambda(\lambda + 1)$ ,  $\lambda'(\lambda' + 1)$ , and  $\lambda''(\lambda'' + 1)$ , respectively,  $\lambda, \lambda', \lambda''$  having the same ranges as l. In each tridimensional subspace we can also select two axes to define a plane and the remaining one plays the role of the polar axis. Any change of the polar axis, say, from the z axis (m projection quantum number) can be performed by means of a Wigner's rotation matrix:

$$\langle lm|lm' 
angle = (-)^{m-m'} \mathcal{D}_{mm'}^{l} \left(\frac{\pi}{2}, \frac{\pi}{2}, \pi\right)$$
  
=  $(i)^{m} d_{mm'}^{l} \left(\frac{\pi}{2}\right).$  (2)

In this way every spherical coordinate set, corresponding to the canonical chain reduction [18] of the [(xy)z]w type, is related to a hyperspherical harmonic (and therefore to a momentum space hydrogenic orbital) labeled by *n*, by the eigenvalue of the rotation operator of one of the tridimensional subspaces and by the eigenvalue of one of its projections. Because of the fact that for the identification of a plane or of a three-dimensional 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 [19]. This enumeration leads to 12 different harmonics starting from the 96 coupling schemes for the variables [16] among which are the polar basis  $|lm\rangle$  and the Zeeman basis  $|\lambda m\rangle$ , the other corresponding to different angular momenta  $(\lambda' \text{ or } \lambda'')$  or to different projection operators  $(m', m'', \mu, \mu', \mu'')$ . Similarly, the 24 systems of coupling schemes for the coordinates parametrizing the decoupled chain reduction lead to only three different bases:  $|m\mu\rangle$ ,  $|m'\mu''\rangle$ ,  $|m''\mu''\rangle$ .

We now turn to the classification of the connecting coefficients among the 15 distinct bases, which can be calculated by direct integration [20] and illustrated in a graph (as in Fig. 1). Three types of transformation coefficients occur: (i) vector coupling coefficients [Eq. (1)], connecting bases which belong to different chain reductions; (ii) the rotation matrix elements [Eq. (2)], which change the polar axis; (iii) the third type of coefficient which,



FIG. 1. The 15 bases are represented at the crossings of six lines in a projective plane (also shown is Leonardo's view of the corresponding polyhedron, which he calls "truncated dodecahedron"). Bases occur at vertices of 10 triangles and 6 pentagons, and the sides represent connecting coefficients. They can be classified as (i) vector coupling coefficients [solid segments, e.g.,  $\langle lm|m\mu\rangle$ , Eq. (1) in the text], (ii) rotation matrix elements [dotted segments, Eq. (2)], (iii) Z coefficients [zig-zag segments, Eq. (3)]. Straight lines and pentagons imply sum rules involving five coefficients such  $\sum_{m\lambda} \langle lm' | lm \rangle \langle lm | \lambda m \rangle \langle \lambda m | \lambda \mu' \rangle \langle \check{\lambda} \mu' | \mu' m' \rangle = \langle lm' | \mu' m' \rangle$ as from which Eqs. (6) and (7) in the text follow. Sum rules such as  $\sum_{\lambda} \langle lm | \lambda m \rangle \langle \lambda m | m \mu \rangle = \langle lm | m \mu \rangle$  can be read from 6 of the triangles and lead, e.g., to Eq. (5) in the text. The other four triangles lead to sum rules such as, for each l (and similarly for any of the  $\lambda$ 's),  $\sum_{m''} \langle lm' | lm'' \rangle \langle lm'' | lm \rangle = \langle lm' | lm \rangle$ .

apart from a normalizing phase, will be called Z,  $\langle lm | \lambda m \rangle = (-1)^{l+\lambda} Z_{l\lambda}^{nm}$ , connecting the polar and Zeeman basis (or any two bases with different threedimensional angular momenta). This coefficient has been previously defined indirectly through the steps: Spherical

basis  $\rightarrow$  Stark basis  $\rightarrow$  Zeeman basis and calculated as a sum on two vector coupling coefficients [6,7]. By direct integration or by specializing overlap coefficients between alternative harmonics [21], we are able to write it directly as a single sum of the Racah type:

$$Z_{l,\lambda}^{n,m} = \left[C(l)C(\lambda)\right]^{1/2} \sum_{r} \frac{\left(-\right)^{r} \Gamma\left(\frac{m+l+p(l)+1}{2} + r\right) \left(\frac{n-m-p(l)-p(\lambda)-1}{2} - r\right)! \Gamma\left(\frac{m+\lambda+p(\lambda)+1}{2} + r\right)}{r! \left(\frac{l-m-p(l)}{2} - r\right)! \left(\frac{\lambda-m-p(\lambda)}{2} - r\right)! \left(\frac{m+p(\lambda)+1}{2} + r\right)! \left(m+r\right)!},$$
(3)

where

$$C(k) = \frac{\left(\frac{n+k-1}{2} + p(k)\right)! \left[\frac{k+m}{2} - q(k)\right]! \left[\frac{k-m}{2} - q(k)\right]! \Gamma\left[\frac{n-k}{2} + p(k)\right]}{\Gamma\left[\frac{n+k+2}{2} + p(k)\right] \Gamma\left[\frac{m+k+1}{2} + q(k)\right] \Gamma\left[\frac{k-m+1}{2} + q(k)\right] \left[\frac{n-k-1}{2} - p(k)\right]!}$$
$$p(k) = -\frac{1 + (-1)^{k-n}}{4} \quad \text{and} \quad q(k) = \frac{(-1)^{k-m} - 1}{4}.$$

Note that  $Z_{l,\lambda}^{n,m}$  is zero when  $n + l + \lambda + m$  is even and shows the symmetries  $Z_{l,\lambda}^{n,m} = Z_{l,\lambda}^{n,-m}$  and  $Z_{l,\lambda}^{n,m} = Z_{\lambda,l}^{n,m}$ . The sum in (3) [22] is a hypergeometric function  $_4F_3$  of unit argument and can be connected with Racah polynomials [21], although it cannot be reduced to the ordinary Racah's or 6-*i* 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  $\lambda$ ), but contains a projection quantum number. The Z coefficient can be compactly written as a generalized 6-j symbol [23]:

$$Z_{l,\lambda}^{n,m} = (-)^{(l+\lambda)/2+1+p(l)+p(\lambda)} \sqrt{\left(l+\frac{1}{2}\right) \left(\lambda+\frac{1}{2}\right) \left\{ \begin{array}{ccc} p(\lambda) & -\frac{1}{4} & \frac{n-1}{2} & \frac{\lambda}{2} & -\frac{1}{4} \\ p(l) & -\frac{1}{4} & \frac{m-1}{2} & \frac{l}{2} & -\frac{1}{4} \end{array} \right\}$$
(4)

and enjoys most properties of ordinary 6-i symbols, such as several recurrence relationships [24], including a three-term one which allows accurate and efficient calculations [25] even for high values of the arguments.

Figure 1 also shows how sum rules and expansion formulas for this coefficient can be derived. Following the sides of the triangle where *m* is conserved,  $Z_{l,\lambda}^{n,m}$  can be written as a sum involving two Clebsch-Gordan coefficients:

$$Z_{l,\lambda}^{n,m} = \sum_{\mu} (-)^{\alpha} \left\langle \frac{n-1+m}{2}, -\frac{\mu}{2}; \frac{n-1-m}{2}, \frac{\mu}{2} \right| l, 0 \right\rangle \left\langle \frac{n-1+m}{2}, -\frac{\mu}{2}; \frac{n-1-m}{2}, \frac{\mu}{2} \right| \lambda, 0 \right\rangle$$
(5)

(the phase  $\alpha = \frac{n-1-m-\mu}{2} + l + \lambda$  is an integer: If it were omitted, the sum would be  $\delta_{l\lambda}$ ). We recognize on the right hand side *the transformation coefficient used for the definition of the Zeeman basis* [6]. An alternative sum rule can be obtained from Fig. 1, following the sides of a pentagon (or equivalently of a

straight line):

$$Z_{l,\lambda}^{n,m} = \sum_{m',\mu'} (-1)^{\mu'+m'} d_{m',m}^{l} \left(\frac{\pi}{2}\right) d_{m,\mu'}^{\lambda} \left(\frac{\pi}{2}\right) \left\langle \frac{n-1+m'}{2}, -\frac{\mu'}{2}, \frac{n-1-m'}{2}, \frac{\mu'}{2}; l, 0 \right\rangle$$

$$\times \left\langle \frac{n-1+\mu'}{2}, -\frac{m'}{2}, \frac{n-1-\mu'}{2}, \frac{m'}{2}; \lambda, 0 \right\rangle.$$
(6)

This formula, or equivalently

$$d_{m,m'}^{l}\left(\frac{\pi}{2}\right)Z_{l,\lambda}^{n,m} = \sum_{\mu'}(-1)^{m+\mu'}d_{m,\mu'}^{\lambda}\left(\frac{\pi}{2}\right)\left\langle\frac{n-1+m'}{2}, -\frac{\mu'}{2}, \frac{n-1-m'}{2}, \frac{\mu'}{2}; l, 0\right\rangle \times \left\langle\frac{n-1+\mu'}{2}, -\frac{m'}{2}, \frac{n-1-\mu'}{2}, \frac{m'}{2}; \lambda, 0\right\rangle,$$
(7)

belongs to the family of well-known "pentagonal" relationships of angular momentum theory [26], such as the Biedenharn and Elliott identity (but also the Clebsch-Gordan series itself). Other sum rules can be derived from Fig. 1 (some of them are well known, as the addition formula for rotation matrices, obtained following the sides of the triangle where l is conserved). Thus Fig. 1 represents an "abacus" to obtain relationships among ordinary elements of angular momentum algebra, augmented by the Z coefficient. Figure 1 is a projective plane representation,  $RP^2$ , where lengths of segments or values of angles are not

meaningful. A visualization of its symmetry can be made by mapping the graph on the surface of a sphere, where the six lines become six great circles. (From this sphere, where each face, side, and vertex appears twice,  $RP^2$  is obtained by identifying antipodes). The corresponding semiregular solid is an Archimedean polyhedron, the icosidodecahedron (20 triangles and 12 pentagons), which in Fig. 1 is depicted reproducing a drawing from the collection of tables which Leonardo da Vinci prepared for the lecture notes of Luca Pacioli on the golden section (De Divina Proportione, Venice, 1502).

The classification presented in this paper is expected to be of help for choosing appropriate basis sets for problems, such as those involving fields where the hyperspherical symmetry is broken, but the perturbation Hamiltonian can still be written in terms of the generators of the fourdimensional group. The new coefficient  $Z_{l,\lambda}^{n,m}$  that we have introduced connects directly the usual spherical basis and the Zeeman basis  $|\lambda m\rangle$ , useful for the treatment of the hydrogen atom diamagnetism [6,7] and of the behavior of Rydberg atoms in a magnetic field [6,27]. Still unexplored are bases of the  $|\lambda\mu'\rangle$  type. Further extensions will concern classifications of harmonics on higher spheres in view of their relationships with multidimensional hydrogen atom orbitals [2] which are relevant as many-electron and molecular orbital expansion basis sets. The connecting coefficients will be of interest as elements of hyperangular momentum algebra and as discrete analogs of hyperspherical harmonics, which are their high quantum number (semiclassical) limits. As such, they are basic tools for the numerical implementation of the "hyperquantization" algorithm [13].

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- [1] V. Aquilanti, S. Cavalli, C. Coletti, and G. Grossi, Chem. Phys. **209**, 405 (1996). Notations and phase conventions are as in this reference.
- [2] V. Aquilanti, S. Cavalli, and C. Coletti, Chem. Phys. 214, 1 (1997).
- [3] H. Schull and P.O. Löwdin, J. Chem. Phys. 30, 617 (1959).
- [4] V. Aquilanti and J. Avery, Chem. Phys. Lett. **267**, 1 (1997), and references therein.
- [5] I. Shibuya and C.E. Wulfman, Proc. R. Soc. London A 286, 376 (1965).
- [6] J. J. Labarthe, J. Phys. B 14, L-467 (1981); D. R. Herrick, Phys. Rev. A 26, 323 (1982); D. Delande and J. C. Gay, Europhys. Lett. 5, 303 (1988).
- [7] D. Delande and J. C. Gay, Phys. Rev. Lett. 59, 1809 (1987); J. C. Gay, in *Spectrum of Atomic Hydrogen*, edited by G. W. Series (World Scientific, Singapore, 1988); F. Penent, D. Delande, and J. C. Gay, Phys. Rev. A 37, 4707 (1988). These authors also emphasize that relationships among bases are given by four-dimensional rotations.
- [8] V. Fock, Z. Phys. 98, 145 (1935).
- [9] C.E. Wulfman, in *Group Theory and its Applications*, edited by E.M. Loebl (Academic Press, New York, 1971), Vol. 2, p. 145; E.G. Kalnins, W. Miller, and P. Winternitz, SIAM J. Appl. Math. **30**, 630 (1976).
- [10] M. Bander and C. Itzykson, Rev. Mod. Phys. 38, 330 (1966).
- [11] M.J. Englefield, Group Theory and the Coulomb Problem (Wiley-Interscience, New York, 1972); B.G. Wybourne, Classical Groups for Physicists (Wiley and Sons, New York, 1972); L.C. Biedenharn and J.D. Louck, Angular Momentum in Quantum Physics. Theory and Applications

(Addison-Wesley, Reading, MA, 1981), pp. 335–364; B.R. Judd, *Angular Momentum Theory for Diatomic Molecules* (Academic Press, New York, 1975).

- [12] J. Avery and D. R. Herschbach, Int. J. Quantum Chem. 41, 673 (1992).
- [13] V. Aquilanti, S. Cavalli, C. Coletti, D. De Fazio, and G. Grossi, in *New Methods in Quantum Theory*, edited by C. A. Tsipis, V. S. Popov, D. R. Herschbach, and J. S. Avery (Kluwer, Dordrecht, 1996), pp. 233–250.
- [14] D. Park, Z. Phys. 36, 155 (1960).
- relationships [15] In Ref. [1] among alternative notations for "parabolic" quantum numbers are presented. Expression (1) is preferred for the form of the coefficient rather than  $\langle lm | \mu m \rangle =$  $(-1)^{(n-1+m-\mu)/2} \langle \frac{n-1}{2}, \frac{m-\mu}{2}; \frac{n-1}{2}, \frac{m+\mu}{2} | l, m \rangle,$ which is normally found in literature and from which it follows by Regge's symmetry [1]. This leads to the physical interpretation of the transformation as one to a body fixed reference frame, where the quantization axis is such that the orbital angular momentum has zero projection and  $\mu$ appears as a helicity quantum number.
- [16] N.P. Klepikov, Sov. J. Nucl. Phys. 19, 462 (1974).
- [17] V. Aquilanti, S. Cavalli, and G. Grossi, J. Chem. Phys. 85, 1362 (1986).
- [18] The two classes are also a manifestation of the two basic reduction chains for the four dimensional rotation group [9], the *canonical*  $O(4) \supset O(3) \supset O(2)$  and the *decoupled*  $O(4) \simeq O(2) \times O(2)$ . Other reduction chains lead to separations of coordinates, but not to explicit form for the eigenfunctions. Similarly, in configuration space, spheroidal coordinates lead to separation. For progress in solving the corresponding tridiagonal eigenvalue problem, see S. M. Sung and D. R. Herschbach, J. Chem. Phys. **95**, 7437 (1991) and A. R. P. Rau, Rep. Prog. Phys. **53**, 181 (1990).
- [19] Care is needed to define the angles associated with rotations on different planes: Different definitions lead to different phases for the harmonics. Explicitly, our definition [1] leads to a real swapping phase:  $|m\mu\rangle = (-1)^{(n-m-\mu-1)/2} |\mu m\rangle$  for the *Stark bases*.
- [20] M.S. Kil'dyushov, Sov. J. Nucl. Phys. 15, 113 (1972).
- [21] A. F. Nikiforov, S. K. Suslov, and V. B. Uvarov, *Classical Orthogonal Polynomials of a Discrete Variable* (Springer-Verlag, Berlin, 1991); S. K. Suslov, Sov. J. Nucl. Phys. 38, 829 (1983).
- [22] C. Coletti, Ph.D. thesis, Università di Perugia, 1997. Numerical tables and further details are given here.
- [23] J. Raynal, J. Nucl. Phys. 19, 467 (1978); V. Aquilanti,
   S. Cavalli, and D. De Fazio, J. Phys. Chem. 99, 15694 (1995).
- [24] D. A. Varshalovich, A. N. Moskalev, and V. K. Khersonskii, *Quantum Theory of Angular Momentum* (World Scientific, Singapore, 1988).
- [25] K. Schulten and R.G. Gordon, J. Math. Phys. 16, 1961 (1975).
- [26] V. Aquilanti, S. Cavalli, and G. Grossi, Z. Phys. D 36, 215 (1996).
- [27] A. Bommier, D. Delande, and J.C. Gay, in *Atoms in Strong Fields*, edited by C.A. Nicolaides *et al.* (Plenum Press, New York, 1990); D. Delande and J.C. Gay, Phys. Rev. Lett. **57**, 2006 (1986); J.C. Gay and D. Delande, Comments At. Mol. Phys. **19**, 35 (1986).