Hierarchical Structure of the Atomic Orbital Wave Functions of *D*-Dimensional Atom

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The hierarchical structure of the set of atomic orbital wave functions of *D*-dimensional atoms is discussed by using the set of their rectangular coordinate expressions.

Introduction

From the very early stage of the progress in quantum mechanical study of the structures of atoms and molecules in the real 3-dimensional world, it has been pointed out that the essence of these theories would easily be understandable if their mathematics is constructed in the nonrelativistic hyperspace worlds especially for the so-called Kepler problem.[1,2] However, the main roads of the quantum theories of atomic structures have not actually been paved with hyperspace bricks, except for those problems involving the Lee algebra.[3−8]

Although interesting papers on the structure of atoms in other dimensions have been sporadically but continually published in physics journals,[9−16] it was quite recently approved that the dimensional scaling technique can bring out fair advancement in the study of various facets of hydrogenic atoms.[17] However, rigorous analytical expressions of higher dimensional atomic wave functions have not widely been publicized until quite recently.

The present author has shown that the number of degeneracies of the angular momentum of a *D*-dimensional (*D*-space) atom can quite easily be obtained from the "asymmetric Pascal triangle",[18] and also has devised a simple algebraic method for deriving the analytical forms of the hyperspace wave functions.[19] In this paper the interesting features of the hierarchical structure of the wave functions of the angular part of the *D*-space atomic orbitals will be demonstrated and discussed. It is to be noted here that all the discussions in this paper are irrelevant to the nature and mathematical form of the central force.[20]

D-Space Coordinate Systems

Let the relation between the rectangular $\{x_1, x_2, ..., x_D\}$ and polar $\{r, \alpha_2, \alpha_3, ..., \alpha_D\}$ coordinate systems for the *D*-space be defined as follows:[21,22]

$$x_1 = r \sin \alpha_D \sin \alpha_{D-1} \dots \sin \alpha_3 \sin \alpha_2$$

$$x_2 = r \sin \alpha_D \sin \alpha_{D-1} \dots \sin \alpha_3 \cos \alpha_2$$

$$x_3 = r \sin \alpha_D \sin \alpha_{D-1} \dots \cos \alpha_3$$

$$\vdots$$

$$x_{D\text{-}1} = r \sin \alpha_D \cos \alpha_{D\text{-}1}$$

$$x_D = r \cos \alpha_D$$

$$x_1{}^2 + x_2{}^2 + \dots + x_D{}^2 = r^2 \qquad (1)$$

where $0 \le r \le \infty$, $0 \le \alpha_2 \le 2\pi$, $0 \le \alpha_3, ..., \alpha_{D\text{-}1}, \alpha_D \le \pi$. The volume element, $dx^{(D)}$, and the solid angle element, $d\Omega^{(D)}$, of the two coordinate systems are respectively defined by

$$dx^{(D)} = dx_1\, dx_2 \dots dx_D = r^{D-1}\, dr\, d\Omega^{(D)} \qquad (2)$$

$$d\Omega^{(D)} = (\sin \alpha_D)^{D-2} (\sin \alpha_{D\text{-}1})^{D-3} \dots \sin \alpha_3\, d\alpha_D \dots d\alpha_2 \qquad (3)$$

The total solid angle S_D in *D*-space is obtained to be[22,23]

$$S_D = \int d\Omega^{(D)} = 2\pi^{D/2}/\Gamma(D/2) = 2^{[(D+1)/2]}\pi^{[D/2]}/(D-2)!! \qquad (4)$$

where Γ stands for the gamma function, $[x]$ represents the largest integer which does not exceed x, and the double factorial is defined by

$$N!! = N(N-2)(N-4) \dots 1 \text{ or } 2 \qquad (5)$$

with $0!! = (-1)!! = 1$.

Consider vector r of a unit length emanating from the origin of *D*-space. The squared average of its direction cosine with respect to any of the rectangular coordinate axes should be $1/D$. That is, one can expect the relation

$$\int (x_j/r)^2\, d\Omega^{(D)} \Big/ \int d\Omega^{(D)} = 1/D \qquad (6)$$

As an extension of this relation the squared average of the power product of more than one direction cosines can be obtained as[19,24]

$$\langle x_i^{2n_1} x_j^{2n_2} x_k^{2n_3} \dots \rangle_D = \int \frac{x_i^{2n_1} x_j^{2n_2} x_k^{2n_3} \dots}{r^{2(n_1+n_2+n_3+\dots)}} d\Omega^{(D)} \Big/ \int d\Omega^{(D)} = \frac{(2n_1-1)!!(2n_2-1)!!(2n_3-1)!!\dots(D-2)!!}{(2n_1+2n_2+2n_3+\dots+D-2)!!} \qquad (7)$$

This relation is useful for obtaining the normalized expressions for the angular parts of the *D*-space atomic functions in terms of rectangular coordinates.

Degeneracy of *D*-Space Atomic Orbitals

Although the angular parts of the atomic wave functions are usually expressed in complex form using the polar coordinates, we will mainly be concerned with those in real form using the rectangular coordinates. For example, in 3-space case instead of using $Y_{l,m}(\theta,\phi)$ in complex form, we use $r^l[4\pi/(2l + 1)]^{1/2}Y_{l,m}(\theta,\phi)$ in real rectangular coordinate form, such as x, y, and z for $l = 1$. Thus neither explicit formulation of (hyper)-spherical harmonics[25] nor calculus of differential equation is needed in this treatment.

By extending the 3-space quantum mechanical atomic theory[26] to *D*-space, it is straightforward that the wave functions

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TABLE 1: Number of Degeneracies, $g(D,l)$, of Angular Momentum l of the Hydrogen Atom in D-Space and the Asymmetric Pascal's Triangle To Generate These Numbers

l	0	1	2	3	4	5
D	s	p	d	f	g	h
1	1	1	0	0	0	0
2	1	2	2	2	2	2
3	1	3	5	7	9	11
4	1	4	9	16	25	36
5	1	5	14	30	55	91
6	1	6	20	50	105	196

Asymmetrical Pascal's Triangle[a]

1
2 1
2 3 1
2 5 4 1
2 7 9 5 1
2 9 16 14 6 1
2 11 25 30 20 7 1

[a] Starting from the top three numbers (1,2,1) all other entries can be generated as in the conventional Pascal's triangle to form "asymmetrical Pascal's triangle", giving $g(D,l)$'s.

for D-space l-orbitals (D-l's) should form such a set of orthonormal independent homogeneous harmonic polynomials of order l composed of D rectangular coordinates. Then the number of degeneracy, $g(D,l)$, of the D-l's is given by[18,24,27]

$$g(D,l) = \frac{D+2l-2}{l}\binom{D+l-3}{l-1} \qquad (l \neq 0)$$
$$= \frac{D+2l-2}{D-2}\binom{D+l-3}{l} \qquad (D \neq 2) \qquad (8)$$

whose values for smaller members are given in Table 1. One of the most important aspects of the mathematical structure of the set of D-l's is that they originate from the set of all the $(D-1)$-k's with $0 \le k \le l$. That is, the recursive relation

$$g(D,l) = g(D-1,0) + g(D-1,1) + ... + g(D-1,l) \qquad (9)$$

is observed as in Table 1. It has also been shown that they can quite easily be derived from the so-called asymmetrical Pascal's triangle (see also Table 1).[18,19]

Hierarchical Structure of *D*-Space Atomic Wave Functions

The main purpose of the present paper is to look into the details of this hierarchical structure of the wave functions of D-space atoms. The explicit rectangular coordinate expressions for the lower members of the D-l-orbitals have been derived by the present author.[18,19] For $l \le 3$ general expressions for an arbitrary D have also been obtained. The essence of these derivations is summarized in the following four mathematical constraints:[19] (i) orthonormality; (ii) hierarchical structure (eq 9); (iii) sphericity (see the discussion below); and (iv) equivalency (eq 6).

By taking these properties of the whole set of the wave functions of a D-space atom into account, we can draw the diagrams illustrating the hierarchical structure of these wave-functions as in Tables 2 and 3. For detailed discussions see the Appendix.

Let us begin with d-functions, since the structure of p-functions in D-space is so obvious. In Table 2 all the sets of the normalized d-orbitals from 2- to 5-space in rectangular coordinates are tabulated. It is easily verified by taking their squared sum that a pair of d-functions, $2x_1x_2$ and $x_1{}^2 - x_2{}^2$, can span r^4 in 2-space. The normalization constants for these two

TABLE 2: Hierarchical Structure of D-Space d-Orbitals

level code[a]					D: 5 $\times\sqrt{5/8}$	4 $\times\sqrt{2/3}$	3 $\times\sqrt{3}/2$	2 $\times 1$	weight[c]
5	4	3	2	1					
2	2	2	2	1	$2x_1x_2$	*b*	*b*	*b*	$\times 1$
2	2	2	2	0	$x_1^2 - x_2^2$	*b*	*b*	*b*	$\times 1$
2	2	2	1	1	$2x_1x_3$	*b*	*b*		$\times 1$
2	2	2	1	0	$2x_2x_3$	*b*	*b*		$\times 1$
2	2	2	0	0	$x_1^2 + x_2^2 - 2x_3^2$	*b*	*b*	*b*	$\times 1/\sqrt{3}$
2	2	1	1	1	$2x_1x_4$	*b*			$\times 1$
2	2	1	1	0	$2x_2x_4$	*b*			$\times 1$
2	2	1	0	0	$2x_3x_4$	*b*			$\times 1$
2	2	0	0	0	$x_1^2 + x_2^2 + x_3^2 - 3x_4^2$	*b*			$\times 1/\sqrt{6}$
2	1	1	1	1	$2x_1x_5$				$\times 1$
2	1	1	1	0	$2x_2x_5$				$\times 1$
2	1	1	0	0	$2x_3x_5$				$\times 1$
2	1	0	0	0	$2x_4x_5$				$\times 1$
2	0	0	0	0	$x_1^2 - 3x_2^2 + x_3^2 + x_4^2 - 4x_5^2$				$\times 1/\sqrt{10}$

[a] For explanation see Appendix. [b] Same as the left-neighbor column. [c] The normalization constant for a given entry is the product of the two weights corresponding to its row and column. Example: for $x_1^2 + x_2^2 - 2x_3^2$ in 4-space is $\sqrt{2/3} \times 1/\sqrt{3} = \sqrt{2}/3$. Its level code 22200 means that this function became a member of d-orbitals already in 3-space.

TABLE 3: Hierarchical Structure of D-Space f-Orbitals

level code[a]				D: 4 $\times 1/\sqrt{2}$	3 $\times\sqrt{5/8}$	2 $\times 1$	weight[c]
4	3	2	1				
3	3	3	1	$x_1(x_1^2 - 3x_2^2)$	*b*	*b*	$\times 1$
3	3	3	0	$x_2(x_2^2 - 3x_1^2)$	*b*	*b*	$\times 1$
3	3	2	1	$2x_1x_2x_3$	*b*		$\times\sqrt{6}$
3	3	2	0	$(x_1^2 - x_2^2)x_3$	*b*		$\times\sqrt{6}$
3	3	1	1	$x_1(x_1^2 + x_2^2 - 4x_3^2)$	*b*		$\times\sqrt{3/5}$
3	3	1	0	$x_2(x_1^2 + x_2^2 - 4x_3^2)$	*b*		$\times\sqrt{3/5}$
3	3	0	0	$(3x_1^2 + 3x_2^2 - 2x_3^2)x_3$	*b*		$\times\sqrt{2/5}$
3	2	2	1	$2x_1x_2x_4$			$\times\sqrt{6}$
3	2	2	0	$(x_1^2 - x_2^2)x_4$			$\times\sqrt{6}$
3	2	1	1	$2x_1x_3x_4$			$\times\sqrt{6}$
3	2	1	0	$2x_2x_3x_4$			$\times\sqrt{6}$
3	2	0	0	$(x_1^2 + x_2^2 - 2x_3^2)x_4$			$\times\sqrt{2}$
3	1	1	1	$x_1(x_1^2 + x_2^2 + x_3^2 - 5x_4^2)$			$\times\sqrt{2/5}$
3	1	1	0	$x_2(x_1^2 + x_2^2 + x_3^2 - 5x_4^2)$			$\times\sqrt{2/5}$
3	1	0	0	$x_3(x_1^2 + x_2^2 + x_3^2 - 5x_4^2)$			$\times\sqrt{2/5}$
3	0	0	0	$(3x_1^2 + 3x_2^2 + 3x_3^2 - 3x_4^2)x_4$			$\times\sqrt{2/3}$

[a] For explanation see Appendix. [b,c] See the corresponding explanations in Table 2.

orbitals in 2-space are both unity, which is obtained by multiplication of the two weight factors given in Table 2.

It can be interpreted that the former function, $2x_1x_2$, is derived when the dimesionality of the space is increased from 1 to 2. That is, the only p-orbital, x_1, in 1-space is multiplied by $2x_1$ to give one of the two d-orbitals in 2-space. On the contrary, the function $2x_1x_2$, together with its counterpart, $x_1{}^2 - x_2{}^2$, keeps its membership in all the higher spaces. However, their relative weight in the whole set of D-d functions decreases with $[D/2(D-1)]^{1/2}$. All these historical trails of this pair of d-orbitals from 1- to 5-space are respectively encoded as 22221 and 22220 in terms of "level code". The digits 0, 1, and 2 represent the angular quantum number of a given function in each dimension, and one can trace the historical trail of each wave function along the path drawn on Chart 1. Consult also the Appendix for more detailed discussion on the "level codes" and "step codes" which make the mathematical structure of these wave functions clearer.

CHART 1

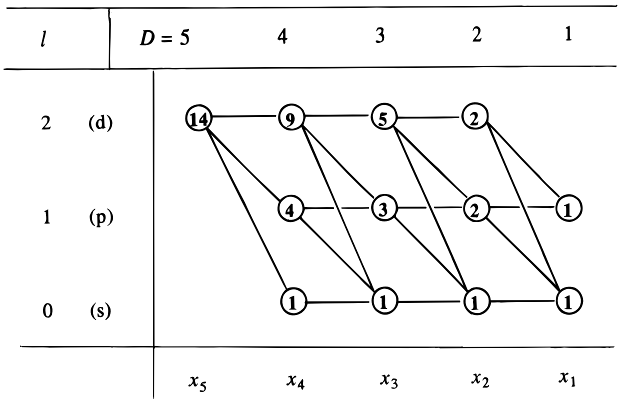
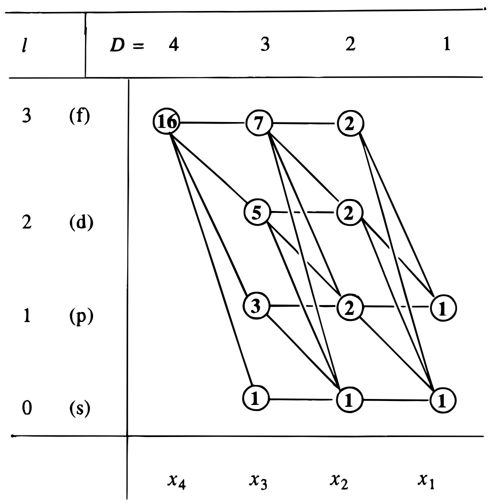


CHART 2



The squared sum of the $g(D,l)$ functions for a given pair of D and l should be r^{2l}. This property may be called the sphericity of the set of these wave functions (vide infra). The simplest case is the set of D p-orbitals in D-space, where their squared sum gives r^2 as in eq 1. The squared sum of the set of $(D + 2)(D - 1)/2$ d-orbitals in D-space as shown in Table 2 yields r^4.

Similarly for f-orbitals of 2- to 4-spaces the normalized rectuangular coordinate expressions are given in Table 3 together with the Chart 2. The squared sum of the set of $D(D - 1)(D + 4)/6$ orbitals gives r^6. The relative weight in the whole set of D-f functions decreases with $[(D + 2)/4(D - 1)]^{1/2}$. One can observe various features of the hierarchical structure of D-f functions in Table 3 as in the case of D-d functions. However, the analytical formulas and relations rapidly get complicated as D increases. Thus, there is no point in extending this type of discussion to g and higher angular momenta.

All the results obtained in this study provide us clear and global understanding of the mathematical structure of the atomic orbitals in our 3-space real world not only for researchers but also for students.

Appendix: Proof of Diagramatic Enumeration of ${}_D\mathbf{H}_l$ and $g(D,l)$

(i) The number of homogeneous products $x_i^p x_j^q x_k^r$ of order $l = p + q + r$ composed of D variables, $x_1, x_2, ..., x_D$, is equal to the repeated combination of l selections out of D, i.e.,

TABLE 4: 1−1 Correspondence among the Homogeneous Harmonic Polynomials and Step and Level Codes for the Diagram Given in Figure 1

step code[a]	monomial	level code
0 0 0 2	x_4^2	2 2 2 2 0
0 0 1 1	x_3x_4	2 2 2 1 0
0 0 2 0	x_3^2	2 2 2 0 0
0 1 0 1	x_2x_4	2 2 1 1 0
0 1 1 0	x_2x_3	2 2 1 0 0
0 2 0 0	x_2^2	2 2 0 0 0
1 0 0 1	x_1x_4	2 1 1 1 0
1 0 1 0	x_1x_3	2 1 1 0 0
1 1 0 0	x_1x_2	2 1 0 0 0
2 0 0 0	x_1^2	2 0 0 0 0

[a] Nonnegative solutions of $x_1 + x_2 + x_3 + x_4 = 2$.

$$K(D,l) = {}_D\mathbf{H}_l = \binom{D + l - 1}{l}$$

(ii) This value is equal to the number of nonnegative integer solutions of $x_1 + x_2 + ... + x_D = l$. If a solution is expressed by a sequence of D digits, $x_1x_2...x_D$, it can be deemed as a D-digit integer. For the case with $l > 9$ the integer may be interpreted as l-adic.

(iii) Rearrange all the set of ${}_D\mathbf{H}_l$ D-digit integers of (ii) in increasing order. An example is shown in Table 4 with $D = 4$ and $l = 2$, where all the set of D-digit integers and the corresponding monomials of order 2 composed out of x_1,x_2,x_3,x_4 are given.

(iv) Arrange $(l + 1) \times (D - 1)$ points to form a square lattice, and put two additional points, A and Z, respectively, to form the top left and bottom right wings as in Figure 1a so that these two points respectively sit on the top and bottom rows. Starting from A and finishing at Z, draw all the possible horizontal and downward lines between the pair of points sitting on neighboring pairs of columns. The number of D-step paths from A to Z is equal to ${}_D\mathbf{H}_l$, because each of such paths can be represented by a D-digit integer in l-adic expression if a nonnegative integer, k, is assigned to a rightward step that goes down by k stairs. Let us call this D-digit integer "step code". An example is illustrated with the sequence of four arrows, whose step code is 0002. Every possible D-step path from A to Z in Figure 1a can find its counterpart in the first column in Table 4.

(v) Transform the step code into "level code" with $(D + 1)$ digits for the set of D-step paths so that each digit represents the level of the point in a given path from level-l to level-0. The level code for the path exemplified in (iv) is 22220. All the level codes corresponding to the step codes given in (iv) are given in the third column of Table 4, where the level codes appear in decreasing order. Note that the numbers of elements in (i)−(v) are all equal to ${}_D\mathbf{H}_l$, or $K(D,l)$.

(vi) For each point of the diagram used in (iv) and (v), one can count the number of possible ways for going down to Z by the shortest steps. These numbers can easily be obtained as follows by starting at Z, for which 1 is assigned naturally.

All the points that are direct neighbors of Z are also given 1. To each point in the next column assign such a number that is the sum of the numbers already assigned to the right neighbors. The numerals encircled in Figure 1a are obtained according to this method and are equal to ${}_D\mathbf{H}_l$, or $K(D,l)$. Although Figure 1a was drawn for a special pair of D and l, this diagram can endlessly grow up reversively from Z to infinitely large D and l values, providing the same numbers in Table 1 but more information as to their hierarchical structure.

(vii) As already stated,[18] the number of degeneracy of the angular momentum l of the atomic orbitals of a D-space atom,

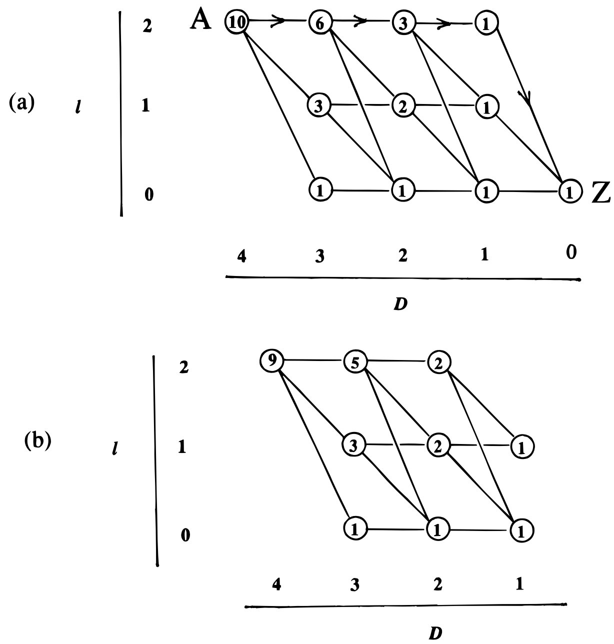


Figure 1. (a) Diagram showing the number of homogeneous products of order l composed of D variables. The number encircled at point (D,l) gives its ${}_D\mathbf{H}_l$ value. The sequence of the four consecutive arrows shows one of the possible paths from A to Z, whose step and level codes are respectively 0002 and 22220. See also Table 4. (b) Diagram showing the number of degeneracy of D-l-orbitals. This diagram can be expanded freely to larger D and l values.

$g(D,l)$, is the difference between ${}_D\mathbf{H}_l$ and ${}_{D\text{-}2}\mathbf{H}_l$. By realizing the meaning of the processes (iv) and (vi) one can immediately find that this number can be enumerated from the diagram, shown in Figure 1b, which are derived from Figure 1a by deleting Z and the direct neighbors of Z except for the bottom two (i.e., $D = 1$ and $l = 0$ and 1). One can then prepare the tables of the step and level codes for a given set of $g(D,l)$ straightforwardly. In this example, only the top entry in Table 4 has been deleted to give Figure 1b, and thus the tabulation of the new set of paths from A to Z is omitted here. However, in this stage the correspondence between the paths from A to Z and monomials as in Table 4 is lost. Instead, the functional forms of the homogeneous harmonic polynomials with proper normalization constants as in Tables 2 and 3 are needed, where the order of $\{x_j\}$ is reversed. This process is guaranteed from a symmetrical reason.

For each point in Figure 1b one can obtain the corresponding $g(D,l)$ value, which satisfies the recursive relation, eq 9. This process and the results obtained can explain what is meant in the asymmetrical Pascal triangle proposed by the presenmt author.[18,19]

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