# A New View of Hybridized Atomic Orbitals from *N*-dimensional World

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By taking a birds-eye view from the *n*-dimensional world (or *n*-space), it was found that the conventionally used sp, $sp^2$, and $sp^3$ hybridized atomic orbitals belong to the $sp^n$ hybridization and their geometrical shapes correspond to *n*-simplexes, which are, respectively, the smallest geometrical objects in *n*-space. Similarly, sp, $sp^2d$, and $sp^2d^3$ hybridizations are found to belong to the $sp^nd^{n-1}$ hybridization, whose geometrical shapes correspond to *n*-cross polytopes (obtained from $2n$ vertices equidistantly located on *n* rectangular coordinate axes). Another series of *n*-cube hybridization is also discussed, whose 3-space member is 8-coordinated cubic hybridization, $sp^3d^3f$. General analytical forms of the wavefunctions of these three series of hybridized atomic orbitals in *n*-space are obtained. The periodic table and related problems of atoms and molecules in *n*-space are discussed.

## INTRODUCTION TO *N*-SPACE

Even in the modern quantum chemistry course the number of degeneracy of s, p, d, and f atomic orbitals (AOs) is usually taught merely as the solution of Schrödinger equation of hydrogen atom without giving any mathematical background. However, according to our recent study on the algebraic structure of *n*-dimensional (*n*-D) world, or *n*-space,[1–4] the number of degeneracy of the angular part of them can be obtained and explained quite easily by using the asymmetrical Pascal's triangle. Some knowledge of the spherical harmonics and wavefunctions of atoms in higher dimension is helpful not only to students but also to researchers for global understanding of the mathematical structure of atoms in our 3-D world. Further, the periodic table of the hypothetical 4-space was also predicted and discussed recently by the present authors in connection with those of 2-space[5,6] and 3-space.[7]

For extending the discussion on *n*-space from atoms to molecules the algebraic structure of the hybridized AOs need to be analyzed. Among a number of hybridized AOs in 3-D molecules, we could find two interesting groups, *i.e.*, $sp^n$ and $sp^nd^{n-1}$ types. Namely, the geometrical forms spanned by sp, $sp^2$, and $sp^3$ hybridizations can be deemed as the smallest geometrical objects (*n*-simplexes), respectively, in 1-D, 2-D, and 3-D worlds. Then it is easy to formulate the $sp^4$ hybridization in 4-D world, and so on. The sp hybridization can also be deemed as the starting member of $sp^nd^{n-1}$ group in *n*-D world to span the *n*-cross polytopes which are composed of $2n$ vertices sitting equidistantly on *n* rectangular coordinate axes passing thorough the origin. Thus by taking a birds-eye view from the higher dimensional world, the relations among seemingly independent hybridized AOs of various spatial arrangements in 3-D world can be understood more clearly and systematically.

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## What is N-*space and Polytopes?*

A minimum number of terminologies and concepts for understanding *n*-space problems will be given here as premises. In *n*-space one can draw *n* mutually perpendicular lines through a given point **O** as the origin. With these lines as the coordinate axes the relative position of point **P** is uniquely determined in *n*-space. This coordinate system is quite different from the one used in Einstein's theory of relativity which brings »time« into the fourth axis to establish his 4-D world.

Table I is helpful for clarifying the relations among the various geometrical elements and objects defined in the spaces of different dimensionality *n*.

As judged from this table some terminologies, especially those given in the first and second rows, are not or cannot be given a rigorous definition, because they had long been used before *n*-D mathematics was born.

## Definition of N-*simplex and* N-*cross Polytope*[9]

Polytope is a convex region of *n*-space and enclosed by a finite number of polytopes, or hyperplanes of $(n-1)$-space. For example, polyhedron and polygon are, respectively, 3-D and 2-D objects, and are enclosed by a finite number of polygons and line segments, which are, respectively, hyperplanes in 2- and 1-spaces. The term polychoron is sometimes used for a polytope in 4-space.[10]

As seen in the last row of Table I the *n*-simplexes line up as vertex, line segment, triangle, tetrahedron, 5-cell, and so on. Their perspective views are shown in Figure 1 together with the numbers, $N_{n,k}$, of *k*th elements in *n*-space, such as V (vertex), E (edge), F (face), and C (cell). They are given by[9]

$$N_{n,k} = \binom{n+1}{k+1}. \tag{1}$$

The 0-simplex is a vertex. The 1-simplex is a line segment, which is constructed from (1+1) vertices and cannot lie on 0-simplex. Then consider 2-simplex, a triangle. It is constructed from (2+1) vertices and enclosed by (2+1) edges which do not lie in an axis, or $(2-1)$-space, and is the smallest polygon. Tetrahedron (3-simplex) is constructed from (3+1) vertices, which do not lie in a plane, or $(3-1)$-space. It is enclosed by (3+1) trian-

| $n$ | $n$-simplex | V $k=0$ | E 1 | F 2 | C 3 |
|---|---|---|---|---|---|
| 0 | ∘ | 1 | | | |
| 1 | | 2 | 1 | | |
| 2 | | 3 | 3 | 1 | |
| 3 | | 4 | 6 | 4 | 1 |
| 4 | | 5 | 10 | 10 | 5 |

$$N_{n,k} = \binom{n+1}{k+1}$$

Figure 1. *N-simplexes and the number of kth elements.*

gles (2-simplexes) and is known as the smallest polyhedron or cell.

Thus in general, *n*-simplex, which is the smallest polytope in *n*-space, is constructed from such $(n + 1)$ vertices that cannot lie in $(n - 1)$-space, and is enclosed by $(n + 1)$ $(n - 1)$-simplexes. In this paper the lengths of all the edges of these objects are to be taken as unity. Then they may be called »regular.«

The 4-simplex, or 5-cell, is shown to have five vertices, ten edges, ten faces (triangles), and five 3-simplexes (tetrahedra). Note that although this is a geometrical object, the graph representing this structure is the so-called pentagram, or complete graph, $K_5$, as shown in Figure 1. There are five different ways for taking out a vertex from 5-cell and the remaining four vertices form a tetrahedron, and in total five tetrahedra are contained in it leading to its name of 5-cell.

There are two other series of important polytopes in each space. Namely, one is polycube and the other is cross polytope. Discussion on the former will be given

TABLE I. Terms describing *n*-D spaces and objects

| $n$ | 0 | 1 | 2 | 3 | 4 |
|---|---|---|---|---|---|
| $n$-space | vertex | line | plane | »space« | 4-D space |
| $n$-D element | vertex | edge | face | cell | 4-D object |
| polytope (hyperplane) | vertex | line segment | polygon | polyhedron | polychoron polytope |
| $n$-simplex | vertex | line segment | triangle | tetrahedron | 5-cell |

| $n$ | $n$-cross polytope | V $k = 0$ | E 1 | F 2 | C 3 |
|---|---|---|---|---|---|
| 1 |  (a) | 2 | 1 | | |
| 2 |  | 4 | 4 | 1 | |
| 3 |  | 6 | 12 | 8 | 1 |
| 4 | ‑‑‑ (b)  | 8 | 24 | 32 | 16 |
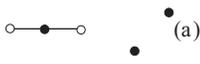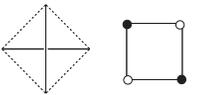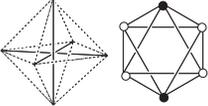
(a) See text. $N_{n,k} = 2^{k+1}\binom{n}{k+1}$ $(0 \le k \le n-1)$, $N_{n,n} = 1$.

(b) Complicated figure is omitted.

Figure 2. N-cross polytopes and the number of kth elements.

composed of mutually perpendicular $n$ axes drawn through point $O$, and on each axis a pair of vertices sit equidistantly from $O$. The enclosed geometrical objects thus obtained are, line segment, square, regular octahedron, hexadecachoron, etc.

Another series of figures in Figure 2 are drawn so that the process of growing with $n$ is easily followed.[9] Start from 1-cross polytope, a pair of vertices with an edge joining them. However, in this figure the edge is omitted from some reason. Now go to 2-cross polytope, a square, which is formed by adding a pair of black vertices to 1-cross polytope which is marked with white vertices. Then draw edges between all the pairs of black and white vertices. Before going from $n$-cross polytope to the next higher one let all the existing vertices turn to white. By following this rule it is easy to get the number of $n$-dimensional elements, $N_{n,k}$, of $n$-cross polytope, as

$$N_{n,k} = 2^{k+1}\binom{n}{k+1} \qquad (0 \le k \le n-1) \qquad (2)$$

and

$$N_{n,n} = 1.$$

These values are given in Figure 2.

in the end of this paper. A pair of vertices equidistant from the origin are situated on both sides of each coordinate axis to form the skeleton of $n$-cross polytope in $n$-space as seen in Figure 2, where two kinds of figures are given. One is the so-called Cartesian frame[9] which is

## sp$^n$ HYBRIDIZED AOs

With the above-mentioned fundamental knowledge on $n$-space geometry, let us take a global look at the algebraic expressions of sp-, sp$^2$-, and sp$^3$-hybridized atomic orbitals as given in Table II, each of them is composed

TABLE II. Wavefunctions of $\chi_{n,m}$ for sp, sp$^2$, sp$^3$, and sp$^4$ hybridized AOs

| sp hybridization in 1-D | sp$^2$ hybridization in 2-D |
|---|---|
| $\chi_{1,1} = \dfrac{1}{\sqrt{2}}s + \dfrac{1}{\sqrt{2}}p_x$ | $\chi_{2,1} = \dfrac{1}{\sqrt{3}}s + \sqrt{\dfrac{2}{3}}p_x$ |
| $\chi_{1,2} = \dfrac{1}{\sqrt{2}}s - \dfrac{1}{\sqrt{2}}p_x$ | $\chi_{2,2} = \dfrac{1}{\sqrt{3}}s - \dfrac{1}{\sqrt{6}}p_x + \dfrac{1}{\sqrt{2}}p_y$ |
| | $\chi_{2,3} = \dfrac{1}{\sqrt{3}}s - \dfrac{1}{\sqrt{6}}p_x - \dfrac{1}{\sqrt{2}}p_y$ |

| sp$^3$ hybridization in 3-D | sp$^4$ hybridization in 4-D |
|---|---|
| $\chi_{3,1} = \dfrac{1}{2}s + \dfrac{\sqrt{3}}{2}p_x$ | $\chi_{4,1} = \dfrac{1}{\sqrt{5}}s + \dfrac{2}{\sqrt{5}}p_x$ |
| $\chi_{3,2} = \dfrac{1}{2}s - \dfrac{1}{\sqrt{12}}p_x + \sqrt{\dfrac{2}{3}}p_y$ | $\chi_{4,2} = \dfrac{1}{\sqrt{5}}s - \dfrac{1}{\sqrt{20}}p_x + \dfrac{\sqrt{3}}{2}p_y$ |
| $\chi_{3,3} = \dfrac{1}{2}s - \dfrac{1}{\sqrt{12}}p_x - \dfrac{1}{\sqrt{6}}p_y + \dfrac{1}{\sqrt{2}}p_z$ | $\chi_{4,3} = \dfrac{1}{\sqrt{5}}s - \dfrac{1}{\sqrt{20}}p_x - \dfrac{1}{\sqrt{12}}p_y + \sqrt{\dfrac{2}{3}}p_z$ |
| $\chi_{3,4} = \dfrac{1}{2}s - \dfrac{1}{\sqrt{12}}p_x - \dfrac{1}{\sqrt{6}}p_y - \dfrac{1}{\sqrt{2}}p_z$ | $\chi_{4,4} = \dfrac{1}{\sqrt{5}}s - \dfrac{1}{\sqrt{20}}p_x - \dfrac{1}{\sqrt{12}}p_y - \dfrac{1}{\sqrt{6}}p_z + \dfrac{1}{\sqrt{2}}p_w$ |
| | $\chi_{4,5} = \dfrac{1}{\sqrt{5}}s - \dfrac{1}{\sqrt{20}}p_x - \dfrac{1}{\sqrt{12}}p_y - \dfrac{1}{\sqrt{6}}p_z - \dfrac{1}{\sqrt{2}}p_w$ |

of two, three, and four equivalent lobes, respectively. Although all of these three types of hybridized orbitals have been proposed to be defined for the spatial arrangement or pointing direction of electron around a carbon atom in a molecule, they can be deemed as a set of vectors emanating from the origin toward each end of $n$-simplex.

By noticing the orthonormality condition for the wavefunction of each lobe it is straightforward to obtain the general form of sp$^n$ hybridized atomic orbtials in $n$-space using one s- and $n$ p-orbitals as in Table III. The s-orbital is equally shared by $n + 1$ lobes. Then the first lobe $\chi_{n,1}$ is chosen to direct along the first axis, or $x$-axis, and takes the major portion of the p-orbital in this axis. All other lobes equally share the minor and negative portion of that p-orbital. The second lobe $\chi_{n,2}$ is chosen to lie in the plane determined by the first ($x$) and second ($y$) axes. Follow successively this rule up to the $n$-th lobe, which will automatically take just a half portion of the $n$-th p-orbital. Finally the last $(n + 1)$-th lobe takes the same contribution from each p-orbital except for the $n$-th one. In this way one can obtain all the wavefunctions of $\chi_{n,m}$ for the sp$^n$ hybridized AOs in $n$-space as given in Table III.

The more compact general expression is obtained as

$$\chi_{n,m} = \frac{1}{\sqrt{n+1}} s - \sum_{k=1}^{m-1} \frac{1}{\sqrt{(n+2-k)(n+1-k)}} p_k +$$

$$+ \frac{\sqrt{n-(m-1)}}{\sqrt{n-(m-2)}} p_m.$$

$$(n = 0,1,2,...; \; m = 1,2,3,..., n, n+1) \qquad (3)$$



Figure 3. Calculation of the angle between a pair of lobes of sp$^n$ hybridized orbitals.

Each of the resultant $n + 1$ lobes of sp$^n$ hybridized atomic orbtials in $n$-space possesses quite an equal position and spatial relationship, or angle, between any other lobe is also quite the same. This property can be derived as in the following analysis.

Consider first the angle between the first and second lobes. As seen in Figure 3 the $x$-components of $\chi_{n,1}$ and $\chi_{n,2}$ are, respectively, $\sqrt{n/(n+1)}$ and $1/\sqrt{n(n+1)}$, while their $y$-components are, respectively, none and $\sqrt{(n-1)/n}$. Then by using the direction cosines of $\chi_{n,1}$ and $\chi_{n,2}$ one gets

$$\cos(\angle \chi_{n,1} \cdot \chi_{n,2}) =$$

$$\sqrt{\frac{n}{n+1}} \left( \frac{-1}{\sqrt{n(n+1)}} \right) \Big/ \left( \sqrt{\frac{n}{n+1}} \right)^2 = -\frac{1}{n}. \qquad (4)$$

TABLE III. Wavefunctions of $\chi_{n,m}$ for the sp$^n$ hybridized AOs in $n$-space

$$\chi_{n,1} = \frac{1}{\sqrt{n+1}} s + \sqrt{\frac{n}{n+1}} p_1$$

$$\chi_{n,2} = \frac{1}{\sqrt{n+1}} s - \frac{1}{\sqrt{n(n+1)}} p_1 + \sqrt{\frac{n-1}{n}} p_2$$

$$\chi_{n,3} = \frac{1}{\sqrt{n+1}} s - \frac{1}{\sqrt{n(n+1)}} p_1 - \frac{1}{\sqrt{n(n-1)}} p_2 + \sqrt{\frac{n-2}{n-1}} p_3$$

$$\chi_{n,4} = \frac{1}{\sqrt{n+1}} s - \frac{1}{\sqrt{n(n+1)}} p_1 - \frac{1}{\sqrt{n(n-1)}} p_2 - \frac{1}{\sqrt{(n-1)(n-2)}} p_3 + \sqrt{\frac{n-3}{n-2}} p_4$$

......

$$\chi_{n,k} = \frac{1}{\sqrt{n+1}} s - \frac{1}{\sqrt{n(n+1)}} p_1 - \frac{1}{\sqrt{n(n-1)}} p_2 - \cdots \frac{1}{\sqrt{(n-k+3)(n-k+2)}} p_{k-1} + \sqrt{\frac{n-k+1}{n-k+2}} p_k$$

......

$$\chi_{n,n} = \frac{1}{\sqrt{n+1}} s - \frac{1}{\sqrt{n(n+1)}} p_1 - \frac{1}{\sqrt{n(n-1)}} p_2 - \cdots - \frac{1}{\sqrt{6}} p_{n-1} + \frac{1}{\sqrt{2}} p_n$$

$$\chi_{n,n+1} = \frac{1}{\sqrt{n+1}} s - \frac{1}{\sqrt{n(n+1)}} p_1 - \frac{1}{\sqrt{n(n-1)}} p_2 - \cdots - \frac{1}{\sqrt{6}} p_{n-1} - \frac{1}{\sqrt{2}} p_n$$

TABLE IV. Geometrical structure of sp$^n$ hybridized orbitals

| $n$ | sp$^n$ | $x_1$ | Geometrical Structure | $\cos\theta$ | $\theta$ |
|---|---|---|---|---|---|
| 1 | sp | $\frac{1}{\sqrt{2}}s + \frac{1}{\sqrt{2}}p_x$ | Line segment | $-\frac{1}{1}$ | 180°00' |
| 2 | sp$^2$ | $\frac{1}{\sqrt{3}}s + \sqrt{\frac{2}{3}}p_x$ | Regular triangle | $-\frac{1}{2}$ | 120°00' |
| 3 | sp$^3$ | $\frac{1}{\sqrt{4}}s + \sqrt{\frac{3}{4}}p_x$ | Regular tetrahedron | $-\frac{1}{3}$ | 109°28' |
| 4 | sp$^4$ | $\frac{1}{\sqrt{5}}s + \sqrt{\frac{4}{5}}p_x$ | Regular 5-cell | $-\frac{1}{4}$ | 104°29' |

The relation between $\chi_{n,1}$ and any other $\chi_{n,k}$ is all the same, because their $x$-component is the same as $\chi_{n,2}$, and $\chi_{n,1}$ has no p-component of other axes. Thus $\chi_{n,1}$ is shown to have the same angle (1.4) at all other $\chi_{n,k}$'s.

The angle between $\chi_{n,2}$ and other $\chi_{n,k}$ is also shown by the following calculation with $\chi_{n,2}$ taken as an example,

$$\cos(\angle\chi_{n,2}\cdot\chi_{n,3}) = \left\{\left(\frac{-1}{\sqrt{n(n+1)}}\right)^2 + \sqrt{\frac{n-1}{n}}\left(\frac{-1}{\sqrt{n(n+1)}}\right)\right\} / $$
$$\left\{\left(\frac{-1}{\sqrt{n(n+1)}}\right)^2 + \left(\sqrt{\frac{n-1}{n}}\right)^2\right\} = -\frac{1}{n} \qquad (5)$$

By doing this type of calculation one can make sure that all the angles between any pair of $\{\chi_n\}$ are the same as $\cos^{-1}(-1/n)$, whose values for $n = 1\sim4$ are given in Table IV. Now it is concluded that the angles of 180°, 120°, and 109°28', respectively, for the sp, sp$^2$, and sp$^3$ hybridizations of carbon atom originally proposed by Pauling[11] are nothing else but the angle spanning a pair of vertices from the center of 1-, 2-, and 3-simplexes. The corresponding angle for the sp$^5$ and sp$^6$ hybridized AOs in 4- and 5-spaces are, respectively, 104°29' and 101°32'.

## sp$^n$d$^{n-1}$ HYBRIDIZED AOs

Among various hybridized AOs involving d-orbitals the four-coordinating sp$^2$d and six-coordinating sp$^3$d$^2$ are the most common. However, there seems to have never been discussed about their mathematical connection. Now look at the wavefunctions of sp-, sp$^2$d-, and sp$^3$d$^2$-hybridized AOs given in Table V, where beautiful block or fractal structure is observed. Namely, although the coefficients depend on the dimensionality, the set of sp$^3$d$^2$ hybridiza-

TABLE V. Wavefunctions of $\chi_{n,m}$ for sp, sp$^2$d, sp$^3$d$^2$ hybridized AOs

| sp hybridization in 1-D | sp$^2$d hybridization in 2-D | | |
|---|---|---|---|
| $\chi_{1,1} = \frac{1}{\sqrt{2}}s + \frac{1}{\sqrt{2}}p_x$ | $\chi_{2,1} = \frac{1}{2}s + \frac{1}{\sqrt{2}}p_x$ | | $+\frac{1}{2}d_{x^2-y^2}$ |
| $\chi_{1,2} = \frac{1}{\sqrt{2}}s - \frac{1}{\sqrt{2}}p_x$ | $\chi_{2,2} = \frac{1}{2}s - \frac{1}{\sqrt{2}}p_x$ | | $+\frac{1}{2}d_{x^2-y^2}$ |
| | $\chi_{2,3} = \frac{1}{2}s$ | $+\frac{1}{\sqrt{2}}p_y$ | $-\frac{1}{2}d_{x^2-y^2}$ |
| | $\chi_{2,4} = \frac{1}{2}s$ | $-\frac{1}{\sqrt{2}}p_y$ | $-\frac{1}{2}d_{x^2-y^2}$ |

| sp$^3$d$^2$ hybridization in 3-D | | | |
|---|---|---|---|
| $\chi_{3,1} = \frac{1}{\sqrt{6}}s + \frac{1}{\sqrt{2}}p_x$ | | $+\frac{1}{2}d_{x^2-y^2} - \frac{1}{\sqrt{12}}d_{z^2}$ | |
| $\chi_{3,2} = \frac{1}{\sqrt{6}}s - \frac{1}{\sqrt{2}}p_x$ | | $+\frac{1}{2}d_{x^2-y^2} - \frac{1}{\sqrt{12}}d_{z^2}$ | |
| $\chi_{3,3} = \frac{1}{\sqrt{6}}s$ | $+\frac{1}{\sqrt{2}}p_y$ | $-\frac{1}{2}d_{x^2-y^2} - \frac{1}{\sqrt{12}}d_{z^2}$ | |
| $\chi_{3,4} = \frac{1}{\sqrt{6}}s$ | $-\frac{1}{\sqrt{2}}p_y$ | $-\frac{1}{2}d_{x^2-y^2} - \frac{1}{\sqrt{12}}d_{z^2}$ | |
| $\chi_{3,5} = \frac{1}{\sqrt{6}}s$ | $+\frac{1}{\sqrt{2}}p_z$ | $+\frac{1}{\sqrt{3}}d_{z^2}$ | |
| $\chi_{3,6} = \frac{1}{\sqrt{6}}s$ | $-\frac{1}{\sqrt{2}}p_z$ | $+\frac{1}{\sqrt{3}}d_{z^2}$ | |

tion contains the set of sp$^2$d, which in turn contains sp. All these hybridized orbitals are directed along one of the axes of the rectangular coordinate system. This means that the sp$^n$d$^{n-1}$ hybridized orbitals (n≥1) are the realization of $n$-cross polytopes. Then it is easy to get the sp$^4$d$^3$-hybridized AOs in 4-space as in Table VI, where the block of sp$^3$d$^2$ is contained.

The analytical forms of the three d-orbitals in $n$-space appearing in Table VI are represented, respectively, as[1]

$$d_{x^2-y^2} = \sqrt{\frac{n}{2(n-1)}}(x_1^2 - x_2^2),$$

$$d_{z^2} = \sqrt{\frac{n}{2\cdot3(n-1)}}(x_1^2 + x_2^2 - 2x_3^2),$$

$$d_{w^2} = \sqrt{\frac{n}{12(n-1)}}(x_1^2 + x_2^2 + x_3^2 - 3x_4^2). \qquad (6)$$

It was not so straightforward but the general expressions for the sp$^n$d$^{n-1}$ hybridized AOs in $n$-space were obtained as in Table VII.

The wavefunctions of typical lobes of four sp$^n$d$^{n-1}$ hybridized AOs (n = 1~4) are compared in Table VIII. It

TABLE VI. Wavefunctions of $\chi_{n,m}$ for sp$^4$d$^3$ hybridized AOs in 4-space

$$\chi_{4,1} = \frac{1}{\sqrt{8}}s + \frac{1}{\sqrt{2}}p_x \qquad\qquad +\frac{1}{2}d_{x^2-y^2} - \frac{1}{\sqrt{12}}d_{z^2} - \frac{1}{\sqrt{24}}d_{w^2}$$

$$\chi_{4,2} = \frac{1}{\sqrt{8}}s - \frac{1}{\sqrt{2}}p_x \qquad\qquad +\frac{1}{2}d_{x^2-y^2} - \frac{1}{\sqrt{12}}d_{z^2} - \frac{1}{\sqrt{24}}d_{w^2}$$

$$\chi_{4,3} = \frac{1}{\sqrt{8}}s \qquad +\frac{1}{\sqrt{2}}p_y \qquad -\frac{1}{2}d_{x^2-y^2} - \frac{1}{\sqrt{12}}d_{z^2} - \frac{1}{\sqrt{24}}d_{w^2}$$

$$\chi_{4,4} = \frac{1}{\sqrt{8}}s \qquad -\frac{1}{\sqrt{2}}p_y \qquad -\frac{1}{2}d_{x^2-y^2} - \frac{1}{\sqrt{12}}d_{z^2} - \frac{1}{\sqrt{24}}d_{w^2}$$

$$\chi_{4,5} = \frac{1}{\sqrt{8}}s \qquad +\frac{1}{\sqrt{2}}p_z \qquad +\frac{1}{\sqrt{3}}d_{z^2} - \frac{1}{\sqrt{24}}d_{w^2}$$

$$\chi_{4,6} = \frac{1}{\sqrt{8}}s \qquad -\frac{1}{\sqrt{2}}p_z \qquad +\frac{1}{\sqrt{3}}d_{z^2} - \frac{1}{\sqrt{24}}d_{w^2}$$

$$\chi_{4,7} = \frac{1}{\sqrt{8}}s \qquad +\frac{1}{\sqrt{2}}p_w \qquad +\frac{3}{\sqrt{24}}d_{w^2}$$

$$\chi_{4,8} = \frac{1}{\sqrt{8}}s \qquad -\frac{1}{\sqrt{2}}p_w \qquad +\frac{3}{\sqrt{24}}d_{w^2}$$

TABLE VII. General form of sp$^n$d$^{n-1}$ hybridized AOs in $n$-space

$$n = 0,1,2,...; \quad m = 1,2,3,...,2n \qquad\qquad l = \left\lfloor \frac{m+1}{2} \right\rfloor$$

for $1 \leq m \leq 4$

$$\chi_{n,m} = \frac{1}{\sqrt{2n}}s + (-1)^{m-1}\frac{1}{\sqrt{2}}p_{x_l} + (1-\delta_{n1})\left\{ (-1)^l \frac{1}{2}d_{x_1^2-x_2^2} - \sum_{k=3}^{n}\frac{1}{\sqrt{2k(k-1)}}d_{x_k^2} \right\}$$

for $m \geq 5$ $(n \geq 3)$

$$\chi_{n,m} = \frac{1}{\sqrt{2n}}s + (-1)^{m-1}\frac{1}{\sqrt{2}}p_{x_l} + \sqrt{\frac{l-1}{2l}}d_{x_l^2} - \sum_{k=l+1}^{n}\frac{1}{\sqrt{2k(k-1)}}d_{x_k^2}$$

is a natural consequence that the weight of s-, p-, and d--orbitals in each hybridized lobe is proportional to the number of the same $l$ orbitals supplied to the hybridization.

Nowadays, *ab initio* molecular orbital calculations are so easily performed by using available programs and the result can be automatically obtained even without any prior knowledge of hybridized AOs developed in this paper. However, the readers will realize the beauty of the mathematical structure of these hybridized AOs in $n$-space. Relation among various hybridized orbitals can be grasped from Figure 4, where possible sp$^m$d$^n$ hybridizations are systematically arranged. By following the bold lines one can easily understand that sp hybridization is the starting member of not only sp$^n$ but also sp$^n$d$^{n-1}$ series.

TABLE VIII. Geometrical structure of sp$^n$d$^{n-1}$ hybridized orbitals

| $n$ | sp$^n$d$^{n-1}$ | $x_{n,2n}$ | Geometrical Structure | $\theta$ |
|---|---|---|---|---|
| 1 | sp | $\frac{1}{\sqrt{2}}s - \frac{1}{\sqrt{2}}p_x$ | Line segment | 180° |
| 2 | sp$^2$d | $\frac{1}{2}s - \frac{1}{\sqrt{2}}p_y - \frac{1}{2}d_{x^2-y^2}$ | Square | 90° |
| 3 | sp$^3$d$^2$ | $\frac{1}{\sqrt{6}}s - \frac{1}{\sqrt{2}}p_z + \frac{1}{\sqrt{3}}d_{z^2}$ | Regular octahedron | 90° |
| 4 | sp$^4$d$^3$ | $\frac{1}{\sqrt{8}}s - \frac{1}{\sqrt{2}}p_w + \frac{3}{\sqrt{24}}d_{w^2}$ | Hexadecachoron | 90° |

dimension        coordination number
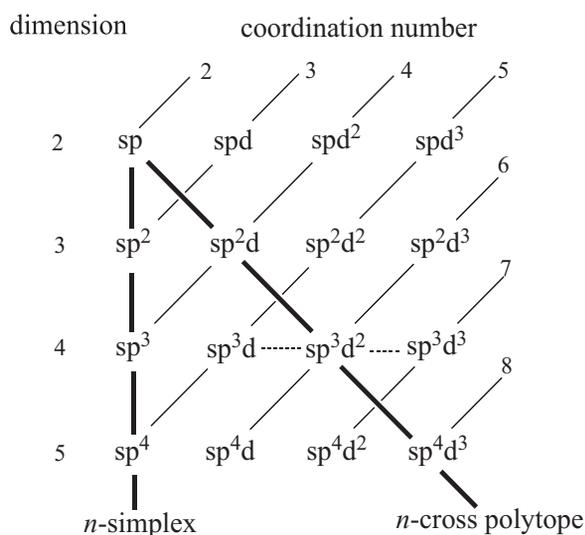


Figure 4. Catalog of $sp^m d^n$ hybridization.

Trigonal and pentagonal bipyramids are described, respectively, by $sp^3d$ and $sp^3d^3$ hybridizations, while octahedron of $sp^3d^2$ hybridization may be called tetragonal bipyramid. Then the dotted line in Figure 4 connects another series of hybridized AOs. However, no $n$-space problem evolves from this group. It is difficult to find other interesting series of hybridized AOs composed of only s, p, and d orbitals. One need to throw away this restriction for finding further possibilities.

## N-CUBIC HYBRIDIZED AOs

Finally consider $n$-cubes, which are the most popular $n$-space polytopes and sometimes called »measure polytopes«,[9] because they are used as a measuring unit in each $n$-space. As shown in Figure 5, the $n$-cubes line up from vertex, line segment, square, cube (3-cube), 4-cube, etc. An $n$-cube is defined as a polytope constructed from $2^n$ vertices and enclosed by $2n$ $(n-1)$-cube. The number of $k$th elements is generally given by $2^{n-k}\binom{n}{k}$ Two different kinds of figures are drawn in Figure 5. Those in the right side column illustrate the growth process of $n$-cube from a pair of $(n-1)$-cubes, white and black, which are connected by the horizontal edges in the figure. The figures in the left side column are drawn to minimize the number of crossing points in the projection.

In Table V we have already seen square planar $sp^2d$ hybridization, in which each lobe lies along either $x$- or $y$-axis. However, we are seeking such $sp^2d$ whose lobes emanate from the origin toward the four corners of a square. The answer is given in Table IX which was obtained just by the rotation of 45 degrees. The $d_{x^2-y^2}$ is replaced with $d_{xy}$, and each lobe is contributed equally from s, $p_x$, $p_y$, and $d_{xy}$, and the sign of $d_{xy}$ component is

TABLE IX. Wavefunctions of $\chi_{n,l}$ for $n$-cube hybridized AOs

sp hybridization in 1-D

$$\begin{pmatrix} \chi_{1,1} \\ \chi_{1,2} \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} + & + \\ + & - \end{pmatrix} \begin{pmatrix} s \\ p_x \end{pmatrix}$$

$sp^2d$ hybridization in 2-D

$$\begin{pmatrix} \chi_{2,1} \\ \chi_{2,2} \\ \chi_{2,3} \\ \chi_{2,4} \end{pmatrix} = \frac{1}{2} \begin{pmatrix} + & + & + & + \\ + & + & - & - \\ + & - & + & - \\ + & - & - & + \end{pmatrix} \begin{pmatrix} s \\ p_x \\ p_y \\ d_{xy} \end{pmatrix}$$

$sp^3d^3f$ hybridization in 3-D

$$\begin{pmatrix} \chi_{3,1} \\ \chi_{3,2} \\ \chi_{3,3} \\ \chi_{3,4} \\ \chi_{3,5} \\ \chi_{3,6} \\ \chi_{3,7} \\ \chi_{3,8} \end{pmatrix} = \frac{1}{\sqrt{8}} \begin{pmatrix} + & + & + & + & + & + & + & + \\ + & + & + & - & + & - & - & - \\ + & + & - & + & - & - & + & - \\ + & + & - & - & - & + & - & + \\ + & - & + & + & - & + & - & - \\ + & - & + & - & - & - & + & + \\ + & - & - & + & + & - & - & + \\ + & - & - & - & + & + & + & - \end{pmatrix} = \begin{pmatrix} s \\ p_x \\ p_y \\ p_z \\ d_{xy} \\ d_{yz} \\ d_{zx} \\ f_{xyz} \end{pmatrix}$$

determined as the product of the signs of the components of the pair of $p_x$ and $p_y$. It is to be noted that the coefficient matrix shown in Table IX is the same as what

| $n$ | $n$-cube | | V $k = 0$ | E 1 | F 2 | C 3 |
|---|---|---|---|---|---|---|
| 0 | • | ○ | 1 | | | |
| 1 | —— | •——○ | 2 | 1 | | |
| 2 | | | 4 | 4 | 1 | |
| 3 | | | 8 | 12 | 6 | 1 |
| 4 | | | 16 | 32 | 24 | 8 |

$$N_{n,k} = 2^{n-k}\binom{n}{k}$$

Figure 5. N-cubes and the number of $k$th elements.

TABLE X. Block or fractal structure of *n*-cube hybridized AOs for *n*=1~3



TABLE XI. Geometrical structure of *n*-cube hybridized orbitals

| *n* hybridization | $\chi_{n,1}$ | $\cos\theta$ | $\theta$ |
|---|---|---|---|
| 1 sp | $\frac{1}{\sqrt{2}}(s + p_x)$ | $-\frac{1}{1}$ | 180°00' |
| 2 sp²d | $\frac{1}{2}(s + p_x + p_y + d_{xy})$ | 0 | 90°00' |
| 3 sp³d³f | $\frac{1}{\sqrt{8}}(s + p_x + p_y + p_z + d_{xy} + d_{xz} + d_{yz} + f_{xyz})$ | $\frac{1}{3}$ | 70°32' |
| 4 sp⁴d⁶f⁴g | $\frac{1}{4}(s + p_x + p_y + p_z + p_w + d_{xy} + d_{xz} + d_{xw} + d_{yz} + d_{yw} + d_{zw} + f_{xyz} + f_{xyw} + f_{xzw} + f_{yzw} + g_{xyzw})$ | $\frac{1}{2}$ | 60°00' |

was proposed by Pauling[9] for sp³ as another representation of sp³ hybridization,

$$\begin{pmatrix}\chi_{3,1}\\\chi_{3,2}\\\chi_{3,3}\\\chi_{3,4}\end{pmatrix} = \frac{1}{2}\begin{pmatrix}+&+&+&+\\+&+&-&-\\+&-&+&-\\+&-&-&+\end{pmatrix}\begin{pmatrix}s\\p_x\\p_y\\p_z\end{pmatrix} \quad (7)$$

However, mathematical meaning of these two matrices is quite different from each other. While each component of (7), one s and three p's, is independent from each other, the sp²d hybridization in Table IX is factorable as symbolically expressed by

$$(1 \pm x)(1 \pm y) = 1 \pm x \pm y \pm xy,$$

where $(1 \pm x)$ and $(1 \pm y)$ represent the $2 \times 2$ matrix as given in Table IX for 1-D sp hybridization. Recall that the spherical harmonics, $d_{xy}$, is obtained by the product of a pair of the lower members of spherical harmonics, $p_x$ and $p_y$.

Now it is straightforward to extend this idea to construct the 8-coordinated 3-cube hybridization, sp³d³f, as shown in Table IX by using the following scheme,

$$(1 \pm x)(1 \pm y)(1 \pm z) = 1 \pm x \pm y \pm z \pm xy \pm xz \pm yz \pm xyz.$$

This means that 3-cube hybridized AOs are composed of one s, three p's (*x*, *y*, and *z*), three d's (*xy*, *yz*, and *zx*), and one f (*xyz*). In these processes one can realize that for constructing the *n*-cube hybridization the number of AOs of angular momentum *l* is determined by the binomial distribution as in the following expression,

$$s\binom{n}{0}p\binom{n}{1}d\binom{n}{2}f\binom{n}{3}\ldots l\binom{n}{l}\ldots \quad (8)$$

In the $8 \times 8$ matrix for sp³d³f hybridization, the blocks of sp²d (dotted lines) and of sp (straight lines) hybridization can be seen as in Table X.

Although possible use of f orbitals for 8-coordinated hybridized AOs has been pointed out in a very limited number of literatures,[12] to the authors' awareness, no explicit representation has ever been published. Since the energy difference between d and f orbitals is rather small in heavier atoms, it is possible for 8-coordinated molybdenum complexes may take some cubic structure.

Since it is no point in writing the whole expression of $16 \times 16$ 4-cube hybridization, sp⁴d⁶f⁴g, only the wavefunction of $\chi_{4,1}$ lobe is given in Table XI, where the angle between a pair of two lobes of *n*-cube hybridization is also given.

The wavefunctions of the 1st and 2nd lobes of *n*-cube hybridization in *n*-space have the following forms as

$$\chi_{n,1} = $$
$$\frac{1}{\sqrt{2^n}}[s + (p_{x1} + p_{x2} + \ldots p_{x(n-1)} + p_{xn}) + (d_{x1x2} + \ldots) + \ldots]$$

$$\chi_{n,2} = $$
$$\frac{1}{\sqrt{2^n}}[s + (p_{x1} + p_{x2} + \ldots p_{x(n-1)} - p_{xn}) + (d_{x1x2} + \ldots) + \ldots]. \quad (9)$$

The angle between them can be obtained by the product sum of the direction cosines of only p components. Thus we have a neat result as

$$\cos(\angle\chi_{n,1} \cdot \chi_{n,2}) = \frac{(n-1)-1}{n} = \frac{n-2}{n} \quad (10)$$

where the normalization coefficient common to all the components has nothing to do with the final result.

It is to be remarked here that the 3-cube hybridized AOs, which have not only mathematical beauty but also an important role in stereochemistry, was derived from the $n$-space analysis as developed in this paper.

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# SAŽETAK

## Novi pogled iz $n$-dimenzionalnog svijeta na hibridizirane atomske orbitale

### Haruo Hosoya, Fuyuko Kido i Sumio Tokita

Pogledom iz ptičje perspektive $n$-dimenzionalnog svijeta ($n$-svijeta) utvrđeno je da uobičajene sp, sp$^2$ i sp$^3$ hibridizirane atomske orbitale pripadaju sp$^n$ hibridizaciji dok njihovi geometrijski oblici odgovaraju $n$-simpleksima, najmanjim geometrijskim objektima u $n$-prostoru. Slično tome, sp, sp$^2$d i sp$^3$d$^2$ hibridi pripadaju sp$^n$d$^{n-1}$ hibridizaciji, a njihovi geometrijski oblici $n$-križnim politopima dobivenima od $2n$ čvorova koji su ekvidistantno smješteni na $n$ međusobno okomitih koordinatnih osi. U radu se također razmatra niz $n$-kocka hibridizacija čiji je član u 3-dimenzionalnom svijetu 8-koordinirana kubna sp$^3$d$^3$f hibridizacija. Izvedeni su opći analitički oblici valnih funkcija za gornja tri niza hibridiziranih atomskih orbitala u $n$-prostoru. Raspravlja se i o periodnom sustavu i srodnim problemima za atome i molekule u $n$-prostoru.

## APPENDIX

The electronic configurations of atoms in 4-space forming a 4-D periodic table was recently proposed by the present authors.[7] However, due to fatal mistake by the publisher the main body of the periodic table of atoms in 4-D in Ref. 7 was wrongly printed. Here the correct form of the periodic table of atoms is printed as Table A.

TABLE AI. Periodic tables of the elements up to Ar in 2, 3, and 4 dimensions

| | 2D | | 3D | | 4D | |
|---|---|---|---|---|---|---|
| H | 1 | $1s$ | 1 | $1s$ | 1 | $1s$ |
| He | 2 | $1s^2$ | 2 | $1s^2$ | 2 | $1s^2$ |
| Li | 3 | $1s^22s$ | 3 | $1s^22s$ | 3 | $1s^22s$ |
| Be | 4 | $1s^22s^2$ | 4 | $1s^22s^2$ | 4 | $1s^22s^2$ |
| B | | | 5 | $1s^22s^22p$ | 5 | $1s^22s^22p$ |
| Cb[a] | | | | | 6 | $1s^22s^22p^2$ |
| C | 5 | $1s^22s^22p$ | 6 | $1s^22s^22p^2$ | 7 | $1s^22s^22p^3$ |
| N | 6 | $1s^22s^22p^2$ | 7 | $1s^22s^22p^3$ | 8 | $1s^22s^22p^4$ |
| On[b] | | | | | 9 | $1s^22s^22p^5$ |
| O | | | 8 | $1s^22s^22p^4$ | 10 | $1s^22s^22p^6$ |
| F | 7 | $1s^22s^22p^3$ | 9 | $1s^22s^22p^5$ | 11 | $1s^22s^22p^7$ |
| Ne | 8 | $1s^22s^22p^4$ | 10 | $1s^22s^22p^6$ | 12 | $1s^22s^22p^8$ |
| | 8 | (KL) | 10 | (KL) | 12 | (KL) |
| Na | 9 | KL3s | 11 | KL3s | 13 | KL3s |
| Mg | 10 | $KL3s^2$ | 12 | $KL3s^2$ | 14 | $KL3s^2$ |
| Al | | | 13 | $KL3s^23p$ | 15 | $KL3s^23p$ |
| Sl[c] | | | | | 16 | $KL3s^23p^2$ |
| Si | 11 | $KL3s^23p$ | 14 | $KL3s^23p^2$ | 17 | $KL3s^23p^3$ |
| P | 12 | $KL3s^23p^2$ | 15 | $KL3s^23p^3$ | 18 | $KL3s^23p^4$ |
| Sp[d] | | | | | 19 | $KL3s^23p^5$ |
| S | | | 16 | $KL3s^23p^4$ | 20 | $KL3s^23p^6$ |
| Cl | 13 | $KL3s^23p^3$ | 17 | $KL3s^23p^5$ | 21 | $KL3s^23p^7$ |
| Ar | 14 | $KL3s^23p^4$ | 18 | $KL3s^23p^6$ | 22 | $KL3s^23p^8$ |
| | 14 | [Ar] | 18 | [Ar] | 22 | [Ar] |

[a] carboron; [b] oxytrogen; [c] siliminum; [d] sulphorus.

TABLE AII. Periodic tables of atoms from Ar to Kr in 2, 3, and 4 dimensions

| | 2D | | 3D | | 4D | |
|---|---|---|---|---|---|---|
| Ar | 14 | $KL3s^23p^4$ | 18 | $KL3s^23p^6$ | 22 | $KL3s^23p^8$ |
| K | 15 | [Ar]4s | 19 | [Ar]4s | 23 | [Ar]4s |
| Ca | 16 | $[Ar]4s^2$ | 20 | $[Ar]4s^2$ | 24 | $[Ar]4s^2$ |
| Sc | 17 | $[Ar]\underline{3d^24s}$ | 21 | $[Ar]3d4s^2$ | 25 | $[Ar]3d4s^2$ |
| Qa | | | | | 26 | $[Ar]3d^24s^2$ |
| Qb | | | | | 27 | $[Ar]3d^34s^2$ |
| Qc | | | | | 28 | $[Ar]3d^44s^2$ |
| Qd | | | | | 29 | $[Ar]3d^54s^2$ |
| Ti | | | 22 | $[Ar]3d^24s^2$ | 30 | $[Ar]3d^64s^2$ |
| V | | | 23 | $[Ar]3d^34s^2$ | 31 | $[Ar]3d^74s^2$ |
| Cr | | | 24 | $[Ar]3d^\underline{5}4s$ | 32 | $[Ar]3d^94s$ |
| Mn | 18 | $[Ar]3d^24s^2$ | 25 | $[Ar]3d^54s^2$ | 33 | $[Ar]3d^94s^2$ |
| Fe | | | 26 | $[Ar]3d^64s^2$ | 34 | $[Ar]3d^{10}4s^2$ |
| Co | | | 27 | $[Ar]3d^74s^2$ | 35 | $[Ar]3d^{11}4s$ |
| Ni | | | 28 | $[Ar]3d^84s^2$ | 36 | $[Ar]3d^{12}4s^2$ |
| Qe | | | | | 37 | $[Ar]3d^{13}4s^2$ |
| Qf | | | | | 38 | $[Ar]3d^{14}4s^2$ |
| Qg | | | | | 39 | $[Ar]3d^{15}4s^2$ |
| Qh | | | | | 40 | $[Ar]3d^{16}4s^2$ |
| Cu | 19 | $[Ar]3d^34s^2$ | 29 | $[Ar]\underline{3d^{10}4s}$ | 41 | $[Ar]3d^{\underline{18}}4s$ |
| Zn | 20 | $[Ar]3d^44s^2$ | 30 | $[Ar]3d^{10}4s^2$ | 42 | $[Ar]3d^{18}4s^2$ |
| Ga | | | 31 | $[Ar]3d^{10}4s^24p$ | 43 | $[Ar]3d^{18}4s^24p$ |
| Qi | | | | | 44 | $[Ar]3d^{18}4s^24p^2$ |
| Ge | 21 | $[Ar]3d^44s^24p$ | 32 | $[Ar]3d^{10}4s^24p^2$ | 45 | $[Ar]3d^{18}4s^24p^3$ |
| As | 22 | $[Ar]3d^44s^24p^2$ | 33 | $[Ar]3d^{10}4s^24p^3$ | 46 | $[Ar]3d^{18}4s^24p^4$ |
| Qj | | | | | 47 | $[Ar]3d^{18}4s^24p^5$ |
| Se | | | 34 | $[Ar]3d^{10}4s^24p^4$ | 48 | $[Ar]3d^{18}4s^24p^6$ |
| Br | 23 | $[Ar]3d^44s^24p^3$ | 35 | $[Ar]3d^{10}4s^24p^5$ | 49 | $[Ar]3d^{18}4s^24p^7$ |
| Kr | 24 | $[Ar]3d^44s^24p^4$ | 36 | $[Ar]3d^{10}4s^24p^6$ | 50 | $[Ar]3d^{18}4s^24p^8$ |
| | 24 | [Kr] | 36 | [Kr] | 50 | [Kr] |