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Magic Numbers in Polygonal and Polyhedral Clusters

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Received March 15, 1985

Certain values for the nuclearity of clusters tend to occur more frequently than others. This paper gives a mathematical derivation of the preferred values of nuclearity (the "magic numbers") corresponding to various symmetrical, close-packed polygons (in two dimensions) and polyhedra (in three dimensions). Simple general formulas are obtained for the numbers of atoms in these clusters. Explicit coordinates are given for the atoms. Application of these *atom-counting* results to *electron counting* of close-packed high-nuclearity metal clusters is illustrated.

I. Introduction

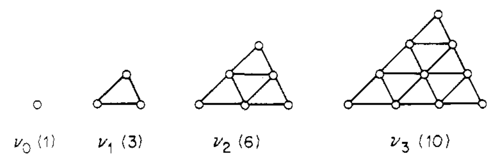
Cluster science has now developed to the stage where, on the one hand, clusters containing up to 44 metal atoms (up to 15 Å in diameter) have been synthesized and structurally characterized and, on the other hand, microscopic metal crystallites of 25 Å or more in diameter can be produced.[1-3] While large molecular clusters created by chemical means have a single, well-defined size and shape (i.e. a δ-function size distribution), small metal crystallites produced by physical means generally have a broader distribution of size and shape. It is known that as the cluster size increases there is a transition from one extreme of chemical and physical behavior of molecular species, in small clusters of up to e.g. 15 Å (with tens of atoms), to the other extreme of bulk properties in large crystallites of more than 30 Å (with thousands or more atoms). It is generally believed, and in some cases has been demonstrated, that unusual size-dependent structural, chemical, and physical properties (e.g. kinetics, catalysis, semiconductivity, superconductivity, magnetism, nucleation and melting behavior, latent heat, surfaces, optical properties, and light scattering) occur in the transition region where there are tens or hundreds of atoms. These unusual properties may lead to technological advances such as homogeneous or heterogeneous catalysis, new thin-film or other microscopic materials, Josephson junction, crystal growth, colloids, etc. Such prospects have sparked intensive interdisciplinary efforts in the production, characterization, and spectroscopic studies of large molecular clusters and small metal particles or crystallites.

Central to the chemical and physical study of clusters is a basic understanding of their molecular and electronic structures. A first step toward such understanding is to determine the number of atoms in a cluster of given size and shape and their arrangement or disposition. We shall call this *atom counting*. This is the subject of the present paper.

It is well-known that clusters containing certain special numbers of atoms occur much more frequently than others. For example clusters[1-3] of three atoms (forming a triangle), four atoms (a tetrahedron), six atoms (an octahedron), and eight atoms (a cube) are far more common than clusters of five, seven, or nine atoms. This is presumably because arrangements of three, four, six, or eight spheres of equal or nearly equal size are more compact and symmetrical than arrangements of five, seven, or nine spheres. Mathematicians from Pythagoras' day to the present have given special names, such as *triangular numbers*, or *polygonal*, *polyhedral*, *figurate numbers*, etc., to numbers of spheres that can be arranged into various symmetrical figures. A comprehensive historical account is given by Dickson,[4] while Hogben[5] has some excellent pictures. The numbers 3, 4, 6, and 8 are in fact the smallest nontrivial triangular, tetrahedral, octahedral, and cubic numbers. We shall refer to all these special numbers as simply *magic numbers*. These same numbers have also been observed in other branches of chemistry and physics.[6]

It is the purpose of this paper to calculate the magic numbers corresponding to the commonest two-dimensional figures (or *polygons*) and three-dimensional bodies (or *polyhedra*). We have discovered some remarkably simple general formulas for these magic numbers. Some special cases of these formulas were discovered earlier by Buckminster Fuller and Coxeter. Section

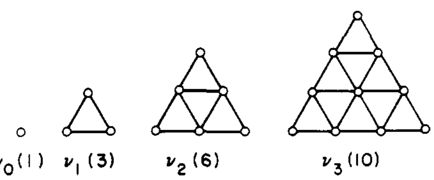
Chart I. Triangles of Frequency 0, 1, 2, and 3[a]



ν_0 (1) ν_1 (3) ν_2 (6) ν_3 (10)

[a] The triangles need not have equal sides. The numbers of points (the triangular numbers t_0, t_1, t_2, t_3) are given in parentheses. A triangle of frequency n, or a ν_n triangle, contains $n+1$ points on each edge.

Chart II. Equilateral Triangles of Frequency 0, 1, 2, and 3[a]



ν_0 (1) ν_1 (3) ν_2 (6) ν_3 (10)

[a] In all these figures the numbers of atoms are given in parentheses, and in most cases nearest neighbors are joined. In this chart $p = 3$ and $F = 1$ (see text).

(1) For reviews on boranes, carboranes, metallaboranes, and metallacarboranes, see: (a) Lipscomb, W. N. "Boron Hydrides"; W. A. Benjamin: New York, 1963. (b) Muetterties, E. L., Ed. "Boron Hydride Chemistry"; Academic Press: New York, 1975. (c) Muetterties, E. L.; Knoth, W. H. "Polyhedral Boranes"; Marcel Dekker: New York, 1968. (d) Rudolph, R. W. *Acc. Chem. Res.* **1976**, *9*, 446. (e) Grimes, R. N. "Carboranes"; Academic Press: New York, 1970. (f) Grimes, R. N., Ed. "Metal Interactions with Boron Clusters"; Plenum Press: New York, 1982. (g) O'Neill, M. E.; Wade, K. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 1, Chapter 1. Onak, T. *Ibid.*, Chapter 5.4. Grimes, R. N. *Ibid.*, Chapter 5.5.

(2) For reviews on main-group clusters, see: (a) Corbett, J. D. *Prog. Inorg. Chem.* **1976**, *21*, 129. (b) Gillespie, R. J. *Chem. Soc. Rev.* **1979**, *8*, 315.

(3) For reviews on transition-metal clusters, see: (a) Chini, P. *Gazz. Chim. Ital.* **1979**, *109*, 225. (b) Chini, P. *J. Organomet. Chem.* **1980**, *200*, 37. (c) Chini, P.; Longoni, G.; Albano, V. G. *Adv. Organomet. Chem.* **1976**, *14*, 285. (d) "Transition Metal Clusters"; Johnson, B. F. G., Ed.; Wiley-Interscience: Chichester, 1980. (e) Benfield, R. E.; Johnson, B. F. G. *Top. Stereochem.* **1981**, *12*, 253. (f) Mingos, D. M. P. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 1.

(4) (a) Dickson, L. E. "History of the Theory of Numbers"; Chelsea: New York, 1966; Vol. II, Chapter 1. See also: (b) Federico, P. J. "Descartes on Polyhedra"; Springer-Verlag: New York, 1982.

(5) Hogben, L. "Chance and Choice by Cardpack and Chessboard"; Chanticleer Press: New York, 1950; Vol. I, Chapter 1.

(6) (a) Borel, J.-P.; Buttet, J. "Small Particles and Inorganic Clusters"; North-Holland: Amsterdam, 1981; and references cited therein. (b) Wronka, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1984**, *106*, 67. (c) Meckstroth, W. K.; Ridge, D. P.; Reents, W. D., Jr., private communication, 1984. (d) Leutwyler, S.; Hermann, A.; Woeste, L.; Schumacher, E. *Chem. Phys.* **1980**, *48*, 253. (e) Powers, D. E.; Hansen, S. G.; Geusic, M. E.; Puiu, A. C.; Hopkins, J. B.; Dietz, T. G.; Duncan, M. A.; Langridge-Smith, P. R. R.; Smalley, R. E. *J. Phys. Chem.* **1982**, *86*, 2556. (f) Gole, J. L.; English, J. H.; Bondybey, U. E. *J. Phys. Chem.* **1982**, *86*, 2560. (g) Barlak, T. M.; Wyatt, J. R.; Colton, R. J.; deCorpo, J. J.; Campana, J. E. *J. Am. Chem. Soc.* **1982**, *104*, 1212. (h) Lichtin, D. A.; Bernstein, R. B.; Vaida, V. *J. Am. Chem. Soc.* **1982**, *104*, 1831. (i) Magnera, T. F.; David, D. E.; Tian, R.; Stulik, D.; Michl, J. *J. Am. Chem. Soc.* **1984**, *106*, 5040.

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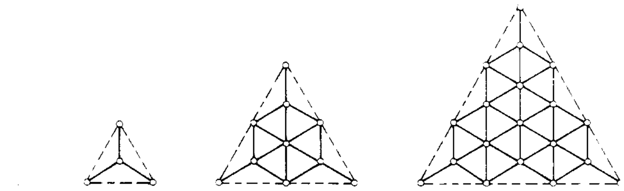
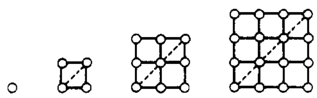
Chart III. Centered Equilateral Triangles of Frequency 0, 1, and 2 and the Centered Triangular Numbers[a]



$\nu_0(1)$ $\nu_1(4)$ $\nu_2(10)$ $\nu_3(19)$

[a] The centered polygons are divided into p triangles from a central point. Here $p = F = 3$.

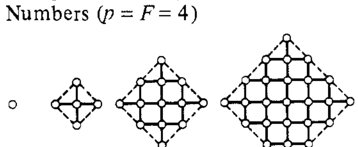
Chart IV. Squares of Frequency 0, 1, 2, and 3 and the Square Numbers[a]



$\nu_0(1)$ $\nu_1(4)$ $\nu_2(9)$ $\nu_3(16)$

[a] The dashed lines show the decomposition into $F = 2$ ν_n triangles.

Chart V. Centered Squares of Frequency 0, 1, 2, and 3 and the Centered Square Numbers ($p = F = 4$)



$\nu_0(1)$ $\nu_1(5)$ $\nu_2(13)$ $\nu_3(25)$

II deals with two-dimensional figures, section III gives formulas for the number of points in a general three-dimensional figure, and section IV studies particular examples of three-dimensional figures. Section V gives coordinates for all the figures. These coordinates should be particularly useful for theoretical investigations such as molecular orbital calculations, since they describe the idealized, most symmetrical configurations. The magic numbers themselves are collected in Tables V–VII. The final section contains a summary and further discussions, including a number of counterintuitive concepts and the application of the magic numbers in *electron counting* of close-packed high-nuclearity metal clusters.

II. Two-Dimensional Figures

A triangular arrangement of atoms, or points, such as is shown in Chart I, with $n + 1$ atoms along each edge, is called a *triangle of frequency n*, or a *ν_n triangle*. (The triangle need not be equilateral, i.e., need not have equal sides.) The total number of atoms in a ν_n triangle is denoted by t_n. Since there are rows of 1, 2, 3, ..., $n + 1$ atoms

$$t_n = 1 + 2 + 3 + ... + (n + 1) = \tfrac{1}{2}(n + 1)(n + 2) \qquad (1)$$

(see Jolley[7,8]). The numbers t_n are called *triangular*[9] *numbers*;

(7) Jolley, L. B. W. "Summation of Series", 2nd ed.; Dover: New York, 1961.

(8) (a) t_n is also the binomial coefficient

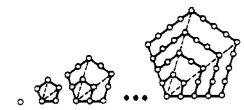
$$\binom{n+2}{n}$$

the number of ways of choosing two objects out of $n + 2$. (b) More generally the rth *figurate* number of order n is the binomial coefficient

$$\binom{r+n-1}{n}$$

(see p 7 of ref 4a). This gives the number of points in an n-dimensional triangular pyramid.

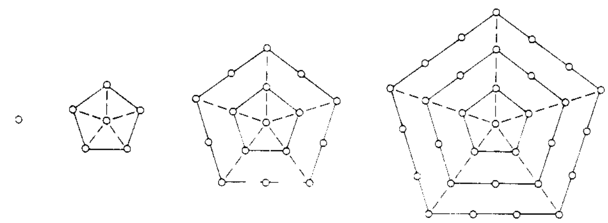
Chart VI. Regular Pentagons of Frequency 0, 1, 2, and 4 and the Classical Pentagonal Numbers[a]



$\nu_0(1)$ $\nu_1(5)$ $\nu_2(12)$ $\nu_4(35)$

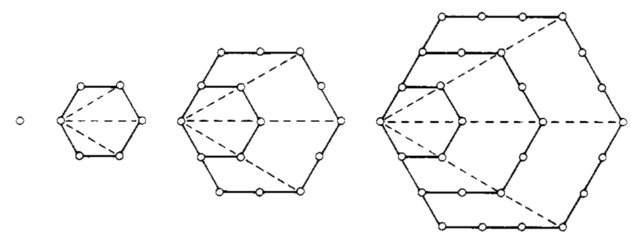
[a] Again the dashed lines show the decomposition into $F = 3$ ν_n triangles.

Chart VII. Centered Pentagons of Frequency 0, 1, 2, and 3 and the Centered Pentagonal Numbers ($p = F = 5$)



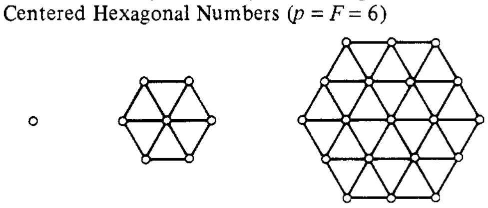
$\nu_0(1)$ $\nu_1(6)$ $\nu_2(16)$ $\nu_3(31)$

Chart VIII. Regular Hexagons of Frequency 0, 1, 2, and 3 and the Classical Hexagonal Numbers ($p = 6$, $F = 4$)



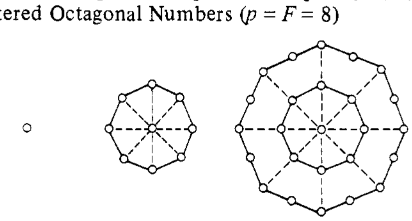
$\nu_0(1)$ $\nu_1(6)$ $\nu_2(15)$ $\nu_3(28)$

Chart IX. Centered Regular Hexagons of Frequency 0, 1, and 2 and the Centered Hexagonal Numbers ($p = F = 6$)



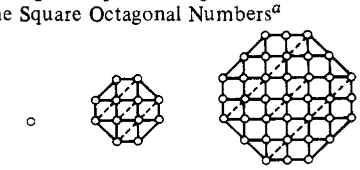
$\nu_0(1)$ $\nu_1(7)$ $\nu_2(19)$

Chart X. Centered Regular Octagons of Frequency 0, 1, and 2 and the Centered Octagonal Numbers ($p = F = 8$)



$\nu_0(1)$ $\nu_1(9)$ $\nu_2(25)$

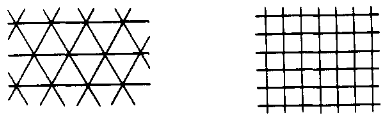
Chart XI. Semiregular Square Octagons Drawn on the Square Lattice, and the Square Octagonal Numbers[a]



$\nu_0(1)$ $\nu_1(12)$ $\nu_2(37)$

[a] ν_n is obtained by removing the corners from a ν_{3n} square. The dashed lines show the decomposition into $F = 14$ triangles.

Chart XII. Hexagonal (a) and Square (b) Lattices



(a) (b)

the first few values can be found in Table V.

We are interested in those two-dimensional figures, or *polygons*, that are made up of ν_n triangles. Charts II–XI show equilateral triangles, squares, and regular[10] pentagons, hexagons, and octagons that are constructed from ν_n triangles. The division into triangles is indicated by dashed lines. In general let P be a convex[11] polygon with p sides. We say that P is a *polygon of frequency n*, or a ν_n *polygon*, if it is the union of a number of ν_n triangles, where the triangles may meet only along edges. It is also required that, when two triangles have a common edge, the two sets of $n + 1$ atoms along the edges must coincide. In Charts II–XI we also indicate p, the number of sides, and F, the number of triangular *faces* into which the polygon is divided.

Notice that each polygon may be divided in (at least!) two different ways. In the first the polygon is subdivided from one corner, and the total number of triangles is $F = p - 2$. This is illustrated in Charts II, IV, VI, and VIII, and the total numbers of atoms in these figures are the classical *polygonal numbers*.[12] We have already mentioned the *triangular* numbers (eq 1). The numbers of points in Charts IV, VI, and VIII are called *square*, *pentagonal*, and *hexagonal* numbers, respectively.

In the second decomposition the polygon is subdivided from the center, and the total numbers of triangles is $F = p$. This is illustrated in Charts III, V, VII, IX, and X, and the numbers of atoms are the *centered polygonal numbers*.[13] Thus Charts III, V, VII, IX, and X show the *centered triangular*, *square*, *pentagonal*, *hexagonal*, and *octagonal* numbers, respectively.

Note that both versions of the square (Charts IV and V) can be drawn on the square lattice in two dimensions (Chart XIIb). The octagon (Chart X) cannot, but the semiregular figure shown in Chart XI, the *square octagon*, or truncated ν_3 square, can be drawn on the square lattice.

Both versions of the (equilateral) triangle (Charts II and III) and the regular hexagon (Charts VIII and IX) can be drawn on the hexagonal lattice (Chart XIIa). It is known[14] that no other regular polygons can be drawn on either of these two lattices.

General Formulas. There are simple general formulas for the numbers of points in these figures. Let G_n denote the *total* number of points in a ν_n polygon, S_n the number on the *boundary* (or perimeter), and $I_n = G_n - S_n$ the number in the *interior*. The general formulas for a p-sided polygon (which can be decomposed into F triangles) are

$$G_n = \tfrac{1}{2}Fn^2 + \tfrac{1}{2}pn + 1 \qquad (2)$$

$$S_n = pn \qquad (3)$$

$$I_n = \tfrac{1}{2}Fn^2 - \tfrac{1}{2}pn + 1 \qquad (4)$$

Remarks. (i) By comparing eq 2 and 4, we see that I_n may be obtained by replacing n by $-n$ in the formula for G_n! We indicate this symbolically by writing

$$I_n = G_{-n} \qquad (5)$$

(9) (a) Reference 4a, p 1. These numbers also appear as sequence 1002 of: (b) Sloane, N. J. A. "A Handbook of Integer Sequences"; Academic Press: New York, 1973.

(10) A regular figure has all angles, all edges, all faces, etc. equal. See, for example: Coxeter, H. S. M. "Regular Polytopes", 3rd ed.; Dover: New York, 1973.

(11) Massey, W. S. "Algebraic Topology: An Introduction"; Harcourt, Brace and World: New York, 1967; p 67.

(12) Reference 4a, p 1. Reference 5, p 20. Reference 9b.

(13) Reference 4a, p 5. Reference 5, p 22.

(14) Patruno, G. N. *Elemente Math.* **1983**, *38*, 69.

Table I. Formulas for G_n, the Total Numbers of Points in a Polygon of Frequency n (p = Number of Sides, F = Number of Triangular Faces)

Polygon	p	F	Formula for G_n
triangle	3	1	$t_n = \tfrac{1}{2}(n+1)(n+2)$
centered triangle	3	3	$\tfrac{1}{2}(3n^2 + 3n + 2)$
square or parallelogram	4	2	$(n+1)^2$
centered square	4	4	$2n^2 + 2n + 1$
pentagon	5	3	$\tfrac{1}{2}(n+1)(3n+2)$
centered pentagon	5	5	$\tfrac{1}{2}(5n^2 + 5n + 2)$
hexagon	6	4	$(n+1)(2n+1)$
centered hexagon	6	6	$3n^2 + 3n + 1$
octagon	8	6	$(n+1)(3n+1)$
centered octagon	8	8	$(2n+1)^2$
square octagon	8	14	$7n^2 + 4n + 1$

This is a special case of eq 25 below.

(ii) The two different decompositions of a polygon (decomposed either from a corner or from the center) have F values differing by 2. It follows from eq 2–4 that

$$G_n(\text{centered polygon}) = G_n(\text{polygon}) + n^2 \qquad (6)$$

$$S_n(\text{centered polygon}) = S_n(\text{polygon}) \qquad (7)$$

$$I_n(\text{centered polygon}) = I_n(\text{polygon}) + n^2 \qquad (8)$$

Examples. We now discuss three examples of these formulas (2)–(4); others will be found in Table I. The corresponding magic numbers themselves are shown in Table V. For a triangle (Charts I and II) of course $p = 3$, $F = 1$, and eq 2–4 become

$$G_n = \tfrac{1}{2}n^2 + \tfrac{3}{2}n + 1 = \tfrac{1}{2}(n + 1)(n + 2) = t_n$$

in agreement with eq 1, $S_n = 3n$, and $I_n = \tfrac{1}{2}(n - 1)(n - 2)$. Note that eq 5 is satisfied. For a square divided into two triangles, as in Chart IV, we have $p = 4$, $F = 2$

$$G_n = n^2 + 2n + 1 = (n + 1)^2 \qquad S_n = 4n \qquad I_n = (n - 1)^2$$

For a centered square, divided into four triangles as in Chart V, $p = F = 4$

$$G_n = 2n^2 + 2n + 1 \qquad S_n = 4n \qquad I_n = 2n^2 - 2n + 1$$

in agreement with eq 6–8.

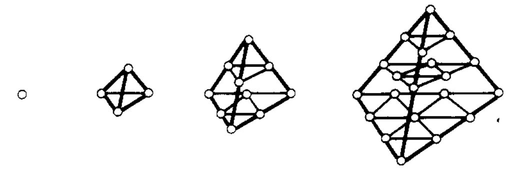
Proofs of Eq 2–4. The proofs are straightforward. Equation 3 is immediate, and (4) follows from (2) and (3). To prove eq 2 we use Euler's formula[15] for a convex polygon. This states that if a polygon contains V nodes (or vertices), E edges, and F faces, then

$$V - E + F = 1 \qquad (9)$$

Suppose our p-sided polygon, when divided into triangles, contains V_i internal vertices and E_i internal edges (i.e. vertices and edges that are not part of the boundary). Then the total number of nodes is $V = V_i + p$, and the total number of edges is $E = E_i + p$ (since

(15) In other words, the Euler characteristic of a convex polygon is equal to 1. See, for example: (a) Spanier, E. H. "Algebraic Topology"; McGraw-Hill: New York, 1966. (b) Hilton, P. J.; Wylie, S. "Homology Theory"; Cambridge University Press: Cambridge, 1960. (c) Aleksandrov, P. S. "Combinatorial Topology"; Graylock Press: Rochester, NY, 1956. See also ref 11.

Chart XIII. Tetrahedra of Frequency 0, 1, 2, and 3[a]



$\nu_0(1)$ $\nu_1(4)$ $\nu_2(10)$ $\nu_3(20)$

[a] The numbers in parentheses are the tetrahedral numbers σ_n (see eq 41).

there are p vertices and edges on the boundary). It follows from eq 9 that

$$V_i - E_i + F = 1 \qquad (10)$$

Each of the F triangular faces has three edges, each internal edge meets two faces, and each boundary edge meets one face, so

$$3F = 2E_i + p \qquad (11)$$

Using the principle of inclusion–exclusion,[16] we see that the total number of points is

$$\begin{aligned} G_n &= Ft_n - E_i(n+1) + V_i \\ &= \tfrac{1}{2}F(n+1)(n+2) - E_i(n+1) + V_i \\ &= \tfrac{1}{2}Fn^2 + \tfrac{1}{2}(3F - 2E_i)n + (F - E_i + V_i) \\ &= \tfrac{1}{2}Fn^2 + \tfrac{1}{2}pn + 1 \end{aligned} \qquad (12)$$

using eq 10 and 11. This proves eq 2.

III. Three-Dimensional Figures: General Theory

Three-dimensional figures of frequency n are defined in a way similar to that for two-dimensional figures. The difference is that the building block is now a *tetrahedron of frequency n* or a *ν_n tetrahedron*. This is a not necessarily regular tetrahedron consisting of $n + 1$ layers containing $t_0, t_1, t_2, ..., t_n$ atoms, respectively, where the t_n are the triangular numbers of eq 1. In particular, a ν_n tetrahedron has $n + 1$ atoms along each edge. Chart XIII shows regular tetrahedra of frequency 0, 1, 2, and 3. The diagram is drawn in such a way as to emphasize the triangular layers.

The total number of atoms in a ν_n tetrahedron is denoted by σ_n. We have[17]

$$\begin{aligned} \sigma_n &= t_0 + t_1 + t_2 + ... + t_n \\ &= \sum_{i=0}^{n} \tfrac{1}{2}(i+1)(i+2) \\ &= \tfrac{1}{6}(n+1)(n+2)(n+3) \end{aligned} \qquad (13)$$

These are called *tetrahedral numbers*; the first few values can be found in Table VI.

We consider those three-dimensional figures, or *polyhedra*, that are made up of ν_n tetrahedra. Charts XIV, XVI, XVII, XIX–XXX, ... show examples. In general let P be a convex[11] polyhedron. We say that P is a *polyhedron of frequency n* if it is the union of a number of ν_n tetrahedra, where the tetrahedra may meet only along triangular faces. It is also required that, when two tetrahedra have a triangular face in common, the two sets of t_n atoms on the faces must coincide. A number of specific examples are described in Section IV.

General Formulas. There are simple general formulas for the numbers of points in these figures, analogous to eq 2–4. Again we let G_n denote the *total* number of points in a ν_n polyhedron, S_n the number of points on the *surface* or outermost *shell*, and

$$I_n = G_n - S_n \qquad (14)$$

the number of *interior* points. Whereas formulas 2–4 involve only two parameters p and F, the three-dimensional formulas now depend on three parameters. These are C, the number of ν_n tetrahedral *cells* into which the polyhedron is divided, F_s, the number of triangular faces on the *surface*, and V_i, the number of vertices in the *interior*. For example, an icosahedron (cf. Chart XVII) may be decomposed into 20 tetrahedra by placing a vertex at the center and joining it to the 12 boundary vertices. Each of the 20 tetrahedra has one of the 20 triangular faces as its base and the central vertex as its apex. Thus we have $C = 20$, $F_s = 20$, and $V_i = 1$.

We can now state the general formulas:

$$G_n = \alpha n^3 + \tfrac{1}{2}\beta n^2 + \gamma n + 1 \quad n \geq 0 \qquad (15)$$

where

$$\alpha = C/6 \qquad (16a)$$

$$\beta = \tfrac{1}{2}F_s \qquad (16b)$$

$$\gamma = F_s/4 + V_i + 1 - C/6 \qquad (16c)$$

$S_0 = 1$

$$S_n = \beta n^2 + 2 \quad n \geq 1 \qquad (17)$$

and $I_0 = 0$

$$\begin{aligned} I_n &= G_n - S_n \\ &= \alpha n^3 - \tfrac{1}{2}\beta n^2 + \gamma n - 1 \quad n \geq 1 \end{aligned} \qquad (18)$$

For later use we also define certain other parameters. V_s and E_s are respectively the number of vertices and edges on the surface of P, and E_i and F_i are respectively the number of internal edges and internal triangular faces. For the original polyhedron P, before it is divided into tetrahedra, $\phi_3, \phi_4, \phi_5, ...$ denote the number of faces with 3, 4, 5, ... sides, and $F = \phi_3 + \phi_4 + \phi_5 + ...$ is the total number of faces.

Remarks. (i) Note that

$$V_i = I_1 \qquad (19)$$

In words, V_i is equal to the number of internal nodes in the ν_1 polyhedron. To prove this, set $n = 1$ in eq 15–18:

$$I_1 = G_1 - S_1 = (\alpha + \tfrac{1}{2}\beta + \gamma + 1) - (\beta + 2) = V_i$$

Similarly, the number of surface atoms in P is given by

$$V_s = S_1 \qquad (20)$$

(ii) In most cases all the ν_n tetrahedra have the same volume. If so, C is (by definition) equal to the volume of P divided by the volume of a ν_n tetrahedron.

(iii) An alternative formula for the number of surface atoms is worth mentioning. Suppose the polyhedron P has ϕ_3 triangular faces, ϕ_4 square faces, ϕ_5 centered-pentagonal faces, ϕ_6 centered-hexagonal faces, and ϕ_8 square-octagonal faces (this covers all the examples we shall meet in section IV). Then $S_0 = 1$

$$S_n = \beta n^2 + 2 \quad n \geq 1 \qquad (21)$$

where

$$\beta = \tfrac{1}{2}(\phi_3 + 2\phi_4 + 5\phi_5 + 6\phi_6 + 14\phi_8) \qquad (22)$$

This formula has the advantage that it can be proved directly,[18]

(16) The product Ft_n counts the $n + 1$ points on each of the E_i internal edges twice, so we must subtract $E_i(n + 1)$. But now the internal vertices have been counted zero times, so we must add V_i. This gives eq 12.

(17) For the evaluation of this sum, which has been known for at least 1500 years, see ref 4a, p 4. σ_n, equal to

$$\binom{n+3}{3}$$

is also a third-order figurate number in the notation of ref 8b. See sequence 1363 of ref 9b.

(18) Let P have V vertices, E edges, and F faces (which need not be triangular) on its surface. Then $V - E + F = 2$ from Euler's formula (eq 32), and $F = \phi_3 + \phi_4 + \phi_5 + \phi_6 + \phi_8$ and $E = \tfrac{1}{2}(3\phi_3 + 4\phi_4 + 5\phi_5 + 6\phi_6 + 8\phi_8)$ (by counting edges). Let p_n be the nth central pentagonal number, h_n the nth central hexagonal number, and o_n the nth square octahedral number. Then $S_n = (\phi_3 t_n + \phi_4(n+1)^2 + \phi_5 p_n + \phi_6 h_n + \phi_8 o_n) - E(n+1) + V$ (by inclusion/exclusion), and eq 21 and 22 follow after some algebra.

Table II. Formulas[a] for the Total Number of Points (G_n), the Number of Surface Points (S_n), and the Number of Interior Points (I_n) in Platonic Solids of Frequency n[d]

Polyhedron	V_s	V_i	E_s	F	F_s	C	Formulas
tetrahedron	4	0	6	4	4	1	$G_n = \sigma_n = \frac{1}{6}(n+1)(n+2)(n+3)$ $S_n = 2n^2 + 2$ $I_n = \frac{1}{6}(n-1)(n-2)(n-3)$
centered tetrahedron[b]	4	1	6	4	4	4	$G_n = \frac{1}{3}(2n+1)(n^2 + n + 3)$
hexahedron or cube	8	0	12	6	12	6	$G_n = (n+1)^3$ $S_n = 6n^2 + 2$ $I_n = (n-1)^3$
centered cube[c]	8	1	18	6	12	12	$G_n = (2n+1)(n^2 + n + 1)$
octahedron	6	0	12	8	8	4	$G_n = \frac{1}{3}(n+1)(2n^2 + 4n + 3)$ $S_n = 4n^2 + 2$ $I_n = \frac{1}{3}(n-1)(2n^2 - 4n + 3)$
centered icosahedron	12	1	30	20	20	20	$G_n = \frac{1}{3}(2n+1)(5n^2 + 5n + 3)$ $S_n = 10n^2 + 2$ $I_n = \frac{1}{3}(2n-1)(5n^2 - 5n + 3)$
centered dodecahedron	32	1	90	12	60	60	$G_n = (2n+1)(5n^2 + 5n + 1)$ $S_n = 30n^2 + 2$ $I_n = (2n-1)(5n^2 - 5n + 1)$

[a] The formulas for G_n are valid for $n \geqslant 0$, while the formulas for S_n and I_n are value for $n \geqslant 1$, with $S_0 = 1$, $I_0 = 0$. [b] S_n for a centered tetrahedron is the same as for a tetrahedron. [c] S_n for a centered cube is the same as for a cube. [d] See text for definitions of V_s, ..., C.

without first decomposing P into tetrahedra. Equation 22 implies that

$$F_s = \phi_3 + 2\phi_4 + 5\phi_5 + 6\phi_6 + 14\phi_8 \tag{23}$$

Equation 17 (and 21) is unexpectedly simple. Special cases of this formula for bodies that can be embedded in the face-centered cubic lattice (see section V) were discovered earlier by Buckminster Fuller[19] and proved by Coxeter.[20]

(iv) A comparison of eq 15 and 18 reveals the surprising fact that I_n may be obtained from the expression for G_n by replacing n by $-n$ and then negating the whole expression. We may indicate this by the remarkably simple formula

$$I_n = -G_{-n} \quad n \geqslant 1 \tag{24}$$

For example, for a cube we have $G_n = (n + 1)^3$, $I_n = -(-n + 1)^3 = (n - 1)^3$ (see Table II). Equations 5 and 24 can be generalized to d-dimensional bodies:

$$I_n = (-1)^d G_{-n} \tag{25}$$

Equation 25 has been known for a number of years[21] (although rediscovered by the present authors). It is an example of a "combinatorial reciprocity law".

(v) There is no direct analogue of eq 6–8 in three dimensions. But the following formulas for centered polyhedra are useful. Suppose a polyhedron is divided into C tetrahedral cells from a central vertex, so that $V_i = 1$ and $F_s = C$. Then eq 15–18 become

$$G_n = \tfrac{1}{12}(2n + 1)(Cn^2 + Cn + 12) \quad n \geqslant 0 \tag{26}$$

$$S_n = \tfrac{1}{2}Cn^2 + 2 \quad n \geqslant 1 \tag{27}$$

$$I_n = \tfrac{1}{12}(2n - 1)(Cn^2 - Cn + 12) \quad n \geqslant 1 \tag{28}$$

In this case we also have, besides eq 24, the identity

$$I_n = G_{n-1} \tag{29}$$

Therefore, from eq 14

$$\begin{aligned} G_n &= S_n + I_n = S_n + G_{n-1} \\ &= S_n + S_{n-1} + G_{n-2} \\ &= \ldots \\ &= S_n + S_{n-1} + S_{n-2} + \ldots + S_1 + S_0 \end{aligned} \tag{30}$$

We shall mention these formulas again in section VI.

Proof of Eq 15, 17, and 18. The proofs of eq 15 and 17 are similar to the proof of eq 2, and we shall not give as much detail.[22] Equation 18 follows immediately from eq 15 and 17. To prove eq 17, we begin with Euler's formula for the *surface* of a convex polyhedron,[23] which states that

$$\text{nodes} - \text{edges} + \text{faces} = 2 \tag{31}$$

For our polyhedron P this reads

$$V_s - E_s + F_s = 2 \tag{32}$$

where V_s and E_s are respectively the number of vertices and edges on the surface of P. Instead of eq 11 we have

$$3F_s = 2E_s \tag{33}$$

and so, from eq 32 and 33

$$E_s = \tfrac{3}{2}F_s \qquad V_s = 2 + \tfrac{1}{2}F_s \tag{34}$$

From the principle of inclusion–exclusion we get

$$\begin{aligned} S_n &= F_s t_n - E_s(n + 1) + V_s \\ &= \tfrac{1}{2}F_s(n + 1)(n + 2) - \tfrac{3}{2}F_s(n + 1) + 2 + \tfrac{1}{2}F_s \\ &= \tfrac{1}{2}F_s n^2 + 2 \end{aligned} \tag{35}$$

using eq 34, which proves eq 17. To prove eq 15, we begin with Euler's formula for a *solid* convex polyhedron,[25] which states that

$$\text{nodes} - \text{edges} + \text{faces} - \text{cells} = 1 \tag{36}$$

For our polyhedron P this reads

$$(V_s + V_i) - (E_s + E_i) + (F_s + F_i) - C = 1$$

where E_i and F_i are the numbers of internal edges and triangular faces in P. After subtracting eq 32, we get

$$V_i - E_i + F_i - C = -1 \tag{37}$$

Since each cell has four triangular faces

$$4C = 2F_i + F_s \tag{38}$$

and so, from eq 37 and 38

$$F_i = 2C - \tfrac{1}{2}F_s \qquad E_i = V_i + C + 1 - \tfrac{1}{2}F_s \tag{39}$$

From inclusion–exclusion we have

$$\begin{aligned} G_n &= C\sigma_n - F_i t_n + E_i(n + 1) - V_i \\ &= \tfrac{1}{6}C(n + 1)(n + 2)(n + 3) - \tfrac{1}{2}F_i(n + 1)(n + 2) + \\ &\qquad E_i(n + 1) - V_i \end{aligned} \tag{40}$$

and eq 15 follows immediately by eliminating F_i and E_i via eq 39.

IV. Three-Dimensional Figures: Examples

This section contains a number of examples of polyhedra of frequency n. We begin with the five Platonic solids[27] (the regular convex polyhedra), followed by the Archimedean sōlids and their

(19) Marks, R. W. "The Dymaxion World of Buckminster Fuller"; Southern Illinois University Press: Carbondale, IL, 1960.
(20) Coxeter, H. S. M. In "For Dirk Struik"; Cohen, R. S., et al., Eds.; Reidel: Dordrecht, Holland, 1974; p 25.
(21) (a) Ehrhart, E. *C. R. Seances Acad. Sci., Ser. A* **1967**, *265*, 91. (b) MacDonald, I. G. *J. London Math. Soc.* **1971**, *4*, 181. (c) Stanley, R. P. *Adv. Math.* **1974**, *14*, 194. See also ref 20.
(22) Underlying the proofs of eq 15 and 17 is the observation that our polyhedron P when decomposed into its C tetrahedra is a "simplicial complex" in the language of topology (see for example Chapter 1 of ref 15b).
(23) Reference 11, p 33.
(24) The first term on the right side of eq 35 overcounts the points on the edges. This is compensated for by the $E_s(n + 1)$ term. But now the vertices have been counted zero times, so we must add V_s.
(25) Reference 11, pp 42–43.
(26) Equation 40 is an immediate generalization of eq 35.
(27) Reference 10, p 5.

Table III. Formulas[a] for the Total Number of Points (G_n), the Number of Surface Points (S_n), and the Number of Interior Points (I_n) in Archimedean and Other Figures of Frequency n[b]

Polyhedron	V_s	V_i	E_s	F	F_s	C	Formulas
truncated tetrahedron	16	0	42	8	28	23	$G_n = \frac{1}{6}(n+1)(23n^2 + 19n + 6)$ $S_n = 14n^2 + 2$ $I_n = \frac{1}{6}(n-1)(23n^2 - 19n + 6)$
cuboctahedron or twinned cuboctahedron	12	1	30	14	20	20	$G_n = \frac{1}{3}(2n+1)(5n^2 + 5n + 3)$ $S_n = 10n^2 + 2$ $I_n = \frac{1}{3}(2n-1)(5n^2 - 5n + 3)$
truncated octahedron	32	6	90	14	60	96	$G_n = 16n^3 + 15n^2 + 6n + 1$ $S_n = 30n^2 + 2$ $I_n = 16n^3 - 15n^2 + 6n - 1$
truncated ν_3 cube	48	8	138	14	92	154	$G_n = \frac{1}{3}(77n^3 + 69n^2 + 19n + 3)$ $S_n = 46n^2 + 2$ $I_n = \frac{1}{3}(77n^3 - 69n^2 + 19n - 3)$
triangular prism	6	0	12	5	8	3	$G_n = \frac{1}{2}(n+1)^2(n+2)$ $S_n = 4n^2 + 2$ $I_n = \frac{1}{2}(n-1)^2(n+2)$

[a] The formulas for G_n are valid for $n \geq 0$, while the formulas for S_n and I_n are valid for $n \geq 1$, with $S_0 = 1$, $I_0 = 0$. [b] See text for definitions of V_s, ..., C.

Table IV. Formulas[a] for the Total Number of Points (G_n), the Number of Surface Points (S_n), and the Number of Interior Points (I_n) in Archimedean and Other Figures of Frequency n[b]

Polyhedron	V_s	V_i	E_s	F	F_s	C	Formulas
hexagonal prism	14	0	36	8	24	18	$G_n = (n+1)(3n^2 + 3n + 1)$ $S_n = 12n^2 + 2$ $I_n = (n-1)(3n^2 - 3n + 1)$
rhombic dodecahedron	14	1	36	12	24	24	$G_n = (2n+1)(2n^2 + 2n + 1)$ $S_n = 12n^2 + 2$ $I_n = (2n-1)(2n^2 - 2n + 1)$
square pyramid or triangular bipyramid	5	0	9	5	6	2	$G_n = \frac{1}{6}(n+1)(n+2)(2n+3)$ $S_n = 3n^2 + 2$ $I_n = \frac{1}{6}(n-1)(n-2)(2n-3)$
tricapped triangular prism	9	0	21	14	14	9	$G_n = \frac{1}{2}(n+1)(3n^2 + 4n + 2)$ $S_n = 7n^2 + 2$ $I_n = \frac{1}{2}(n-1)(3n^2 - 4n + 2)$

[a] The formulas for G_n are valid for $n \geq 0$, while the formulas for S_n and I_n are valid for $n \geq 1$, with $S_0 = 1$, $I_0 = 0$. [b] See text for definitions of V_s, ..., C.

duals,[28] and conclude with some further figures. Any given polyhedron can be decomposed into tetrahedra in several different ways. We have not attempted to describe all the possibilities but have concentrated on the most natural decompositions. We have given preference to those decompositions that result in either ν_n polyhedra that can be embedded in the cubic lattice, face-centered cubic lattice, body-centered cubic lattice, or ν_n polyhedra in which the distances between neighboring points are equal (so that points can be replaced by nonoverlapping spheres of equal radius). To

(28) (a) Fejes Tōth, L. "Regular Figures"; Pergamon Press: Oxford, England, 1964; Figure 17/2. (b) Cundy, H. M.; Rollett, A. P. "Mathematical Models"; Oxford University Press: Oxford, England, 1957, §3.7.

Table V. Total Number of Points G_n in Various Polygons of Frequency n

Polygon	n=0	1	2	3	4	5	6	7	8	9	10
triangle	1	3	6	10	15	21	28	36	45	55	66
centered triangle	1	4	10	19	31	46	64	85	109	136	166
square (parallelogram)	1	4	9	16	25	36	49	64	81	100	121
centered square	1	5	13	25	41	61	85	113	145	181	221
pentagon	1	5	12	22	35	51	70	92	117	145	176
centered pentagon	1	6	16	31	51	76	106	141	181	226	276
hexagon	1	6	15	28	45	66	91	120	153	190	231
centered hexagon	1	7	19	37	61	91	127	169	217	271	331
octagon	1	8	21	40	65	96	133	176	225	280	341
centered octagon	1	9	25	49	81	121	169	225	289	361	441
square octagon	1	12	37	76	129	196	277	372	481	604	741

Table VI. Number of Surface Points (S_n) and the Total Number of Points (G_n) in Platonic Solids of Frequency n[a]

Polyhedron	n	0	1	2	3	4	5	6	7	8	9	10
tetrahedron	S_n	1	4	10	20	34	52	74	100	130	164	202
	G_n	1	4	10	20	35	56	84	120	165	220	286
centered tet.*	G_n	1	5	15	35	69	121	195	295	425	589	791
cube	S_n	1	8	26	56	98	152	218	296	386	488	602
	G_n	1	8	27	64	125	216	343	512	729	1000	1331
centered cube*	G_n	1	9	35	91	189	341	559	855	1241	1729	2331
octahedron	S_n	1	6	18	38	66	102	146	198	258	326	402
	G_n	1	6	19	44	85	146	231	344	489	670	891
centered	S_n	1	12	42	92	162	252	362	492	642	812	1002
icosahedron	G_n	1	13	55	147	309	561	923	1415	2057	2869	3871
centered	S_n	1	32	122	272	482	752	1082	1472	1922	2432	3002
dodecahedron	G_n	1	33	155	427	909	1661	2743	4215	6137	8569	11571

[a] Asterisks denote that S_n is the same as for the previous entry.

save space, and because they have not yet been found in chemistry, some more complicated figures have been omitted, such as the "great rhombicuboctahedron".[29] However, these figures, as well as nonconvex bodies such as the "great icosidodecahedron",[30] can be handled in exactly the same way as the others.

The results are summarized in Tables II–IV, VI, and VII.

Tetrahedron. The most natural decomposition of a tetrahedron is of course to take it as it stands, with no further subdivision. Chart XIII shows regular tetrahedra of frequency 0, 1, 2, 3, ... A tetrahedron of frequency n has $n + 1$ points on each edge. In this case we have $C = 1$, $F_s = 4$, $V_i = 0$, so from eq 15–18 we find that there are a total of

$$G_n = \tfrac{1}{6}(n + 1)(n + 2)(n + 3) = \sigma_n \quad n \geq 0 \qquad (41)$$

points, in agreement with eq 13

$$S_n = 2n^2 + 2 \quad n \geq 1 \qquad (42)$$

points on the surface, and

$$I_n = \tfrac{1}{6}(n - 1)(n - 2)(n - 3) \quad n \geq 1 \qquad (43)$$

interior points (see Tables I and V). Note that

(29) Reference 28b, §3.7.12.
(30) Reference 28b, §3.9.2.

$$I_n = G_{n-4} \quad n \geq 5 \tag{44}$$

From this we obtain, exactly as in eq 30

$$G_n = S_n + S_{n-4} + S_{n-8} + ... \tag{45}$$

in steps of 4, the last term in eq 45 being one of S_0, S_1, S_2, or S_3. Note that $I_0 = I_1 = I_2 = I_3 = 0$.

Centered Tetrahedron. A tetrahedron may also be decomposed into four tetrahedra from a central node (the three-dimensional analogue of the centered triangle shown in Chart III). Now $V_i = 1$, $C = F_s = 4$, and eq 26–28 give

$$G_n = \tfrac{1}{3}(2n + 1)(n^2 + n + 3) \quad n \geq 0$$

$$S_n = 2n^2 + 2 \quad n \geq 1$$

$$I_n = \tfrac{1}{3}(2n - 1)(n^2 - n + 3) \quad n \geq 1$$

The number of surface atoms in a centered tetrahedron is still given by eq 42 (just as in two dimensions we have eq 7).

Hexahedron or Cube. A cube of frequency n is shown in Chart XIV, and the corresponding dissection into six tetrahedra is given in Chart XV. Each square face is divided into two triangles. Thus $C = 6$, $F_s = 2 \times 6 = 12$, and $V_i = 0$, so from eq 15–18 we obtain

$$G_n = (n + 1)^3 \quad n \geq 1$$

$$S_n = 6n^2 + 2 \quad n \geq 0$$

$$I_n = (n - 1)^3 \quad n \geq 0$$

Note that

$$I_n = G_{n-2} \quad n \geq 2 \tag{46}$$

$$G_n = I_n + I_{n-2} + I_{n-4} + ... \tag{47}$$

in steps of 2, the last term being either I_0 or I_1.

(Body-) Centered Cube. An alternative decomposition of the cube is obtained by first dividing it into six square pyramids from a central vertex and then dividing each square pyramid into two triangular pyramids. Then we have $V_i = 1$ and $C = F_s = 12$, and eq 26–28 give

$$G_n = (2n + 1)(n^2 + n + 1) \quad n \geq 0$$

$$S_n = 6n^2 + 2 \quad n \geq 1$$

$$I_n = (2n - 1)(n^2 - n + 1) \quad n \geq 1$$

Octahedron. A ν_n octahedron[31] (Chart XVI) may be decomposed into four tetrahedra (slicing it for example along the equatorial plane and by a vertical plane through the north and south poles). Thus $C = 4$, $F_s = 8$, and $V_i = 0$, and from eq 15–18 we obtain the formulas for G_n, S_n, and I_n shown in Table II. Equations 46 and 47 also apply to the octahedron.

Icosahedron. An icosahedron[32] (Chart XVII) may be decomposed into 20 tetrahedra as described in section III (just before eq 15). Thus $C = F_s = 20$ and $V_i = 1$, and we obtain the formulas shown in Table II. In this case eq 29 and 30 hold.

Dodecahedron. The most symmetric decomposition of a dodecahedron[33] (Chart XVIII) is obtained by dividing each pentagonal face into five triangles via a point at the center of each face and the joining each of these triangles to a point at the center of the dodecahedron. Thus $C = F_s = 5 \times 12 = 60$ and $V_i = 1$. Equations 29 and 30 also hold for the centered dodecahedron.

Truncated Tetrahedron. A ν_n truncated tetrahedron,[34] the first of the Archimedean solids, is shown in Chart XIX. This is obtained by removing the four corners (which are ν_{n-1} tetrahedra) from a ν_{3n} tetrahedron. If greater precision is needed, this could also be called a "ν_n truncated ν_3 tetrahedron", but we prefer the simpler notation. A similar remark applies to the ν_n truncated octahedron described below.

A ν_n truncated tetrahedron may be decomposed into 23 ν_n tetrahedra, as the following argument shows. Equivalently, we show that a ν_{3n} tetrahedron may be decomposed into 27 ν_n tet-

(31) Reference 28b, §3.5.3.
(32) Reference 28b, §3.5.5.
(33) Reference 28b, §3.5.4.
(34) Reference 28b, §3.7.1.

Chart XIV. Cubes of Frequency 0, 1, 2, and 3

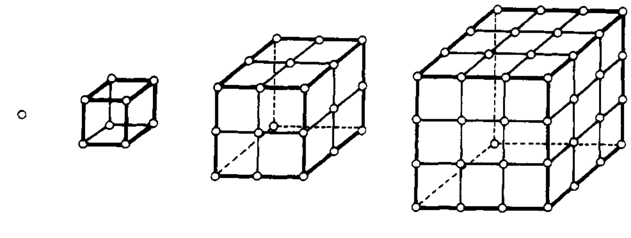
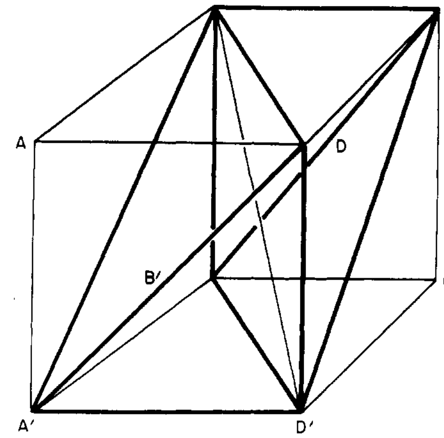


Chart XV. Decomposition of a ν_n Cube into Six ν_n Tetrahedra, by Cutting it along the Planes BDD′B′, BCD′A′, BDA′, and CD′B′[a]



[a] The six tetrahedra are ABDA′, BB′D′A′, BDD′A′, CC′D′B′, BB′D′C, and BDD′C.

Chart XVI. Octahedra of Frequency 0, 1, and 2

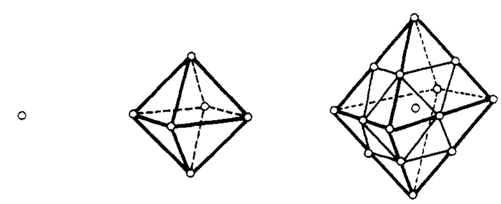


Chart XVII. Centered Icosahedron of Frequency 1

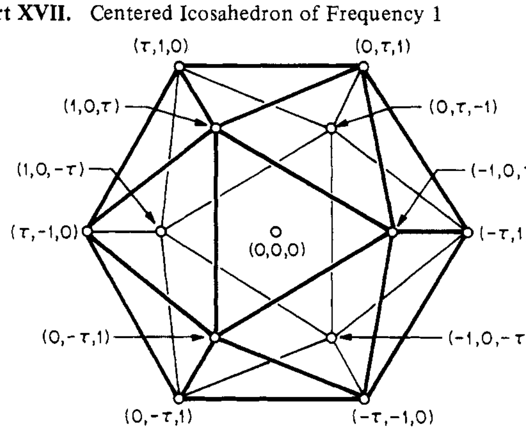


Chart XVIII. Dodecahedron

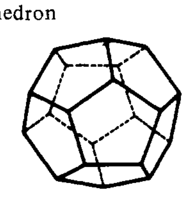
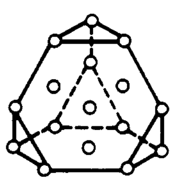


Table VII. Number of Surface Points (S_n) and the Total Number of Points (G_n) for Various Archimedean and Other Figures

Polyhedron	n	0	1	2	3	4	5	6	7	8	9	10
truncated	S_n	1	16	58	128	226	352	506	688	898	1136	1402
tetrahedron	G_n	1	16	68	180	375	676	1106	1688	2445	3400	4576
cubocta-	S_n	1	12	42	92	162	252	362	492	642	812	1002
-hedron[a]	G_n	1	13	55	147	309	561	923	1415	2057	2869	3871
truncated	S_n	1	32	122	272	482	752	1082	1472	1922	2432	3002
octahedron	G_n	1	38	201	586	1289	2406	4033	6266	9201	12934	17561
truncated	S_n	1	48	186	416	738	1152	1658	2256	2946	3728	4602
ν_3 cube	G_n	1	56	311	920	2037	3816	6411	9976	14665	20632	28031
triangular	S_n	1	6	18	38	66	102	146	198	258	326	402
prism	G_n	1	6	18	40	75	126	196	288	405	550	726
hexagonal	S_n	1	14	50	110	194	302	434	590	770	974	1202
prism	G_n	1	14	57	148	305	546	889	1352	1953	2710	3641
rhombic	S_n	1	14	50	110	194	302	434	590	770	974	1202
dodecahedron	G_n	1	15	65	175	369	671	1105	1695	2465	3439	4641
square	S_n	1	5	14	29	50	77	110	149	194	245	302
pyramid[b]	G_n	1	5	14	30	55	91	140	204	285	385	506
tricapped	S_n	1	9	30	65	114	177	254	345	450	569	702
prism	G_n	1	9	33	82	165	291	469	708	1017	1405	1881

[a] The numbers for a cuboctahedron also apply to a twinned cuboctahedron. [b] The numbers for a square pyramid also apply to a triangular bipyramid.

Chart XIX. Truncated Tetrahedron of Frequency 1



ν_1 (16)

rahedra. We first decompose the tetrahedron by planes parallel to each of the four faces, the planes being at $^1/_3$ and $^2/_3$ of the total height.[35] These 8 planes decompose the tetrahedron into 11 ν_n tetrahedra (4 at the corners, 6 at the centers of the edges, and 1 in the very center) and 4 ν_n octahedra. We have just seen that each ν_n octahedron can be decomposed into 4 ν_n tetrahedra, so in all we obtain 27 ν_n tetrahedra, as claimed.

Each hexagonal face of the truncated tetrahedron is divided into six triangles, so $F_s = 4 + 4 \times 6 = 28$, $C = 23$, and $V_i = 0$, and from eq 15–18 we obtain

$$G_n = \tfrac{1}{6}(23n^3 + 42n^2 + 25n + 6) = \tfrac{1}{6}(n + 1)(23n^2 + 19n + 6) \quad n \geq 0 \qquad (48)$$

$$S_n = 14n^2 + 2 \quad n \geq 1 \qquad (49)$$

$$I_n = \tfrac{1}{6}(n - 1)(23n^2 - 19n + 6) \quad n \geq 1 \qquad (50)$$

as given in Table III.

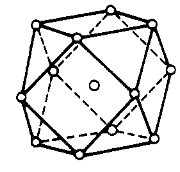
These equations may also be derived directly, without first decomposing the truncated tetrahedron into tetrahedra. Since these are $\phi_3 = 4$ triangular faces and $\phi_6 = 4$ hexagonal faces, eq 49 follows from eq 21 and 22. Since a truncated tetrahedron is obtained by removing the corners from a ν_{3n} tetrahedron

$$G_n = G_{3n}(\text{tetrahedron}) - 4G_{n-1}(\text{tetrahedron})$$

and using eq 41 we get eq 48. Finally $I_n = G_n - S_n$ gives eq 50. This second method of analysis is preferable for polyhedra that are difficult to decompose into tetrahedra.

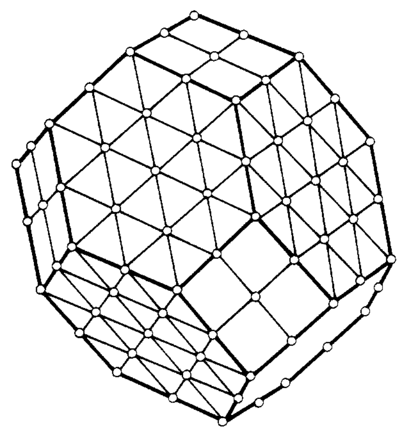
(35) A vivid illustration of this decomposition is found in the tetrahedral version of the Rubik cube, sold under the name of Pyraminx.

Chart XX. Cuboctahedron of Frequency 1



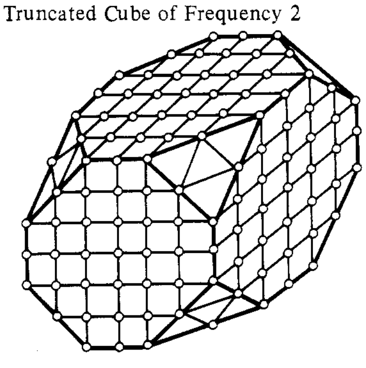
ν_1 (13)

Chart XXI. Truncated Octahedron of Frequency 2



ν_2 (201)

Chart XXII. Truncated Cube of Frequency 2



ν_2 (311)

We note that in this case there is no identity of the form $G_n = S_n + S_m + S_l + ...$, in contrast to the previous figures.

Cuboctahedron. A ν_n cuboctahedron[36] (Chart XX) may be formed by removing either eight corners from a ν_{2n} cube or six corners from a ν_{2n} octahedron. To decompose it into tetrahedra, we place a node at the center and joint it to the 12 vertices, obtaining $C = F_s = 20$ and $V_i = 1$. The formulas for G_n, S_n, and I_n are given in Table III. Equations 29 and 30 apply here also.

Truncated Octahedron. A ν_n truncated octahedron[37] (Chart XXI) is best analyzed by the second method, since the decomposition into tetrahedra (which we do not give) requires $I_1 = V_i = 6$ internal nodes, $C = 96$ cells, and $F_s = 60$. There are $\phi_4 = 6$ square faces and $\phi_6 = 8$ hexagonal faces, so from eq 21 and 22, $\beta = 30$ and

$$S_n = 30n^2 + 2 \quad n \geq 1$$

This figure is obtained from a ν_{3n} octahedron by removing the six corners, each of which is a ν_{n-1} square pyramid containing $n(n + 1)(2n + 1)/6$ atoms (see Table IV). Therefore

$$G_n = G_{3n}(\text{octahedron}) - n(n + 1)(2n + 1) = 16n^3 + 15n^2 + 6n + 1 \quad n \geq 0$$

(36) Reference 28b, §3.7.2.
(37) Reference 28b, §3.7.4.

Chart XXIII. Triangular Prism

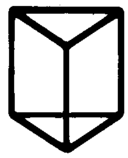


Chart XXIV. Decomposition of a ν_n Triangular Prism into the Three ν_n Tetrahedra ABCA′, BB′C′A′, and BCC′A′

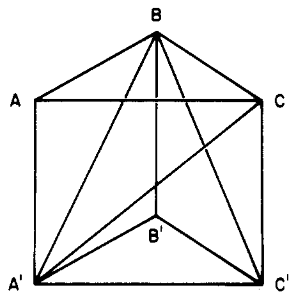
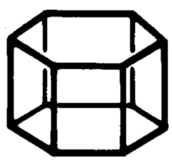


Chart XXV. Hexagonal Prism



Truncated Cube. The Archimedean version of a truncated cube[38] cannot be embedded in the cubic lattice (since it has faces that are regular octagons, and we know from section II that these cannot be embedded in the cubic lattice). But the semiregular truncated cube shown in Chart XXII, having the square octagons of Chart XI as faces, can be embedded in the cubic lattice, and so we describe this polyhedron instead. This ν_n truncated cube is obtained by removing eight ν_{n-1} tetrahedral pyramids from the corners of a ν_{3n} cube, and we have (again analyzing it by the second method)

$$G_n = G_{3n}(\text{cube}) - 8G_{n-1}(\text{tetrahedron}) = \tfrac{1}{3}(77n^3 + 69n^2 + 19n + 3) \quad n \geq 0$$

$$S_n = 46n^2 + 2 \quad n \geq 1$$

$$I_n = \tfrac{1}{3}(77n^3 - 69n^2 + 19n - 3) \quad n \geq 1$$

The decomposition into tetrahedra requires $I_1 = V_i = 8$ internal nodes, $C_i = 154$ cells, and $F_s = 92$.

Triangular Prism. For a ν_n triangular prism (Chart XXIII) we have $\phi_3 = 2$ and $\phi_4 = 3$, so from eq 21 and 22

$$S_n = 4n^2 + 2 \quad n \geq 1$$

(the same as for an octahedron), and from eq 1 and 14

$$G_n = (n + 1)t_n = \tfrac{1}{2}(n + 1)^2(n + 2) \quad n \geq 0$$

$$I_n = \tfrac{1}{2}(n - 1)^2(n - 2) \quad n \geq 1$$

Alternatively this figure may be decomposed into $C = 3$ tetrahedra as illustrated in Chart XXIV.

Hexagonal Prism. Similarly for a ν_n hexagonal prism (Chart XXV) we have

$$G_n = (n + 1)(3n^2 + 3n + 1) \quad n \geq 1$$

$$S_n = 12n^2 + 2 \quad n \geq 0$$

$$I_n = (n - 1)(3n^2 - 3n + 1) \quad n \geq 1$$

This figure may be decomposed into 6 triangular prisms and thence into 18 tetrahedra.

We omit the remaining Archimedean solids: the other regular prisms and antiprisms, the small and great rhombicuboctahedra,

(38) Reference 28b, §3.7.3.

Chart XXVI. Centered Rhombic Dodecahedron of Frequency 1

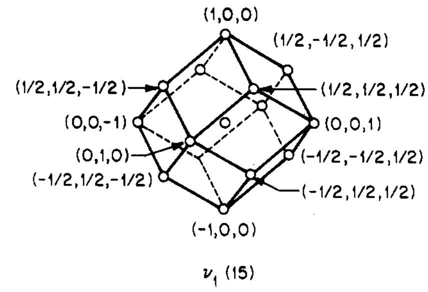


Chart XXVII. Square Pyramid of Frequency 4

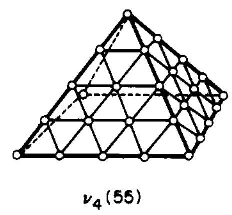


Chart XXVIII. Triangular Bipyramid

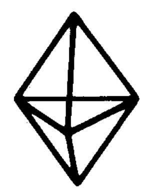


Chart XXIX. Tricapped Triangular Prism

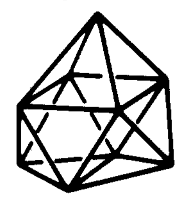
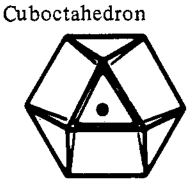


Chart XXX. Twinned Cuboctahedron



the snub cube, etc.[39] We shall only discuss one of the Archimedean dual solids, the rhombic dodecahedron.

Rhombic Dodecahedron. The rhombic dodecahedron[40] (Chart XXVI) may be decomposed into 24 tetrahedra via a vertex at the center. The formulas are shown in Table IV.

Finally we mention four non-Archimedean figures.

Square Pyramid. A square pyramid of frequency n (Chart XXVII) can be decomposed into two tetrahedra (by a vertical cut through a pair of opposite corners). The formulas are given in Table IV.

Triangular Bipyramid. A ν_n triangular bipyramid (Chart XXVIII) is obtained by reflecting a ν_n tetrahedron in its base. We have $C = 2$, $F_s = 6$, and $V_i = 0$, as for the square pyramid, and so the same formulas apply.

Tricapped Triangular Prism. A ν_n tricapped triangular prism (Chart XXIX) is obtained by adding ν_{n-1} square pyramids to the three square faces of a triangular prism. Thus $C = 3 \times 2 + 3 = 9$, $F_s = 14$, and $V_i = 0$ (cf. Table IV).

Twinned Cuboctahedron. A ν_n twinned cuboctahedron (Chart XXX) contains the same number of points as a ν_n cuboctahedron,

(39) Reference 28b, §3.7.
(40) Reference 28b, §3.8.1.

and the same formulas apply (cf. Table III).

V. Coordinates

In this section we give coordinates for the points in various figures of frequency n. As mentioned in section II, the (two-dimensional) triangular and hexagonal figures can be embedded in the hexagonal lattice (Chart XIIa), whereas the square and semiregular octagonal figures can be embedded in the square lattice (Chart XIIb). We see now from the coordinates of the three-dimensional figures that the cube and semiregular truncated cube of frequency n can be embedded in the *simple cubic lattice*, the tetrahedron, centered tetrahedron, octahedron, truncated tetrahedron, truncated octahedron, cuboctahedron, and square pyramid can be embedded in the *face-centered cubic lattice*, and the centered cube can be embedded in the *body-centered cubic lattice*. A ν_1 twinned octahedron can be embedded in the *hexagonal close-packing* arrangement, but not a ν_n twinned octahedron for $n > 1$. (The latter can be embedded in a packing consisting of the face-centered cubic lattice above the xy plane and a mirror image of this lattice below the xy plane.) The figures with fivefold symmetry (the icosahedron, dodecahedron, etc.) cannot be embedded in any lattice.

Throughout this section the individual coordinates i, j, k, l all represent (positive or negative) integers, except in a few places where $i = (-1)^{1/2}$.

We begin with a useful observation. Suppose a triangle has vertices P_1, P_2, and P_3, written in any system of coordinates. Let us place $n + 1$ points along each edge and corresponding points in the interior so as to obtain a ν_n triangle, with a total of t_n points. Then the coordinates of these t_n points are given by

$$(iP_1 + jP_2 + kP_3)/n$$

where i, j, k range over all integers 0, 1, 2, ..., n subject to $i + j + k = n$. If integer coordinates are preferred (which is the form we use in this section), we may multiply this expression by n, obtaining

$$iP_1 + jP_2 + kP_3 \qquad 0 \leq i,j,k \leq n \qquad i + j + k = n \tag{51}$$

Similarly if P_1, P_2, P_3, and P_4 are the vertices of a tetrahedron, the coordinates of the atoms in the corresponding ν_n tetrahedron are

$$\begin{gathered} iP_1 + jP_2 + kP_3 + lP_4 \qquad 0 \leq i,j,k,l \leq n \\ i + j + k + l = n \end{gathered} \tag{52}$$

With the aid of (51) and (52) it is possible to give the coordinates of any ν_n polyhedron, once the vertices of the tetrahedral decomposition are known.

Triangle. Conventional two-dimensional coordinates for the points of a ν_n triangle are messy. It is far better to use three-dimensional coordinates.[41] A ν_n triangle consists of the points

$$(i, j, k){:}\;\; i \geq 0, j \geq 0, k \geq 0, i + j + k = n \tag{53}$$

(This is obtained from eq 51 by taking $P_1 = (1, 0, 0)$, $P_2 = (0, 1, 0)$, and $P_3 = (0, 0, 1)$.) For example, the points of a ν_3 triangle are

```
            300
        210     201
    120     111     102
030     021     012     003
```

To convert these to standard two-dimensional coordinates, simply multiply by the matrix

$$M_2 = \begin{bmatrix} 1 & 0 \\ -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{1}{2} & -\frac{\sqrt{3}}{2} \end{bmatrix} \tag{54}$$

(41) Since these points lie on the plane $i + j + k = n$, the figure is indeed two-dimensional.

Thus (2, 1, 0) becomes

$$(2, 1, 0)M_2 = [3/2, 3^{1/2}/2]$$

Similarly (again eq 51) a ν_n centered triangle consists of the points

$$\begin{gathered} (3i + k, 3j + k, k) \qquad (3i + k, k, 3j + k) \\ (k, 3i + k, 3j + k) \end{gathered} \tag{55}$$

subject to $0 \leq i,j,k \leq n$, $i + j + k = n$.

Square. There are two convenient ways to specify the points of a ν_n square. Either

$$(i, j){:}\;\; 0 \leq i,j \leq n \tag{56}$$

or[42]

$$(i, j){:}\;\; i \equiv j \equiv n (\text{mod } 2),\ |i|,|j| \leq n \tag{57}$$

Equation 56 is the more natural definition, but eq 57 (and the analogous definition (67) for the cube) is better for constructing the truncated figures.

A centered ν_n square consists of the points

$$(i, j){:}\;\; |i| + |j| \leq n \tag{58}$$

Pentagon. The points of the (noncentered) pentagon and hexagon are loosely packed, and therefore of much less interest, so we omit them. A centered pentagon is best described with use of complex coordinates. Let $\alpha = \cos (2\pi/5) + i \sin (2\pi/5)$, where $i = (-1)^{1/2}$, so that $\alpha^5 = 1$. A ν_n centered pentagon consists of the points

$$\alpha^r(j + k\alpha){:}\;\; 0 \leq r \leq 4, j \geq 0, k \geq 0, j + k \leq n \tag{59}$$

Hexagon. The points of a ν_n centered hexagon are

$$(i, j, k){:}\;\; 0 \leq i,j,k \leq 2n;\ i + j + k = 3n \tag{60}$$

This formula may be derived by taking a ν_{3n} triangle, $\{(i, j, k,){:}\ 0 \leq i,j,k;\ i + j + k = 3n\}$ (see eq 53), and removing the corners by imposing the additional constraints $i,j,k, \leq 2n$.

Example. The points of a ν_2 hexagon are

```
        420     411     402
    330     321     312     303
240     231     222     213     204
    141     132     123     114
        042     033     024
```

To convert 60 to two-dimensional coordinates, we again multiply by M_2 (see eq 54).

Octagon. The points of a ν_n centered octagon are

$$\alpha^r(j + k\alpha){:}\;\; 0 \leq r \leq 7, j \geq 0, k \geq 0, j + k \leq n \tag{61}$$

where $\alpha = \cos (2\pi/8) + i \sin (2\pi/8) = (1 + i)/2^{1/2}$, with $\alpha^8 = 1$ (compare eq 59).

The points of the ν_n square octagon shown in Chart XI are

$$(i, j){:}\;\; i \equiv j \equiv n (\text{mod } 2),\ |i|, |j| \leq 3n,\ |i| + |j| \leq 4n \tag{62}$$

Tetrahedron. Conventional three-dimensional coordinates for a ν_n tetrahedron are messy. The following four-dimensional coordinates (obtained from eq 52) are far better:

$$(i, j, k, l){:}\;\; i,j,k,l \geq 0,\ i + j + k + l = n \tag{63}$$

To convert to three-dimensional coordinates, multiply by

$$M_3 = \begin{bmatrix} 1 & 0 & 0 \\ -\frac{1}{3} & 2\frac{\sqrt{2}}{3} & 0 \\ -\frac{1}{3} & -\frac{\sqrt{2}}{3} & \frac{\sqrt{6}}{3} \\ -\frac{1}{3} & -\frac{\sqrt{2}}{3} & -\frac{\sqrt{6}}{3} \end{bmatrix} \tag{64}$$

(42) The conditions $i \equiv n(\text{mod } 2)$ means that i and n must have the same parity, i.e. are both even or both odd. $i \equiv j \equiv n(\text{mod } 2)$ means that i, j, and n must all have the same parity.

Similarly (compare eq 55) a ν_n centered tetrahedron consists of the points

$$(4i + l, 4j + l, 4k + l, l):\ 0 \leqslant i,j,k,l \leqslant n,\ i + j + k + l = n \tag{65}$$

and all permutations of these coordinates.

Cube. For a ν_n cube either

$$(i, j, k):\ 0 \leqslant i,j,k \leqslant n \tag{66}$$

or

$$(i, j, k):\ i \equiv j \equiv k \equiv n(\text{mod } 2),\ |i|,|j|,|k| \leqslant n \tag{67}$$

For a ν_n centered cube

$$(i, j, k):\ i \equiv j \equiv k,\ |i|,|j|,|k| \leqslant n \tag{68}$$

Octahedron:

$$(i, j, k):\ i + j + k \equiv n(\text{mod } 2),\ |i| + |j| + |k| \leqslant n \tag{69}$$

The last condition could also be written as

$$-n \leqslant i + j + k \leqslant n \qquad -n \leqslant i + j - k \leqslant n$$
$$-n \leqslant i - j + k \leqslant n \qquad -n \leqslant -i + j + k \leqslant n$$

which are the eight faces of the octahedron. An example is given in section VI.

Icosahedron. The 12 vertices of an icosahedron (cf. Chart XVII) may be taken to be[43]

$$(\pm\tau, \pm1, 0),\ (0, \pm\tau, \pm1),\ (\pm1, 0, \pm\tau)$$

where $\tau = (1 + 5^{1/2})/2$, $\tau^2 = \tau + 1$, with all possible combinations of signs. Using eq 52, we find that the points of a ν_n centered icosahedron are

$$(\pm(i\tau + j), \pm(k\tau + j), \pm(j\tau + k))$$
$$(\pm i\tau, \pm\{(j + k)\tau + i\}, \pm(j - k))$$
$$(\pm(j - k), \pm i\tau, \pm\{(j + k)\tau + i\})$$
$$(\pm\{(j + k)\tau + i\}, \pm(j - k), \pm i\tau)$$

where $i, j, k, \geqslant 0$, $i + j + k \leqslant n$.

Dodecahedron. The 20 vertices of a dodecahedron (cf. Chart XVIII) may be taken to be[44]

$$(\pm1, \pm1, \pm1),\ (0, \pm1/\tau, \pm\tau),\ (\pm\tau, 0, \pm1/\tau),\ (\pm1/\tau, \pm\tau, 0)$$

and from this we can obtain the coordinates of a ν_n centered dodecahedron using eq 52.

Truncated Tetrahedron:

$$(i, j, k, l):\ 0 \leqslant i,j,k,l \leqslant 2n,\ i + j + k + l = 3n$$

(obtained from eq 63).

Cuboctahedron:

$$(i, j, k):\ |i|,|j|,|k| \leqslant n,\ |i| + |j| + |k| \leqslant 2n,\quad i + j + k \equiv 0(\text{mod } 2)$$

(The first set of constraints corresponds to the six faces of the cube and the second to the eight faces of the octahedron; cf. eq 70.)

Truncated Octahedron:

$$(i, j, k):\ |i|,|j|,|k| \leqslant 2n,\ |i| + |j| + |k| \leqslant 3n,\quad i + j + k \equiv n(\text{mod } 2) \tag{70}$$

See section VI for an example.

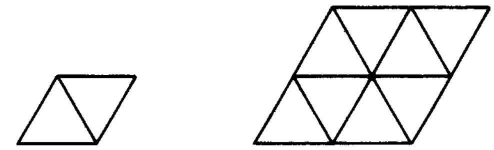
Semiregular Truncated Cube:

$$(i, j, k):\ |i|,|j|,|k| \leqslant 3n,\ |i| + |j| + |k| \leqslant 7n,\quad i \equiv j \equiv k \equiv n(\text{mod } 2)$$

The coordinates for the prisms are easily obtained from the coordinates for the corresponding polygons (see eq 53 and 60).

(43) Reference 10, §3.7.
(44) Reference 10, §3.7.

Chart XXXI. Parallelograms of Frequency 1 and 2



$\nu_1(4)$ $\nu_2(9)$

The coordinates for a ν_n rhombic dodecahedron can be obtained from the coordinates of the vertices given in Chart XXVI.

Square Pyramid:

$$(i, j, k):\ i + j + k \equiv n(\text{mod } 2),\ i \geqslant 0,\ i + |j| + |k| \leqslant n$$

VI. Results and Discussions

The two-dimensional polygons and three-dimensional polyhedra discussed in this paper are depicted in Charts I–XI and Charts XIII–XXXI, respectively. Equations for the polygonal numbers of the two-dimensional figures are given in eq 2–4 (see eq 6–8 for centered polygons) and in Table I for specific polygons. Examples illustrating the utility of eq 2–4 can be found in section II. Equations for the total number of atoms (G_n), the number of surface atoms (S_n), and the number of interior atoms (I_n) of the three-dimensional polyhedra are given in eq 15–18 (see eq 26–28 for centered polyhedra) in general, and in Tables II–IV for specific polyhedra. The magic numbers themselves are tabulated in Tables V–VII. Examples illustrating the utility of eq 15–18 are given in section IV.

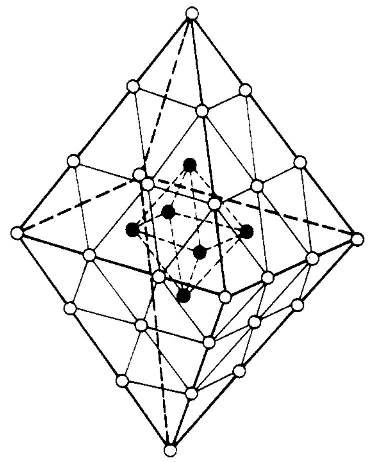
Further Comments on the Formulas. Although we have only proved eq 15–18 for convex bodies, these formulas are valid for a much larger class of bodies. However, as the discussion by Lakatos[45] shows, the precise conditions under which Euler's formulas are valid are fairly complicated. The hypothesis of convexity avoids these difficulties and covers all the figures studied in this paper.

It is difficult to establish priorities in a subject as old as this one. The references to polygonal and polyhedral numbers in Dickson[4a] go as far back as Pythagoras (570–501 B.C.), who described the triangular numbers. The Hindu mathematician Aryabhatta[46] of the 5th century A.D. knew the formula for the tetrahedral numbers σ_n (eq 13). Many mathematicians in the past 300 years have studied these numbers, and Dickson,[4a] writing in 1919, already gives 240 references. Coxeter's 1974 paper[20] contains our formulas for the total number of points in a ν_n octahedron, cuboctahedron, truncated tetrahedron, and truncated octahedron. So it would not surprise us if most of these formulas can be found somewhere scattered through the immense mathematical literature. Nevertheless, we have not found any paper that treats the problem in the way we do, and we know of no source where all these formulas are collected together (cf. Tables I–VII). The two closest works are Descartes/Federico[4b] and Coxeter.[20] The former takes a different point of view altogether and has almost none of our formulas. Coxeter has some of our formulas but only treats the Platonic and Archimedean polyhedra that can be embedded in the face-centered cubic lattice and only gives an ad hoc case-by-case derivation, not our general formulas (15), (17), and (18). Furthermore, none of these references are concerned with the applications to cluster chemistry.

Polygonal Systems. Despite tremendous efforts by many groups over the last decade or so, only a small number of planar metal clusters of high nuclearity are known. The most abundant planar cluster is of ν_1 triangular shape (Chart II), of which $Os_3(CO)_{12}$[47] is an example. The corresponding ν_2 triangular cluster (Chart II), represented by the raftlike cluster $Os_6(CO)_{17}(P(OMe)_3)_4$[48]

(45) Lakatos, I. "Proofs and Refutations"; Cambridge University Press: Cambridge, England, 1976.
(46) Reference 4a, p 4.
(47) (a) Corey, E. R.; Dahl, L. F. *Inorg. Chem.* **1962**, *1*, 521. (b) Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1977**, *16*, 878.

Chart XXXII. "Peeling an Onion": A ν_3 Octahedron, Showing the Surface Atoms (the "Skin", Hollow Circles) and the Interior Atoms (the "Core", Solid Circles)



○ $S_3 = 38$
● $I_3 = 6$

and $Cu_3Fe_3(CO)_{12}^{3-}$,[50b] is rather scarce. Similarly, the square series (Chart IV) is dominated by ν_1 square clusters such as $Co_4(PPh)_2(CO)_{10}$.[49] The ν_1 and ν_2 parallelograms (Chart XXXI) are represented by $[Re_4(CO)_{16}]^{2-}$[50a] and $Cu_5Fe_4(CO)_{16}^{3-}$,[50b] respectively. The latter has four $Fe(CO)_4$ moieties occupying the corners of the ν_2 parallelogram. Note that a ν_n parallelogram has the same atom count as a ν_n square.

To the best of our knowledge, no *centered* triangular, square, pentagonal, etc. metal cluster systems have yet been synthesized.

The preparation of large planar metal clusters in solution is clearly a great synthetic challenge. Perhaps some sort of "template" is needed for the cluster to "grow" on.

Polyhedral Systems. As in the case of polygonal systems, the known (three-dimensional) polyhedral systems are mainly examples of ν_n polyhedra with $n \leq 3$. Some of the known examples follow.

The commonest three-dimensional metal cluster is probably the ν_1 tetrahedron (Chart XIII). One example is $Co_4(CO)_{12}$.[51] The ν_2 tetrahedral cluster $Os_{10}C(CO)_{24}^{2-}$[52] has only recently been synthesized and structurally characterized.

The next most common cluster is the ν_1 octahedron (Chart XVI) as represented by $Rh_6(CO)_{16}$.[53] As far as we know, a ν_2 octahedron has not yet been synthesized. However, the ν_3 octahedral cluster (Chart XXXII) $[Ni_{38}Pt_6(CO)_{48}H]^{5-}$,[54] with 38 nickel surface atoms and 6 platinum interior atoms, has recently been synthesized.

The ν_1 cubic metal cluster (Chart XIV) is represented by $Ni_8(PPh)_6(CO)_8$.[55] No discrete higher nuclearity cubic metal clusters are known at present. The ν_1 icosahedral structure (Chart XVII) occurs in $[Au_{13}(PMe_2Ph)_{10}Cl_2]^{3+}$.[56a] The ν_1, ν_2, and ν_3 icosahedral structures, containing 13, 55, and 147 atoms, have been observed in inert-gas (e.g., Xe) clusters formed by adiabatic jet expansion.[56b] A ν_1 centered dodecahedron (with 33 atoms, 20 at the vertices, 12 at the centers of the faces, and 1 at the center) is not known, although $C_{20}H_{20}$[57] has the structure of a simple dodecahedron (Chart XVIII).

The ν_1 truncated octahedron (the ν_2 analogue is shown in Chart XXI) is found in $[Pt_{38}(CO)_{44}H_x]^{2-}$.[58] The ν_1 triangular prismatic structure (Chart XXIII) can be found in $[Rh_6C(CO)_{15}]^{2-}$.[59] One example of a ν_1 square pyramid (the ν_4 analogue is shown in Chart XXVII) is $Ru_5C(CO)_{15}$.[60] Two examples of a ν_1 triangular bipyramid (Chart XXVIII) are $Os_5(CO)_{16}$[61] and $[Ni_5(CO)_{12}]^{2-}$[62] with different electron counts. No higher nuclearity analogues are known.

A ν_1 tricapped triangular prism (Chart XXIX) is found in Ge_9^{2-},[63] and a ν_1 twinned cuboctahedron (Chart XXX) is found in $[Rh_{13}(CO)_{24}H_{5-q}]^{q-}$, where q = 2, 3, 4.[64a-c] The ν_1 cuboctahedron (Chart XX), minus the central atom, can be found in the $Cu_{12}S_8^{4-}$ tetraanion.[64d] In the latter cluster, the eight sulfur atoms cap the eight triangular faces of the cuboctahedron.

Again there is the great synthetic challenge of preparing ν_n clusters with higher values of n.

Counterintuitive Concepts: "Peeling Onions" and "Slicing Cheese". We made several counterintuitive discoveries in the course of this work. In order to understand the packing of spheres (or atoms) in a ν_n polyhedron, it is helpful to introduce the concepts of "peeling an onion" and "slicing a cheese".

"Peeling an onion" refers to the removal of the S_n surface atoms (the "skin") to reveal the I_n interior atoms (the "core"). It is natural to ask (1) does the new polyhedron have the same *shape* as the original and, if so, (2) what is its *size* or, more precisely, is the core a ν_{n-1} polyhedron? The answer to both question is, surprisingly, "not necessarily".

This can be seen from the results in sections IV and V and Tables VI and VII. There are in fact three classes of figures. In the first class, exemplified by the centered polyhedra (centered tetrahedron, centered cube, icosahedron, etc.), and the cuboctahedron and twinned cuboctahedron, the removal of the surface atoms does produce a ν_{n-1} polyhedron of the same shape, and the answer to both questions is positive. For these figures $I_n = G_{n-1}$ and $G_n = S_n + S_{n-1} + S_{n-2} + ... + S_1 + S_0$ (see eq 29 and 30). The latter equation expresses the fact that in this case the whole "onion" can be built up from layers of the same shape.

The second class of objects is exemplified by a ν_n cube, which has the property that the removal of the outer shell produces a ν_{n-2} cube, not a ν_{n-1} cube. The answer to the first question is positive, but the answer to the second question is negative. For the cube we have $I_n = G_{n-2}$ and $G_n = I_n + I_{n-2} + I_{n-4} + ...$ (see eq 46 and 47). The "onion" is now composed of layers of the same shape, but the sizes of the layers decrease by 2 each time. A ν_n octahedron behaves in the same way. For a ν_n square pyramid or triangular bipyramid the interior is a ν_{n-3} polyhedron of the same shape. For a ν_n tetrahedron the interior is a ν_{n-4} tetrahedron,[65] and we have $I_n = G_{n-4}$ and $G_n = S_n + S_{n-4} + S_{n-8} + ...$ (see eq 44 and 45), in steps of 4.

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(65) This may be proved as follows, using the coordinates in eq 63. The boundary points have one or more of i, j, k, l equal to 0. The interior points have $i, j, k, l \geq 1$. Set $i' = i - 1$, $j' = j - 1$, etc. Then the interior consists of (i', j', k', l') with $i' + j' + k' + l' = n - 4$, which is a ν_{n-4} tetrahedron.

Table VIII. Values of s, K, T_n, and B_n for Some Close-Packed ν_n Polygonal and Polyhedral Metal Clusters Where n = 1, 2, 3, ...

Cluster	Chart	s	K^a	T_n^b	B_n^c
triangle	II	3	6,6,7, ···	24,42,67,96, ···	6,6,13,24, ···
parallelogram	XXXI	2	7,7, ···	31,61,103,157, ···	7,13,31,61, ···
centered hexagon	IX	1	7, ···	49,121,229,373, ···	13,49,121,229, ···
tetrahedron	XIII	4	6,7,6,7, ···	30,67,126,217, ···	6,7,6,13, ···
triangular bipyramid	XXVIII	3	6,6,7, ···	36,90,187,336, ···	6,6,13,36, ···
octahedron	XVI	2	7,7, ···	43,121,271,517, ···	7,13,43,121, ···
centered cuboctahedron^d	XX	1	7, ···	85,337,889,1861, ···	13,85,337,889, ···
truncated octahedron	XXI	–	7,7, ···	235,1213,3523, ···	43,481,1891, ···

^{a} K = 7, 6, 6, 7, ... for clusters centered at an atom, a triangle, a tetrahedral hole, an octahedral hole, ... Note that K repeats itself after s steps. ^{b} $T_n = 6G_n + K$. ^{c} $B_n = T_n - 6S_n$. ^{d} The s, K, T_n, and B_n values apply also to a centered icosahedron (Chart XVII) and twinned cuboctahedron (Chart XXX).

The remaining figures considered in section IV (and in fact most polyhedra) belong to the third class, where the interior polyhedron has a shape different from the original. For example, removing the outer shell from a ν_n truncated octahedron (cf. Chart XXI) does not produce a ν_k truncated octahedron for any value of k. The core of a ν_1 truncated octahedron is a ν_1 octahedron, but this does not generalize. Another example is a truncated tetrahedron. It can be shown that removing the outer shell from a ν_n truncated tetrahedron produces a figure that is a ν_{3n-4} tetrahedron with four corners removed, each corner being a ν_{n-3} tetrahedron. Thus, for the third type of polyhedra, the answer to both questions is negative.

In other words, not all polyhedra can be built up out of shells of the same shape. Even when this is possible, it is not necessarily true that the frequencies of the layers increase by steps of 1. Steps of size 2, 3, and 4 are also possible. The step size s for some close-packed polygonal and polyhedral clusters are tabulated in Table VIII.

The concept of "slicing a cheese" involves removing the atoms layer by layer, i.e. in planar layers, each layer being parallel to the next. Once again, removal of a facial layer of atoms from a ν_n polyhedron does not necessarily produce a polyhedron of the shape shape. In other words, it is not always possible to build up a polyhedral cluster from parallel layers of the same shape. In fact, of all the polyhedra considered in section IV, only two can be built in this fashion: (a) the ν_n tetrahedron (Chart XIII) by adding a ν_n triangle (Chart I) to a ν_{n-1} tetrahedron, and (b) the ν_n square pyramid (Chart XXVII) by adding a ν_n square (Chart IV) to a ν_{n-1} square pyramid. In both cases the step size is 1.

Electron Counting of Close-Packed High-Nuclearity Metal Clusters. There are many potential applications of the results presented in this paper. In metal cluster chemistry, the enumeration of the number and disposition of atoms within a cluster may be termed simply as *atom counting*. In fact, these atom-counting results (especially the counterintuitive concepts described in the previous part) not only provide new insight but also serve as a vehicle for *electron countings* of close-packed polygonal (2-D) or polyhedral (3-D) metal cluster systems. We shall discuss one such atom–electron counting here.

Within the context of the topological electron counting (TEC)[66–70] rule, a polyhedral metal cluster (not necessarily close packed) with S_n vertices (cf. Tables I–VII) is required to have a total of T_n topological electron pairs:[68]

$$T_n = 6S_n + B_n \tag{71}$$

where B_n is the number of *shell electron pairs*.[71] For small clusters (mostly n = 1), B_n can be interpreted as the number of *bonding cluster orbitals*.[71] For a *close-packed* high-nuclearity metal cluster, T_n can be rewritten[69,72] as

$$T_n = 6G_n + K \tag{72}$$

where G_n is the total number of atoms (cf. Tables I–VII) and K is related to the B value of the "center" of the cluster. For example, for clusters centered at an atom, a triangle, a tetrahedral hole, or an octahedral hole, K = 7, 6, 6, and 7, respectively.[68,69] The K values for some representative close-packed polygonal and polyhedral clusters are tabulated in Table VIII. Note that since these clusters repeat its overall shape (the peeling onion concept) in steps of s (also listed in Table VIII), only s values of K are given. Take the tetrahedron as an example, it repeats itself in steps of 4 (cf. Chart XIII): (1) since ν_1, ν_5, ν_9, ... tetrahedra all center at a tetrahedral hole, K = 6; (2) since ν_2, ν_6, ν_{10}, ... tetrahedra all center at an octahedral hole, K = 7; (3) since ν_3, ν_7, ν_{11}, ... tetrahedra all center at a tetrahedral hole, K = 6; (4) since ν_4, ν_8, ν_{12}, ... tetrahedra all center at an atom, K = 7.

Using these K and s values (cf. Table VIII) and the G_n and S_n values (cf. Tables I–VII) in conjection with eq 71 and 72, one can calculate the T_n and B_n values for various ν_n polygonal or polyhedral clusters. For example, a ν_n octahedral cluster is predicted to have

$$T_n = 2(n + 1)(2n^2 + 4n + 3) + 7$$

topological electron pairs (via eq 72) and

$$B_n = 2(n - 1)(2n^2 - 4n + 3) + 7$$

shell electron pairs (via eq 71).

While it is possible to write down analytical expressions for T_n and B_n for a given close-packed polygonal or polyhedral cluster, it is more convenient to use the computed G_n and S_n numbers listed in Table V–VII. Some results are tabulated in Table VIII. It is interesting to compare these predicted values of T_n and B_n with the observed ones. For example, the observed T_n and B_n values for some ν_n polygonal or polyhedral clusters are as follows: (1) ν_1 triangle, 24 and 6, as in $Os_3(CO)_{12}$,[47] and ν_2 triangle, 42 and 6, as in $Cu_3Fe_3(CO)_{12}^{3-}$;[50b] (2) ν_1 parallelogram, 31 and 7, as in $Re_4(CO)_{16}^{2-}$,[50a] and ν_2 parallelogram, 61 and 13, as in $Cu_5Fe_4(CO)_{16}^{3-}$;[50b] (3) ν_1 tetrahedron, 30 and 6, as in $Co_4(CO)_{12}$,[51] and ν_2 tetrahedron, 67 and 7, as in $Os_{10}C(CO)_{24}^{2-}$;[52] (4) ν_1 triangular bipyramid, 36 and 6, as in $Os_5(CO)_{16}$;[61] (5) ν_1 octahedron, 43 and 7, as in $Rh_6(CO)_{16}$,[53] and ν_3 octahedron, 271 and 43, as in $[Ni_{38}Pt_6(CO)_{48}H]^{5-}$;[54] (6) ν_1 twinned cuboctahedron, 85 and 13, as in $[Rh_{13}(CO)_{24}H_{5-q}]^{q-}$ where q = 2, 3, 4;[64a–c] (7) ν_1 truncated octahedron, 235 + $x/2$ and 43 + $x/2$, as in $[Pt_{38}(CO)_{44}H_x]^{2-}$.[58]

It is evident from Table VIII that, in most cases, $B_n = T_{n-s}$. In other words, the number of shell electron pairs of a ν_n cluster is exactly equal to the number of topological electron pairs of a (smaller) ν_{n-s} cluster. This is actually not too surprising because in the previous section we have shown that the figures can be built up in step size of s or, equivalently, that a ν_{n-s} polygon or polyhedron can be completely encapsulated within a ν_n figure of the same shape (the "onion" concept). In fact, we can generalize this principle by taking the difference of eq 71 and 72

$$B_n = 6I_n + K \tag{73}$$

since $G_n = S_n + I_n$. Now if there is a smaller cluster containing $G_{n'} = I_n$ atoms

$$\begin{aligned} B_n &= 6G_{n'} + K \\ &= T_{n'} \end{aligned} \tag{74}$$

In other words, in order for a cluster (denoted by n) to completely

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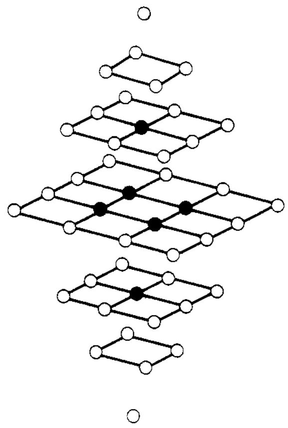
(67) Teo, B. K.; Longoni, G.; Chung, F. R. K. *Inorg. Chem.* **1984**, *23*, 1257.
(68) Teo, B. K. *Inorg. Chem.* **1985**, *24*, 1627.
(69) Teo, B. K. *Inorg. Chem.* **1985**, *24*, 4209.
(70) Teo, B. K., submitted for publication.

(71) Strictly speaking, T_n, B_n, and S_n in this paper correspond to T, B, and V_m in ref 68 (cf. eq 7) *only* for small clusters. That is, in most cases, $B_1 = B$, which is also equivalent to the *skeletal electron pairs* (cf. ref 6 of ref 68 in this paper). For larger clusters, this connection is lost. In this context, B_n is better described as the number of *shell electron pairs*.

(72) Ciani, G.; Sironi, A. *J. Organomet. Chem.* **1980**, *197*, 233.
(73) Teo, B. K. *J. Chem. Soc., Chem. Commun.* **1983**, 1362.

Chart XXXIII. "Slicing a Cheese": The ν_3 Octahedron Divided into Horizontal Slices



encapsulate a smaller cluster (denoted by n'), $B_n = T_{n'}$. For example, a ν_3 octahedron and ν_1 truncated octahedron both have 43 shell electron pairs, which exactly satisfy the 43 topological electron pairs of a ν_1 octahedron. Indeed, both $[Ni_{38}Pt_6(CO)_{48}H]^{5-}$ [54] and $[Pt_{38}(CO)_{44}H_x]^{2-}$ [58] contain a completely encapsulated Pt_6 octahedron.

We note that this *inclusion principle* (and the cage size concept) has already been pointed out in ref 66 and 69 (though for somewhat smaller clusters).[74] For further discussions on the "bulk connection" of close-packed high-nuclearity metal clusters, see ref 73.

Atomic Coordinates. Examples showing the determination of atomic coordinates of two-dimensional figures have been given in section V and will not be repeated here.

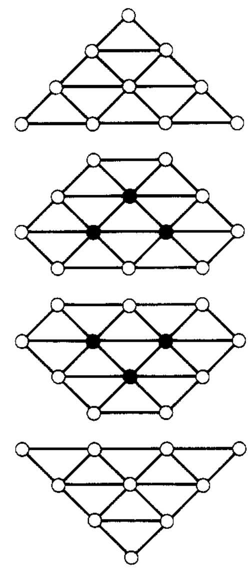
We shall illustrate the determination of atomic coordinates of three-dimensional figures from the formulas given in section V with two examples.

The atomic coordinates for a ν_3 octahedron can be obtained from eq 69. There are 6 interior atoms at $(\pm 1, 0, 0)$, 6 vertex atoms at $(\pm 3, 0, 0)$, 24 edge atoms at $(\pm 2, \pm 1, 0)$, and 8 face atoms at $(\pm 1, \pm 1, \pm 1)$, where it is to be understood that all permutations of the coordinates and all possible sign combinations are permitted. (For example, $(\pm 1, 0, 0)$ refers to the six atoms $(\pm 1, 0, 0)$, $(0, \pm 1, 0)$, $(0, 0, \pm 1)$). The last 3 groups describe the 38 surface atoms (cf. Table VI). Note that the coordinates of the $I_3 = 6$ interior atoms satisfy the relation $|i| + |j| + |k| = 1$, whereas the $S_3 = 38$ surface atoms satisfy $|i| + |j| + |k| = 3$ (compare eq 69), as illustrated in Chart XXXII. This corresponds to the "peeling onion" concept.

The "slicing cheese" concept may be illustrated by considering the layers along the (001) direction or z axis (Chart XXXIII). It is seen that the layers are ν_n squares. For z equal to $-3, -2, -1, 0, 1, 2$, and 3 there are respectively 1, 4, 9, 16, 9, 4, and 1 points (the square numbers) in the corresponding layer.

(74) As pointed out in ref 69, $B_n \geq T_{n'}$ in order for a cluster n to completely encapsulate a smaller cluster n'. If $B_n < T_{n'}$, incomplete encapsulation will occur.

Chart XXXIV. The ν_3 Octahedron Divided into Slices in the (111) Direction



Another way of slicing the ν_3 octahedron is along the (111) direction as shown in Chart XXXIV. Here the layers are distinguished according to the value of $i + j + k$. For $i + j + k$ equal to $-3, -1, 1$, and 3 there are respectively 10, 12, 12, and 10 points in the layer.

As a second example we consider a ν_2 truncated octahedron (Chart XXI). From eq 70 we find that the points of a ν_2 truncated octahedron are

coords	no.	coords	no.
420	24	310	24
411	24	220	12
400	6	211	24
330	12	200	6
321	48	110	12
222	8	000	1

(again allowing all permutations and all sign combinations), for a total of $G_3 = 201$ points. The $S_3 = 122$ points in the first column lie on the surface, while the remaining 79 points (which do not form a truncated octahedron) are in the interior (cf. Table VII). The surface points all satisfy $|i| + |j| + |k| = 6$, except for the six points $(\pm 4, 0, 0)$. Note that the 79 interior points correspond to a truncated ν_4 octahedron $(85 - 6 = 79$, see Table VI). In other words, a ν_2 truncated octahedron is made up of shells of follows: (1) 1 atom with $|i| + |j| + |k| = 0$; (2) 18 atoms with $|i| + |j| + |k| = 2$; (3) 60 atoms with $|i| + |j| + |k| = 4$; (4a) 6 atoms with $|i| + |j| + |k| = 4$ but only one nonzero coordinate; (4b) 116 atoms with $|i| + |j| + |k| = 6$. The fourth shell contains the 6 + 116 = 122 surface atoms. The 19 atoms of shells 1 and 2 form a ν_2 octahedron. The union of shells 1, 2, 3, and 4a is a ν_4 octahedron containing 85 atoms.