

# Generating functions for the cage isomers of the $C_{20n}$ icosahedral fullerenes

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Received 27 April 1992; revised 1 February 1993

The number of isomeric cages for the  $C_{20n}$  icosahedral fullerenes (Goldberg polyhedra), is given by the coefficient of  $n^{-s}$  in the expansion of the Dirichlet generating function

$$\zeta(s)L[s, \chi(3)].$$

When this coefficient is even, the cages occur as chiral pairs of point symmetry  $I$ ; when odd, there is one structural isomer of point symmetry  $I_h$ , and the other isomers, if any, occur as chiral pairs. Asymptotic estimates are given for the number of isomers of each type.

## 1. Introduction

The discovery [1] and subsequent isolation [2] of the icosahedral molecule, buckminsterfullerene, has also produced a great deal of interest in possible homologues, particularly those of a highly symmetric nature. These are suspected to be constituents of soot and interstellar matter [3], and include the known  $C_{70}$ , as well as several postulated series, the “magic numbers” [4], recently extended to ionic species [5], and the icosahedral  $C_{20n}$  series [6]. According to [5], stable fullerenes are likely to be those polyhedra with 12 pentagonal faces and the remaining faces hexagons, and with the following properties: (1) isolated pentagons, (2) large delocalisation energies and HOMO-LUMO gaps, (3) low steric strain.

Considering the infinite icosahedral series, these will clearly satisfy criteria (1) and (3), and when the lower members were considered from a quantum mechanical viewpoint, several, such as  $C_{80}^{2+}$  [5] and  $C_{240}$  [6], were indeed adjudged to have high stability. The corresponding polyhedra are named after their discoverer, Goldberg [7], and, in addition to their application as geodesic domes, their properties have been used by Caspar and Klug [8] to describe possible icosahedral virus particles. In light of the growing interest – recently reviewed [9] – in the relationship between crystallography and clusters of fivefold symmetry, it is interesting to note that the

rule that  $n$  must be expressible in the form  $(h^2 + hk + k^2)$ , with  $h$  and  $k$  integers such that  $h > 0$  and  $k \geq 0$ , can be related to similar restrictions applying to the indices of points of a hexagonal crystal lattice [7,8,10]. However the underlying number theory which applies to integer solutions of the quadratic form  $(h^2 + hk + k^2)$  appears not to have been recognised in a crystallographic context before the work of Senechal [11]. Only very recently [12,13] has there been any systematic attempt to introduce number theory methods into crystallography, specifically multiplicative arithmetic functions and their Dirichlet generating functions [14]. These functions allow ready enumeration, often including asymptotic estimation, for derivative lattices by their symmetry classes.

Although the appropriate generating functions are already known in the crystallographic context [12], the asymptotic properties of these particular arithmetic functions have not previously been examined. Since the distribution of isomers in the title series is very unusual and irregular, the distribution was considered worth this more detailed study, especially since it has now been shown that all fullerene cages composed solely of pentagons and hexagons can also be arranged in families,  $C_{nx}$ , each with the same isomer distribution as this icosahedral series [15]. It was concluded that the distribution of isomers could be linked to the properties of the Dirichlet generating functions, which are the appropriate tools for enumeration in the case of the Goldberg polyhedra, rather than the more familiar power series type. As such, it is the first application of these functions to finite molecular systems. In fact the reason that they apply is, as we shall see, that the major aspects of the enumerations can be carried across directly from a specific lattice-based problem.

## 2. Derivative lattice enumerations

The way in which a planar map of an icosahedral geodesic dome may be formed, by placing an arrangement of large equilateral triangles on a net of smaller equilateral triangles, has been described by Coxeter [10]. The smaller triangles form a regular hexagonal net, and the vertices of the larger triangles must lie on a geometrically similar net, which is then a crystallographic derivative lattice [16] of the first. This lattice projection construction has since been used to predict fullerene structures of icosahedral and other symmetries [17]. In the case of icosahedral fullerenes, the unit cell of this derivative lattice contains some integer number  $n$  graphite hexagons and therefore  $2n$  carbon atoms, since each carbon atom is shared by 3 hexagons. Since the rhomboidal unit cell contains the equivalent of 2 triangular icosahedron faces, each face will contain  $n$  carbon atoms, and the polyhedron as a whole  $20n$  carbon atoms. Thus the problem may be completely transformed into an enumeration of the two-dimensional hexagonal derivative lattices.

We next develop the results of ref. [12], particularly regarding the hexagonal

plane groups p6 (No. 16) and p6mm (No. 17). We use Dirichlet generating functions of the form

$$F(s) = \sum_{n=1}^{\infty} f(n)n^{-s},$$

where  $f(n)$  is the corresponding arithmetic function, and we define the derivative lattice by the index  $(h, k)$  in hexagonal co-ordinates of its closest lattice point in the sextant  $h > 0, k \geq 0$ . the symmetry of the resulting structure will be p6mm if  $k = 0$  or  $k = h$ , otherwise it will be p6. The total number of such derivative lattices is given by  $\{r_{\text{hex}}/6\}$ , where  $r_{\text{hex}}$  is the total number of representations of  $n$  of the form  $(h^2 + hk + k^2)$ .  $\{r_{\text{hex}}/6\}$  is in turn enumerated by

$$F(\text{p6}) = \zeta(s)L[s, \chi(3)], \tag{1}$$

where

$$\zeta(s) = 1 + 2^{-s} + 3^{-s} + 4^{-s} + 5^{-s} + 6^{-s} + \dots$$

is the Riemann zeta function, and

$$L[s, \chi(3)] = 1 - 2^{-s} + 4^{-s} - 5^{-s} + 7^{-s} - 8^{-s} + \dots$$

is a Dirichlet  $L$ -function. Their product becomes

$$F(\text{p6}) = 1 + 3^{-s} + 4^{-s} + 2 \times 7^{-s} + 9^{-s} + 12^{-s} + 2 \times 13^{-s} + \dots,$$

where the coefficient  $f(n)$  of  $n^{-s}$  gives the number of stereoisomers for that value of  $n$ . Thus, for  $n = 1 (h = 1, k = 0)$ , we have one structure, the dodecahedrane cage C<sub>20</sub>, for  $n = 3, (h = 1, k = 1)$ , one, buckminsterfullerene, for C<sub>80</sub>,  $(h = 2, k = 0)$ , also one, but for C<sub>140</sub>, two, corresponding to  $(2, 1)$  and  $(1, 2)$ , which give enantiomeric structures. Similarly there are two enantiomers for C<sub>260</sub>, namely  $(3, 1)$  and  $(1, 3)$ . The number of isomers may increase still further; for example, for  $n = 49$  it is three,  $(5, 3), (3, 5)$  and  $(7, 0)$ , and for  $n = 91$ , four, namely  $(9, 1), (8, 3), (3, 8)$  and  $(1, 9)$ .

Since  $F(\text{p6})$  is a multiplicative function, we may derive a formula for it in terms of the contributions of the individual prime numbers. The Dirichlet series involved here have all prime product forms; in fact these are

$$\zeta(s) = \prod_p (1 - p^{-s})^{-1}$$

and

$$L[s, \chi(3)] = \left\{ \prod_{p \equiv -1 \pmod 3} (1 + p^{-s})^{-1} \right\} \left\{ \prod_{p \equiv +1 \pmod 3} (1 - p^{-s})^{-1} \right\}.$$

Multiplying these two functions together gives a formula in which the prime 3 has a unique role:

$$F(6) = \frac{1}{(1-3^{-s})} \left\{ \prod_{p=-1 \bmod 3} (1-p^{-2s})^{-1} \right\} \left\{ \prod_{p=+1 \bmod 3} (1-p^{-s})^{-2} \right\}. \quad (2)$$

Detailed examination of this equation shows that:  $f(n)$  is always 1 for  $n = 3^\alpha$ , independent of  $\alpha$ ; for  $n = p_i^{\beta_i}$ ,  $p_i = -1 \bmod 3$ , either  $f(n) = 0$  or  $f(n) = 1$ , depending on whether  $\beta_i$  is odd or even; and only for  $n = p_j^{\gamma_j}$ ,  $p_j = +1 \bmod 3$ , can the value of  $f(n)$  be greater than 1, being, in fact,  $f(n) = (\gamma_j + 1)$ . Thus, for a general

$$n = 3^\alpha \left\{ \prod_{p_i=-1 \bmod 3} p_i^{\beta_i} \right\} \left\{ \prod_{p_j=+1 \bmod 3} p_j^{\gamma_j} \right\},$$

using the multiplicative property of  $f(n)$ , the isomer count is either zero when one or more  $\beta_i$ 's are odd [17a], or

$$f(n) = \prod_{p_j=+1 \bmod 3} (\gamma_j + 1)$$

when all the  $\beta_i$ 's are even.

Further analysis of the symmetries involved depends on whether or not mirror planes occur. Thus whether the plane group symmetry of the hexagonal structure is  $p6$  or  $p6mm$ , depending on whether the two-dimensional point group of the individual triangle is  $3$  or  $3m1$ . Similarly the symmetry of the resulting polyhedron is  $I$  (235) or  $I_h$  ( $m\bar{3}5$ ), depending on whether the individual face belongs to  $3$  or  $3m1$ . Thus we see that the lattice projection method maps plane group  $p6$  into point group  $I$ ,  $p6mm$  into  $I_h$ . This in turn allows us to apply the results of the corresponding crystallographic enumerations to distinguish the polyhedra by symmetry group, since it is also possible to treat independently the derivative lattices of symmetry  $p6mm$ , for which  $k = 0$  or  $k = h$ . The function here, also involving a unique role for the prime 3, is

$$F(p6mm) = \frac{(1-3^{-2s})}{(1-3^{-s})} \zeta(2s) = 1 + 3^{-s} + 4^{-s} + 9^{-s} + 12^{-s} + 16^{-s} + \dots \quad (3)$$

Here the series coefficient of  $n^{-s}$  is unity where the previous series coefficient was odd, and is zero where the previous coefficient was even. This illustrates that the function  $F(p6)$  counts the cage isomers in such a way that when a coefficient is even, the cages occur as chiral pairs of point symmetry  $I$ ; when odd, there is one structural isomer of point symmetry  $I_h$ , and the other isomers, if any, occur as chiral pairs.

### 3. Asymptotic estimation of the number of isomers

In many cases Dirichlet generating functions readily provide asymptotic estimations of the average value of the corresponding arithmetic function for large values of the index  $n$ . Methods given by Knopfmacher [18] have already been used to

derive such estimates for certain crystallographic objects [13]. These methods yield in this case the following. From (20) we get the asymptotic density of the relevant solutions of  $n = (h^2 + hk + k^2)$ , corresponding to all icosahedral cages, to be

$$\rho(I + I_h) = L[1, \chi(3)] = \frac{\pi}{3\sqrt{3}},$$

and from (3) we get the corresponding density of  $I_h$  isomers

$$\rho(I_h) = \frac{4}{3}n^{-1/2}.$$

This shows that the total number of isomers remains on average independent of  $n$ ; however, the number of isomers of point symmetry  $I_h$  tends to zero, and for large  $n$ , as we might expect, almost all isomers have point symmetry  $I$ .

The average number of isomers for a specific  $n$  we saw was  $\pi/3\sqrt{3}$ . However, making use of (2) we see that  $f(n)$  being zero depends only on the prime factors of the type  $-1 \pmod 3$ , and, in fact, by using simple combinatorics and geometric series, the fraction of non-zero coefficients proves to be

$$\prod_{p \equiv -1 \pmod 3} (1 + p^{-1})^{-1} = \prod_{p \equiv -1 \pmod 3} \frac{p}{p+1} = \frac{2}{3} \times \frac{5}{6} \times \frac{11}{12} \dots$$

Thus we may identify the other term,

$$\prod_{p \equiv +1 \pmod 3} (1 - p^{-1})^{-1} = \prod_{p \equiv +1 \pmod 3} \frac{p}{p-1} = \frac{7}{6} \times \frac{13}{12} \times \frac{19}{18} \dots,$$

as the average magnitude of a non-zero term. However, by rearranging (2) and setting  $s = 1$ , we find

$$\prod_{p \equiv +1 \pmod 3} (1 - p^{-1})^{-2} = (1 - 3^{-1}) \left\{ \prod_{p \equiv -1 \pmod 3} (1 - p^{-2}) \right\} L[1, \chi(3)] \zeta(1).$$

Since the first three terms on the right-hand side are finite positive constants, (they have values  $\frac{3}{2}$ , 0.75560..., and  $\pi/3\sqrt{3}$  respectively), and  $\zeta(1)$  is well known to be divergent:

$$\zeta(1) = 1 + \frac{1}{2} + \frac{1}{3} + \frac{1}{4} + \dots,$$

Table 1  
Distribution of icosahedral fullerene isomers  $C_{20n}$  with  $n \leq 100$ .

Range of $n$	Molecular symmetry		Total	Number of non-zero terms
	$I_h$	$I$		
1-20	6	6	12	9
21-40	3	10	13	8
41-60	2	8	10	5
61-80	2	12	14	8
81-100	2	8	10	5

then the left-hand side also diverges. This means that the average magnitude of a non-zero term increases without limit. This in turn can only occur, given a fixed overall average value of  $\pi/3\sqrt{3}$ , if the set of non-zero terms in the series has asymptotic measure zero.

Thus, as  $n$  increases, the values of  $n$  for which isomers can exist at all become progressively scarcer, while the average number of isomers, where they do occur, continues to increase. All of these trends are illustrated in table 1, which shows the statistics for  $n \leq 100$ , grouped in twenties; i.e.  $\rho(I + I_h)$  fluctuates around its average value of  $\pi/3\sqrt{3} = 0.60460\dots$ , while  $\rho(I_h)$  decreases, and the average non-zero number of isomers increases, with increasing  $n$ .

## References

- [1] H.W. Kroto, J.E. Heath, S.C. O'Brien, R.F. Curl and R.E. Smalley, *Nature* 318 (1985) 162.
- [2] W. Kratschmer, L.D. Lamb, K. Fostiropoulos and D.R. Huffman, *Nature* 347 (1990) 354.
- [3] H.W. Kroto, *Proc. R. Inst.* 58 (1986) 45; *Science* 242 (1988) 1017.
- [4] P.W. Fowler, *Chem. Phys. Lett.* 131 (1986) 444.
- [5] P.W. Fowler and D.E. Manolopoulos, *Nature* 355 (1992) 428.
- [6] D.J. Klein, W.A. Seitz and T.G. Schmalz, *Nature* 323 (1986) 703.
- [7] M. Goldberg, *Tohoku Math. J.* 43 (1937) 104.
- [8] D.L.D. Caspar and A. Klug, *Cold Spring Harbor Symp. Quant. Bio.* 27 (1962) 1.
- [9] A.L. Mackay, in: *Quasicrystals, Networks, and Molecules of Fivefold Symmetry*, ed. I. Hargittai (VCH, New York, 1990) p. 1.
- [10] H.S.M. Coxeter, in: *A Spectrum of Mathematics: Essays presented to H.G. Forder*, ed. J.C. Butcher (Adelaide University Press/Oxford University Press, Adelaide/Oxford, 1971) p. 98.
- [11] M. Senechal, *Discrete Appl. Math.* 1 (1979) 51.
- [12] J.S. Rutherford, *Acta Cryst.* A42 (1992) 500.
- [13] J.S. Rutherford, *Acta Cryst. A*, in press.
- [14] G.H. Hardy and E.M. Wright, *An Introduction to the Theory of Numbers*, 5th Ed. (Oxford University Press, Oxford, 1979) p. 244.
- [15] J.S. Rutherford, *Inorg. Chem.*, in press.
- [16] Y. Billiet and E.F. Bertaut, in: *International Tables for Crystallography*, Vol. A, ed. T. Hahn (Riedel, Dordrecht, 1983) p. 810.
- [17] (a) P.W. Fowler, J.E. Cremona and J.I. Steer, *Theor. Chim. Acta* 73 (1988) 1;  
(b) M. Fujita, R. Saito, G. Dresselhaus and M. Dresselhaus, *Phys. Rev.* B45 (1992) 13834.
- [18] J. Knopfmacher, *Abstract Analytical Number Theory* (Dover, New York, 1990).