

Arrangements of Point Charges Having Zero Electric-Field Gradient. II

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In Part I [Knop, Palmer & Robinson (1975). *Acta Cryst.* A31, 19–31] arrangements of point charges at the vertices of polyhedra of cubic and icosahedral symmetry were described which produce a zero electric-field gradient (ZEFG) at a reference point $s_0(0,0,0)$. Further infinite classes of ZEFG configurations have now been identified, among them regular polygons having particular metric properties relative to s_0 , and combinations of such polygons. Any ZEFG configuration of charges on a sphere can be generated by combining suitable irreducible (minimal) ZEFG sets of charges. The numbers $J(n)$ of irreducible ZEFG sets of n equal charges of the same sign on a sphere are known only for $n \leq 4$: $J(1)=0$, $J(2)=0$, $J(3)=1$ (any three vertices of a regular octahedron, no two forming a centrosymmetric pair), and $J(4)=3$ (any four vertices of a cube, no two forming a centrosymmetric pair).

For n discrete charges having values u_c and Cartesian coordinates (x_i, y_i, z_i) to produce a zero electric-field gradient (ZEFG) at point $s_0(0,0,0)$ the electric-field gradient tensor **EFG** must be a null matrix (*cf.* part I, Knop, Palmer & Robinson, 1975). For a set of unit charges of equal sign situated on a sphere of unit radius with centre at s_0 , $x_i^2 + y_i^2 + z_i^2 = 1$, the **EFG**=(0) condition may be written as

$$\begin{pmatrix} x_1 & y_1 & z_1 \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ x_n & y_n & z_n \end{pmatrix} \begin{pmatrix} x_1 \dots x_n \\ y_1 \dots y_n \\ z_1 \dots z_n \end{pmatrix} = (n/3) \quad (1)$$

or, in an extended form, as

$$\sum_1^n (3x_i^2 - 1) = \sum_1^n (3y_i^2 - 1) = \sum_1^n (3z_i^2 - 1) = 0$$

or

$$\sum_1^n x_i^2 = \sum_1^n y_i^2 = \sum_1^n z_i^2 = n/3 \quad (1)$$

$$\sum_1^n x_i y_i = \sum_1^n x_i z_i = \sum_1^n y_i z_i = 0. \quad (2)$$

In part I we have shown that conditions 1 and 2 are satisfied by sets of charges which are minimum subsets \mathcal{S}_j of sets \mathcal{S} of vertices of centrosymmetric polyhedra of cubic and icosahedral symmetry inscribed in the unit sphere, and by sums and combinations of such subsets. In the present paper we describe further infinite classes of ZEFG configurations.

Unit charges on a unit sphere

Consider n like unit charges on the unit sphere located at the vertices of a regular n -gon in a plane parallel to the equatorial (xy) plane. The coordinates of this set

of point charges are $[x \cos (i-1)\alpha, x \sin (i-1)\alpha, z]$, $i=1, 2, \dots, n$, $\alpha=2\pi/n$. This set satisfies the ZEFG conditions 1 and 2 at s_0 :

$$(1) \quad \sum_1^n (3x_i^2 - 1) = 3x^2 \sum_1^n \cos^2 (i-1)\alpha = \frac{1}{2}n(3x^2 - 2),$$

$$\sum_1^n (3y_i^2 - 1) = 3x^2 \sum_1^n \sin^2 (i-1)\alpha = \frac{1}{2}n(3x^2 - 2),$$

$$\sum_1^n (3z^2 - 1) = n(3z^2 - 1);$$

$$(2) \quad \sum_1^n x_i y_i = \frac{1}{2}x^2 \sum_1^n \sin 2(i-1)\alpha = 0,$$

$$\sum_1^n x_i z = z \sum_1^n \cos (i-1)\alpha = 0,$$

$$\sum_1^n y_i z = z \sum_1^n \sin (i-1)\alpha = 0.$$

Setting $\frac{1}{2}n(3x^2 - 2) = 0$ and $n(3z^2 - 1) = 0$, we have $x = \pm \sqrt{\frac{2}{3}}$, $z = \pm \sqrt{\frac{1}{3}}$, and $x_i^2 + y_i^2 + z_i^2 = x^2[\cos^2 (i-1)\alpha + \sin^2 (i-1)\alpha] + z^2 = 1$; hence the ZEFG conditions are satisfied for any $n \geq 3$. Thus regular n -gons of unit charges inscribed in a circle of radius $\sqrt{\frac{2}{3}}$ on a unit sphere constitute an infinite class of ZEFG solutions of *axial* symmetry.

For $n=3$ and 4 the n -gons are the face of a regular octahedron and the face of a cube respectively, and hence solutions of cubic symmetry (ZEFG configurations No. 1 on the octahedron and cube, Table 7 of Part 1).

Since a regular n -gon inscribed in a circle of radius $\sqrt{\frac{2}{3}}$ is a ZEFG configuration, any combination of such polygons is a ZEFG configuration, and the values of n need not be the same. Some such combinations with the polygons in special relationship can be singled out:

(3) Combine an n_1 -gon (x_1, y_1, z_1) with an n_2 -gon (x_2, y_2, z_2) in parallel planes. To satisfy the ZFEG conditions,

$$\frac{1}{2}n_1(1 - 3z_1^2) + \frac{1}{2}n_2(1 - 3z_2^2) = 0,$$

i.e.

$$n_1z_1^2 + n_2z_2^2 = (n_1 + n_2)/3.$$

(3a) $n_1 = n_2 = n$, $z_1 = -z_2$: two n -gons in parallel planes symmetric about s_0 . Since the rotational displacement of the two n -gons relative to each other does not matter, any n -gonal prism of symmetry C_n inscribed in a circular cylinder of a height-to-radius ratio equal to $\sqrt{2}$ is a ZFEG configuration. From an infinity of skew prisms C_n one can single out the infinite class of right n -gonal prisms D_{nh} and antiprisms D_{nd} . The cube is a solution of symmetry $D_{4h} \subset O_h$ (*i.e.* $4/mmm \subset m3m$), the octahedron is a solution of symmetry $D_{3d} \subset O_h$ (*i.e.* $\bar{3}m \subset m3m$).

Combining such prisms and antiprisms produces further ZFEG configurations, some of them belonging to the cubic and icosahedral classes. For example, a combination of three cubes $[\pm\sqrt{(\frac{2}{3})}, 0, \pm\sqrt{(\frac{1}{3})}]$, $[\pm\sqrt{(\frac{2}{3})}, \pm\sqrt{(\frac{1}{3})}, 0]$, *etc.*, $[\pm\sqrt{(\frac{1}{3})}, \pm\sqrt{(\frac{2}{3})}, 0]$, *etc.*] produces a truncated octahedron, a ZFEG configuration of symmetry $m3m$.

(3b) $n_1, n_2, z_1 = z_2$: a regular n_1 -gon and a regular n_2 -gon inscribed in the same circle, of radius $\sqrt{(\frac{2}{3})}$, and rotated through an arbitrary angle relative to each other. This generates an infinite class of ZFEG $(n_1 + n_2)$ -gons. For $n_1 = n_2 = n$ and a displacement angle $2\pi/n$ a regular $2n$ -gon results, or otherwise a $2n$ -gon having n pairs of vertices.

(3c) $n_1, n_2, z_1 = -z_2$: in general, irregular polyhedra with parallel basal planes. When $n_2 = kn_1$, $(n_1 + n_2 + 2)$ -hedra of symmetries C_{nv} and C_n are possible.

(3d) $n_1 = n_2, z_1 = -z_2: z_1 = \pm\sqrt{(\frac{1}{3})}$, as under (3a).

(3e) $z_2 = \pm 1$ requires $2n_2 \leq n_1$. But if $z_2 = \pm 1$, the n_2 -gon is reduced to a point at the pole, hence $n_2 = 1$, $n_1 \geq 2$. This corresponds to an infinite ZFEG class of n -gonal pyramids defined by the vertex $(0, 0, 1)$ and by $x = [(2n + 2)/3n]^{1/2}$, $z = \pm[(n - 2)/3n]^{1/2}$. The limiting values x_∞ and z_∞ for $n \rightarrow \infty$ are $\sqrt{(\frac{2}{3})}$ and $\pm\sqrt{(\frac{1}{3})}$ respectively, *i.e.* the effect of the charge at $(0, 0, 1)$ disappears and the limiting configuration is the above cylinder with $n_1 = n_2, z_1 = -z_2$, defined by the two circles of circumference $s = 2\pi\sqrt{(\frac{2}{3})}$ and uniform charge density $dn/ds = 1$.

For $n_1 = 3$, the solution with $z_1 = \frac{1}{3}$ is equivalent to configuration No. 2 ($C_{3v} - 3m$) and with $z_1 = -\frac{1}{3}$, to configuration No. 3 ($T_d - \bar{4}3m$) on the cube (Table 7, Part 1).

(3f) $z_1 = 0$ requires $n_1 \leq 2n_2$. When $n_1 = n_2 = n$, $x_2 = \pm\sqrt{(\frac{1}{3})}$, $z_2 = \pm\sqrt{(\frac{2}{3})}$; with the two n -gons properly oriented a truncated pyramid of symmetry C_{nv} results. When $n_2 = 1$, $n_1 \leq 2$; taking $n_1 = 2, z_2 = \pm 1$. Because of $x_1^2 + y_1^2 = 1$ and rotational indefiniteness one may choose $x_1 = 1/\sqrt{2}$, whence $z_1 = \pm 1/\sqrt{2}$. This solution defines a face of a regular octahedron.

(4) Combine an n_1 -gon (x_1, y_1, z_1) with two n_2 -gons $(x_2, y_2, \pm z_2)$ in parallel planes: $n_1z_1^2 + 2n_2z_2^2 = (n_1 + 2n_2)/3$. A special case with $n_1 = 6, n_2 = 3, z_1 = 0$, is the cuboctahedron O_h .

(4a) $n_1 = n_2 = n, z_1 = 0: x_2 = \pm 1/\sqrt{2}, z_2 = \pm 1/\sqrt{2}$. Depending on the relative orientation of the n -gons, this combination yields a truncated n -gonal bipyramid or a right n -gonal prism augmented on all vertical faces.

(4b) $z_1 = 0, z_2 = 1: 2n_2 = (n_1 + 2n_2)/3, n_1 = 4n_2$. However, $n_2 = 1$ when $z_2 = 1$; hence a regular octahedron is the only solution of this type.

(4c) Combine an n -gon (x_1, y_1, z_1) with a charge at $(0, 0, 1)$ and an n -gon $(x_2, y_2, z_2): z_1^2 + z_2^2 = \frac{2}{3} - (2/3n)$. When $z_1 = 0, z_2^2 = \frac{2}{3} - (2/3n)$.

Obviously a large variety of further types of ZFEG configurations can be obtained by combining the regular ZFEG polygons, some of them of high symmetry, but a general discussion of these possibilities would be out of place here.

Combination to centrosymmetric arrangements of maximum symmetry

Whenever a combination of ZFEG polygons has a centre of symmetry at s_0 , the constituent polygons correspond to the \mathcal{S}_j ZFEG subsets discussed in part I and the $\mathcal{S}_j + \mathcal{S}_j^*$ sums have the properties associated with self-duality. For example, two square pyramids \mathcal{S}_1 and \mathcal{S}_1^* described under (3e) can be combined to a bicapped tetragonal prism $\mathcal{S}_1 + \mathcal{S}_1^*$ of symmetry D_{4h} , with vertices $(0, 0, \pm 1), [\sqrt{(\frac{2}{3})}, 0, \pm\sqrt{(\frac{1}{3})}]$, *etc.* Any set of five vertices of this polyhedron, no two of them related by the centre of symmetry, will be a ZFEG configuration and thus a new \mathcal{S}_j subset. The bicapped prisms, bicapped antiprisms, and $2n$ -gonal bipyramids are among the more important classes of centrosymmetric arrangements. The results for unequal charges discussed in part I can be applied in an analogous manner.

The enumeration principle for self-dual configurations (*cf.* part I) can be applied to any such centrosymmetric ZFEG arrangement in the same manner as has been described for the cubic and icosahedral symmetries. For the bicapped tetragonal prism D_{4h} , for example, the cycle index Z is that of a bicapped cube of symmetry D_{4h} (Knop, Barker & White, 1975):

$$Z = \frac{1}{16}(t_1^{10} + 2t_1^2t_4^2 + 3t_1^2t_2^4 + 3s_1^2t_2^4 + 2s_2^3t_2^2 + 2s_2^2t_4^2 + s_2^5 + 2t_1^2t_2^2).$$

Setting $s_k = 0$ and $t_k = \sqrt{2}$ yields $N_1 = 6$ for the number of distinct self-dual \mathcal{S}_j subsets (up to rotation and reflexion).

Irreducible ZFEG sets of unit charges on a unit sphere

Any ZFEG configuration of n unit charges of equal sign is the sum of irreducible (minimal) ZFEG sets \mathcal{S}_j . The number of distinct (up to rotation and reflexion) irreducible ZFEG sets $J(n)$ corresponding to a

given n is not known at present for $n > 4$. For $n = 2$ no ZFEG configuration exists in real E^3 space. For $n = 3$, placing one charge at $(0, 0, 1)$, $z_2^2 + z_3^2 = 0$, whence $z_2 = z_3 = 0$ and, if $x_2 = 1$, $y_2 = x_3 = 0$ and $y_3 = \pm 1$ up to rotation, *i.e.* any orthogonal triplet of radius vectors of unit length is a solution and no other class of solutions exists. A triplet of this kind defines a subset \mathcal{S}_1 of three vertices of an octahedron $O_h - m\bar{3}m$, so that $J(3) = 1$ and the irreducible ZFEG set belongs to the cubic class described in part I, $J(3) = N_1$ (octahedron).

For $n = 4$, choosing $x_1 = y_1 = x_2 = 0$, $z_1 = 1$, solving equations (1) and (2) and transforming the coordinates yields $(\pm\sqrt{3}/3, \pm\sqrt{3}/3, \pm\sqrt{3}/3)$, *i.e.* four vertices of the cube, no two forming a centrosymmetric pair. This solution is unique and identical with the bicapped trigonal antiprism obtained by combining two trigonal pyramids of (3e). It corresponds to $J(4) = N_1$ (cube) = 3.

For $n \geq 5$ the problem of determining $J(n)$ is diophantine and for larger values of n probably intractable. For $n = 6$, for example, the ZFEG configurations Nos. 1 and 4 on the icosahedron (*cf.* Table 7 of Part 1) are pentagonal pyramids of (3e) defined by $(2/\sqrt{5}, 0, \pm 1/\sqrt{5}; \text{etc.})$ and $(0, 0, 1)$; Nos. 2 and 3 consist of equilateral triangles at heights z_1 and $\pm z_2$, $z_1^2 + z_2^2 = \frac{2}{3}$ [*cf.* (3)]. The ZFEG configuration No. 2 on the cuboctahedron corresponds to two equilateral triangles at heights $\sqrt{(\frac{2}{3})}$ and 0, as under (3f), but Nos. 1 and 3 seem to be irreducible relative to 1 and 4. The regular hexagon at $z = \pm 1/\sqrt{3}$ is a special class of two concentric equilateral triangles combined to give D_{6h} symmetry (C_{6v} relative to s_0).

Combinations producing multiple charges

k congruent ZFEG n -gons of unit charges inscribed in the same circle may be rotated in their own plane so as to produce coincidence of the k sets of vertices. This would be equivalent to having a ZFEG n -gon of k -tuple charges. Similarly, k irreducible orthogonal triplets of unit charges on the unit sphere can be combined in such a way that one vertex is placed in $(0, 0, 1)$ and is common to all k triplets, no other vertices coinciding. A ZFEG configuration of $2k + 1$ charges will result, $2k$ of them unit charges and one k -tuple. In this manner one can generate an infinite set of ZFEG configurations containing multiple charges.

Embedding in three-dimensional lattices

In contrast to the ZFEG configurations on cubic polyhedra, the noncubic ZFEG configurations described in this paper cannot be embedded in crystallo-

graphic lattices to give ZFEG structures, even when the point-group symmetry of the configuration is crystallographic and therefore admissible as site symmetry. Not only must the particular metric properties of the noncubic and nonicosahedral ZFEG configurations be preserved: even if the dimensions of the lattice satisfy this requirement, the charges at lattice points not belonging to the ZFEG configuration but related by translation will violate the ZFEG condition at the reference point s_0 of the configuration. The ZFEG condition could be approximated, *locally*, if the distances of the charges external to the ZFEG configuration were sufficiently great to produce only a small contribution to the EFG at s_0 , as a result of the EFG dependence on the inverse cube of distance. However, this would be an exceptional case.

Effect of distance from s_0

If unit charges outside the unit sphere are considered, the effect of the distance $r_i = |(x_i^2 + y_i^2 + z_i^2)^{1/2}|$ must be included. The ZFEG conditions 1 and 2 then become

$$\sum_i r_i^{-3}(3x_i'^2 - 1) = \sum_i r_i^{-3}(3y_i'^2 - 1) = \sum_i r_i^{-3}(3z_i'^2 - 1) = 0 \quad (3)$$

$$\sum_i r_i^{-3}x_i'y_i' = \sum_i r_i^{-3}x_i'z_i' = \sum_i r_i^{-3}y_i'z_i' = 0, \quad (4)$$

where $x_i' = x_i/r_i$ *etc.* In the simplest case, that of k sets of charges on concentric spheres centred at s_0 , the results obtained above for ZFEG configurations on the unit sphere hold but must be scaled by r_k .

An interesting result follows from the limiting values x_∞ and z_∞ under (3e). The two parallel circles of radius $\sqrt{(\frac{2}{3})}$ on the unit sphere at $z = \pm \sqrt{(\frac{1}{3})}$ define a conical surface generated by a straight line passing through s_0 and forming an angle $\varphi = \arccos \sqrt{(\frac{1}{3})}$ with the z axis. Any charge distribution on this cone rotationally symmetric about the cone axis, will produce a ZFEG at s_0 . The angle φ is in fact the tetrahedral angle $109^\circ 28' 14''$.

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