M, R, and N centers is the appeal in promoting a deeper understanding of a broad class of defects in alkali halide crystals.

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Point-Charge Calculations of Energy Levels of Magnetic Ions in Crystalline Electric Fields*

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I. Introduction

The calculation of energy levels of magnetic ions in crystalline electric fields is often the cause of considerable confusion. This confusion largely arises, not through the fundamental theoretical principles which are now well established, but from the large number of different and often not fully defined notations used, occasional errors, and the fact that one author seldom gives an example of calculation from start to finish. This discussion contains no original contribution to the problem, but it is hoped that by illustrating how the energy levels may be calculated on the basis of a simple point-charge ionic model of the crystal lattice, the connection between the

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various forms of crystal-field Hamiltonians will be clarified. Particular reference will be made to fields of cubic symmetry.

If the crystalline electric field effects are taken as a perturbation on the appropriate free-ion wave functions and energy levels, the problem becomes that of finding the perturbing Hamiltonian and its matrix elements. The energy levels in the crystal field can then be found from standard perturbation theory. The simple point-charge model used to calculate the Hamiltonian is known to possess several weaknesses. It neglects the finite extent of charges on the ions, the overlap of the magnetic ions' wave functions with those of neighboring ions, and the complex effects of "screening" of the magnetic electrons by the outer electron shells of the magnetic ion. However, it serves as a first approximation to illustrate the principles involved, and may be used to calculate ratios of terms of the same degree in the Hamiltonian for lattice sites of high symmetry, since these ratios are independent of the model used and are determined solely by the symmetry. Certain refinements of the ionic model for rare-earth compounds, for which it is most applicable, have been discussed by Hutchison and Wong,[1] Hutchings and Ray,[2] and Lenander and Wong.[3]

2 II. Determination of the Perturbing Hamiltonian

On the basis of a simple point-charge ionic model the determination of the perturbing Hamiltonian is primarily the evaluation of the electrostatic potential $V(r, \theta, \phi)$ due to the surrounding point charges, at a point (r, θ, ϕ) near the origin at the magnetic ion in question:

$$V(r, \theta, \phi) = \sum_j \frac{q_j}{|(\mathbf{R}_j - \mathbf{r})|} \tag{II.1}$$

where q_j is the charge at the jth neighboring ion, a distance R_j from the origin.

If the magnetic ion has charge q_i at (r_i, θ_i, ϕ_i), then the perturbing crystalline potential energy will be

$$W_c = \sum_i q_i V_i = \sum_i \sum_j \frac{q_i q_j}{|(\mathbf{R}_j - \mathbf{r}_i)|}. \tag{II.2}$$

We are normally only concerned with $\sum_i$ over electrons in unfilled shells, as the crystal field affects closed shells only in a high order of perturbation. This is also true for ions in an S state, and throughout we shall omit such ions from the discussion.

[1] C. A. Hutchison and E. Y. Wong, *J. Chem. Phys.* **29**, 754 (1958).
[2] M. T. Hutchings and D. K. Ray, *Proc. Phys. Soc. (London)* **81**, 663 (1963).
[3] C. J. Lenander and E. Y. Wong, *J. Chem. Phys.* **38**, 2750 (1963).

The crystalline potential, Eq. (II.1), may be calculated in Cartesian coordinates, or directly in terms of spherical harmonics. These two methods and their connection will be illustrated below for crystal fields of cubic symmetry.

1. Evaluation of the Crystalline Electric Potential near a Magnetic Ion in Terms of Cartesian Coordinates

As an illustration we shall calculate the potential at a point (x, y, z) near the magnetic ion as origin for three arrangements of charges giving a cubic crystalline electric field, that is, near an origin of cubic point symmetry. The simplest three such arrangements are:

(1) When the charges are placed at the corners of an octahedron (sixfold coordination).
(2) When the charges are placed at the corners of a cube (eightfold coordination).
(3) When the charges are placed at the corners of a tetrahedron (fourfold coordination).

We shall see later (Section 4a) that it is only necessary to expand the potential up to terms of sixth degree.

a. Sixfold Cubic Coordination

Consider the potential $V(x, y, z)$ at a point P, (x, y, z), due to point charges of charge q at the corners of an octahedron; i.e., at $(a, 0, 0)$, $(-a, 0, 0)$, $(0, a, 0)$, $(0, -a, 0)$, $(0, 0, a)$, and $(0, 0, -a)$, as shown in Fig. 1. Then $V(x, y, z) = V_x + V_y + V_z$, where

$R^2 = x^2+y^2+z^2$

$$V_x = q\left[\frac{1}{(r^2 + a^2 - 2ax)^{1/2}} + \frac{1}{(r^2 + a^2 + 2ax)^{1/2}}\right],$$

V_y = etc., and $r^2 = x^2 + y^2 + z^2$. Now let $A = (r^2 + a^2)$, $B = r^2/a^2$, and

$$X = \frac{2ax}{A} = \frac{2x}{a}\frac{1}{(1+B)}; \qquad Y = \frac{2ay}{A}; \qquad Z = \frac{2az}{A}.$$

Expanding up to terms of sixth degree, for $R_j = a > r$:

$$V(x, y, z) = (q/A^{1/2})[(1 + X)^{-1/2} + (1 - X)^{-1/2} + (1 + Y)^{-1/2} + (1 - Y)^{-1/2} + (1 + Z)^{-1/2} + (1 - Z)^{-1/2}].$$

Now,

$$(1+X)^{-\frac{1}{2}} + (1-X)^{-\frac{1}{2}} = 2 + \frac{3}{4}X^2 + \frac{35}{64}X^4 + \frac{\overset{231}{\cancel{693}}}{64\cdot \underset{8}{24}}X^6.$$

Therefore,

$$V(x,y,z) = \frac{q}{A^{\frac{1}{2}}}\left[6 + \frac{3}{4}(X^2+Y^2+Z^2) + \frac{35}{64}(X^4+Y^4+Z^4) + \frac{693}{64\cdot 24}(X^6+Y^6+Z^6)\right]$$

$$= \frac{q}{a}\left[6(1+B)^{-\frac{1}{2}} + \frac{3\cdot 4}{4}\frac{(x^2+y^2+z^2)}{a^2(1+B)^{5/2}} + \frac{35\cdot 16}{64}\frac{(x^4+y^4+z^4)}{a^4(1+B)^{9/2}} + \frac{693\cdot 64}{64\cdot 24a^6}\frac{(x^6+y^6+z^6)}{(1+B)^{13/2}}\right]$$

$$= \frac{q}{a}\left\{6 - 3\frac{(x^2+y^2+z^2)}{a^2} + \frac{9}{4}\frac{(x^2+y^2+z^2)^2}{a^4} - \frac{15}{8}\frac{(x^2+y^2+z^2)^3}{a^6} + \frac{(x^2+y^2+z^2)}{a^2} \times \left[3 - \frac{15}{2}\frac{(x^2+y^2+z^2)}{a^2} + \frac{105}{8}\frac{(x^2+y^2+z^2)^2}{a^4}\right] + \frac{(x^4+y^4+z^4)}{a^4}\left[\frac{35}{4} - \frac{35\cdot 9}{8}\frac{(x^2+y^2+z^2)}{a^2}\right] + \frac{693}{24a^6}(x^6+y^6+z^6)\right\}.$$

Therefore, collecting terms,

$$V(x,y,z) = \frac{6q}{a} - \frac{21q}{4a^5}(x^2+y^2+z^2)^2 + \frac{35q}{4}\frac{(x^4+y^4+z^4)}{a^5} + \frac{90q}{8}\frac{(x^2+y^2+z^2)^3}{a^7} + \frac{231q}{8}\frac{(x^6+y^6+z^6)}{a^7} - \frac{35\cdot 9q}{8}\frac{(x^2+y^2+z^2)(x^4+y^4+z^4)}{a^7}.$$

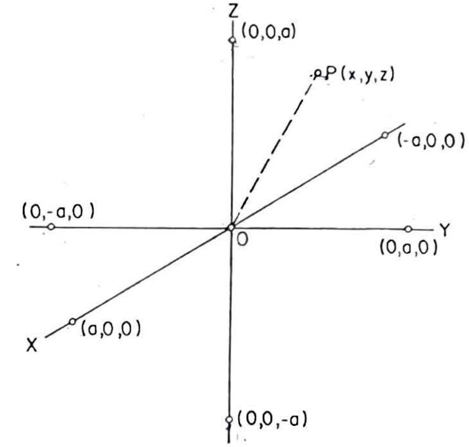


FIG. 1. Sixfold cubic coordination.

We now make use of several expansions listed below. (These include also some which will be required later.)

$$(x+y+z)^2 = x^2+y^2+z^2+2(zy+xz+xy) = r^2+2(zy+xz+xy)$$

$$(x+y+z)^3 = x^3+y^3+z^3 + 3(xy^2+xz^2+yx^2+yz^2+zx^2+zy^2) + 6xyz$$

$$(x+y+z)^4 = r^4 + 4r^2(xy+yz+zx) + 4(x^2y^2+y^2z^2+z^2x^2) + 8(xy^2z+x^2yz+xz^2y)$$

$$(x+y+z)^6 = x^6+y^6+z^6+15(x^2y^4+x^2z^4+y^2x^4+y^2z^4+z^2x^4+z^2y^4) + 90x^2y^2z^2 + \text{terms where } x, y, \text{ or } z \text{ occur to an odd power.}$$

$$r^2 = x^2+y^2+z^2$$

$$r^4 = x^4+y^4+z^4+2x^2y^2+2y^2z^2+2z^2x^2$$

$$r^6 = x^6+y^6+z^6+3(x^4y^2+x^4z^2+y^4x^2+y^4z^2+z^4x^2+z^4y^2) + 6x^2y^2z^2. \quad (1.1)$$

Using these we find

$$V(x,y,z) = \frac{6q}{a} + \left(\frac{35q}{4a^5}\right)\left[(x^4+y^4+z^4) - \tfrac{3}{5}r^4\right] + \left(\frac{-21q}{2a^7}\right) \times \left[(x^6+y^6+z^6) + \tfrac{15}{4}(x^2y^4+x^2z^4+y^2x^4+y^2z^4+z^2x^4+z^2y^4) - \tfrac{15}{14}r^6\right]. \quad (1.2)$$

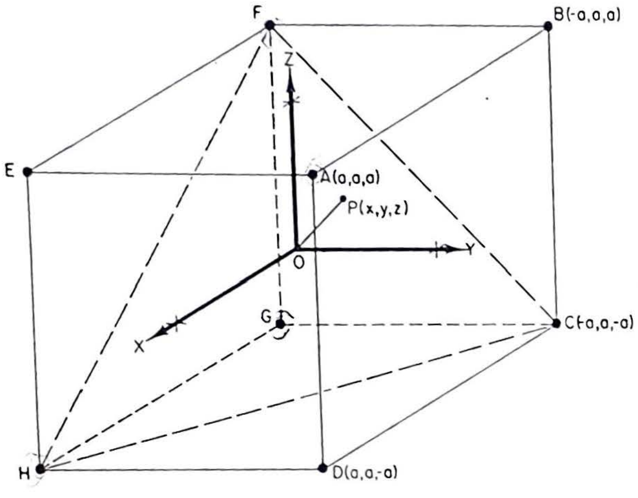


FIG. 2. Eightfold cubic coordination.

An alternative method of calculating this result is to make use of Taylor's series, expanding up to $n = 6$:

$$V(x, y, z) = \sum_{n=0}^{n=6} \frac{1}{n!}\left[x\left(\frac{\partial}{\partial x}\right)_0 + y\left(\frac{\partial}{\partial y}\right)_0 + z\left(\frac{\partial}{\partial z}\right)_0\right]^n V(x, y, z).$$

b. Eightfold Cubic Coordination

We now repeat the same calculation for eight charges at the corners of a cube; that is, we consider the potential at a point (x, y, z) due to eight point charges q at positions: (a, a, a), $(-a, a, a)$, $(a, -a, a)$, $(a, a, -a)$, $(a, -a, -a)$, $(-a, a, -a)$, $(-a, -a, a)$, and $(-a, -a, -a)$, as shown in Fig. 2.

In principle this is a similar case to that of sixfold coordination, but requires more tedious algebraic manipulation.

Choosing axes as shown in Fig. 2, we calculate the potential V_A, at a point P, (x, y, z), due to the charge q at A, (a, a, a). Consider the plane

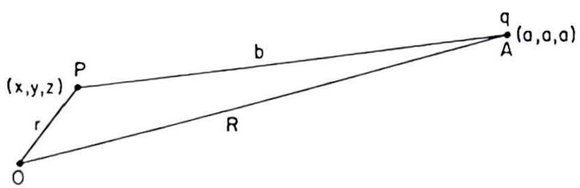


FIG. 3. (See text.)

containing the origin O, the point P, and the charge at A, when $R_j = a\sqrt{3} > r$ (where $r^2 = x^2 + y^2 + z^2$). Let $AP = b$ (Fig. 3):

$$V_A = \frac{+q}{b} = \frac{+q}{[(a-x)^2 + (a-y)^2 + (a-z)^2]^{1/2}}$$

$$= \frac{+q}{[A - 2a(x+y+z)]^{1/2}} = \frac{+q}{A^{1/2}}\frac{1}{(1+Y)^{1/2}},$$

where $A = 3a^2 + r^2$ and $Y = -2a(x+y+z)/A$. Expanding,

$$(1+Y)^{-1/2} = 1 - \tfrac{1}{2}Y + \frac{3}{2^3}Y^2 - \frac{5}{2^4}Y^3 + \frac{35}{2^7}Y^4 - \frac{63}{2^8}Y^5 + \frac{231}{2^{10}}Y^6 \cdots.$$

Therefore,

$$V_A = q\left[\frac{1}{A^{1/2}} + \frac{a(x+y+z)}{A^{3/2}} + \frac{3}{2}\frac{a^2(x+y+z)^2}{A^{5/2}} + \frac{5}{2}\frac{a^3(x+y+z)^3}{A^{7/2}}\right.$$

$$+ \frac{35}{2^3}\frac{a^4(x+y+z)^4}{A^{9/2}} + \frac{63}{2^3}\frac{a^5(x+y+z)^5}{A^{11/2}}$$

$$\left. + \frac{231}{2^4}\frac{a^6(x+y+z)^6}{A^{13/2}} \cdots\right]$$

Now let $X = r^2/3a^2$; i.e., $A = 3a^2(1+X)$. Then denoting each term in the square brackets by Roman numerals, and expanding up to powers of sixth degree, with $r^2 = x^2 + y^2 + z^2$, we have

$$\mathrm{I} = \frac{1}{(3a^2)^{1/2}}(1+X)^{-1/2} = \frac{1}{(3a^2)^{1/2}}\left[1 - \frac{1}{2}\frac{(x^2+y^2+z^2)}{3a^2}\right.$$

$$\left. + \frac{3}{8}\frac{(x^2+y^2+z^2)^2}{9a^4} - \frac{5}{2^4}\frac{(x^2+y^2+z^2)^3}{27a^6} + \cdots\right];$$

$$\mathrm{II} = \frac{a}{(3a^2)^{3/2}}(x+y+z)(1+X)^{-3/2}$$

$$= \frac{a}{(3a^2)^{3/2}}\left[(x+y+z) - \frac{(x^2+y^2+z^2)(x+y+z)}{2a^2}\right.$$

$$\left. + \frac{5}{24a^4}(x^2+y^2+z^2)^2(x+y+z) + \cdots\right];$$

$$\mathrm{III} = \frac{3}{2}\frac{a^2}{(3a^2)^{5/2}}(x+y+z)^2(1+X)^{-5/2}$$

$$= \frac{3}{2}\frac{a^2}{(3a^2)^{5/2}}\Big[(x+y+z)^2 - \frac{5}{6a^2}(x^2+y^2+z^2)(x+y+z)^2$$

$$+ \frac{35}{8\cdot 9a^4}(x^2+y^2+z^2)^2(x+y+z)^2 + \cdots\Big];$$

$$\mathrm{IV} = \frac{5}{2}\frac{a^3}{(3a^2)^{7/2}}(x+y+z)^3(1+X)^{-7/2} = \frac{5a^3}{2(3a^2)^{7/2}}$$

$$\times\Big[(x+y+z)^3 - \frac{7}{6a^2}(x^2+y^2+z^2)(x+y+z)^3 + \cdots\Big];$$

$$\mathrm{V} = \frac{35}{8}\frac{a^4}{(3a^2)^{9/2}}(x+y+z)^4(1+X)^{-9/2} = \frac{35}{8}\frac{a^4}{(3a^2)^{9/2}}$$

$$\times\Big[(x+y+z)^4 - \frac{9}{6a^2}(x^2+y^2+z^2)(x+y+z)^4 + \cdots\Big];$$

$$\mathrm{VI} = \frac{63}{8}\frac{a^5}{(3a^2)^{11/2}}(x+y+z)^5[1+\cdots];$$

$$\mathrm{VII} = \frac{231}{2^4}\frac{a^6}{(3a^2)^{13/2}}(x+y+z)^6[1+\cdots].$$

We must now add the potential due to each of the other seven charges. However, we note that the potential at (x, y, z) due to charge at $(-a, a, a)$, for example, is $V_B = q/[(-a-x)^2 + (a-y)^2 + (a-z)^2]^{\frac{1}{2}}$, which is the same as that at $(-x, y, z)$ due to q at (a, a, a). Therefore we need merely add all the corresponding terms occurring in V_A with $x \to -x$. For all the charges, the potential will be the sum of all terms arising from the different combinations of $\pm x$, $\pm y$, $\pm z$. The result is that all *odd* degree terms cancel, as do all terms in which x, y, or z occurs to an odd power; e.g., xy, x^2yz, etc. Terms in which x, y, and z each occur to an even power will be the same for each charge, and simply add.

The relevant terms in V_A are, therefore,

$$V_A = q\Bigg\{\frac{1}{(3a^2)^{1/2}} + \Big[\frac{-1}{2(3a^2)^{3/2}}(x^2+y^2+z^2) + \frac{3}{2}\frac{a^2}{(3a^2)^{5/2}}(x+y+z)^2\Big]$$

$$+\Big[\frac{3}{(3a^2)^{1/2}}\frac{1}{8\cdot 9a^4}(x^2+y^2+z^2)^2$$

$$-\frac{3}{2}\frac{a^2}{(3a^2)^{5/2}}\frac{5}{6a^2}(x^2+y^2+z^2)(x+y+z)^2$$

$$+\frac{35}{8}\frac{a^4}{(3a^2)^{9/2}}(x+y+z)^4\Big]$$

$$+\Big[\frac{-1}{(3a^2)^{1/2}}\frac{5}{2^4}\frac{(x^2+y^2+z^2)^3}{27a^6}$$

$$+\frac{3}{2}\frac{a^2}{(3a^2)^{5/2}}\frac{35}{8\cdot 9a^4}(x^2+y^2+z^2)^2(x+y+z)^2$$

$$-\frac{35a^4}{8(3a^2)^{9/2}}\frac{9}{6a^2}(x^2+y^2+z^2)(x+y+z)^4$$

$$+\frac{231}{2^4}\frac{a^6}{(3a^2)^{13/2}}(x+y+z)^6\Big]\Bigg\} + \text{odd-degree terms.}$$

Using the expansions in Eqs. (1.1), and adding the contribution from all eight ions, we find, after cancellation of the remaining odd terms,

$$V(x, y, z) = q\Bigg(\frac{8}{d} + \Big[-\frac{8}{2d^3}r^2 + \frac{3\cdot 8}{6d^3}r^2\Big] + \Big\{\frac{3\cdot 8}{8d^5}r^4 - \frac{3\cdot 5\cdot 8}{2\cdot 6d^5}r^4$$

$$+\frac{35}{8\cdot 9}\frac{8}{d^5}[r^4 + 2r^4 - 2(x^4+y^4+z^4)]\Big\}$$

$$+\Big\{-\frac{5\cdot 8}{16d^7}r^6 + \frac{3\cdot 8\cdot 35r^6}{2d^7\cdot 24} - \frac{35}{8}\frac{8}{d^7}\frac{1}{2}$$

$$\times[r^6 + 4r^2(x^2y^2+y^2z^2+z^2x^2)] + \frac{77}{9}\frac{8}{16d^7}$$

$$\times[15r^6 - 14(x^6+y^6+z^6)$$

$$- 30(x^2y^4 + x^2z^4 + y^2x^4 + y^2z^4 + z^2x^4 + z^2y^4)]\Big\}\Bigg)$$

... Van Nostrand, Princeton, New Jersey, 1956.

where $d = \sqrt{3}a$ = distance of the eight charges from the origin. The sixth-degree term simplifies to

$$\left\{-\frac{5}{2}\frac{r^6}{d^7} + \frac{35}{2}\frac{r^6}{d^7} - \frac{35r^6}{2d^7} - \frac{35}{2d^7}\left[2r^6 - 2(x^6 + y^6 + z^6) - 2(x^2y^4 + \cdots)\right]\right.$$

$$\left. + \frac{77}{18}\frac{1}{d^7}\left[15r^6 - 14(x^6 + y^6 + z^6) - 30(x^2y^4 + \cdots)\right]\right\}.$$

Collecting terms, we find that the total potential, expressed in the same form as for sixfold cubic coordination, is

$$V(x, y, z) = \frac{8q}{d} + \left(-\frac{70q}{9d^5}\right)\left[(x^4 + y^4 + z^4) - \tfrac{3}{5}r^4\right] + \left(\frac{-224q}{9d^7}\right)$$

$$\times \left[(x^6 + y^6 + z^6) + \tfrac{15}{4}(x^2y^4 + x^2z^4 + y^2x^4 + y^2z^4 + z^2x^4 + z^2y^4) - \tfrac{15}{14}r^6\right] \tag{1.3}$$

c. Fourfold Cubic Coordination

If the axes are chosen carefully, the potential at a point P near the origin due to a tetrahedron of charges follows immediately from Section 1b. In Fig. 2, if we consider the cube to be made up of two tetrahedra, AFHC and EBGD, it follows that the contribution to the even-degree terms in the potential from each of these is just half that from the total, as they are equivalent except for a rotation of the axes of 90 deg about the z axis. This rotation will not affect even terms in V because of the symmetry in x, y, and z and the fact that they are each raised to even powers. There will in this case be further odd-degree terms, but we shall see in Section 4a that these do not affect the energy levels if only one configuration is considered.

d. Summary: Cubic Potential in Cartesian Coordinates

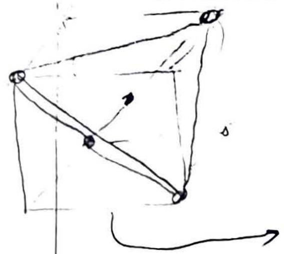
The potential energy of a charge q' at (x, y, z) in the potentials we have just calculated will be of the form

$$W_c = C_4\left[(x^4 + y^4 + z^4) - \tfrac{3}{5}r^4\right] + D_6\left[(x^6 + y^6 + z^6)\right.$$

$$\left. + \tfrac{15}{4}(x^2y^4 + x^2z^4 + y^2x^4 + y^2z^4 + z^2x^4 + z^2y^4) - \tfrac{15}{14}r^6\right], \tag{1.4}$$

where the coefficients are given in Table I; d is now the distance of the point charges q from the origin in each case ($d > r$). Axes are chosen in the manner discussed above. The initial term in Eq. (1.3) only affects the zero of energy and has been omitted.

TABLE I. COEFFICIENTS C_4 AND D_6 (EQ. 1.4) FOR THE THREE COORDINATIONS



	C_4	D_6
Eightfold coordination	$-\frac{70qq'}{9d^5}$	$-\frac{224qq'}{9d^7}$
Sixfold coordination	$+\frac{35qq'}{4d^5}$	$-\frac{21qq'}{2d^7}$
Fourfold coordination	$-\frac{35qq'}{9d^5}$	$-\frac{112qq'}{9d^7}$

The form of the expression for W_c given in Eq. (1.4) is frequently quoted, but there is often confusion over the magnitude and sign of the coefficients [see, for example, Low,[4] p. 15. There is an error in sign of D_6 in his Eq. (5.5)]. Before its matrix elements can be conveniently found from tables, it must be rearranged as in Section 6a.

2. EVALUATION OF THE CRYSTALLINE ELECTRIC POTENTIAL NEAR A MAGNETIC ION IN TERMS OF SPHERICAL HARMONICS

It is far more convenient to express the crystalline electric potential due to surrounding point charges in spherical harmonics, or tesseral harmonics, for two reasons. Firstly, a general formula for its evaluation can easily be derived; secondly, it is far easier to calculate the matrix elements of the potential energy in this form.

The method of calculation is discussed by Griffith,[5] page 199, and Prather,[6] page 6. It is based on the spherical harmonic addition theorem. This expresses the angle ω between two vectors $\mathbf{r}$ and $\mathbf{R}$ in terms of their polar angles (θ_i, ϕ_i) and (θ_j, ϕ_j):

$$P_n^0(\cos\omega) = \frac{4\pi}{(2n+1)}\sum_{m=-n}^{n}(-1)^m Y_n^{-m}(\theta_j, \phi_j)\, Y_n^m(\theta_i, \phi_i). \tag{2.1}$$

(See Griffith,[5] page 75, for example.) Here the Legendre functions, P_n^m (where we use the term Legendre functions to cover both the Legendre polynomials P_n^0 and the associated Legendre polynomials P_n^m ($m \neq 0$),

[4] W. Low, *Solid State Phys.* Suppl. 2, (1960).
[5] J. S. Griffith, "The Theory of Transition-Metal Ions." Cambridge Univ. Press, London and New York, 1961.
[6] J. L. Prather, "Atomic Energy Levels in Crystals." N. B. S. Monograph No. 19, 1961.

TABLE II. SOME OF THE MORE COMMONLY OCCURRING LEGENDRE FUNCTIONS (as defined by Eq. (2.2))

$$P_2^0(\cos\theta) = \tfrac{1}{2}(3\cos^2\theta - 1)$$
$$P_2^2(\cos\theta) = 3(1 - \cos^2\theta)$$
$$P_4^0(\cos\theta) = \tfrac{1}{8}(35\cos^4\theta - 30\cos^2\theta + 3)$$
$$P_4^2(\cos\theta) = \tfrac{15}{2}(1 - \cos^2\theta)(7\cos^2\theta - 1)$$
$$P_4^3(\cos\theta) = 105(1 - \cos^2\theta)^{3/2}\cos\theta$$
$$P_4^4(\cos\theta) = 105(1 - \cos^2\theta)^2$$
$$P_6^0(\cos\theta) = \tfrac{1}{16}(231\cos^6\theta - 315\cos^4\theta + 105\cos^2\theta - 5)$$
$$P_6^2(\cos\theta) = \tfrac{105}{8}(1 - \cos^2\theta)(33\cos^4\theta - 18\cos^2\theta + 1)$$
$$P_6^3(\cos\theta) = \tfrac{315}{2}(1 - \cos^2\theta)^{3/2}(11\cos^3\theta - 3\cos\theta)$$
$$P_6^4(\cos\theta) = \tfrac{945}{2}(1 - \cos^2\theta)^2(11\cos^2\theta - 1)$$
$$P_6^6(\cos\theta) = 10{,}395(1 - \cos^2\theta)^3$$

and spherical harmonics, Y_n^m, are defined as

$$\left.\begin{aligned} P_n^0(\mu) &= (1/2^n n!)(d^n/d\mu^n)(\mu^2 - 1)^n \\ P_n^{|m|}(\mu) &= (1 - \mu^2)^{|m|/2}(d^{|m|}/d\mu^{|m|})P_n^0(\mu) \end{aligned}\right\} \quad \mu = \cos\theta$$

$$Y_n^m(\theta, \phi) = (-1)^{(m+|m|)/2}\left[\frac{(2n+1)(n-|m|)!}{2(n+|m|)!}\right]^{1/2} \times \frac{1}{(2\pi)^{1/2}} P_n^{|m|}(\cos\theta) \times \exp(im\phi). \quad (2.2)$$

Some of the more relevant Legendre functions, and spherical harmonics are listed in Tables II and III. More complete lists are given by Prather,[6] page 4 (with different normalization of the Legendre functions from those defined in Eq. (2.2)), and also by Jahnke and Emde,[7] pages 107 and 110.

Now the potential $V(r, \theta, \phi)$, at a point (r, θ, ϕ), due to a number of charges q_j at $\mathbf{R}_j$ is given by Eq. (II.1):

$$V(r, \theta, \phi) = \sum_j \frac{q_j}{|(\mathbf{R}_j - \mathbf{r})|}.$$

[7] E. Jahnke and F. Emde, "Tables of Functions," 4th ed. Dover, New York, 1945.

TABLE III. SOME OF THE MORE COMMONLY OCCURRING SPHERICAL HARMONICS (as defined by Eq. (2.2))

$$Y_2^0 = \frac{1}{4}\left(\frac{5}{\pi}\right)^{1/2}(3\cos^2\theta - 1)$$
$$Y_2^{\pm 2} = \frac{1}{4}\left(\frac{15}{2\pi}\right)^{1/2}\sin^2\theta\, e^{\pm 2i\phi}$$
$$Y_4^0 = \frac{3}{16}\frac{1}{\pi^{1/2}}(35\cos^4\theta - 30\cos^2\theta + 3)$$
$$Y_4^{\pm 2} = \frac{3}{8}\left(\frac{5}{2\pi}\right)^{1/2}\sin^2\theta(7\cos^2\theta - 1)e^{\pm 2i\phi}$$
$$Y_4^{\pm 3} = \mp\frac{3}{8}\left(\frac{35}{\pi}\right)^{1/2}\sin^3\theta\cos\theta\, e^{\pm 3i\phi}$$
$$Y_4^{\pm 4} = \frac{3}{16}\left(\frac{35}{2\pi}\right)^{1/2}\sin^4\theta\, e^{\pm 4i\phi}$$
$$Y_6^0 = \frac{1}{32}\left(\frac{13}{\pi}\right)^{1/2}(231\cos^6\theta - 315\cos^4\theta + 105\cos^2\theta - 5)$$
$$Y_6^{\pm 2} = \frac{1}{64}\left(\frac{2730}{2\pi}\right)^{1/2}\sin^2\theta(33\cos^4\theta - 18\cos^2\theta + 1)e^{\pm 2i\phi}$$
$$Y_6^{\pm 3} = \mp\frac{1}{32}\left(\frac{2730}{2\pi}\right)^{1/2}\sin^3\theta(11\cos^3\theta - 3\cos\theta)e^{\pm 3i\phi}$$
$$Y_6^{\pm 4} = \frac{21}{32}\left(\frac{13}{14\pi}\right)^{1/2}\sin^4\theta(11\cos^2\theta - 1)e^{\pm 4i\phi}$$
$$Y_6^{\pm 6} = \frac{231}{64}\left(\frac{13}{231\pi}\right)^{1/2}\sin^6\theta\, e^{\pm 6i\phi}$$

If ω is the angle between $\mathbf{r}$ and $\mathbf{R}$, then

$$\frac{1}{|(\mathbf{R} - \mathbf{r})|} = \sum_{n=0}^{\infty}\frac{r^n}{R^{(n+1)}}P_n^0(\cos\omega) \qquad R > r. \quad (2.3)$$

(See, for example, Margenau and Murphy,[8] page 100.)

In order to avoid the use of imaginary quantities, we define tesseral

[8] H. Margenau and G. M. Murphy, "The Mathematics of Physics and Chemistry," 2nd ed. Van Nostrand, Princeton, New Jersey, 1956.

harmonics as

$$\left.\begin{aligned} Z_{n0} &= Y_n^0 \\ Z^c_{nm} &= (1/\sqrt{2})[Y_n^{-m} + (-1)^m Y_n^m] \\ Z^s_{nm} &= (i/\sqrt{2})[Y_n^{-m} - (-1)^m Y_n^m] \end{aligned}\right\} \quad m > 0, \tag{2.4}$$

that is,

$$\begin{aligned} Z_{n0} &= Y_n^0 \\ Z^c_{nm} &= \left[\frac{(2n+1)}{2}\frac{(n-m)!}{(n+m)!}\right]^{\frac{1}{2}} P_n^m(\cos\theta)\,\frac{\cos m\phi}{\sqrt{\pi}} \\ Z^s_{nm} &= \left[\frac{(2n+1)}{2}\frac{(n-m)!}{(n+m)!}\right]^{\frac{1}{2}} P_n^m(\cos\theta)\,\frac{\sin m\phi}{\sqrt{\pi}} \end{aligned} \tag{2.5}$$

Then from the spherical harmonic addition theorem, Eq. (2.1),

$$P_n^0(\cos\omega) = \frac{4\pi}{(2n+1)}\sum_\alpha Z_{n\alpha}(\mathbf{r})Z_{n\alpha}(\mathbf{R}), \tag{2.6}$$

where the Z's are evaluated for the points $\mathbf{r}$ and $\mathbf{R}$, and the summation is over α; that is, for each n, there are terms Z_{n0}, Z^c_{nm}, and Z^s_{nm} for all m. Hence, if $V(r, \theta, \phi)$ is due to a charge q_j, at $\mathbf{R}_j$, using Eqs. (2.3) and (2.6) in (II.1),

$$V(r, \theta, \phi) = q_j \sum_{n=0}^{\infty} \frac{r^n}{R_j^{(n+1)}}\left[\sum_\alpha \frac{4\pi}{(2n+1)} Z_{n\alpha}(\theta_j, \phi_j) Z_{n\alpha}(\theta, \phi)\right],$$

and for k charges

$$V(r, \theta, \phi) = \sum_{n=0}^{\infty}\sum_\alpha r^n \gamma_{n\alpha} Z_{n\alpha}(\theta, \phi),$$

where

$$\gamma_{n\alpha} = \sum_{j=1}^{k} \frac{4\pi}{(2n+1)}\, q_j\, \frac{Z_{n\alpha}(\theta_j, \phi_j)}{R_j^{(n+1)}}. \tag{2.7}$$

This is a very convenient form in which to write the potential. If the $Z_{n\alpha}$ are expressed in Cartesian coordinates, there is an immediate correspondence between them and Stevens' "operator equivalents," which can be used for the evaluation of the matrix elements. These will be discussed in Section 5. The tesseral harmonics used here are identical with those of Griffith,[5] page 200, and Prather,[6] page 4, although Prather uses

the notation $\mathbf{C}_n^m \equiv Z^c_{nm}$; $\mathbf{S}_n^m \equiv Z^s_{nm}$. Prather,[6] pages 4 and 5, gives expressions for the $\mathbf{C}_n^m$ and $\mathbf{S}_n^m$ up to order $n = 6$, $m = 6$, in terms of Cartesian coordinates (x, y, z). A few of the more commonly occurring Z^c_{nm} are listed in Table IV.

TABLE IV. SOME OF THE MORE COMMONLY OCCURRING TESSERAL HARMONICS EXPRESSED IN CARTESIAN COORDINATES[a]

$$Z_{20} = \frac{1}{4}\left(\frac{5}{\pi}\right)^{\frac{1}{2}}[(3z^2 - r^2)/r^2]$$

$$Z^c_{22} = \frac{1}{4}\left(\frac{15}{\pi}\right)^{\frac{1}{2}}[(x^2 - y^2)/r^2]$$

$$Z_{40} = \frac{3}{16}\left(\frac{1}{\pi^{\frac{1}{2}}}\right)[(35z^4 - 30z^2r^2 + 3r^4)/r^4]$$

$$Z^c_{42} = \frac{3}{8}\left(\frac{5}{\pi}\right)^{\frac{1}{2}}[(7z^2 - r^2)(x^2 - y^2)/r^4]$$

$$Z^c_{43} = \frac{3}{8}\left(\frac{70}{\pi}\right)^{\frac{1}{2}}[z(x^3 - 3xy^2)/r^4]$$

$$Z^s_{43} = \frac{3}{8}\left(\frac{70}{\pi}\right)^{\frac{1}{2}}[z(3x^2y - y^3)/r^4]$$

$$Z^c_{44} = \frac{3}{16}\left(\frac{35}{\pi}\right)^{\frac{1}{2}}[(x^4 - 6x^2y^2 + y^4)/r^4]$$

$$Z^s_{44} = \frac{3}{16}\left(\frac{35}{\pi}\right)^{\frac{1}{2}}[4(x^3y - y^3x)/r^4]$$

$$Z_{60} = \frac{1}{32}\left(\frac{13}{\pi}\right)^{\frac{1}{2}}[(231z^6 - 315z^4r^2 + 105z^2r^4 - 5r^6)/r^6]$$

$$Z^c_{62} = \frac{1}{64}\left(\frac{2730}{\pi}\right)^{\frac{1}{2}}[(16z^4 - 16(x^2 + y^2)z^2 + (x^2 + y^2)^2)(x^2 - y^2)/r^6]$$

$$Z^c_{63} = \frac{1}{32}\left(\frac{2730}{\pi}\right)^{\frac{1}{2}}[(11z^3 - 3zr^2)(x^3 - 3xy^2)/r^6]$$

$$Z^c_{64} = \frac{21}{32}\left(\frac{13}{7\pi}\right)^{\frac{1}{2}}[(11z^2 - r^2)(x^4 - 6x^2y^2 + y^4)/r^6]$$

$$Z^c_{66} = \frac{231}{64}\left(\frac{26}{231\pi}\right)^{\frac{1}{2}}[(x^6 - 15x^4y^2 + 15x^2y^4 - y^6)/r^6]$$

[a] If required in polar coordinates, they can be found from Table III and Eq. (2.4).

An alternative way of expressing V is to write it directly in spherical harmonics, using the form of the spherical harmonic addition theorem in Eq. (2.1). Dropping the i's,

$$V(r,\theta,\phi) = \sum_j \frac{q_j}{|(\mathbf{R}_j - \mathbf{r})|}$$

$$= \sum_j q_j \sum_n \frac{r^n}{R_j^{(n+1)}} \frac{4\pi}{(2n+1)} \sum_{m=-n}^{n} (-1)^m Y_n^{-m}(\theta_j,\phi_j) Y_n^m(\theta,\phi).$$

Therefore,

$$V(r,\theta,\phi) = \sum_n \sum_{m=-n}^{n} r^n \gamma'_{nm} Y_n^m(\theta,\phi), \tag{2.8}$$

where

$$\gamma'_{nm} = \sum_j \frac{4\pi}{(2n+1)} \frac{q_j}{R_j^{(n+1)}} (-1)^m Y_n^{-m}(\theta_j,\phi_j).$$

To illustrate the use of Eq. (2.7) let us once again determine the potential due to a cubic crystalline environment, using polar coordinates. We shall see that in this case we really require only the following tesseral harmonics:

$$Z_{00} = \frac{1}{2\sqrt{\pi}}; \qquad Z_{40} = \frac{3}{16\sqrt{\pi}}(35\cos^4\theta - 30\cos^2\theta + 3)$$

$$Z_{60} = \frac{1}{32}\left(\frac{13}{\pi}\right)^{\frac{1}{2}}(231\cos^6\theta - 315\cos^4\theta + 105\cos^2\theta - 5)$$

$$\tag{2.9}$$

$$Z^c_{44} = \frac{3}{16}\left(\frac{35}{\pi}\right)^{\frac{1}{2}}\sin^4\theta\cos 4\phi$$

$$Z^c_{64} = \frac{3}{32}\left(\frac{91}{\pi}\right)^{\frac{1}{2}}(11\cos^2\theta - 1)\sin^4\theta\cos 4\phi$$

$= \frac{21}{32}\left(\frac{13}{7\pi}\right)^{\frac{1}{2}}$

We shall first consider the case of octahedral symmetry.

a. Sixfold Cubic Coordination

The surrounding ions are at positions (r,θ,ϕ) of $(a, 0, 0)$; $(a, \pi, 0)$; $(a, \pi/2, 0)$; $(a, \pi/2, \pi)$; $(a, \pi/2, \pi/2)$; and $(a, \pi/2, 3\pi/2)$. Only the angular coordinates vary from ion to ion. We must consider the contribution to terms $Z_{n\alpha}$, for all n and m, up to $n = 6$ (see Section 4a).

From the definitions of the $Z_{n\alpha}$, we see that all γ^s_{nm} with $m = 2, 4,$ and 6, will be zero because $\sin m\phi = 0$ for each charge; and considering each other $\gamma_{n\alpha}$ in turn, it can easily be seen that most of them are equal to zero. For example,

$$Z^c_{31} = \frac{1}{8}\left(\frac{42}{\pi}\right)^{\frac{1}{2}}(5\cos^2\theta - 1)\sin\theta\cos\phi,$$

and therefore

$$\gamma^c_{31} = q\frac{1}{8}\left(\frac{42}{\pi}\right)^{\frac{1}{2}}\cdot\frac{4\pi}{7}\cdot\frac{1}{a^4}$$

$$\times[0 + 0 + (-1)\cdot 1\cdot 1 + (-1)\cdot 1\cdot(-1) + 0 + 0] = 0$$

The only nonvanishing terms are found to be γ_{00}, γ_{40}, γ_{60}, γ^c_{44}, and γ^c_{64}. That is, there are only fourth- and sixth-degree terms, besides γ_{00}. Using Eqs. (2.7) and (2.9), the contribution to these terms is

$$\gamma_{00} = \frac{12\sqrt{\pi}}{a}q$$

$$\gamma_{40} = \frac{3}{16\sqrt{\pi}}[2\cdot(35 - 30 + 3) + 4\cdot 3]\cdot\frac{4\pi}{9}\cdot\frac{q}{a^5} = \frac{7\sqrt{\pi}}{3}\frac{q}{a^5}$$

$$\gamma_{60} = \frac{1}{32}\left(\frac{13}{\pi}\right)^{\frac{1}{2}}[2\cdot(231 - 315 + 105 - 5) - 4\cdot 5]\cdot\frac{4\pi}{13}\frac{q}{a^7} = \frac{3}{2}\left(\frac{\pi}{13}\right)^{\frac{1}{2}}\frac{q}{a^7}$$

$$\gamma^c_{44} = \frac{3}{16}\left(\frac{35}{\pi}\right)^{\frac{1}{2}}[0 + 0 + 1\cdot 1 + 1\cdot 1 + 1\cdot 1 + 1\cdot 1]\cdot\frac{4\pi}{9}\cdot\frac{q}{a^5} = \frac{(35\pi)^{\frac{1}{2}}}{3}\frac{q}{a^5}$$

$$\gamma^c_{64} = \frac{3}{32}\left(\frac{91}{\pi}\right)^{\frac{1}{2}}[2\cdot(11 - 1)\cdot 0 + (-1)\cdot 1\cdot 1 + (-1)\cdot 1\cdot 1 + (-1)\cdot 1\cdot 1$$

$$+ (-1)\cdot 1\cdot 1]\cdot\frac{4\pi}{13}\cdot\frac{q}{a^7} = -\frac{3}{2}\left(\frac{7\pi}{13}\right)^{\frac{1}{2}}\frac{q}{a^7}.$$

Neglecting the Y_0^0 term, which will only affect the zero of energy, we substitute these values in

$$V(r,\theta,\phi) = r^4\gamma_{40}Y_4^0 + r^4(\gamma^c_{44}/\sqrt{2})(Y_4^4 + Y_4^{-4}) + r^6\gamma_{60}Y_6^0$$

$$+ r^6(\gamma^c_{64}/\sqrt{2})(Y_6^4 + Y_6^{-4}), \tag{2.10}$$

and following the notation of Bleaney and Stevens,[9] page 129 (for the fourth-degree terms only), we have

$$V(r, \theta, \phi) = D_4^\dagger[Y_4^0 + (5/14)^{\frac{1}{2}}(Y_4^4 + Y_4^{-4})] + D_6^\dagger[Y_6^0 - (7/2)^{\frac{1}{2}}(Y_6^4 + Y_6^{-4})], \quad (2.11)$$

where

$$D_4^\dagger = \frac{7\sqrt{\pi}}{3}\frac{q}{a^5}r^4, \quad \text{and} \quad D_6^\dagger = \frac{3}{2}\left(\frac{\pi}{13}\right)^{\frac{1}{2}}\frac{q}{a^7}r^6.$$

b. Eightfold Cubic Coordination

Here all the ions are at the same distance $d = \sqrt{3}a$, and again only the angular coordinates differ for each ion. We have charges at $(d, \theta_1, \pi/4)$; $(d, \theta_1, 3\pi/4)$; $(d, \theta_1, 5\pi/4)$; $(d, \theta_1, 7\pi/4)$; $(d, (\pi - \theta_1), \pi/4)$; $(d, (\pi - \theta_1), 3\pi/4)$; $(d, (\pi - \theta_1), 5\pi/4)$; and $(d, (\pi - \theta_1), 7\pi/4)$, where $\theta_1 = \tan^{-1}\sqrt{2}$.

We can see immediately that there will be no contribution to γ^s_{nm} when $m = 4$, or to γ^c_{nm} when $m = 2$ or 6, as $\sin m\phi$ and $\cos m\phi$ vanish in respective cases for each ion. On summing over the coordinates of all eight ions we can easily see that once again we are left with contributions to only γ_{00}, γ_{40}, γ_{60}, γ^c_{44}, and γ^c_{64}.

Substituting θ and ϕ for each ion in these terms and summing, we find that:

$\gamma_{00} = (16\sqrt{\pi}/d)q$ (this is the coefficient of $Y_0^0 = 1/(2\sqrt{\pi})$, and contributes $8q/d$ to the potential, but affects only the zero of energy);

$$\gamma_{40} = -\frac{56}{27}\sqrt{\pi}\cdot\frac{q}{d^5}; \quad \gamma_{60} = \frac{32}{9}\left(\frac{\pi}{13}\right)^{\frac{1}{2}}\cdot\frac{q}{d^7};$$

$$\gamma^c_{44} = -\frac{8(35\pi)^{\frac{1}{2}}}{27}\cdot\frac{q}{d^5}; \quad \gamma^c_{64} = -\frac{32}{9}\left(\frac{7\pi}{13}\right)^{\frac{1}{2}}\cdot\frac{q}{d^7}.$$

Substituting these values in Eq. (2.10) and writing the potential in the same form as Eq. (2.11), we have

$$V(r, \theta, \phi) = D_4^\dagger[Y_4^0 + (5/14)^{\frac{1}{2}}(Y_4^4 + Y_4^{-4})] + D_6^\dagger[Y_6^0 - (7/2)^{\frac{1}{2}}(Y_6^4 + Y_6^{-4})], \quad (2.12)$$

where

$$D_4^\dagger = -\frac{56}{27}\sqrt{\pi}\frac{qr^4}{d^5}, \quad \text{and} \quad D_6^\dagger = \frac{32}{9}\left(\frac{\pi}{13}\right)^{\frac{1}{2}}\frac{qr^6}{d^7}.$$

[9] B. Bleaney and K. W. H. Stevens, *Repl. Progr. Phys.* **16**, 108 (1953).

c. Fourfold Cubic Coordination

If we choose the axes as in Section 1.(c), then by similar symmetry arguments we see that the even-degree terms in the potential are just half those due to the full cube (eightfold coordination).

d. Summary: Cubic Potential in Spherical Harmonics

To summarize, we have for the potential energy W_c of a charge q' at (r, θ, ϕ) in the potential due to charges q, at distances d from the origin $(d > r)$, and arranged with the three coordinations and axes chosen as in Figs. 1 and 2:

$$W_c = D_4'\{Y_4^0(\theta,\phi) + (5/14)^{\frac{1}{2}}[Y_4^4(\theta,\phi) + Y_4^{-4}(\theta,\phi)]\} + D_6'\{Y_6^0(\theta,\phi) - (7/2)^{\frac{1}{2}}[Y_6^4(\theta,\phi) + Y_6^{-4}(\theta,\phi)]\} \quad (2.13)$$

where D_4' and D_6' are given in Table V.

TABLE V. COEFFICIENTS D_4' AND D_6' (EQ. 2.13) FOR THE THREE COORDINATIONS

	D_4'	D_6'
Eightfold coordination	$-\frac{56}{27}(\pi)^{\frac{1}{2}}\frac{qq'r^4}{d^5}$	$+\frac{32}{9}\left(\frac{\pi}{13}\right)^{\frac{1}{2}}\frac{qq'r^6}{d^7}$
Sixfold coordination	$+\frac{7}{3}(\pi)^{\frac{1}{2}}\frac{qq'r^4}{d^5}$	$+\frac{3}{2}\left(\frac{\pi}{13}\right)^{\frac{1}{2}}\frac{qq'r^6}{d^7}$
Fourfold coordination	$-\frac{28}{27}(\pi)^{\frac{1}{2}}\frac{qq'r^4}{d^5}$	$+\frac{16}{9}\left(\frac{\pi}{13}\right)^{\frac{1}{2}}\frac{qq'r^6}{d^7}$

This potential energy, written in a slightly different form, is given by Low,[4] page 13 (with $q' = +e$, $q = +Ze$; there is an error in sign of his coefficient of $(Y_6^4 + Y_6^{-4})$, in the fourfold and eightfold coordination expressions).

e. Cubic Potential Expressed with Respect to Other Choices of Axes

The cubic potential is sometimes required referred to axes other than the fourfold axes considered above, in particular when the polar axis z is a twofold or threefold axis of symmetry. The results for these cases, found using the formulae and procedure discussed so far in Section 2, are summarized below.

The potential energy of a charge q' at (r, θ, ϕ), in the potential due to charges q arranged in the three coordinations at distances d from the origin $(d > r)$, and with the z and x axes chosen to be twofold axes of symmetry and the y axis a fourfold axis, is given by

$$W_c = D_4'^{(2)} \Big\{ Y_4^0(\theta, \phi) - (10)^{1/2}[Y_4^2(\theta, \phi) + Y_4^{-2}(\theta, \phi)] - \frac{3}{7}\left(\frac{35}{2}\right)^{1/2} [Y_4^4(\theta, \phi) + Y_4^{-4}(\theta, \phi)] \Big\} + D_6'^{(2)} \Big\{ Y_6^0(\theta, \phi) + \frac{(105)^{1/2}}{26} [Y_6^2(\theta, \phi) + Y_6^{-2}(\theta, \phi)] - \frac{5}{13}\left(\frac{7}{2}\right)^{1/2} [Y_6^4(\theta, \phi) + Y_6^{-4}(\theta, \phi)] + \frac{(231)^{1/2}}{26} [Y_6^6(\theta, \phi) + Y_6^{-6}(\theta, \phi)] \Big\}. \quad (2.14)$$

where $D_4'^{(2)} = (-1/4)D_4'$ and $D_6'^{(2)} = (-13/8)D_6'$; D_4' and D_6' are the constants in the fourfold-axes potential energy, listed in Table V for the three coordinations.

The potential energy of a charge q' at (r, θ, ϕ), in the potential due to charges q arranged in the three coordinations at distances d from the origin $(d > r)$ and with the polar z axis an axis of threefold symmetry, may be expressed in a concise form if the x axis is chosen consistently. For the sixfold coordination, if we take Oz to lie in the [111] direction referred to axes XYZ of Fig. 1, then we take Ox to lie in the plane zOZ such that $\angle xOZ$ is acute. For the four- and eightfold coordination, if we take Oz to lie along, say, OA in Fig. 2, then we take Ox to lie in the plane AOF such that $\angle xOF$ is acute. The potential energy is then given by

$$W_c = D_4'^{(3)} \Big\{ Y_4^0(\theta, \phi) - \left(\frac{10}{7}\right)^{1/2} [Y_4^{-3}(\theta, \phi) - Y_4^3(\theta, \phi)] \Big\} + D_6'^{(3)} \Big\{ Y_6^0(\theta, \phi) + \frac{1}{12}\left(\frac{105}{2}\right)^{1/2} [Y_6^{-3}(\theta, \phi) - Y_6^3(\theta, \phi)] + \frac{1}{24} (231)^{1/2}[Y_6^{-6}(\theta, \phi) + Y_6^6(\theta, \phi)] \Big\} \quad (2.15)$$

where $D_4'^{(3)} = (-2/3)D_4'$ and $D_6'^{(3)} = (16/9)D_6'$; D_4' and D_6' are the constants in the fourfold-axes potential energy, listed in Table V for the three coordinations.

3. Number of Harmonics Occurring in the Expression for the Potential

We have seen above that the coefficients of most of the tesseral harmonics in the expansion of the potential are zero in the cases considered.

In general the potential function must reflect the point symmetry of the lattice site in question; that is, it must be invariant under the operations of the point group. The less symmetric the site, the more potential terms occur in the expansion. Prather,[6] page 10, lists the nonvanishing γ's for different point groups. It must be noted that the terms occurring depend very much on the axes chosen, and are in their simplest form when the axes are the symmetry axes of the point group, as was the case in our examples.

There are two general rules which may be mentioned at this point. Firstly, if there is a center of inversion at the ion site considered there will be no odd-n terms in the potential; and secondly, if the z axis is an m-fold axis of symmetry, the potential will contain terms Z_{nm}. For some high symmetry cases there exist relations between the coefficients of the tesseral harmonics of the same n occurring in the potential as we have already seen for the case of cubic fields.

It must be noted that not all the nonzero terms in the expansion of the potential will affect the energy levels of the magnetic ion, as their matrix elements may yet be zero.

As an example of the terms occurring in the expression for the crystalline potential, and giving nonzero matrix elements in general, we list below the terms up to $n = 6$ (see Section 4.a) for a few common point groups. (The V_n^m are defined in Section 5.a).

C_{3h}	(ethyl sulfates; some rare-earth trichlorides)	V_2^0, V_4^0, V_6^0, V_6^6, (V_6^{-6})
C_{3v}	(double nitrates)	V_2^0, V_4^0, V_4^3, V_6^0, V_6^3, V_6^6
Cubic	(CaF_2, ThO_2, etc.)	V_4^0, V_4^4, V_6^0, V_6^4
Cubic	(fluosilicates[10])	V_4^0, V_4^3, V_6^0, V_6^3, V_6^6
D_2	(garnets, rare-earth site)	V_2^0, V_2^2, V_4^0, V_4^2, V_4^4, V_6^0, V_6^2, V_6^4, V_6^6

III. Calculation of the Matrix Elements of the Crystalline Potential Perturbing Hamiltonian

We must now evaluate the matrix elements of the perturbing Hamiltonian between free-ion states. The matrix thus formed can then be diagonalized to find the energy levels and eigenfunctions of the ion in the crystalline field. If the classical potential energy of the magnetic ion in the crystalline electric field is, as in Eq. (II.2),

$$W_c = \sum_i q_i V(x_i, y_i, z_i),$$

[10] The six H_2O complex are usually treated as being octahedrally coordinated to first order in these hydrated salts.

the crystal-field perturbing Hamiltonian operator, $\mathcal{H}_c$, will be formed from this by applying the usual rules, $x \to x_{op}$, $y \to y_{op}$, etc. That is, the Hamiltonian operator will simply be the classical potential energy

$$\mathcal{H}_c = W_c = -|e| \sum_i V(x_i, y_i, z_i), \tag{III.1}$$

where we have put $q_i = -|e|$, and the summation is over the magnetic electrons. The free-ion wave functions used will depend on the relative size of W_c to the intraionic interaction energies. For example, to a first approximation for the 3d transition-group ions in ionic compounds, they will be characterized by $|L, S, L_z, S_z\rangle$, as W_c is larger than the spin-orbit coupling; and in the 4f rare-earth group by $|L, S, J, J_z\rangle$, as the spin-orbit coupling is generally larger than W_c. In order to calculate the matrix elements we may use one of two methods which are described briefly in Sections 4 and 5.

4. Direct Integration

This is the fundamental method and is clearly described in Bleaney and Stevens,[9] page 129. The free-ion wave functions are expanded into determinental product states involving single-electron wave functions ϕ_i on which the corresponding terms $V(x_i, y_i, z_i)$ in $\mathcal{H}_c$ act. The matrix elements, expressed in polar coordinates, therefore, reduce the sums of terms of the form

$$\int \phi^*(r_i, \theta_i, \phi_i) r^n Y_n^m(r_i, \theta_i, \phi_i) \phi(r_i, \theta_i, \phi_i)\, d\tau.$$

As the radial part of the wave function $f(r)$ is never accurately known, the radial integral, which separates out, is often taken as a parameter

$$\langle r^n \rangle = \int [f(r)]^2 r^n r^2\, dr$$

There have been several theoretical calculations of $\langle r^n \rangle$ (for example, for rare-earth ions, see Freeman and Watson[11]).

If $V(x_i, y_i, z_i)$ is written in terms of spherical harmonics, the matrix elements and several quite general rules can be found from their expansion, using vector coupling coefficients (see Edmonds,[12] page 37), and orthogonality properties. These rules have been discussed fully by Bleaney and Stevens,[9] pages 128 and 130 and will now be summarized. (More generally they follow from the Wigner–Eckart theorem, see Edmonds,[12] page 75, for example.)

[11] A. J. Freeman and R. E. Watson, *Phys. Rev.* **127**, 2058 (1962).
[12] A. R. Edmonds, "Angular Momentum in Quantum Mechanics." Princeton Univ. Press, Princeton, New Jersey, 1957.

a. *Rules Limiting the Number of Nonzero Matrix Elements*

We have seen in Section 3 that the symmetry of the crystalline electric field limits the number of terms occurring in the expansion of the potential. The rules listed below indicate which of these give nonzero matrix elements:

(i) All terms of $n > 2l$, where l is the orbital quantum number of the single magnetic electrons, vanish. Thus we need only consider the expansion of the crystalline potential up to fourth degree for the 3d-group ions and sixth degree for the 4f-group ions. Or if we use the operator equivalents method (Section 5), terms for which $n > 2L$ or $n > 2J$, vanish; where, for example, L and J are the coupled angular momentum for the 3d-group or 4f-group ions, respectively.

(ii) Operators of the form Z_{nm} have zero matrix elements between two states $\phi_{l'}$ and $\phi_{l''}$, unless $l' + l'' + n =$ even number. This means that within a given configuration, i.e., given l, the matrix elements of odd-n terms vanish, but that they may couple different configurations.

(iii) Operators of the form Z_{nm} have zero matrix elements between two states $\phi_{l'}^{m'}$ and $\phi_{l''}^{m''}$, unless $m = |m' - m''|$. In the coupled system, for example, this will mean that terms Z_{nm} link states of ΔJ_z (or ΔL_z) $= m$.

A very useful check on all calculations may be made using the fact that the number and types of the resulting energy levels can be found by group theoretical methods, but the eigenvalues and eigenfunctions cannot be found without full calculation in most cases.

There is a very important general theorem, dealing with the energy levels of magnetic ions in a crystalline environment, which might be mentioned here. Kramers theorem[13] states that the energy levels of odd-electron ions under electrostatic interaction of any nature are at least twofold and evenly degenerate. A consequence of this theorem is that the matrices of $\mathcal{H}_c$ between states of an odd-electron ion always factorize into at least two similar matrices. (When Kramer's theorem does not apply, Jahn and Teller[14] have shown that the surroundings of a magnetic ion will distort and always tend to give nondegenerate energy levels. Thus, even-electron ions tend to have singlet energy levels in crystals.)

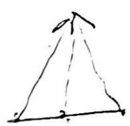
5. Use of Stevens' "Operator Equivalents" Method

This is by far the most convenient method, within its limitations, for evaluating the matrix elements of the crystalline potential between coupled

[13] H. A. Kramers, *Koninki. Ned. Akad. Wetenschap., Proc.* **B33**, 959 (1930).
[14] H. A. Jahn and E. Teller, *Proc. Roy. Soc.* **A161**, 220 (1937).

wave functions specified by one particular value of angular momentum J, (or L), and will be that used in all further discussions here. It eliminates the need to go back to single-electron wave functions each time by the use of an "operator equivalent" to $\mathcal{H}_c$ consisting of angular momentum operators which act on the angular part of the wave function in the coupled system; this is really an application of the Wigner–Eckart theorem (see Edmonds,[12] page 73, for example). The method is described fully by Stevens,[15] and Bleaney and Stevens,[9] page 131. The rules for determining the operator equivalent to the Cartesian Hamiltonian, given by Eq. (III.1), $\mathcal{H}_c = -\sum_i |e| V(x_i, y_i, z_i)$, are given by Stevens.[15] If $f(x, y, z)$ is a Cartesian function of given degree, then to find the operator equivalent to such terms as $\sum_i f(x_i, y_i, z_i)$ occurring in $\mathcal{H}_c$, one replaces, x, y, and z by J_x, J_y, and J_z, respectively, always allowing for the noncommutation of J_x, J_y, and J_z. This is done by replacing products of x, y, and z by an expression consisting of all the possible different combinations of J_x, J_y, and J_z, divided by the total number of combinations. In this way an operator is formed with the same transformation properties under rotation as the potential. It must be noted that although it is conventional to use J or L in the equivalent operator, when evaluating its matrix elements all factors $\hbar$ are dropped.

Some simple examples are



$$\sum_i (3z_i^2 - r_i^2) \equiv \alpha_J \langle r^2 \rangle [3J_z^2 - J(J+1)] = \alpha_J \langle r^2 \rangle O_2^0$$

$$\sum_i (x_i^2 - y_i^2) \equiv \alpha_J \langle r^2 \rangle [J_x^2 - J_y^2] = \alpha_J \langle r^2 \rangle O_2^2$$

$$\sum_i x_i y_i \equiv \alpha_J \langle r^2 \rangle [(J_x J_y + J_y J_x)/2]$$

$$\sum_i (x_i^4 - 6x_i^2 y_i^2 + y_i^4) = \sum_i \{[(x_i + iy_i)^4 + (x_i - iy_i)^4]/2\}$$

$$\equiv \beta_J \langle r^4 \rangle \tfrac{1}{2}[J_+^4 + J_-^4] = \beta_J \langle r^4 \rangle O_4^4 \qquad (5.1)$$

where $J_\pm = J_x \pm iJ_y$.

When the noncommutation effects cannot be immediately taken account of, the determination is more tedious, and will be illustrated in Section 6a.

We therefore have, for example, that the matrix elements of the sum $\sum_i (3z_i^2 - r_i^2)$ between coupled states $|LSJJ_z\rangle$ are equal to those of $\alpha_J \langle r^2 \rangle O_2^0$ between the angular part of the coupled wave functions; i.e.,

$$\langle LSJJ_z' | \sum_i (3z_i^2 - r_i^2) | LSJJ_z \rangle$$

$$\equiv \alpha_J \langle r^2 \rangle \langle LSJJ_z' | [3J_z^2 - J(J+1)] | LSJJ_z \rangle.$$

[15] K. W. H. Stevens, *Proc. Phys. Soc.* (*London*) **A65**, 209 (1952).

The multiplicative factor α_J is a numerical constant depending on l (the orbital quantum number of the electrons in the unfilled shell), n' (the number of them), and J (or L and S). The constant is denoted by β_J for fourth-degree terms, and γ_J for sixth-degree terms. These constants are originally determined by returning to the direct integration method of finding the matrix elements between single-electron wave functions in a specific case. This method of determination is clearly described in Stevens,[15] page 211 and Heine,[16] page 151. (An alternative method is given by Elliott *et al.*,[17] page 518, using fractional parentage coefficients.) Although Stevens' paper relates mainly to matrix elements of rare-earth ions' states characterized by $|LSJJ_z\rangle$, it can be used for d-electron ions, or between states characterized by $|LSL_zS_z\rangle$, provided the correct numerical factors are used; in these cases the operator $\mathbf{J}$ above is replaced by $\mathbf{L}$. The multiplicative factors for rare-earth ions are listed in Table VI; for 3d-group ions (or for matrix elements between states characterized by L and S) they can be found from the general formula of Bleaney and Stevens,[9] page 132, given in Table VII.

To illustrate the method in general we shall again consider the crystalline electric field Hamiltonian given by Eq. (III.1),

$$\mathcal{H}_c = -|e| \sum_i V(x_i, y_i, z_i).$$

If the electrostatic potential $V(x, y, z)$ is determined from a point-charge model as in Section 2, with the tesseral harmonics expressed in Cartesian coordinates, we have,

$$V(x, y, z) = \sum_{n\alpha} r^n \gamma_{n\alpha} Z_{n\alpha}(x, y, z).$$

In order to make full use of operator equivalents whose matrix elements have been tabulated, we define Cartesian functions $f_{n\alpha}(x, y, z)$ which are related to the $Z_{n\alpha}(x, y, z)$ by $Z_{n\alpha} = (\text{const})\, f_{n\alpha}/r^n$. For the Z^c_{nm} listed in Table IV, the f^c_{nm}/r^n are the functions in square brackets. It is these functions $f_{n\alpha}(x, y, z)$, (or rather $f^c_{nm}(x, y, z)$), so defined, which are directly related to the most commonly used operator equivalents O_n^m by the relation that the operator

$$\sum_i f^c_{nm}(x_i, y_i, z_i) \equiv \theta_n \langle r^n \rangle O_n^m, \qquad (5.2)$$

where θ_n is the multiplicative factor; $\theta_2 = \alpha_J$; $\theta_4 = \beta_J$; $\theta_6 = \gamma_J$.

Some common O_n^m are listed in Table VIII. The matrix elements of

[16] V. Heine, "Group Theory in Quantum Mechanics," p. 151. Pergamon Press, New York, 1960.

[17] J. P. Elliott, B. R. Judd, and W. A. Runciman, *Proc. Roy. Soc.* **A240**, 509 (1957).

ver artigo Physical Review B V19, p. 5475 (1979)

TABLE VI. STEVENS' MULTIPLICATIVE FACTORS FOR RARE-EARTH IONS[a]

	Ce^{3+} $4f^1\,{}^2F_{5/2}$	Pr^{3+} $4f^2\,{}^3H_4$	Nd^{3+} $4f^3\,{}^4I_{9/2}$	Pm^{3+} $4f^4\,{}^5I_4$	Sm^{3+} $4f^5\,{}^6H_{5/2}$	Tb^{3+} $4f^8\,{}^7F_6$
$g_J = \langle J \Vert \Lambda \Vert J \rangle$	$\frac{6}{7}$	$\frac{4}{5}$	$\frac{8}{11}$	$\frac{3}{5}$	$\frac{2}{7}$	$\frac{3}{2}$
$\alpha_J = \langle J \Vert \alpha \Vert J \rangle$	$\frac{-2}{5\cdot7}$	$\frac{-2^2\cdot13}{3^2\cdot5^2\cdot11}$	$\frac{-7}{3^2\cdot11^2}$	$\frac{2\cdot7}{3\cdot5\cdot11^2}$	$\frac{13}{3^2\cdot5\cdot7}$	$\frac{-1}{3^2\cdot11}$
$\beta_J = \langle J \Vert \beta \Vert J \rangle$	$\frac{2}{3^2\cdot5\cdot7}$	$\frac{-2^2}{3^2\cdot5\cdot11^2}$	$\frac{-2^3\cdot17}{3^3\cdot11^3\cdot13}$	$\frac{2^3\cdot7\cdot17}{3^3\cdot5\cdot11^3\cdot13}$	$\frac{2\cdot13}{3^3\cdot5\cdot7\cdot11}$	$\frac{2}{3^3\cdot5\cdot11^2}$
$\gamma_J = \langle J \Vert \gamma \Vert J \rangle$	0	$\frac{2^4\cdot17}{3^4\cdot5\cdot7\cdot11^2\cdot13}$	$\frac{-5\cdot17\cdot19}{3^3\cdot7\cdot11^3\cdot13^2}$	$\frac{2^3\cdot17\cdot19}{3^3\cdot7\cdot11^2\cdot13^2}$	0	$\frac{-1}{3^4\cdot7\cdot11^2\cdot13}$

	Dy^{3+} $4f^9\,{}^6H_{15/2}$	Ho^{3+} $4f^{10}\,{}^5I_8$	Er^{3+} $4f^{11}\,{}^4I_{15/2}$	Tm^{3+} $4f^{12}\,{}^3H_6$	Yb^{3+} $4f^{13}\,{}^2F_{7/2}$
$g_J = \langle J \Vert \Lambda \Vert J \rangle$	$\frac{4}{3}$	$\frac{5}{4}$	$\frac{6}{5}$	$\frac{7}{6}$	$\frac{8}{7}$
$\alpha_J = \langle J \Vert \alpha \Vert J \rangle$	$\frac{-2}{3^2\cdot5\cdot7}$	$\frac{-1}{2\cdot3^2\cdot5^2}$	$\frac{2^2}{3^2\cdot5^2\cdot7}$	$\frac{1}{3^2\cdot11}$	$\frac{2}{3^2\cdot7}$
$\beta_J = \langle J \Vert \beta \Vert J \rangle$	$\frac{-2^3}{3^3\cdot5\cdot7\cdot11\cdot13}$	$\frac{-1}{2\cdot3\cdot5\cdot7\cdot11\cdot13}$	$\frac{2}{3^2\cdot5\cdot7\cdot11\cdot13}$	$\frac{2^3}{3^4\cdot5\cdot11^2}$	$\frac{-2}{3\cdot5\cdot7\cdot11}$
$\gamma_J = \langle J \Vert \gamma \Vert J \rangle$	$\frac{2^2}{3^3\cdot7\cdot11^2\cdot13^2}$	$\frac{-5}{3^3\cdot7\cdot11^2\cdot13^2}$	$\frac{2^3}{3^3\cdot7\cdot11^2\cdot13^2}$	$\frac{-5}{3^4\cdot7\cdot11^2\cdot13}$	$\frac{2^2}{3^3\cdot7\cdot11\cdot13}$

[a] After R. J. Elliott and K. W. H. Stevens, *Proc. Roy. Soc.* **A218**, 553 (1953).

TABLE VII. STEVENS' MULTIPLICATIVE FACTORS FOR 3d-GROUP IONS, AND GENERAL FORMULAS[a]

$$\alpha = -\frac{2}{21}, \quad \beta = \frac{2}{63} \quad \text{for} \begin{cases} 3d^1\,{}^2D \\ 3d^6\,{}^5D \end{cases} \qquad \alpha = \frac{2}{21}, \quad \beta = -\frac{2}{63} \quad \text{for} \begin{cases} 3d^4\,{}^5D \\ 3d^9\,{}^2D \end{cases}$$

$$\alpha = -\frac{2}{105}, \quad \beta = -\frac{2}{315} \quad \text{for} \begin{cases} 3d^2\,{}^3F \\ 3d^7\,{}^4F \end{cases} \qquad \alpha = \frac{2}{105}, \quad \beta = \frac{2}{315} \quad \text{for} \begin{cases} 3d^3\,{}^4F \\ 3d^8\,{}^3F \end{cases}$$

In general,
$$\alpha = \mp\frac{2(2l+1-4S)}{(2l-1)(2l+3)(2L-1)}$$

$$\beta = \mp\frac{3(2l+1-4S)[-7(l-2S)(l-2S+1)+3(l-1)(l+2)]}{(2l-3)(2l-1)(2l+3)(2l+5)(L-1)(2L-1)(2L-3)}$$

where a minus sign is used in the first half of the shell and a plus sign is used in the second half of the shell.

[a] After B. Bleaney and K. W. H. Stevens, *Repl. Progr. Phys.* **16**, 108 (1953).

TABLE VIII. LIST OF OPERATOR EQUIVALENTS TO SOME COMMONLY OCCURRING FUNCTIONS WITHIN A MANIFOLD OF GIVEN J, THE SUMMATION BEING OVER THE COORDINATES OF THE MAGNETIC ELECTRONS[a]

$\sum f_{na}$	Stevens' operator equivalent	Standard notation
$\sum(3z^2 - r^2)$	$\equiv \alpha_J \langle r^2\rangle[3J_z^2 - J(J+1)]$	$= \alpha_J\langle r^2\rangle O_2^0$
$\sum(x^2 - y^2)$	$\equiv \alpha_J \langle r^2\rangle \frac{1}{2}[J_+^2 + J_-^2]$	$= \alpha_J\langle r^2\rangle O_2^2$
$\sum(35z^4 - 30r^2z^2 + 3r^4)$	$\equiv \beta_J\langle r^4\rangle[35J_z^4 - 30J(J+1)J_z^2 + 25J_z^2$ $-6J(J+1) + 3J^2(J+1)^2]$	$= \beta_J\langle r^4\rangle O_4^0$
$\sum(7z^2 - r^2)(x^2 - y^2)$	$\equiv \beta_J\langle r^4\rangle\frac{1}{4}[(7J_z^2 - J(J+1) - 5)(J_+^2 + J_-^2)$ $+ (J_+^2 + J_-^2)(7J_z^2 - J(J+1) - 5)]$	$= \beta_J\langle r^4\rangle O_4^2$
$\sum z(x^3 - 3xy^2)$	$\equiv \beta_J\langle r^4\rangle\frac{1}{4}[J_z(J_+^3 + J_-^3) + (J_+^3 + J_-^3)J_z]$	$= \beta_J\langle r^4\rangle O_4^3$
$\sum z(3x^2y - y^3)$	$\equiv -i\beta_J\langle r^4\rangle\frac{1}{4}[J_z(J_+^3 - J_-^3) + (J_+^3 - J_-^3)J_z]$	$= \beta_J\langle r^4\rangle O_4^3(s)$[b]
$\sum(x^4 - 6x^2y^2 + y^4)$	$\equiv \beta_J\langle r^4\rangle\frac{1}{2}[J_+^4 + J_-^4]$	$= \beta_J\langle r^4\rangle O_4^4$
$\sum 4(x^3y - xy^3)$	$\equiv -i\beta_J\langle r^4\rangle\frac{1}{2}[J_+^4 - J_-^4]$	$= \beta_J\langle r^4\rangle O_4^4(s)$[b]
$\sum(231z^6 - 315z^4r^2 + 105z^2r^4 - 5r^6)$	$\equiv \gamma_J\langle r^6\rangle[231J_z^6 - 315J(J+1)J_z^4 + 735J_z^4$ $+ 105J^2(J+1)^2J_z^2 - 525J(J+1)J_z^2 + 294J_z^2$ $- 5J^3(J+1)^3 + 40J^2(J+1)^2 - 60J(J+1)]$	$= \gamma_J\langle r^6\rangle O_6^0$
$\sum\{16z^4 - 16(x^2 + y^2)z^2 + (x^2 + y^2)^2\}(x^2 - y^2)$	$\equiv \gamma_J\langle r^6\rangle\frac{1}{4}\{[33J_z^4 - (18J(J+1) + 123)J_z^2$ $+ J^2(J+1)^2 + 10J(J+1) + 102](J_+^2 + J_-^2)$ $+ (J_+^2 + J_-^2)[33J_z^4 - \text{etc.}]\}$	$= \gamma_J\langle r^6\rangle O_6^2$
$\sum(11z^3 - 3zr^2)(x^3 - 3xy^2)$	$\equiv \gamma_J\langle r^6\rangle\frac{1}{4}[(11J_z^3 - 3J(J+1)J_z - 59J_z)$ $\times (J_+^3 + J_-^3) + (J_+^3 + J_-^3)(11J_z^3 - 3J(J+1)J_z$ $- 59J_z)]$	$= \gamma_J\langle r^6\rangle O_6^3$
$\sum(11z^2 - r^2)(x^4 - 6x^2y^2 + y^4)$	$\equiv \gamma_J\langle r^6\rangle\frac{1}{4}[(11J_z^2 - J(J+1) - 38)(J_+^4 + J_-^4)$ $+ (J_+^4 + J_-^4)(11J_z^2 - J(J+1) - 38)]$	$= \gamma_J\langle r^6\rangle O_6^4$
$\sum(x^6 - 15x^4y^2 + 15x^2y^4 - y^6)$	$\equiv \gamma_J\langle r^6\rangle\frac{1}{2}[J_+^6 + J_-^6]$	$= \gamma_J\langle r^6\rangle O_6^6$

FOOTNOTES TO TABLE VIII

[a] After B. Bleaney and K. W. H. Stevens, *Repl. Progr. Phys.* **16**, 108 (1953); K. W. H. Stevens, *Proc. Phys. Soc. (London)* **A65**, 209 (1952); J. M. Baker, B. Bleaney, and W. Hayes, *Proc. Roy. Soc.* **A247**, 141 (1958); R. J. Elliott and K. W. H. Stevens, *ibid.* **A218**, 553 (1953); B. R. Judd, *ibid.* **A227**, 552 (1955); D. A. Jones, J. M. Baker, and D. F. D. Pope, *Proc. Phys. Soc.* (London) **74**, 249 (1959).

[b] We use the notation $O_n^m(s)$ to represent the operator equivalent to $f^s{}_{nm}$, and O_n^m as the conventional operator equivalent to $f^c{}_{nm}$ (cf. Section 5).

the O_n^m, between states of constant J, or L, have been tabulated in several papers, and these have been reproduced in Tables IX–XIII.

Considering for simplicity the case of a crystal field with axes chosen such that $\gamma^s{}_{nm} = 0$, we re-express the potential energy of an electron in the crystalline potential $V(x, y, z)$ (following the notation of Stevens, Elliott, and Judd; see Bibliography), as,

$$-|e|V(x, y, z) = \sum_{nm} A_n^m f^c{}_{nm}(x, y, z), \tag{5.3}$$

where we have the connection between the coefficients,

$$A_n^m = \gamma^c{}_{nm}\cdot(-|e|)\cdot(\text{a numerical factor occurring in } Z^c{}_{nm}). \tag{5.4}$$

The numerical factor is that outside the square brackets for those $Z^c{}_{nm}$ listed in Table IV. For example, in the case of cubic symmetry, using the notation of Eq. (5.3),

$$\begin{aligned}-|e|V(x_i, y_i, z_i) = {} & A_4^0(35z_i^4 - 30r_i^2z_i^2 + 3r_i^4) + A_4^4(x_i^4 - 6x_i^2y_i^2 + y_i^4)\\ & + A_6^0(231z_i^6 - 315z_i^4r_i^2 + 105z_i^2r_i^4 - 5r_i^6)\\ & + A_6^4(11z_i^2 - r_i^2)(x_i^4 - 6x_i^2y_i^2 + y_i^4).\end{aligned}$$

For a number of electrons, i, in the general potential $V(x, y, z)$ the operator is

$$\mathcal{H}_c = -|e|\sum_i V(x_i, y_i, z_i),$$

or

$$\mathcal{H}_c = \sum_i\sum_{nm} A_n^m f^c{}_{nm}(x_i, y_i, z_i) = \sum_{nm}[A_n^m\langle r^n\rangle\theta_n]O_n^m, \tag{5.5}$$

where we have made use of Eqs. (5.2) and (5.3).

a. Note on Notation

The quantities $A_n^m\langle r^n\rangle$ (or V_n^m in the notation of Elliott and Stevens[18]) are know as the "crystal field parameters," and are usually determined by

[18] R. J. Elliott and K. W. H. Stevens, *Proc. Roy. Soc.* **A219**, 387 (1953).

TABLE IX. Matrix Elements of O_2^0, O_4^0, and O_6^0 within a Manifold of States of Constant J[a]

$$O_2^0 = [3J_z^2 - J(J+1)]$$

J	F[b]	$J_z =$ ±1/2	±3/2	±5/2	±7/2	±9/2	±11/2	±13/2	±15/2
1/2	0	0	—	—	—	—	—	—	—
3/2	3	−1	1	—	—	—	—	—	—
5/2	2	−4	−1	5	—	—	—	—	—
7/2	3	−5	−3	1	7	—	—	—	—
9/2	6	−4	−3	−1	2	6	—	—	—
11/2	1	−35	−29	−17	1	25	55[c]	—	—
13/2	6	−8	−7	−5	−2	2	7	13	—
15/2	3	−21	−19	−15	−9	−1	9	21	35

J	F	$J_z =$ 0	±1	±2	±3	±4	±5	±6	±7	±8
0	0	0	—	—	—	—	—	—	—	—
1	1	−2	1	—	—	—	—	—	—	—
2	3	−2	−1	2	—	—	—	—	—	—
3	3	−4	−3	0	5	—	—	—	—	—
4	1	−20	−17	−8	7	28	—	—	—	—
5	3	−10	−9	−6	−1	6	15	—	—	—
6	3	−14	−13	−10	−5	2	11	22	—	—
7	1	−56	−53	−44	−29	−8	19	52	91	—
8	3	−24	−23	−20	−15	−8	1	12	25	40

$$O_4^0 = [35J_z^4 - 30J(J+1)J_z^2 + 25J_z^2 - 6J(J+1) + 3J^2(J+1)^2]$$

J	F	$J_z =$ ±1/2	±3/2	±5/2	±7/2	±9/2	±11/2	±13/2	±15/2
1/2	0	0	—	—	—	—	—	—	—
3/2	0	0	0	—	—	—	—	—	—
5/2	60	2	−3	1	—	—	—	—	—
7/2	60	9	−3	−13	7	—	—	—	—
9/2	84	18	3	−17	−22	18	—	—	—
11/2	120	28	12	−13	−33	−27	33	—	—
13/2	60	108	63	−13	−92	−132	−77	143	—
15/2	60	189	129	23	−101	−201	−221	−91	273

Nd

Er, Dy

J	F	$J_z =$ 0	1	2	3	4	5	6	7	8
0	0	0	—	—	—	—	—	—	—	—
1	0	0	0	—	—	—	—	—	—	—
2	12	6	−4	1	—	—	—	—	—	—
3	60	6	1	−7	3	—	—	—	—	—
4	60	18	9	−11	−21	14	—	—	—	—
5	420	6	4	−1	−6	−6	6	—	—	—
6	60	84	64	11	−54	−96	−66	99	—	—
7	12	756	621	251	−249	−704	−869	−429	1001	—
8	420	36	31	17	−3	−24	−39	−39	−13	52

$$O_6^0 = [231J_z^6 - 315J(J+1)J_z^4 + 735J_z^4 + 105J^2(J+1)^2J_z^2 - 525J(J+1)J_z^2 + 294J_z^2 - 5J^3(J+1)^3 + 40J^2(J+1)^2 - 60J(J+1)]$$

J	F	$J_z =$ ±1/2	±3/2	±5/2	±7/2	±9/2	±11/2	±13/2	±15/2
1/2	0	0	—	—	—	—	—	—	—
3/2	0	0	0	—	—	—	—	—	—
5/2	0	0	0	0	—	—	—	—	—
7/2	1260	−5	9	−5	1	—	—	—	—
9/2	5040	−8	6	10	−11	3	—	—	—
11/2	7560	−20	4	25	11	−31	11	—	—
13/2	2160	−200	−25	185	227	−11	−319	143	—
15/2	13860	−75	−25	45	87	59	−39	−117	65

Nd

Er, Dy

J	F	$J_z =$ 0	1	2	3	4	5	6	7	8
0	0	0	—	—	—	—	—	—	—	—
1	0	0	0	—	—	—	—	—	—	—
2	0	0	0	0	—	—	—	—	—	—
3	180	−20	15	−6	1	—	—	—	—	—
4	1260	−20	1	22	−17	4	—	—	—	—
5	2520	−40	−12	36	29	−48	15	—	—	—
6	7560	−40	−20	22	43	8	−55	22	—	—
7	3780	−200	−125	50	197	176	−55	−286	143	—
8	13860	−120	−85	2	93	128	65	−78	−169	104

Pr

[a] After K. W. H. Stevens, *Proc. Phys. Soc.* (*London*) **A65**, 209 (1952).
[b] The numbers in column F are multiplying factors common to all elements in the row.
[c] Corrected value.

TABLE X. MATRIX ELEMENTS OF O_2^2, O_4^2, AND O_6^2, WITHIN A MANIFOLD OF STATES OF CONSTANT J[a]

$$O_2^2 = \tfrac{1}{2}(J_+^2 + J_-^2)$$

J	⟨±1 ‖ ∓1⟩	⟨±2 ‖ 0⟩	⟨±3 ‖ ±1⟩	⟨±4 ‖ ±2⟩	⟨±5 ‖ ±3⟩	⟨±6 ‖ ±4⟩	⟨±7 ‖ ±5⟩	⟨±8 ‖ ±6⟩
1	1	—	—	—	—	—	—	—
2	3	$\sqrt{6}$	—	—	—	—	—	—
3	6	$\sqrt{30}$	$\sqrt{15}$	—	—	—	—	—
4	10	$3\sqrt{10}$	$3\sqrt{7}$	$2\sqrt{7}$	—	—	—	—
5	15	$\sqrt{210}$	$2\sqrt{42}$	$6\sqrt{3}$	$3\sqrt{5}$	—	—	—
6	21	$2\sqrt{105}$	$6\sqrt{10}$	$3\sqrt{30}$	$\sqrt{165}$	$\sqrt{66}$	—	—
7	28	$6\sqrt{21}$	$15\sqrt{3}$	$5\sqrt{22}$	$6\sqrt{11}$	$3\sqrt{26}$	$\sqrt{91}$	—
8	36	$6\sqrt{35}$	$\sqrt{1155}$	$3\sqrt{110}$	$2\sqrt{195}$	$\sqrt{546}$	$3\sqrt{35}$	$2\sqrt{30}$

J	⟨±3/2 ‖ ∓1/2⟩	⟨±5/2 ‖ ±1/2⟩	⟨±7/2 ‖ ±3/2⟩	⟨±9/2 ‖ ±5/2⟩	⟨±11/2 ‖ ±7/2⟩	⟨±13/2 ‖ ±9/2⟩	⟨±15/2 ‖ ±11/2⟩
3/2	$\sqrt{3}$	—	—	—	—	—	—
5/2	$3\sqrt{2}$	$\sqrt{10}$	—	—	—	—	—
7/2	$2\sqrt{15}$	$3\sqrt{5}$	$\sqrt{21}$	—	—	—	—
9/2	$5\sqrt{6}$	$3\sqrt{14}$	$2\sqrt{21}$	6	—	—	—
11/2	$3\sqrt{35}$	$2\sqrt{70}$	$6\sqrt{6}$	$3\sqrt{15}$	$\sqrt{55}$	—	—
13/2	$14\sqrt{3}$	$6\sqrt{15}$	$15\sqrt{2}$	$\sqrt{330}$	$3\sqrt{22}$	$\sqrt{78}$	—
15/2	$12\sqrt{7}$	$3\sqrt{105}$	$5\sqrt{33}$	$2\sqrt{165}$	$6\sqrt{13}$	$\sqrt{273}$	$\sqrt{105}$

$$O_4^2 = \tfrac{1}{4}\{[7J_z^2 - J(J+1) - 5](J_+^2 + J_-^2) + (J_+^2 + J_-^2)[7J_z^2 - J(J+1) - 5]\}$$

J	F[b]	⟨±1 ‖ ∓1⟩	⟨±2 ‖ 0⟩	⟨±3 ‖ ±1⟩	⟨±4 ‖ ±2⟩	⟨±5 ‖ ±3⟩	⟨±6 ‖ ±4⟩	⟨±7 ‖ ±5⟩	⟨±8 ‖ ±6⟩
2	3	-4	$\sqrt{6}$	—	—	—	—	—	—
3	3	-20	$-\sqrt{30}$	$6\sqrt{15}$	—	—	—	—	—
4	3	-60	$-11\sqrt{10}$	$10\sqrt{7}$	$30\sqrt{7}$	—	—	—	—
5	21	-20	$-\sqrt{210}$	0	$10\sqrt{3}$	$12\sqrt{5}$	—	—	—
6	3	-280	$-22\sqrt{105}$	$-24\sqrt{10}$	$23\sqrt{30}$	$24\sqrt{165}$	$45\sqrt{66}$	—	—
7	3	-504	$-94\sqrt{21}$	$-130\sqrt{3}$	$15\sqrt{22}$	$116\sqrt{11}$	$121\sqrt{26}$	$66\sqrt{91}$	—
8	7	-360	$-54\sqrt{35}$	$-6\sqrt{1155}$	$-3\sqrt{110}$	$12\sqrt{195}$	$15\sqrt{546}$	$78\sqrt{35}$	$78\sqrt{30}$

J	F	⟨±3/2 ‖ ∓1/2⟩	⟨±5/2 ‖ ±1/2⟩	⟨±7/2 ‖ ±3/2⟩	⟨±9/2 ‖ ±5/2⟩	⟨±11/2 ‖ ±7/2⟩	⟨±13/2 ‖ ±9/2⟩	⟨±15/2 ‖ ±11/2⟩
5/2	3	$-5\sqrt{2}$	$3\sqrt{10}$	—	—	—	—	—
7/2	6	$-4\sqrt{15}$	$\sqrt{5}$	$5\sqrt{21}$	—	—	—	—
9/2	21	$-5\sqrt{6}$	$-\sqrt{14}$	$2\sqrt{21}$	18	—	—	—
11/2	12	$-8\sqrt{35}$	$-3\sqrt{70}$	$5\sqrt{6}$	$13\sqrt{15}$	$9\sqrt{55}$	—	—
13/2	3	$-210\sqrt{3}$	$-62\sqrt{15}$	$-15\sqrt{2}$	$13\sqrt{330}$	$95\sqrt{22}$	$55\sqrt{78}$	—
15/2	6	$-120\sqrt{7}$	$-23\sqrt{105}$	$-15\sqrt{33}$	$8\sqrt{165}$	$80\sqrt{13}$	$25\sqrt{273}$	$39\sqrt{105}$[c]

$$O_6^2 = \tfrac{1}{4}\{[33J_z^4 - 18J_z^2J(J+1) - 123J_z^2 + J^2(J+1)^2 + 10J(J+1) + 102](J_+^2 + J_-^2) + (J_+^2 + J_-^2)[33J_z^4 - 18J_z^2J(J+1) - 123J_z^2 + J^2(J+1)^2 + 10J(J+1) + 102]\}$$

J	F	⟨±1 ‖ ∓1⟩	⟨±2 ‖ 0⟩	⟨±3 ‖ ±1⟩	⟨±4 ‖ ±2⟩	⟨±5 ‖ ±3⟩	⟨±6 ‖ ±4⟩	⟨±7 ‖ ±5⟩	⟨±8 ‖ ±6⟩
3	24	15	$-2\sqrt{30}$	$\sqrt{15}$	—	—	—	—	—
4	30	84[c]	0	$-36\sqrt{7}$	$24\sqrt{7}$	—	—	—	—
5	120[c]	84[c]	$2\sqrt{210}$[c]	$-11\sqrt{42}$[c]	$-42\sqrt{3}$[c]	$-42\sqrt{5}$[c]	—	—	—
6	72	420	$22\sqrt{105}$	$-63\sqrt{10}$	$-84\sqrt{30}$	$-14\sqrt{165}$	$70\sqrt{66}$	—	—
7	1080	70	$10\sqrt{21}$	$-7\sqrt{3}$	$-14\sqrt{22}$	$-21\sqrt{11}$	0	$11\sqrt{91}$	—
8	264	630[c]	$78\sqrt{35}$	$\sqrt{1155}$	$-42\sqrt{110}$	$-49\sqrt{195}$	$-20\sqrt{546}$	$39\sqrt{35}$	$182\sqrt{30}$

J	F	⟨±3/2 ‖ ∓1/2⟩	⟨±5/2 ‖ ±1/2⟩	⟨±7/2 ‖ ±3/2⟩	⟨±9/2 ‖ ±5/2⟩	⟨±11/2 ‖ ±7/2⟩	⟨±13/2 ‖ ±9/2⟩	⟨±15/2 ‖ ±11/2⟩
7/2	24	$7\sqrt{15}$	$-21\sqrt{5}$	$5\sqrt{21}$	—	—	—	—
9/2	240	$7\sqrt{6}$	$-3\sqrt{14}$	$-5\sqrt{21}$	21	—	—	—
11/2	216	$12\sqrt{35}$	$-\sqrt{70}$	$-35\sqrt{6}$	$-14\sqrt{15}$	$14\sqrt{55}$	—	—
13/2	720	$35\sqrt{3}$	$3\sqrt{15}$[c]	$-36\sqrt{2}$	$-4\sqrt{330}$	$-3\sqrt{22}$	$11\sqrt{78}$	—
15/2	1320	$30\sqrt{7}$	$3\sqrt{105}$	$-7\sqrt{33}$	$-7\sqrt{165}$	$-21\sqrt{13}$	$\sqrt{273}$	$13\sqrt{105}$

[a] After D. A. Jones, J. M. Baker, and D. F. D. Pope, *Proc. Phys. Soc. (London)* **74**, 249 (1959).
[b] The numbers in column F are multiplying factors common to all the elements in the row.
[c] Corrected values.

TABLE XI. MATRIX ELEMENTS OF O_4^3 AND O_6^3 WITHIN A MANIFOLD OF STATES OF CONSTANT $J^{a,b}$

$$O_4^3 = \tfrac{1}{4}[J_z(J_+^3 + J_-^3) + (J_+^3 + J_-^3)J_z]$$

J	F^c	⟨2 ‖ −1⟩	⟨3 ‖ 0⟩	⟨4 ‖ 1⟩	⟨5 ‖ 2⟩	⟨6 ‖ 3⟩	⟨7 ‖ 4⟩	⟨8 ‖ 5⟩
2	3	1	—	—	—	—	—	—
3	3	$\sqrt{10}$	$3\sqrt{5}$	—	—	—	—	—
4	3	$5\sqrt{2}$	$3\sqrt{35}$	$5\sqrt{14}$	—	—	—	—
5	3	$5\sqrt{7}$	$6\sqrt{35}$	$10\sqrt{21}$	$7\sqrt{30}$	—	—	—
6	3	$7\sqrt{10}$	$6\sqrt{105}$	$50\sqrt{3}$	$7\sqrt{165}$	$9\sqrt{55}$	—	—
7	3	$14\sqrt{6}$	$15\sqrt{42}$	$25\sqrt{33}$	$35\sqrt{22}$	$9\sqrt{286}$	$11\sqrt{91}$	—
8	3	$6\sqrt{70}$	$3\sqrt{2310}$	$25\sqrt{77}$	$7\sqrt{1430}$	$9\sqrt{910}$	$11\sqrt{455}$	$26\sqrt{35}$

J	F	⟨5/2 ‖ −1/2⟩	⟨7/2 ‖ 1/2⟩	⟨9/2 ‖ 3/2⟩	⟨11/2 ‖ 5/2⟩	⟨13/2 ‖ 7/2⟩	⟨15/2 ‖ 9/2⟩
5/2	3	$\sqrt{10}$	—	—	—	—	—
7/2	3	$4\sqrt{5}$	$2\sqrt{35}$	—	—	—	—
9/2	3	$5\sqrt{14}$	$8\sqrt{14}$	$6\sqrt{21}$	—	—	—
11/2	$12\sqrt{5}$	$\sqrt{14}$	$\sqrt{42}$	$3\sqrt{6}$	$\sqrt{33}$	—	—
13/2	3	$14\sqrt{15}$	$40\sqrt{6}$	$15\sqrt{66}$	$16\sqrt{55}$	$5\sqrt{286}$	—
15/2	6	$4\sqrt{105}$	$5\sqrt{231}$	$30\sqrt{11}$	$4\sqrt{715}$	$10\sqrt{91}$	$3\sqrt{455}$

$$O_6^3 = \tfrac{1}{4}[(11J_z^3 - 3J_zJ(J+1) - 59J_z)(J_+^3 + J_-^3) + (J_+^3 + J_-^3)(11J_z^3 - 3J_zJ(J+1) - 59J_z)]$$

J	F	⟨2 ‖ −1⟩	⟨3 ‖ 0⟩	⟨4 ‖ 1⟩	⟨5 ‖ 2⟩	⟨6 ‖ 3⟩	⟨7 ‖ 4⟩	⟨8 ‖ 5⟩
2	0	0	—	—	—	—	—	—
3	18	$-3\sqrt{10}$	$2\sqrt{5}$	—	—	—	—	—
4	90	$-7\sqrt{2}$	$-2\sqrt{35}$	$4\sqrt{14}$	—	—	—	—
5	180	$-6\sqrt{7}$	$-5\sqrt{35}$	$-\sqrt{21}$	$7\sqrt{30}$	—	—	—
6	36	$-63\sqrt{10}$	$-43\sqrt{105}$	$-175\sqrt{3}$	$14\sqrt{165}$	$84\sqrt{55}$	—	—
7	90	$-70\sqrt{6}$	$-64\sqrt{42}$	$-70\sqrt{33}$	$-21\sqrt{22}$	$21\sqrt{286}$	$66\sqrt{91}$	—
8	198	$-18\sqrt{70}$	$-8\sqrt{2310}$	$-50\sqrt{77}$	$-7\sqrt{1430}$	$3\sqrt{910}$	$22\sqrt{455}$	$104\sqrt{35}$

J	F	⟨5/2 ‖ −1/2⟩	⟨7/2 ‖ 1/2⟩	⟨9/2 ‖ 3/2⟩	⟨11/2 ‖ 5/2⟩	⟨13/2 ‖ 7/2⟩	⟨15/2 ‖ 9/2⟩
5/2	0	0	—	—	—	—	—
7/2	36	$-7\sqrt{5}$	$2\sqrt{35}$	—	—	—	—
9/2	360	$-2\sqrt{14}$	$-\sqrt{14}$	$2\sqrt{21}$	—	—	—
11/2	$36\sqrt{5}$	$-27\sqrt{14}$	$-16\sqrt{42}$	$7\sqrt{6}$	$28\sqrt{33}$	—	—
13/2	360	$-14\sqrt{15}$	$-29\sqrt{6}$	$-4\sqrt{66}$	$6\sqrt{55}$	$6\sqrt{286}$	—
15/2	1980	$-2\sqrt{105}$	$-2\sqrt{231}$	$-7\sqrt{11}$	0	$3\sqrt{91}$	$2\sqrt{455}$

[a] After B. R. Judd, *Proc. Roy. Soc.* **A227**, 552 (1955).
[b] The matrix elements of $\langle -m \mid O_n^3 \mid -m' \rangle = -\langle m \mid O_n^3 \mid m' \rangle$, $n = 4, 6$.
[c] The numbers in column F are multipyling factors common to all the elements in the row.

TABLE XII. MATRIX ELEMENTS OF O_4^4 AND O_6^4 WITHIN A MANIFOLD OF STATES OF CONSTANT J[a]

$$O_4^4 = \tfrac{1}{2}(J_+^4 + J_-^4)$$

J	F[b]	$\langle 2 \| -2\rangle$	$\langle 3 \| -1\rangle$	$\langle 4 \| 0\rangle$	$\langle 5 \| 1\rangle$	$\langle 6 \| 2\rangle$	$\langle 7 \| 3\rangle$	$\langle 8 \| 4\rangle$	
2	12	1	—	—	—	—	—	—	
3	12	5	$\sqrt{15}$	—	—	—	—	—	
4	12	15	$5\sqrt{7}$	$\sqrt{70}$	—	—	—	—	
5	12	35	$5\sqrt{42}$	$3\sqrt{70}$	$\sqrt{210}$	—	—	—	
6	12	70	$21\sqrt{10}$	$15\sqrt{14}$	$5\sqrt{66}$	$3\sqrt{55}$	—	—	
7	12	126	$70\sqrt{3}$	$5\sqrt{462}$	$15\sqrt{33}$	$5\sqrt{143}$	$\sqrt{1001}$	—	
8	12	210	$6\sqrt{1155}$	$15\sqrt{154}$	$5\sqrt{1001}$	$\sqrt{15015}$	$5\sqrt{273}$	$2\sqrt{455}$	
J	F	$\langle 5/2 \| -3/2\rangle$	$\langle 7/2 \| -1/2\rangle$	$\langle 9/2 \| 1/2\rangle$	$\langle 11/2 \| 3/2\rangle$	$\langle 13/2 \| 5/2\rangle$	$\langle 15/2 \| 7/2\rangle$		
5/2	12	$\sqrt{5}$	—	—	—	—	—		
7/2	12	$5\sqrt{3}$	$\sqrt{35}$	—	—	—	—		
9/2	$12\sqrt{7}$	$5\sqrt{3}$	$5\sqrt{2}$	$3\sqrt{2}$	—	—	—		Nd
11/2	$12\sqrt{2}$	35	$3\sqrt{105}$	$5\sqrt{21}$	$\sqrt{165}$	—	—		
13/2	12	$42\sqrt{5}$	$35\sqrt{6}$	$15\sqrt{22}$	$15\sqrt{11}$	$\sqrt{715}$	—		
15/2	12	$42\sqrt{15}$	$10\sqrt{231}$	$15\sqrt{77}$	$5\sqrt{429}$	$\sqrt{5005}$	$\sqrt{1365}$		Er

$$O_6^4 = \tfrac{1}{4}[(11J_z^2 - J(J+1) - 38)(J_+^4 + J_-^4) + (J_+^4 + J_-^4)(11J_z^2 - J(J+1) - 38)]$$

J	F	$\langle 2 \| -2\rangle$	$\langle 3 \| -1\rangle$	$\langle 4 \| 0\rangle$	$\langle 5 \| 1\rangle$	$\langle 6 \| 2\rangle$	$\langle 7 \| 3\rangle$	$\langle 8 \| 4\rangle$	
2	0	0	—	—	—	—	—	—	
3	60	-6	$\sqrt{15}$	—	—	—	—	—	
4	180	-14	$-\sqrt{7}$	$2\sqrt{70}$	—	—	—	—	
5	60	-168	$-13\sqrt{42}$	$12\sqrt{70}$	$15\sqrt{210}$	—	—	—	
6	180	-168	$-35\sqrt{10}$	$8\sqrt{14}$	$21\sqrt{66}$	$28\sqrt{55}$	—	—	
7	60	-1260	$-546\sqrt{3}$	$-6\sqrt{462}$	$147\sqrt{33}$	$126\sqrt{143}$	$45\sqrt{1001}$	—	
8	660	-252	$-6\sqrt{1155}$	$-6\sqrt{154}$	$3\sqrt{1001}$	$2\sqrt{15015}$	$19\sqrt{273}$	$12\sqrt{455}$	
J	F	$\langle 5/2 \| -3/2\rangle$	$\langle 7/2 \| -1/2\rangle$	$\langle 9/2 \| 1/2\rangle$	$\langle 11/2 \| 3/2\rangle$	$\langle 13/2 \| 5/2\rangle$	$\langle 15/2 \| 7/2\rangle$		
5/2	0	0	—	—	—	—	—		
7/2	60	$-7\sqrt{3}$	$3\sqrt{35}$	—	—	—	—		
9/2	$60\sqrt{7}$	$-16\sqrt{3}$	$6\sqrt{2}$	$30\sqrt{2}$	—	—	—		Nd
11/2	$180\sqrt{2}$	-63	$-\sqrt{105}$	$13\sqrt{21}$	$7\sqrt{165}$	—	—		
13/2	360	$-56\sqrt{5}$	$-21\sqrt{6}$	$13\sqrt{22}$	$46\sqrt{11}$	$6\sqrt{715}$	—		
15/2	660	$-42\sqrt{15}$	$-6\sqrt{231}$	$3\sqrt{77}$	$7\sqrt{429}$	$3\sqrt{5005}$	$5\sqrt{1365}$		Er

[a] After J. M. Baker, B. Bleaney, and W. Hayes, *Proc. Roy. Soc.* **A247**, 141 (1958).

[b] The numbers in column F are multiplying factors common to all the elements in the row.

TABLE XIII. MATRIX ELEMENTS OF O_6^6 WITHIN A MANIFOLD OF STATES OF CONSTANT J[a]

$$O_6^6 = \tfrac{1}{2}[(J_z + iJ_y)^6 + (J_z - iJ_y)^6]$$

J	F[b]	$\langle 3 \| -3\rangle$	$\langle 4 \| -2\rangle$	$\langle 5 \| -1\rangle$	$\langle 6 \| 0\rangle$	$\langle 7 \| 1\rangle$	$\langle 8 \| 2\rangle$
3	360	1	—	—	—	—	—
4	360	7	$2\sqrt{7}$	—	—	—	—
5	360	28	$14\sqrt{3}$	$\sqrt{210}$	—	—	—
6	360	84	$14\sqrt{30}$	$7\sqrt{66}$	$2\sqrt{231}$	—	—
7	360	210	$42\sqrt{22}$	$28\sqrt{33}$[c]	$2\sqrt{(21\cdot143)}$[c]	$\sqrt{(21\cdot143)}$[c]	—
8	360	462	$42\sqrt{110}$	$12\sqrt{(13\cdot77)}$	$14\sqrt{(3\cdot143)}$	$7\sqrt{(13\cdot55)}$	$2\sqrt{(14\cdot143)}$

J	F	$\langle 7/2 \| -5/2\rangle$	$\langle 9/2 \| -3/2\rangle$	$\langle 11/2 \| -1/2\rangle$	$\langle 13/2 \| 1/2\rangle$	$\langle 15/2 \| 3/2\rangle$
7/2	360	$\sqrt{7}$	—	—	—	—
9/2	360	14	$2\sqrt{21}$	—	—	—
11/2	360	$28\sqrt{3}$	$7\sqrt{30}$	$\sqrt{462}$	—	—
13/2	720	$21\sqrt{10}$	$7\sqrt{66}$	$7\sqrt{33}$	$\sqrt{429}$	—
15/2	$360\sqrt{11}$	$42\sqrt{5}$	84	$4\sqrt{273}$	$7\sqrt{39}$	$\sqrt{(35\cdot13)}$

[a] After R. J. Elliott and K. W. H. Stevens, *Proc. Roy. Soc.* **A219**, 387 (1953).
[b] The numbers in column F are multiplying factors common to all elements in the row.
[c] Corrected values.

$$B_m^m = -ze^2\langle r^m\rangle \theta_m \left[\frac{4\pi}{2m+1} \sum_{j=1}^{k} \frac{Z_{mm}(\theta_j,\phi_j)}{R_j^{(m+1)}}\right] \times \left[c^{te}\right]$$

Ver PRB 19, 5475 (1979)

$\theta_m = \alpha, \beta, \gamma$ p/ $m = 2, 4, 6$ respectivamente

$[c^{te}] \to c^{te}$ que aparece na frente dos harmônicos tesserais

fitting $\mathcal{H}_c$ to experimental data. (V_n^m is sometimes also used to denote $\sum_i f^c_{nm}(x_i, y_i, z_i)$, e.g., Stevens,[15] page 209.)

The operator equivalent Hamiltonian $\mathcal{H}_c$ is often written

$$\mathcal{H}_c = \sum_{nm} B_n^m O_n^m \qquad \left(\text{or } \mathcal{H}_c = \sum_{nm} B_n^m P_n^m\right), \tag{5.6}$$

where $B_n^m = A_n^m\langle r^n\rangle\theta_n$. The B's rather than the A's will be used in Section 6. (The A's and B's used by Bleaney and Stevens,[9] pages 128–129, are different from those used here, but can easily be related to them.)

Other notations commonly used, including some used in spin Hamiltonians of the form of Eq. (5.6), are listed below (Watanabe[19]):

$$b_2^0 = 3B_2^0 = D \qquad b_6^6 = 1260B_6^6$$
$$b_2^2 = 3B_2^2 = 3E \qquad b_4^m = 60B_4^m$$
$$b_4^0 = 60B_4^0 = \tfrac{1}{3}F \qquad b_6^m = 1260B_6^m$$
$$b_6^0 = 1260B_6^0$$

and, especially for cubic fields,

$$b_4^0 = 60B_4^0 = \tfrac{1}{2}a = \tfrac{1}{4}c$$
$$b_6^0 = 1260B_6^0 = \tfrac{1}{4}d.$$

6. Operator Equivalents for Cubic Potentials

As an example we shall now determine the operator equivalent appropriate to the cubic crystal-field potentials found in Sections 1 and 2. Since these differ only in the coefficients for the three different coordinations, we need only consider how the functions transform into the appropriate operators. The Hamiltonian may of course be found directly from Eqs. (5.4), (5.5), and (2.7).

a. Cubic Potential Expressed in Cartesian Coordinates

If we put $q_i' = -|e|$ in the expression derived in Section 1, Eq. (1.4), and Table I,

$$\mathcal{H}_c = \sum_i \{C_4[(x_i^4 + y_i^4 + z_i^4) - \tfrac{3}{5}r_i^4] + D_6[(x_i^6 + y_i^6 + z_i^6) + \tfrac{15}{4}(x_i^2y_i^4 + x_i^2z_i^4 + y_i^2x_i^4 + y_i^2z_i^4 + z_i^2x_i^4 + z_i^2y_i^4) - \tfrac{15}{14}r_i^6]\}.$$

We rewrite the Cartesian functions, using the expressions listed in Eqs. (1.1), in terms of the $f^c_{nm}(x_i, y_i, z_i)$. These then immediately go over into an operator equivalent in its usual form, i.e., O_4^0, O_4^4, O_6^0, and O_6^4,

[19] H. Watanabe, Private communication, 1962.

ss listed in Table VIII, and whose matrix elements are tabulated. Now

$$[(x^4+y^4+z^4)-\tfrac{3}{5}r^4] = \tfrac{1}{20}[(35z^4-30r^2z^2+3r^4)+5(x^4+y^4-6x^2y^2)]$$

$$= \tfrac{1}{20}\{(35z^4-30r^2z^2+3r^4) + 5[(x+iy)^4+(x-iy)^4]/2\}. \qquad (6.1)$$

We have seen in Section 5 that the matrix elements of

$$\sum_i \left[\frac{(x_i+iy_i)^4+(x_i-iy_i)^4}{2}\right]$$

are identical to those of $\beta_J\langle r^4\rangle O_4^4$ between the angular part of the wave functions. We shall now consider the operator equivalent to

$$\sum_i f_{40} = \sum_i (35z_i^4 - 30r_i^2z_i^2 + 3r_i^4).$$

This is a more lengthy application of Stevens' rules given in Section 5, and we must make use of the commutation relations below:

$$J_xJ_y - J_yJ_x = iJ_z$$

$$J_yJ_z - J_zJ_y = iJ_x$$

$$J_zJ_x - J_xJ_z = iJ_y \qquad \text{(measuring all angular momenta in units of } \hbar).$$

These are used to bring all the different combinations of the operators into similar form; for example, below we reduce them to squares of operators and the product $J_xJ_yJ_z$.

Considering each term in f_{40} separately,

(a) $\underline{z^4 \rightsquigarrow J_z^4}$ (6.2)

(b) $r^2z^2 = x^2z^2 + y^2z^2 + z^4$

$$x^2z^2 \rightsquigarrow \tfrac{1}{6}[J_x^2J_z^2 + J_z^2J_x^2 + J_xJ_zJ_xJ_z + J_xJ_zJ_zJ_x + J_zJ_xJ_zJ_x + J_zJ_xJ_xJ_z],$$

and using the commutation relations,

$$J_xJ_zJ_xJ_z = J_x(iJ_y + J_xJ_z)J_z = iJ_xJ_yJ_z + J_x^2J_z^2$$

$$J_xJ_zJ_zJ_x = J_xJ_z(iJ_y + J_xJ_z) = iJ_xJ_zJ_y + iJ_xJ_yJ_z + J_x^2J_z^2$$

$$= iJ_x(J_yJ_z - iJ_x) + iJ_xJ_yJ_z + J_x^2J_z^2$$

$$= 2iJ_xJ_yJ_z + J_x^2 + J_x^2J_z^2,$$

$$J_zJ_xJ_zJ_x = J_z(J_zJ_x - iJ_y)J_x$$

$$= J_z^2J_x^2 - iJ_zJ_yJ_x$$

$$= J_z^2J_x^2 - iJ_z(J_xJ_y - iJ_z)$$

$$= J_z^2J_x^2 - i[(J_xJ_z + iJ_y)J_y - iJ_z^2]$$

$$= J_z^2J_x^2 - i[J_x(J_yJ_z - iJ_x) + iJ_y^2 - iJ_z^2]$$

$$= J_z^2J_x^2 - iJ_xJ_yJ_z - J_x^2 + J_y^2 - J_z^2,$$

$$J_zJ_xJ_xJ_z = J_zJ_x(J_zJ_x - iJ_y)$$

$$= J_z^2J_x^2 - iJ_xJ_yJ_z - J_x^2 + J_y^2 - J_z^2 - i(iJ_y + J_xJ_z)J_y$$

$$= J_z^2J_x^2 - iJ_xJ_yJ_z - J_x^2 + J_y^2 - J_z^2 + J_y^2 - iJ_x(J_yJ_z - iJ_x)$$

$$= J_z^2J_x^2 - 2iJ_xJ_yJ_z - 2J_x^2 + 2J_y^2 - J_z^2.$$

Adding, we find

$$x^2z^2 \rightsquigarrow \tfrac{1}{6}[3J_x^2J_z^2 + 3J_z^2J_x^2 - 2J_x^2 + 3J_y^2 - 2J_z^2]. \qquad (6.3)$$

Similarly,

$$y^2z^2 \rightsquigarrow \tfrac{1}{6}[3J_y^2J_z^2 + 3J_z^2J_y^2 + 3J_x^2 - 2J_y^2 - 2J_z^2]. \qquad (6.4)$$

If we now use the fact that $J_x^2 + J_y^2 + J_z^2 = J^2$, which when operating on states within a manifold of given J gives a constant $J(J+1)$, which commutes with J_z, and add Eqs. (6.2), (6.3), and (6.4) we find

$$r^2z^2 \rightsquigarrow \tfrac{1}{6}[6J(J+1)J_z^2 + J_x^2 + J_y^2 - 4J_z^2],$$

or

$$\underline{r^2z^2 \rightsquigarrow \tfrac{1}{6}[6J(J+1)J_z^2 + J(J+1) - 5J_z^2]}, \qquad (6.5)$$

(c) $r^4 = (x^2+y^2+z^2)(x^2+y^2+z^2)$

$$= x^4 + y^4 + z^4 + 2(x^2y^2 + y^2z^2 + z^2x^2).$$

Now $x^4 \rightsquigarrow J_x^4$, etc., and in a similar manner as that used in (b) we can show

$$x^2y^2 \rightsquigarrow \tfrac{1}{6}[3J_x^2J_y^2 + 3J_y^2J_x^2 - 2J(J+1) + 5J_z^2]. \qquad (6.6)$$

Using Eqs. (6.3), (6.4), and (6.6),

$$r^4 \rightsquigarrow \tfrac{2}{6}[3J_x^2J_y^2 + 3J_y^2J_x^2 + 3J_x^2J_z^2 + 3J_z^2J_x^2 + 3J_z^2J_y^2 + 3J_y^2J_z^2]$$

$$+ J_x^4 + J_y^4 + J_z^4 + \tfrac{2}{6}[-2J(J+1) + J_x^2 + J_y^2 + J_z^2],$$

which reduces to

$$r^4 \rightsquigarrow [J^2(J+1)^2 - \tfrac{1}{3}J(J+1)]. \qquad (6.7)$$

Finally, using Eqs. (6.2), (6.5), and (6.7), we see that

$$\sum_i [35z_i^4 - 30z_i^2r_i^2 + 3r_i^4]$$

$$\equiv \beta_J\langle r^4\rangle\{35J_z^4 - [30J(J+1) - 25]J_z^2 - 6J(J+1) + 3J^2(J+1)^2\}$$

$$= \beta_J\langle r^4\rangle O_4^0. \qquad (6.8)$$

If we now combine Eqs. (6.1), (5.1), and (6.8), we see that the matrix elements of

$$\sum_i [x_i^4 + y_i^4 + z_i^4 - \tfrac{3}{5}r_i^4] \equiv \text{those of } \tfrac{1}{20}\beta_J\langle r^4\rangle[O_4^0 + 5O_4^4]. \qquad (6.9)$$

Similarly,

$$[x^6 + y^6 + z^6 + \tfrac{15}{4}(x^2y^4 + x^2z^4 + y^2x^4 + y^2z^4 + z^2x^4 + z^2y^4) - \tfrac{15}{14}r^6]$$

$$= -\tfrac{1}{224}\{(231z^6 - 315z^4r^2 + 105z^2r^4 - 5r^6) - 21(11z^2 - r^2) \times [(x+iy)^4 + (x-iy)^4]/2\},$$

using the Eqs. (1.1), and the fact that

$$x^4 + y^4 - 6x^2y^2 = [(x+iy)^4 + (x-iy)^4]/2.$$

The matrix elements of $\sum_i[231z_i^6 - 315z_i^4r_i^2 + 105z_i^2r_i^4 - 5r_i^6]$ between coupled wave functions are the same as those of $\gamma_J\langle r^6\rangle O_6^0$ between the angular part of the wave functions; and those of

$$\sum_i\left[(11z_i^2 - r_i^2)\frac{(x_i+iy_i)^4 + (x_i-iy_i)^4}{2}\right]$$

are the same as those of $\gamma_J\langle r^6\rangle O_6^4$. Therefore, the matrix elements of

$$\sum_i[(x_i^6+y_i^6+z_i^6) + \tfrac{15}{4}(x_i^2y_i^4+x_i^2z_i^4+y_i^2x_i^4+y_i^2z_i^4+z_i^2x_i^4+z_i^2y_i^4) - \tfrac{15}{14}r_i^6]$$

$$\equiv \text{those of } -\tfrac{1}{224}\gamma_J\langle r^6\rangle[O_6^0 - 21O_6^4]. \qquad (6.10)$$

We therefore have that for a crystal field of cubic symmetry,

$$\mathcal{H}_c = (C_4/20)\beta_J\langle r^4\rangle[O_4^0 + 5O_4^4] - (D_6/224)\gamma_J\langle r^6\rangle[O_6^0 - 21O_6^4],$$

or

$$\mathcal{H}_c = B_4^0[O_4^0 + 5O_4^4] + B_6^0[O_6^0 - 21O_6^4]. \qquad (6.11)$$

three coordinations.

TABLE XIV. COEFFICIENTS B_4^0 AND B_6^0 (EQ. 6.11) FOR THE THREE COORDINATIONS

	B_4^0	B_6^0
Eightfold coordination	$+\frac{7}{18}\frac{\lvert e\rvert q}{d^5}\beta_J\langle r^4\rangle$	$-\frac{1}{9}\frac{\lvert e\rvert q}{d^7}\gamma_J\langle r^6\rangle$
Sixfold coordination	$-\frac{7}{16}\frac{\lvert e\rvert q}{d^5}\beta_J\langle r^4\rangle$	$-\frac{3}{64}\frac{\lvert e\rvert q}{d^7}\gamma_J\langle r^6\rangle$
Fourfold coordination	$+\frac{7}{36}\frac{\lvert e\rvert q}{d^5}\beta_J\langle r^4\rangle$	$-\frac{1}{18}\frac{\lvert e\rvert q}{d^7}\gamma_J\langle r^6\rangle$

Where B_4^0 and B_6^0 are given in Table XIV for surrounding point charges of charge q, at distance $d(d > r)$, in various coordinations about the magnetic ion site, and axes are chosen as in Figs. 1 and 2. This is in the same form as the Hamiltonian given, for example, in Baker *et al.*,[20] page 150. We have put $q' = -|e|$ in the values listed in Table I, the signs of the β_J, or γ_J, factors are consistent with this.

b. *Cubic Potential Expressed in Spherical Harmonics*

To illustrate how one rewrites, in terms of operator equivalents, the crystal-field Hamiltonian operator when the potential is expressed in spherical or tesseral harmonics, we again consider the cubic case. We first express the Hamiltonian in terms of tesseral harmonics $Z_{n\alpha}$. Using Eq. (2.13), with $q' = -|e|$,

$$\mathcal{H}_c = \sum_i\{D_4'[Y_4^0 + (5/14)^{1/2}(Y_4^4 + Y_4^{-4})] + D_6'[Y_6^0 - (7/2)^{1/2}(Y_6^4 + Y_6^{-4})]\}$$

$$= \sum_i\{D_4'[Z_{40} + (5/7)^{1/2}Z^c_{44}] + D_6'[Z_{60} - (7)^{1/2}Z^c_{64}]\}.$$

Let $D_4'' = D_4'/r^4$ and $D_6'' = D_6'/r^6$. Then

$$\mathcal{H}_c = \sum_i\{D_4''[r^4Z_{40} + (5/7)^{1/2}r^4Z^c_{44}] + D_6''[r^6Z_{60} - (7)^{1/2}r^6Z^c_{64}]\} \qquad (6.12)$$

We now write $r^4Z^c_{4m}$ and $r^6Z^c_{6m}$ in Cartesian coordinates, using the values of Z^c_{nm} from Table IV. The tesseral harmonics are directly proportional to the $f_{nm}(x, y, z)$ which immediately go over into the operator

[20] J. M. Baker, B. Bleaney, and W. Hayes, *Proc. Roy. Soc.* **A247**, 141 (1958).

FIG. 4. Summary diagram.

form. Thus we get

$$\mathcal{H}_c = D_4''\left[\frac{3}{16}\frac{1}{\sqrt{\pi}}\beta_J\langle r^4\rangle O_4^0 + \left(\frac{5}{7}\right)^{\frac{1}{2}}\frac{3}{16}\left(\frac{35}{\pi}\right)^{\frac{1}{2}}\beta_J\langle r^4\rangle O_4^4\right]$$

$$+ D_6''\left[\frac{1}{32}\left(\frac{13}{\pi}\right)^{\frac{1}{2}}\gamma_J\langle r^6\rangle O_6^0 - (7)^{\frac{1}{2}}\frac{21}{32}\left(\frac{13}{7\pi}\right)^{\frac{1}{2}}\gamma_J\langle r^6\rangle O_6^4\right],$$

$$\mathcal{H}_c = \frac{3}{16\sqrt{\pi}}D_4''\beta_J\langle r^4\rangle[O_4^0 + 5O_4^4] + \frac{1}{32}\left(\frac{13}{\pi}\right)^{\frac{1}{2}}D_6''\gamma_J\langle r^6\rangle[O_6^0 - 21O_6^4], \tag{6.13}$$

and putting $q' = -|e|$ in the values of D_4' and D_6' taken from Table V, we arrive once more at the values of B_4^0 and B_6^0 listed in Table XIV.

c. *Cubic Potential Operators Expressed with Respect to Other Choices of Axes*

As mentioned in Section 2.c, in some compounds the cubic-crystal potential energy operator is required expressed with respect to axes other than the fourfold axes considered above. Using Eqs. (2.7), (5.4), and (5.5), we can show that the operators corresponding to the potential energy of electrons of charge $-|e|$ in the field due to charges in the various coordinations will be given by the expressions below. Axes are chosen as in Section 2.c.

When z is a twofold axis,

$$\mathcal{H}_c = B_4^{0(2)}[O_4^0 - 20O_4^2 - 15O_4^4]^{(2)} + B_6^{0(2)}[O_6^0 + \tfrac{105}{26}O_6^2 - \tfrac{105}{13}O_6^4 + \tfrac{231}{26}O_6^6]^{(2)}, \tag{6.14}$$

where $B_4^{0(2)} = (-1/4)B_4^0$ and $B_6^{0(2)} = (-13/8)B_6^0$; B_4^0 and B_6^0 are the constants in the fourfold-axes Hamiltonian listed in Table XIV for the three coordinations. (This operator may also be found from Eq. (6.11) and the transformations given in Table XV.)

When z is a threefold axis,

$$\mathcal{H}_c = B_4^{0(3)}[O_4^0 - 20\sqrt{2}O_4^3]^{(3)} + B_6^{0(3)}[O_6^0 + (35\sqrt{2}/4)O_6^3 + \tfrac{77}{8}O_6^6]^{(3)}, \tag{6.15}$$

where $B_4^{0(3)} = (-2/3)B_4^0$ and $B_6^{0(3)} = (16/9)B_6^0$; B_4^0 and B_6^0 are the constants in the fourfold-axes Hamiltonian listed in Table XIV for the three coordinations.

TABLE XV. TRANSFORMATION OF SPIN OPERATORS ON ROTATION OF THE z AXIS INTO THE PERPENDICULAR PLANE xy SO THAT z' MAKES AN ANGLE ϕ WITH x AND y' IS PARALLEL TO z[a]

$$O_2^0 \to -\frac{1}{2}O_2^0 - \frac{3}{2}O_2^2$$

$$O_2^2 \to \left(\frac{1}{2}O_2^0 - \frac{1}{2}O_2^2\right)\cos 2\phi - 2iO_2^1\sin 2\phi$$

$$O_4^0 \to \frac{3}{8}O_4^0 + \frac{5}{2}O_4^2 + \frac{35}{8}O_4^4$$

$$O_4^2 \to \left(-\frac{1}{8}O_4^0 - \frac{1}{2}O_4^2 + \frac{7}{8}O_4^4\right)\cos 2\phi + i\left(\frac{1}{2}O_4^1 + \frac{7}{2}O_4^3\right)\sin 2\phi$$

$$O_4^4 \to \left(\frac{1}{8}O_4^0 - \frac{1}{2}O_4^2 + \frac{1}{8}O_4^4\right)\cos 4\phi - i(O_4^1 - iO_4^3)\sin 4\phi$$

$$O_6^0 \to -\frac{5}{16}O_6^0 - \frac{105}{32}O_6^2 - \frac{63}{16}O_6^4 - \frac{231}{32}O_6^6$$

$$O_6^2 \to \left(\frac{1}{16}O_6^0 + \frac{17}{32}O_6^2 + \frac{3}{16}O_6^4 - \frac{33}{32}O_6^6\right)\cos 2\phi - i\left(\frac{1}{4}O_6^1 + \frac{9}{8}O_6^3 + \frac{33}{8}O_6^5\right)\sin 2\phi$$

$$O_6^4 \to \left(-\frac{1}{16}O_6^0 - \frac{5}{32}O_6^2 + \frac{13}{16}O_6^4 - \frac{11}{32}O_6^6\right)\cos 4\phi + i\left(\frac{1}{2}O_6^1 + \frac{5}{4}O_6^3 - \frac{11}{4}O_6^5\right)\sin 4\phi$$

$$O_6^6 \to \left(\frac{1}{16}O_6^0 - \frac{15}{32}O_6^2 + \frac{3}{16}O_6^4 - \frac{1}{32}O_6^6\right)\cos 6\phi - i\left(\frac{3}{4}O_6^1 - \frac{5}{8}O_6^3 + \frac{3}{8}O_6^5\right)\sin 6\phi$$

[a] After D. A. Jones, J. M. Baker, and D. F. D. Pope, *Proc. Phys. Soc. (London)* 74, 249 (1959).

IV. Summary

To summarize, we illustrate the different methods of calculating the crystal-field Hamiltonian, and its matrix elements, by the diagram shown in Fig. 4. The method, using a Cartesian expansion is, however, far too tedious to be used in practice.

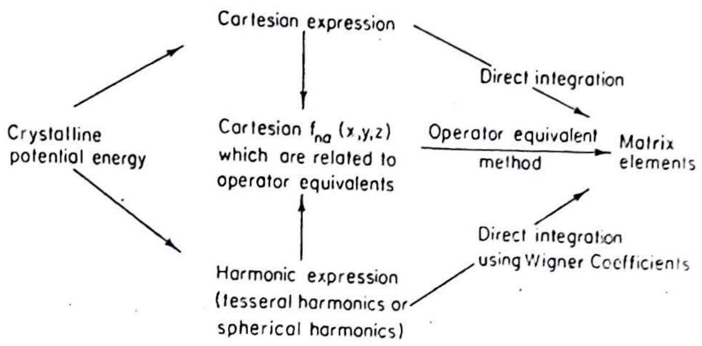


FIG. 4. Summary diagram.