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Houston's Method and Its Application to the Calculation of Characteristic Temperatures of Cubic Crystals

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Houston's formula first derived for an approximate determination of the frequency spectrum of cubic crystals, essentially approximates the integral over the surface of a unit sphere of any function $I(\theta,\varphi)$ which is invariant under the operations of the cubic symmetry group in terms of the values of $I(\theta,\varphi)$ along the three directions (100), (110), and (111). In this paper approximate formulas are given for the integral in terms of the values of $I(\theta,\varphi)$ along the above three and any or all of the (210), (211), and (221) directions. As an application, Debye temperatures Θ are calculated for nine cubic crystals. It appears that the Θ values calculated from the formula containing the values of I along *all* the above six directions may be expected to be correct to about 1% for crystals for which $0.25<\eta<4.0$ [where $\eta\equiv 2c_{44}/(c_{11}-c_{12})$]. For the alkali metals ($\eta\sim 8$), the error can be as large as 10%.

Houston's method involves the expansion of $I(\theta,\varphi)$ in terms of those Kubic harmonics which are invariant under all the operations of the cubic symmetry group. In the Appendix, formulas are derived from which the Kubic harmonics of this type of any degree may be written down readily.

1. HOUSTON'S METHOD AND SCOPE OF THE PRESENT WORK

IN 1948, Houston[1] gave a very convenient method for approximately determining the frequency distribution function of cubic crystals. The ease of the method depends on the fact that there exist in the reciprocal space certain directions along which the secular equation determining the frequencies ω of the normal modes of vibration can be solved exactly. Thus the frequency distribution function $g(\omega,\theta_s,\varphi_s)$ per unit solid angle, per unit frequency range can be obtained easily for several directions θ_s, φ_s in the reciprocal space. The functions $g(\omega,\theta_s,\varphi_s)$ may be expanded in terms of those Kubic harmonics[2] which have the same symmetry properties as $g(\omega,\theta,\varphi)$; thus

$$g(\omega,\theta_s,\varphi_s)=\sum\nolimits'_m a_m(\omega)K_m(\theta_s,\varphi_s), \qquad (1.1)$$

where $K_0=1$ and a prime on the summation sign signifies that $m=1$ is to be excluded from the summation; in the notation employed here, $K_1\equiv$zero (see Sec. 2 and appendix). K_m satisfy the orthogonality conditions

$$\int_0^\pi\int_0^{2\pi} K_mK_n \sin\theta d\theta d\varphi=4\pi\gamma_m\delta_{m,n}. \qquad (1.2)$$

In (1.2), γ_m is a normalization constant and $\delta_{m,n}$ is the usual Kröneker delta function, equal to unity when $m=n$ and zero otherwise. If the number of terms retained in the expansion (1.1) is equal to the number of directions θ_s, φ_s along which $g(\omega,\theta_s,\varphi_s)$ is determined, one may solve for $a_m(\omega)$. The frequency distribution function $G(\omega)$ per unit frequency range is then given by

$$G(\omega)=\int\int g(\omega,\theta,\varphi)\sin\theta d\theta d\varphi=4\pi a_0(\omega). \qquad (1.3)$$

Houston determined $a_0(\omega)$, and hence $G(\omega)$, from the values of $g(\omega,\theta,\varphi)$ along the three principal directions of a cubic crystal, namely the (100), (110), and (111) directions,[3] and obtained the formula[4]

$$G(\omega)=(4\pi/35)[10g_A(\omega)+16g_B(\omega)+9g_C(\omega)], \qquad (1.4)$$

in which the subscripts A, B, and C on g signify its value in the (100), (110), and (111) directions, respectively.

The approximate formula (1.4) has been used recently by several authors[5] to calculate $G(\omega)$, and hence the specific heat C_v at constant volume, for cubic crystals. Houston's method is particularly suited for the calculation of C_v at low temperatures, since, with the help of (1.4), one can easily obtain an analytical expansion of $G(\omega)$ in powers of ω^2.[6] Recently Bhatia and Tauber[7] have used (1.4) also to derive an explicit formula for the characteristic temperature Θ in the limit of vanishing temperature in terms of the elastic constants c_{11}, c_{12}, and c_{44} of a cubic crystal. We may mention, as is obvious, that Houston's method of approximating $G(\omega)$ may be used to evaluate approximately any integral

$$J=\int\int I(\theta,\varphi)\sin\theta d\theta d\varphi, \qquad (1.5)$$

provided that the integrand $I(\theta,\varphi)$ has the correct symmetry properties.

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[1] W. V. Houston, Revs. Modern Phys. **20**, 161 (1948).

[2] F. C. Von der Lage and H. A. Bethe, Phys. Rev. **71**, 612 (1947).

[3] The solutions of the secular equation are particularly simple in these three directions.

[4] The formula (1.4) is written here after allowing for a numerical error in Houston's calculation. Note also that our notation is different from that used in reference 1.

[5] For example, E. Bauer, Phys. Rev. **92**, 58 (1953); A. B. Bhatia, Phys. Rev. **97**, 363 (1955); A. B. Bhatia and G. K. Horton, Phys. Rev. **98**, 1715 (1955).

[6] See last reference in footnote 5.

[7] A. B. Bhatia and G. E. Tauber, Phil. Mag. **45**, 1211 (1954); also erratum; Phil. Mag. **46**, 108 (1955).

Now clearly the number of terms retained in the expansion (1.1) corresponds to a certain degree of approximation. It would be desirable, therefore, to study the effect of retaining more than three terms on the right hand side of (1.1). In Sec. 2 of this paper, Houston's formula (1.4) is extended by retaining up to six terms in the expansion (1.1) and taking the values of the integrand I along the A, B, and C directions and along either one, two, or all of the three directions (210), (211), and (221).[8] This gives us, besides Houston's formula (1.4), seven other approximate formulas for J. In Sec. 3, we use these formulas to calculate Debye characteristic temperatures Θ for nine typical cubic crystals in terms of their elastic constants. It is found that for crystals for which the anisotropy factor η $[\equiv 2c_{44}(c_{11}-c_{12})^{-1}]$ lies outside the range $0.5<\eta<1.5$, the Θ values calculated by retaining six terms in the expansion (1.1) are a distinct improvement over those obtained by retaining three terms only. Application of of the formulas derived in Sec. 3 to the calculation of frequency distribution function $G(\omega)$ will be taken up in a later communication.

The appendix is devoted to the mathematical problem of constructing a Kubic harmonic (K.H.) of any degree. Attention is mainly confined to those K.H. which are invariant under all the operations of the cubic symmetry group, as the functions $I(\theta,\varphi)$ [see Eq. (1.5)] occurring in the type of problems considered here have this property. In the notation of Von der Lage and Bethe,[2] these K.H. are referred to as of α type. They obtained the first four K.H. of this type by orthogonalizing each K.H. with all the preceding ones. This procedure is lengthier the higher the degree of K.H. to be constructed.

In the appendix it is shown that the number of linearly independent K.H. of α type of degree $2n$ is given by the coefficient of x^n in the expansion

$$[(1-x^2)(1-x^3)]^{-1}=1+x^2+x^3+x^4+x^5+2x^6+\cdots. \quad (1.6)$$

Further formulas determining a complete, linearly independent set of K.H. of this type are derived. In this set K.H. of different degrees only are orthogonal to each other. However, where there exist more than one K.H. of the same degree, they may be easily orthogonalized by taking suitable linear combinations of them. Note that up to degree 24 there are at most two K.H. of each degree. It is believed that the method given here may be modified to also construct K.H. of types other than α, enumerated in reference 2.

2. EXTENSION OF HOUSTON'S FORMULA

Since we wish to retain six terms in the expansion (1.1), we need six K.H., $K_0, K_2, K_3, \cdots K_6$ of the α type; we take these to be $(K_1=0)$

$$\begin{aligned}
&K_0=1, \quad K_2=x^4+y^4+z^4-\tfrac{3}{5}\rho^4K_0,\\
&K_3=x^2y^2z^2+(1/22)\rho^2K_2-(1/105)\rho^6K_0,\\
&K_4=x^8+y^8+z^8-(28/5)\rho^2K_3\\
&\qquad\qquad -(210/143)\rho^4K_2-\tfrac{1}{3}\rho^8K_0,\\
&K_5=x^{10}+y^{10}+z^{10}-(45/19)\rho^2K_4-(126/17)\rho^4K_3 \qquad (2.1)\\
&\qquad\qquad -(210/143)\rho^6K_2-(3/11)\rho^{10}K_0,\\
&K_6=x^4y^4z^4+(6/115)\rho^2K_5-(1/2\cdot7\cdot19)\rho^4K_4\\
&\qquad -(54/5\cdot17\cdot19)\rho^6K_3+(3/11\cdot13\cdot17)\rho^8K_2\\
&\qquad\qquad -(1/5\cdot7\cdot11\cdot13)\rho^{12}K_0,
\end{aligned}$$

where $\rho^2=x^2+y^2+z^2$. K_0, K_2, K_3 and K_4 are taken from reference 2.[9] The coefficients of K_4, K_3, etc., in K_5 and of K_5, K_4, etc., in K_6 were determined by the requirement that K_5 and K_6 each be orthogonal on the unit sphere to all the preceding harmonics.[10] The normalization constants γ_m, though not needed in the present work, are given below for the sake of completeness.

$$\begin{aligned}
&\gamma_0=1, \quad \gamma_2=16/(3\cdot5\cdot5\cdot7), \quad \gamma_3=32/[(3\cdot7\cdot11)^2\cdot13],\\
&\gamma_4=256/[3\cdot11\cdot(5\cdot13)^2\cdot17],\\
&\gamma_5=5\cdot512/[7\cdot13\cdot(11\cdot17\cdot19)^2], \qquad (2.2)\\
&\gamma_6=41\cdot1024/[11\cdot(3\cdot7\cdot13\cdot17\cdot19\cdot23)^2].
\end{aligned}$$

For brevity, we shall call the directions (100), (110), (111), (210), (211), and (221) the A, B, C, D, E, and F directions, respectively. Further a subscript A, B, etc., on a symbol for any quantity like $K_m(\theta,\varphi)$ or $I(\theta,\varphi)$ will imply its value in that direction. Then the six equations determining the coefficients a_m in the expansion of $I(\theta,\varphi)$ in terms of K.H. may be written

$$I_A=\sum_{m=0}^{6}{}' a_mK_{m,A}, \quad I_B=\sum_{m=0}^{6}{}' a_mK_{m,B}, \quad \text{etc.} \qquad (2.3)$$

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[8] The choice of these three latter directions is somewhat arbitrary and was governed by the facts that (a) the equations of the elasticity theory for a cubic crystal can be solved for the velocities with ease in these directions, and (b) they are more or less symmetrically distributed in the portion of the total solid angle in which the equations have distinct solutions.

[9] The coefficient of K_0 in K_4 is misprinted in reference 2 as $\frac{1}{6}$ instead of $\frac{1}{3}$.

[10] K_5 may be verified to be identical, apart from a normalization constant, with that given in the appendix [Eq. (A.16)]. K_6, however, is a linear combination of the two linearly independent 12th degree harmonics $K_6^{(1)}$ and $K_6^{(2)}$ of the appendix. We have used here K_6 since most of the numerical work was done prior to developing the general method of constructing Kubic harmonics given in the appendix. The other 12th degree harmonic orthogonal to K_6 is

$$\begin{aligned}
\bar{K}_6=x^{12}+y^{12}+z^{12}-\frac{72\cdot99}{25\cdot41}K_6-\frac{6}{23}\rho^2K_5-\frac{5\cdot9\cdot11}{7\cdot19}\rho^4K_4\\
-\frac{28\cdot99}{17\cdot19}\rho^6K_3-\frac{35\cdot9}{13\cdot17}\rho^8K_2-\frac{3}{13}\rho^{12}K_0.
\end{aligned}$$

The use of this harmonic instead of K_6 in Eqs. (2.3) makes the final formulas more involved without appreciably changing the final results.

The coefficients $K_{m,A}$, $K_{m,B}$, etc., $(m=0, 2, 3, \cdots 6)$, can be readily evaluated from (2.1); these will not be given here as some of them are rather lengthy.

Equations (2.3) were solved for a_0 exactly by eliminating a_2, a_3, $\cdots$, successively and the resulting expression for J in terms of I_A, I_B, $\cdots I_F$ is given below as Eq. (2.4.8). In order to obtain a better idea of the degrees of approximation involved in Houston's three-term formula and in the six-term formula (2.4.8), it was thought desirable to obtain other approximations to J by retaining (a) four terms in the expansion (1.1) and taking I along the directions A, B, C and D or E or F, (b) five terms in the expansion (1.1) and taking I along the direction A, B, C and D and E, E and F, or F and D. The relevant equations for the determination of a_0 for these cases may be obtained by deleting the appropriate terms in Eqs. (2.3). We denote the corresponding approximations to J by J_2, J_3, $\cdots J_7$, respectively. J_1 corresponds to the Houston three-term approximation, while J_8 is the six-term formula (2.4.8). The various expressions for J are

$$J_1=\frac{4\pi}{35}[10I_A+16I_B+9I_C], \quad \text{(Houston's approximation)}, \tag{2.4.1}$$

$$J_2=\frac{4\pi}{945}[45I_A+32I_B+243I_C+625I_D], \tag{2.4.2}$$

$$J_3=\frac{4\pi}{35}[6I_A+8I_B-3I_C+24I_E], \tag{2.4.3}$$

$$J_4=\frac{4\pi}{70}[17I_A-64I_B-126I_C+243I_F], \tag{2.4.4}$$

$$J_5=\frac{4\pi}{10395}[1197I_A+1456I_B+729I_C+3125I_D+3888I_E], \tag{2.4.5}$$

$$J_6=\frac{4\pi}{83160}[7281I_A-13312I_B-13608I_C+59049I_F+43750I_D], \tag{2.4.6}$$

$$J_7=\frac{4\pi}{770}[117I_A+416I_B+294I_C+672I_E-729I_F], \tag{2.4.7}$$

$$J_8=\frac{4\pi}{1081080}[117603I_A+76544I_B+17496I_C+381250I_D+311040I_E+177147I_F]. \tag{2.4.8}$$

3. DEBYE Θ FOR SOME CUBIC CRYSTALS

The calculation of Debye characteristic temperature involves the evaluation of the integral

$$J=\int_0^{\pi}\int_0^{2\pi} I(\theta,\varphi)\,\sin\theta d\theta d\varphi,$$

with

$$I=\textstyle\sum_i\{v_i(\theta,\varphi)\}^{-3}. \tag{3.1}$$

Here $v_i(\theta,\varphi)$, $(i=1, 2, 3)$, are the velocities of the three elastic waves for a given direction (θ,φ) of propagation. In terms of the elastic constants c_{11}, c_{12}, and c_{44} of a cubic crystal, the v_i are given by the well-known Christoffel's equations of the elasticity theory.[11] The Debye Θ and J are related by the equation[12]

$$\Theta=(h/k)(9s/\Delta)^{\frac{1}{3}}J^{-\frac{1}{3}}, \tag{3.2}$$

where Δ is the cell volume, s the number of atoms per cell and h and k have their usual meaning.

On solving the equations of the elasticity theory for the velocities $v_i(\theta,\varphi)$ along the directions A, B, $\cdots F$, one finds the following expressions for I_A, I_B, etc.:

$$\begin{aligned}
I_A&=\rho^{\frac{3}{2}}\{2[c_{44}]^{-\frac{3}{2}}+[c_{44}+\alpha]^{-\frac{3}{2}}\},\\
I_B&=\rho^{\frac{3}{2}}\{[c_{44}]^{-\frac{3}{2}}+[c_{44}+\tfrac{1}{2}(\alpha-\beta)]^{-\frac{3}{2}}+[c_{44}+\tfrac{1}{2}(\alpha+\beta)]^{-\frac{3}{2}}\},\\
I_C&=\rho^{\frac{3}{2}}\{2[c_{44}+\tfrac{1}{3}(\alpha-\beta)]^{-\frac{3}{2}}+[c_{44}+\tfrac{1}{3}(\alpha+2\beta)]^{-\frac{3}{2}}\},\\
I_D&=\rho^{\frac{3}{2}}\{[c_{44}]^{-\frac{3}{2}}+[c_{44}+\tfrac{1}{2}\alpha+\tfrac{1}{10}(9\alpha^2+16\beta^2)^{\frac{1}{2}}]^{-\frac{3}{2}}\\
&\qquad+[c_{44}+\tfrac{1}{2}\alpha-\tfrac{1}{10}(9\alpha^2+16\beta^2)^{\frac{1}{2}}]^{-\frac{3}{2}}\},\\
I_E&=\rho^{\frac{3}{2}}\{[c_{44}+\tfrac{1}{6}(\alpha-\beta)]^{-\frac{3}{2}}+[c_{44}+\tfrac{1}{12}(5\alpha+\beta)\\
&\qquad+\tfrac{1}{12}(9\alpha^2+33\beta^2-6\alpha\beta)^{\frac{1}{2}}]^{-\frac{3}{2}}+[c_{44}+\tfrac{1}{12}(5\alpha+\beta)\\
&\qquad-\tfrac{1}{12}(9\alpha^2+33\beta^2-6\alpha\beta)^{\frac{1}{2}}]^{-\frac{3}{2}}\},\\
I_F&=\rho^{\frac{3}{2}}\{[c_{44}+(4/9)(\alpha-\beta)]^{-\frac{3}{2}}+[c_{44}+(1/18)(5\alpha+4\beta)\\
&\qquad+(1/18)(9\alpha^2+48\beta^2+24\alpha\beta)^{\frac{1}{2}}]^{-\frac{3}{2}}\\
&\qquad+[c_{44}+(1/18)(5\alpha+4\beta)\\
&\qquad-(1/18)(9\alpha^2+48\beta^2+24\alpha\beta)^{\frac{1}{2}}]^{-\frac{3}{2}}\},
\end{aligned} \tag{3.3}$$

where ρ is the density of the substance and where, for convenience, we have written

$$\alpha=c_{11}-c_{44} \quad \text{and} \quad \beta=c_{12}+c_{44}. \tag{3.4}$$

We may now calculate Debye Θ for a cubic crystal by substituting for J any of the eight approximations given by Eqs. (2.4) in Eq. (3.2). We denote a Θ value obtained by using for J a given J_μ $(\mu=1, 2, \cdots 8)$ by Θ_μ. We have calculated Θ_μ $(\mu=1, 2, \cdots 8)$ for nine typical cubic crystals and these results are collected in Table I. For this calculation the values of the elastic constants, density, etc., were taken from Blackman's paper.[13] In the last column of the table the Θ values obtained by Blackman by numerical integration are given. We also give (second column) values for

$$\eta=2c_{44}/(c_{11}-c_{12}); \tag{3.5}$$

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[11] A. E. H. Love, *Mathematical Theory of Elasticity* (Dover Publications, New York, 1944), fourth edition, p. 299.

[12] See, for example, reference 13 or 7.

[13] M. Blackman, Proc. Roy. Soc. (London) **A164**, 62 (1938): The values of the elastic constants are taken from here rather than any later data in order to be able to compare the Θ values computed in this paper with those obtained by Blackman by numerical integration. For lead, the elastic constants and the Θ value given in the last column of Table I are taken from C. Kittel, *Introduction to Solid State Physics* (John Wiley and Sons, Inc., New York, 1953).

TABLE I. Debye Θ in various approximations. Θ_1 corresponds to the three-term approximation to J of reference 7; Θ_2, Θ_3, Θ_4 and Θ_5, Θ_6, Θ_7 correspond respectively to the three four-term and three five-term approximations to J mentioned in the text; Θ_8 is obtained with the six-term formula (2.4.8) for J, and Θ_B (last column) are the values obtained by Blackman by numerical integration.

Substance	$\eta=\dfrac{2c_{44}}{c_{11}-c_{12}}$	Θ_1	Θ_2	Θ_3	Θ_4	Θ_5	Θ_6	Θ_7	Θ_8	Θ_B
NaCl	0.762	302.7	303.3	303.3	303.5	303.3	303.3	303.3	303.3	302
KCl	0.370	220.2	224.5	226.7	234.4	225.7	226.4	224.8	225.9	227
MgO	1.51	943	946	939	940	946	946	947.0	946.0	946
Al	1.23	405.0	406.0	406.0	405.5	406.0	406.0	406.0	406.0	398
Cu	3.26	328.1	349.4	340.7	336.4	344.5	346.5	341.8	345.0	342
Ag	2.96	203.6	214.9	210.6	207.5	212.8	213.3	213.1	212.7	212
Pb	4.0	82.7	91.9	87.7	87.5	89.5	90.9	87.9	89.8	88
Li	7.80	323	391	353	449	368	401	337	375	354
Na	8.10	129	161	143	188	150	166	137	153	143

the deviation of η from unity is a measure of the elastic anisotropy of the crystal. [For elastically isotropic crystals ($\eta=1$), $\Theta_1=\Theta_2=\cdots\Theta_8=\Theta_{\text{exact}}$.]

Discussion

From the table it will be seen that for NaCl, MgO, and Al for which $\eta=0.762$, 1.51, and 1.23, respectively, the various approximations to Θ differ from each other and from Θ_B (Blackman's values) by less than 0.5 percent. For KCl, Cu, and Ag for which $\eta=0.37$, 3.26, and 2.96, respectively, the three five-term approximations Θ_5, Θ_6, and Θ_7 and the six-term approximation Θ_8 differ from each other and from Θ_B by at most 1%; for Pb ($\eta=4.0$) this difference is about 3%. However, the three-term and the three four-term approximations are comparatively poor for these substances. For the highly anisotropic metals Na and Li ($\eta\sim8$), we find that though Θ_5, Θ_6, Θ_7, and Θ_8 are much closer to each other and to Θ_B than are Θ_1, Θ_2, Θ_3, and Θ_4, even Θ_8 (the six-term approximation) differs from Θ_B by about 7%. We may mention that we have also tried other five-term approximations in which we evaluated Θ by taking values of $I(\theta,\varphi)$ along the directions C, D, E, and two of A, B, and F. The various approximations to Θ differ again only little from each other for substances other than Na and Li. For the latter metals, however, they remain unsatisfactory, and even become more so. These results for the alkali metals are to be expected to some extent since, because of their large anisotropy, the function $I(\theta,\varphi)$ varies with θ and φ within much wider limits than for the less anisotropic crystals.

Mention may be made here of the graphical methods of calculating Debye Θ for cubic crystals given by Quimby and Sutton[14] and Sutton[14] and a numerical method due to de Launay.[15] The Debye Θ for silver calculated by the graphical methods,[14] with the same elastic constants as used in the present paper, is 211.3°K as compared to $\Theta_8=212.7$°K.

From the preceding discussion it may be concluded that for cubic crystals for which $\eta[=2c_{44}/(c_{11}-c_{12})]$ lies between 0.5 and 1.5, the three-term approximation to Θ is in error by at most a fraction of a percent. For η in the range $0.3\leqslant\eta\leqslant3.3$, the six-term approximation [characterized by Eqs. (2.4.8), (3.2), and (3.3)] to Θ is in error by at most 1% and the error is not much greater for η lying in the range $0.25\leqslant\eta\leqslant4.0$. For the alkali metals, however, for which $\eta\sim8$, one would have to take more than six terms in the expansion (1.1) to obtain Θ values to this order of accuracy. We may remark that, as far as is known to us, there are hardly any cubic crystals, except the alkalis, for which η does not lie in the range $0.25\leqslant\eta\leqslant4.0$.

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APPENDIX

A Kubic Harmonic is defined as a homogeneous polynomial solution of Laplace's equation which obeys certain symmetry properties with respect to the operations of the cubic symmetry group. Following Von der Lage and Bethe[2] we say that a Kubic Harmonic is of α type if it is invariant under all the operations of the cubic symmetry group. Restricting ourselves to Kubic Harmonics of α type, we shall: (1) determine the number of polynomials in a complete, linearly independent, set of Kubic Harmonics of degree $2n$; (2) give formulas that determine a complete, linearly independent, set of Kubic Harmonics of degree $2n$; (3) indicate a method for forming a complete set of Kubic Harmonics which are orthogonal over the unit sphere.

Polynomials which are invariant to reflexive symmetries, of the type $x\leftrightarrow -x$, etc., must be polynomials of the form $P(x^2,y^2,z^2)$. If we introduce a symmetrization operation S by

$$SP(x^2,y^2,z^2)=\tfrac{1}{6}[P(x^2,y^2,z^2)+P(y^2,x^2,z^2)+P(z^2,x^2,y^2)+P(y^2,z^2,x^2)+P(x^2,z^2,y^2)+P(z^2,y^2,x^2)],\quad (\text{A}.1)$$

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[14] S. L. Quimby and P. M. Sutton, Phys. Rev. **91**, 1122 (1953); P. M. Sutton, Phys. Rev. **99**, 1826 (1955).

[15] J. de Launay, J. Chem. Phys. **22**, 1676 (1954).

then every polynomial of the form $SP(x^2,y^2,z^2)$ has cubic symmetry.

Our major problem is to determine the polynomials of the form $SP(x^2,y^2,z^2)$ which are also solutions of Laplace's equation $\nabla^2 V=0$. As a partial step in solving this problem, we seek solutions of the form

$$V=z^{2r+2s}F(u,v),\quad u=-x^2/z^2,\quad v=-y^2/z^2,\qquad r,s=0,1,2\cdots. \tag{A.2}$$

In order that V be a harmonic it is easily shown that F must satisfy

$$u(1-u)\frac{\partial^2 F}{\partial u^2}+v(1-v)\frac{\partial^2 F}{\partial v^2}-2uv\frac{\partial^2 F}{\partial u\partial v}+[\tfrac{1}{2}-(\tfrac{3}{2}-2r-2s)u]\frac{\partial F}{\partial u}+[\tfrac{1}{2}-(\tfrac{3}{2}-2r-2s)v]\frac{\partial F}{\partial v}-(r+s)(r+s-\tfrac{1}{2})F=0. \tag{A.3}$$

Equation (A.3) is satisfied by the Appell polynomials[16]

$$F=F_2(\tfrac{1}{2}-r-s,\,-r,\,-s,\,\tfrac{1}{2},\,\tfrac{1}{2},\,u,\,v), \tag{A.4}$$

where $F_2(\alpha,\beta,\beta',\gamma,\gamma',u,v)$ is given by

$$F_2=\frac{\Gamma(\gamma)\Gamma(\gamma')}{\Gamma(\alpha)\Gamma(\beta)\Gamma(\beta')}\sum_{k=0}^{\infty}\sum_{k'=0}^{\infty}\times\frac{\Gamma(\alpha+k+k')\Gamma(\beta+k)\Gamma(\beta'+k')u^k v^{k'}}{\Gamma(\gamma+k)\Gamma(\gamma'+k')k!k'!}. \tag{A.5}$$

By introducing the new variables

$$\xi=x^2,\quad \eta=y^2,\quad \zeta=z^2, \tag{A.6}$$

and using the known[16] properties of the Appell polynomials, it is possible to derive a Rodrique-type formula, for the harmonic V, of the form

$$V=A_{rs}(\xi,\eta,\zeta)=\frac{\Gamma^2(\frac{1}{2})(\xi\eta\zeta)^{\frac{1}{2}}}{\Gamma(r+\frac{1}{2})\Gamma(s+\frac{1}{2})}\frac{\partial^{r+s}}{\partial\xi^r\partial\eta^s}\times(\xi^{r-\frac{1}{2}}\eta^{s-\frac{1}{2}}\zeta^{r+s-\frac{1}{2}}). \tag{A.7}$$

During differentiation, ζ is treated as if it were equal to $1-\xi-\eta$. However, in the powers of ζ that remain after differentiation, ζ is again taken to be independent of ξ, η.

The following properties of the Appell polynomials $A_{rs}(\xi,\eta,1-\zeta-\eta)$, in the two variables ξ, η, are well known[16]: 1. The polynomials $A_{rs}(\xi,\eta,1-\zeta-\eta)$ form an orthogonal set for different values of $n=r+s$, over the triangles $\zeta\geq 0$, $\eta\geq 0$, $\zeta+\eta\leq 1$. 2. The weight function for orthogonalization is $[\xi\eta(1-\xi-\eta)]^{\frac{1}{2}}$. 3. The polynomials $A_{rs}(\xi,\eta,1-\xi-\eta)$ are linearly independent.

From these properties and (A.7), it is easily shown that the polynomial harmonics $A_{rs}(x^2,y^2,z^2)$ have the following properties: 1. $A_{rs}(x^2,y^2,z^2)$ are homogeneous polynomial harmonics of degree $2n$, where $n=r+s$. 2. This set of polynomials is linearly independent. 3. For different values of $n=r+s$, the set $A_{rs}(x^2,y^2,z^2)$ is orthogonal over the unit sphere. 4. The weight function is unity. 5. For fixed n and varying r and s, the polynomials so generated are not orthogonal over the unit sphere.

Further, by symmetrization, the set of polynomials $K_{rs}(x^2,y^2,z^2)$ defined by

$$K_{rs}(x^2,y^2,z^2)=SA_{rs}(x^2,y^2,z^2) \tag{A.8}$$

are all Kubic Harmonics. Hence we can say that a complete set of linearly independent Kubic Harmonics must be contained within the set K_{rs}. Since some of the K_{rs} are zero and others are linearly dependent, we have not as yet determined the number of polynomials in a complete set of linearly independent Kubic Harmonics. For example, $K_{0,1}=K_{1,0}=0$, $K_{2,0}=K_{1,1}=K_{0,2}$.

The total number of polynomials A_{rs} such that $r+s\leq n$ is $(n+1)(n+2)/2$. If $\rho^2=x^2+y^2+z^2$, then it is easily seen that the set of polynomials $\rho^{2n-2r-2s}A_{rs}$, $(r+s\leq n)$, form a set of $(n+1)(n+2)/2$ linearly independent homogeneous polynomials of degree $2n$. This in turn implies that every homogeneous polynomial $P(x^2,y^2,z^2)$ of degree $2n$ can be written as a linear combination of $\rho^{2n-2r-2s}K_{rs}$. Hence every polynomial $SP(x^2,y^2,z^2)$, with cubic symmetry, can be written as a linear combination of $\rho^{2n-2r-2s}K_{rs}$.

It is easily shown that the number of polynomials, in a linearly independent, complete, set of polynomials with cubic symmetry of degree $2n$, is $p_3(n)$. By $p_3(n)$ we mean the number of ways of partitioning a number n into at most three parts a, b, c such that $n=a+b+c$. The values and properties of $p_3(n)$ are well known.[16]

The preceding analysis shows that a linearly independent, complete, set of Kubic Harmonics must contain at least $p_3(n)$ polynomials. We shall now prove that this inequality also runs the other way.

Let us consider a complete set T of linearly independent polynomials with the following properties: (a) every polynomial of T is homogeneous and has cubic symmetry. (b) every two polynomials of T, whose degrees are different, are orthogonal over the unit sphere. Since T is complete, it is clear that every K_{rs} can be written as a linear combination of the polynomials of T. Let us denote by $f(n)$ the number of polynomials of T whose degree is $\leq 2n$. The number of polynomials of T whose degree $=2n$ is $f(n)-f(n-1)$. We have already shown that there are $p_3(n)$ linearly independent polynomials with cubic symmetry of degree $2n$. Out of these we can construct $p_3(n)-f(n-1)$ such polynomials that will also have the required orthog-

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[16] Erdelyi, Magnus, Oberhettinger, and Tricomi, *Higher Transcendental Functions* (McGraw-Hill Book Company, Inc., New York, 1953), Vol. 2.

onal property. Hence $f(n)=p_3(n)$. Finally a complete set of linearly independent Kubic Harmonics, of degree $\leq 2n$, can have no more than $p_3(n)$ polynomials in the set. Hence we obtain the following results: 1. The total number of polynomials in a complete, linearly independent, set of Kubic Harmonics of degree $\leq 2n$ is $p_3(n)$. 2. The total number of polynomials in a linearly independent, complete, set of Kubic Harmonics of degree $2n$ is $p_3(n)-p_3(n-1)$.

The generating function for $p_3(n)$ is[16]

$$1+\sum_{n=1}^{\infty} p_3(n)x^n=[(1-x)(1-x^2)(1-x^3)]^{-1}. \quad \text{(A.9)}$$

Hence

$$1+\sum_{n=1}^{\infty} [p_3(n)-p_3(n-1)]x^n=[(1-x^2)(1-x^3)]^{-1}$$
$$=1+x^2+x^3+x^4+x^5+2x^6+x^7+2x^8\cdots. \quad \text{(A.10)}$$

We see from (A.10), that there is at most one independent Kubic Harmonic of each degree up to degree 10. Further, up to degree 24 there are at most two such harmonics for each degree. From the point of view of expansion purposes, it is desirable to have a completely orthogonal set. Our set is orthogonal only for different degrees. However, up to fairly large degrees, the construction of a completely orthogonal set from our set is relatively easy. For example, to orthogonalize up to degree 14 we need only orthogonalize $K_{0,6}$ and a linear combination of $K_{0,6}$ and $K_{2,4}$.

From (A.7) we can derive the following explicit formula for $A_{rs}(x^2,y^2,z^2)$:

$$A_{rs}=\frac{(2r+2s)!r!s!}{(r+s)!}\sum_{a=0}^{r}\sum_{b=0}^{s} \times\frac{(-1)^{r+s-a-b}(a+b)!x^{2r-2a}y^{2s-2b}z^{2a+2b}}{a!b!(2a+2b)!(2r-2a)!(2s-2b)!}, \quad \text{(A.11)}$$

and of course

$$K_{rs}=SA_{rs}(x^2,y^2,z^2). \quad \text{(A.12)}$$

If we let $i=\sqrt{(-1)}$, and as usual $Rl(a+ib)=a$, we find from (A.11) that

$$A_{0,s}=Rl(z+iy)^{2s}. \quad \text{(A.13)}$$

If is odd, $SA_{0,s}=0$. If $s=2n$, then

$$K_{0,2n}=S[Rl(z+iy)^{4n}] \quad \text{(A.14)}$$

is a Kubic Harmonic of degree $4n$. Similarly, we can show that

$$K_{1,2n}=\tfrac{1}{2}S\{Rl(z+iy)^{4n}[y^2+z^2-(8n+2)x^2]\} \quad \text{(A.15)}$$

is a Kubic Harmonic of degree $4n+2$. The set of polynomials $K_{0,2n}$, $K_{1,2n}$ form a set of Kubic Harmonics containing every degree. Further, the members of the set are orthogonal to each other over the unit sphere. Unfortunately they are not complete beyond degree 10.

Notation

Although the notation K_{rs} is useful in our derivation of Kubic Harmonics, it seems better, in their application, to use the following notation.

If $n=r+s$, we write a linearly independent set of Kubic Harmonics of degree $2n$ as $K_n^{(1)}$, $K_n^{(2)}$, $\cdots$, $K_n^{p_3(n)-p_3(n-1)}$. If the set contains only one element, we drop the superscript. In this notation, the Kubic Harmonics up to degree 12 can be written

$$K_0=1, \quad K_1=0, \quad K_2=S(2x^4-6x^2y^2),$$
$$K_3=S(x^6-15x^4y^2+180x^2y^2z^2),$$
$$K_4=S(2x^8-56x^6y^2+70x^4y^4),$$
$$K_5=S(x^{10}-45x^8y^2+42x^6y^4-630x^4y^4z^2+504x^2y^6z^2),$$
$$K_6^{(1)}=K_{0,6}=S(2x^{12}-132x^{10}y^2+990x^8y^4-924x^6y^6),$$
$$K_6^{(2)}=K_{2,4}=S[x^{12}-66x^{10}y^2+297x^8y^4-(924/5)x^6y^6$$
$$+594x^8y^2z^2-2772x^6y^4z^2+2310x^4y^4z^4]. \quad \text{(A.16)}$$