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Point Group Symmetries and Gaussian Integration*

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A computationally efficient and exact method of symmetrizing a complete set of angular functions using Gaussian integration is presented. This technique will be useful in situations such as crystal field-type calculations, full potential electronic structure calculations, and wherever symmetrized functions of a given irreducible representation are needed. As an example, combinations of spherical harmonics transforming as the completely symmetric irreducible representation are given for all the 32 crystallographic point groups in three dimensions.
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INTRODUCTION

The use of symmetrized functions in solid state physics is nearly as old as the subject itself. Early on Wigner, von Neuman, Weyl, and others demonstrated [1] the usefulness of group theory in solid state physics. A non-empty collection of $n \times n$ rotation matrices that satisfy the group postulates is called a faithful representation of a crystallographic point group, if at a given point, the n-dimensional crystal lattice transforms into itself under the action of an arbitrary member of the collection and this collection contains all such rotations. This requirement of leaving the lattice invariant, severely restricts the number of otherwise infinite number of finite groups that can be formed using these rotation matrices. In three dimensions, this number is 32, while in two dimensions it equals 10.

It is clearly useful to work with functions that transform according to the symmetries of the lattice as many of the early researchers of solid state physics (e.g., von der Lage and Bethe [2]) realized in the 1930s and 1940s. In later work, Altmann, Cracknell, Bradley [3, 4], and others extended some of these early ideas to generally practical and computational levels. Some of the computational techniques used to obtain these symmetrized functions, however, are not always straightforward, in a computational sense. As an example, when rotations of axes are involved, specification of Euler angles may be necessary.

What we are about to describe is a simple algorithm for obtaining these symmetrized functions using a Gaussian integration technique. It will be useful in situations that involve crystal field-type calculations, full-potential methods, and in constructing eigenfunctions that transform according to a given irreducible representation. This method, we believe, is computationally superior and less cumbersome, compared to other techniques involving Euler angles. It also has the flexibility of calculating symmetry coefficients for arbitrary axes. Although this technique can easily be generalized, we limit our discussion to three-dimensional crystalline symmetries, in particular to the determination of the completely symmetric lattice harmonics of the 32 crystallographic point groups.

Most importantly, this method should be regarded as an alternate way of carrying out symmetrization, that can be easily automated. For the symmetrized spherical harmonics shown in our tables, the technique turns out to be exact. With automation, we have an efficient scheme that can be used to handle, for example, higher l values, or nonstandard axes as demonstrated here.

SYMMETRIZATION

The basis for symmetrization is the theorem that if $\Gamma^{(1)}$, $\Gamma^{(2)}$, ..., $\Gamma^{(n)}$ are all the distinct irreducible representations

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of a group of operators $\mathbf{R}$, then any function F in the space of the operators $\mathbf{R}$ can be decomposed into a sum

$$F = \sum_{j=1}^{n} \sum_{v=1}^{l_j} f_v^{(j)}, \tag{1}$$

where $f_v^{(j)}$ belongs to the vth row of the jth irreducible representation of dimension l_j. Combining this result with theorems regarding the properties (especially orthogonality) of representations, yields

$$f_v^{(j)} = \frac{l_j}{h} \sum_{\mathbf{R}} \Gamma^{(j)}(\mathbf{R})_{vv}^{*} \mathbf{R} F, \tag{2}$$

where h is the order of the group. The action of the operators $\mathbf{R}$ on a function (in the active representation) is

$$\mathbf{R} F(\mathbf{r}) = F(\mathbf{R}^{-1}\mathbf{r}). \tag{3}$$

If a complete set of functions is substituted into the above equations, then the set of $f_v^{(j)}$ will be a complete set of *symmetrized* basis functions.

At this point we specialize to the case of the spherical harmonics $Y_{lm}(\hat{r})$, which form a complete set over angular functions. Generalizations to other complete sets is straightforward. The symmetrized functions for a given l can be written as

$$\begin{aligned} K_{lv}^{(j)}(\hat{r}) &= \sum_{m} c_{vm}^{l(j)} Y_{lm}(\hat{r}) \\ &= \frac{l_j}{h} \sum_{\mathbf{R}} \Gamma^{(j)}(\mathbf{R})_{vv}^{*} Y_{l\mu}(\mathbf{R}^{-1}\hat{r}). \end{aligned} \tag{4}$$

If F is given as an arbitrary combination of Y_{lm}'s, then applying Eq. (2) will generate the symmetrized basis functions needed. Equivalently, as in Eq. (4), we can apply the projection operator given in Eq. (2) to each $Y_{l\mu}$ ($\mu = -l, ..., l$) separately and keep only the non-zero functions. In this case, the lattice harmonic coefficients are given by

$$\begin{aligned} c_{vm}^{l(j)}(\mu) &= \frac{l_j}{h} \sum_{\mathbf{R}} \Gamma^{(j)}(\mathbf{R})_{vv}^{*} \\ &\quad \times \int d\hat{r}\, Y_{lm}^{*}(\hat{r})\, Y_{l\mu}(\mathbf{R}^{-1}\hat{r}). \end{aligned} \tag{5}$$

By considering all values of μ, a set of symmetrized basis functions will be generated.

The coefficients of all the lattice harmonics that transform according to a given irreducible representation can be generated by this procedure. In the (rather common) case that there are more than one symmetrized function that transform according to a given irreducible representation, orthonormalization can be carried out using the standard Gram–Schmidt procedure. The standard way of calculating the integral in Eq. (5) involves the use of Euler angles. What we propose is to use Gaussian quadrature to directly and *exactly* calculate this integral. The advantage of this method is that once given a representation of the rotation matrices $\mathbf{R}$, the integrals are obtained quite simply. As an example where this feature is important, consider the density or potential in a complicated crystal structure. These functions transform according to the completely symmetric representation of the space group. Locally about each site, the point group symmetry will be a subgroup of the global space group symmetry, but often with rotated principal axes compared to the standard settings. While it is obviously possible to determine the Euler angles, the method suggested in this paper needs only the representations of the $\mathbf{R}$ operators in the global coordinate system and the positions of the sites to generate the local point group symmetry and the corresponding lattice harmonics. This simplification allows the group theory to be done easily and exactly by computer.

GAUSSIAN INTEGRATION

Gaussian quadrature is an efficient method of numerically evaluating a definite integral [5]. In contrast to Newton–Cotes-type integration methods in which the integral is approximated by the sum of the integrand evaluated at equally spaced points and multiplied by properly chosen weights, in Gaussian quadrature methods, both the abscissas and the weights in the approximation can be chosen, effectively doubling the number of degrees of freedom. The method is closely tied to a set of polynomials orthogonal over a weight function $W(x)$ in an interval (a, b); the abscissas are the roots of the polynomials and the weights are related to the derivatives. Thus, an N-point approximation has the important property that

$$\int_a^b W(x)\, f(x)\, dx \approx \sum_{i=1}^{N} w_i f(x_i) \tag{6}$$

is *exact* if $f(x)$ is a polynomial of order $2N-1$ or less. (It can be shown that the error term that is associated with this approximation is proportional to the $2N$th derivative of f evaluated at some point inside the interval (a, b)). As an example, any definite integral $\int_{-1}^{1} f(x)\, dx$, of a well behaved function f, may be approximated by the above formula with weights w_j given by

$$w_j = 2/\{(1-a_j^2)(P'_N(a_j))^2\}. \tag{7}$$

The P'_Ns are derivatives of Legendre polynomials and the a_js are the roots of P_Ns.

As discussed in the previous section, any rotated Y_{lm} can be expressed in terms of spherical harmonics of the same l. Thus the integrand in Eq. (5) consists of terms of the form

$$\frac{2l+1}{4\pi}\sqrt{\frac{(l-m)!\,(l-m')!}{(l+m)!\,(l+m')!}}\int_{-1}^{1} dx\, P_l^m(x) \times P_{l'}^{m'}(x)\int_0^{2\pi} d\phi\, e^{i(m'-m)\phi}. \quad (8)$$

The integral over ϕ is related to the discrete Fourier transform, as well as to Gaussian quadrature. The number of uniformly spaced points (with uniform weights) necessary to exactly evaluate the ϕ integral is determined by the maximum values of the integers $m'-m$, via the Nyquist frequency. The result is, of course, $2\pi\delta_{m,m'}$. Thus the numerical integral projects out the $m=m'$ component.

Given that $m=m'$, it is simple to show that $P_l^m(x)\, P_{l'}^m(x)$ is a polynomial of order $l+l'$: Since

$$P_l^m(x)=(-1)^m\,(1-x^2)^{m/2}\,\frac{d^m}{dx^m}\,P_l(x), \quad (9)$$

then

$$P_l^m(x)\,P_{l'}^m(x)=(1-x^2)^m\,\frac{d^m}{dx^m}\,P_l(x)\,\frac{d^m}{dx^m}\,P_{l'}(x), \quad (10)$$

which is a polynomial of order $2m+(l-m)+(l'-m)=l+l'$. Thus Gaussian integration will give *exact* results for integrals of the type in Eqs. (5) and (8) if the weight function is chosen as $W(x)=1$ for the θ (or $x=\cos\theta$) angular integration, as long as the number of quadrature points N

TABLE I

Triclinic Groups: Lattice Harmonics

1. Point group C_1 (1)

Harmonics 1–256

$m=0$	Y_{l0}
$m\neq 0$	$\frac{1}{\sqrt{2}}\{Y_{lm}+(-1)^m\,Y_{l-m}\}$
	$\frac{i}{\sqrt{2}}\{Y_{lm}-(-1)^m\,Y_{l-m}\}$

2. Point group C_i ($\bar{1}$)

Harmonics 1–120, l even

$m=0$	Y_{l0}
$m\neq 0$	$\frac{1}{\sqrt{2}}\{Y_{lm}+(-1)^m\,Y_{l-m}\}$
	$\frac{i}{\sqrt{2}}\{Y_{lm}-(-1)^m\,Y_{l-m}\}$

TABLE II

Monoclinic Groups: Lattice Harmonics

3. Point group C_2 (2)

Harmonics 1–128

$m=0$	Y_{l0}
$m=2, 4, \ldots$	$\frac{1}{\sqrt{2}}\{Y_{lm}+Y_{l-m}\}$
	$\frac{i}{\sqrt{2}}\{Y_{lm}-Y_{l-m}\}$

4. Point group C_{1h} (m)

Harmonics 1–136, $l+m$ even

$m=0$	Y_{l0}
$m\neq 0$	$\frac{1}{\sqrt{2}}\{Y_{lm}+(-1)^m\,Y_{l-m}\}$
	$\frac{i}{\sqrt{2}}\{Y_{lm}-(-1)^m\,Y_{l-m}\}$

5. Point group C_{2h} ($2/m$)

Harmonics 1–64, l even

$m=0$	Y_{l0}
$m=2, 4, \ldots$	$\frac{1}{\sqrt{2}}\{Y_{lm}+Y_{l-m}\}$
	$\frac{i}{\sqrt{2}}\{Y_{lm}-Y_{l-m}\}$

TABLE III

Orthorhombic Groups: Lattice Harmonics

6. Point group D_2 (222)

Harmonics 1–64

$m=0$, l even	Y_{l0}
$m=2, 4, \ldots$	$\frac{i^l}{\sqrt{2}}(Y_{lm}+(-1)^l\,Y_{l-m})$

7. Point group C_{2v} ($mm2$)

Harmonics 1–72

$m=0$	Y_{l0}
$m=2, 4, \ldots$	$\frac{1}{\sqrt{2}}(Y_{lm}+Y_{l-m})$

8. Point group D_{2h} (mmm)

Harmonics 1–36, l even

$m=0$	Y_{l0}
$m=2, 4, \ldots$	$\frac{1}{\sqrt{2}}(Y_{lm}+Y_{l-m})$

TABLE IV

Tetragonal Groups: Lattice Harmonics

9. Point group C_4 (4)	
Harmonics 1–64	
$m=0$	Y_{l0}
$m=4, 8, \ldots$	$\frac{1}{\sqrt{2}}(Y_{lm}+Y_{l-m})$
	$\frac{i}{\sqrt{2}}(Y_{lm}-Y_{l-m})$
10. Point group S_4 ($\bar{4}$)	
Harmonics 1–64	
$m=0$, l even	Y_{l0}
$m=2, 6, \ldots$, l odd	$\frac{1}{\sqrt{2}}(Y_{lm}+Y_{l-m})$
	$\frac{i}{\sqrt{2}}(Y_{lm}-Y_{l-m})$
$m=4, 8, \ldots$, l even	$\frac{1}{\sqrt{2}}(Y_{lm}+Y_{l-m})$
	$\frac{i}{\sqrt{2}}(Y_{lm}-Y_{l-m})$
11. Point group C_{4h} ($4/m$)	
Harmonics 1–32, l even	
$m=0$	Y_{l0}
$m=4, 8, \ldots$	$\frac{1}{\sqrt{2}}(Y_{lm}+Y_{l-m})$
	$\frac{i}{\sqrt{2}}(Y_{lm}-Y_{l-m})$
12. Point group D_4 (422)	
Harmonics 1–32	
$m=0$, l even	Y_{l0}
$m=4, 8, \ldots$	$\frac{i^l}{\sqrt{2}}(Y_{lm}+(-1)^l\, Y_{l-m})$
13. Point group C_{4v} ($4mm$)	
Harmonics 1–40	
$m=0$	Y_{l0}
$m=4, 8, \ldots$	$\frac{1}{\sqrt{2}}(Y_{lm}+Y_{l-m})$
14. Point group D_{2d} ($\bar{4}2m$)	
Harmonics 1–36	
$m=0$, l even	Y_{l0}
$m=2, 6, \ldots$, l odd	$\frac{i}{\sqrt{2}}(Y_{lm}-Y_{l-m})$
$m=4, 8, \ldots$, l even	$\frac{1}{\sqrt{2}}(Y_{lm}+Y_{l-m})$
15. Point group D_{4h} ($4/mmm$)	
Harmonics 1–20, l even	
$m=0$	Y_{l0}
$m=4, 8, \ldots$	$\frac{1}{\sqrt{2}}(Y_{lm}+Y_{l-m})$

satisfy $l+l' < 2N$. This choice corresponds to the standard Gauss–Legendre quadrature formulas. Generalization to products of more spherical harmonics is straightforward.

TABLES OF SYMMETRIZED HARMONICS

Our tables give the symmetrized combinations of spherical harmonics that transform according to the completely symmetric irreducible representations for the 32 crystallographic point groups in three dimensions. These so-called lattice harmonics can always be chosen to be real. In

TABLE V

Trigonal Groups: Lattice Harmonics

16. Point group C_3 (3)	
Harmonics 1–86	
$m=0$	Y_{l0}
$m=3, 6, \ldots$	$\frac{1}{\sqrt{2}}(Y_{lm}+(-1)^m\, Y_{l-m})$
	$\frac{i}{\sqrt{2}}(Y_{lm}-(-1)^m\, Y_{l-m})$
17. Point group C_{3i} ($\bar{3}$)	
Harmonics 1–40, l even	
$m=0$	Y_{l0}
$m=3, 6, \ldots$	$\frac{1}{\sqrt{2}}(Y_{lm}+(-1)^m\, Y_{l-m})$
	$\frac{i}{\sqrt{2}}(Y_{lm}-(-1)^m\, Y_{l-m})$
18. Point group D_3 (32)	
Harmonics 1–43	
$m=0$, l even	Y_{l0}
$m=3, 6, \ldots$	$\frac{i^{l+m}}{\sqrt{2}}(Y_{lm}+(-1)^l\, Y_{l-m})$
19. Point group C_{3v} ($3m$)	
Harmonics 1–51	
$m=0$	Y_{l0}
$m=3, 6, \ldots$	$\frac{i^m}{\sqrt{2}}(Y_{lm}+Y_{l-m})$
20. Point group D_{3d} ($\bar{3}m$)	
Harmonics 1–24, l even	
$m=0$	Y_{l0}
$m=3, 6, \ldots$	$\frac{i^m}{\sqrt{2}}(Y_{lm}+Y_{l-m})$

TABLE VI

Hexagonal Groups: Lattice Harmonics

21. Point group C_6 (6)

Harmonics 1–44

$m=0$	Y_{l0}
$m=6, \ldots$	$\frac{1}{\sqrt{2}}(Y_{lm}+Y_{l-m})$
	$\frac{i}{\sqrt{2}}(Y_{lm}-Y_{l-m})$

22. Point group C_{3h} ($\bar{6}$)

Harmonics 1–46, $l+m$ even

$m=0$	Y_{l0}
$m=3, 6, \ldots$	$\frac{1}{\sqrt{2}}(Y_{lm}+(-1)^m Y_{l-m})$
	$\frac{i}{\sqrt{2}}(Y_{lm}-(-1)^m Y_{l-m})$

23. Point group C_{6h} ($6/m$)

Harmonics 1–22, l even

$m=0$	Y_{l0}
$m=6$	$\frac{1}{\sqrt{2}}(Y_{l6}+Y_{l-6})$
	$\frac{i}{\sqrt{2}}(Y_{l6}-Y_{l-6})$

24. Point group D_6 (622)

Harmonics 1–22

$m=0$, l even	Y_{l0}
$m=6$	$\frac{i^l}{\sqrt{2}}(Y_{l6}+(-1)^l Y_{l-6})$

25. Point group C_{6v} ($6mm$)

Harmonics 1–30

$m=0$	Y_{l0}
$m=6$	$\frac{1}{\sqrt{2}}(Y_{l6}+Y_{l-6})$

26. Point group D_{3h} ($\bar{6}m2$)

Harmonics 1–27, $l+m$ even

$m=0$	Y_{l0}
$m=3, 6, \ldots$	$\frac{1}{\sqrt{2}}(Y_{lm}+(-1)^m Y_{l-m})$

27. Point group D_{6h} ($6/mmm$)

Harmonics 1–15, l even

$m=0$	Y_{l0}
$m=6$	$\frac{1}{\sqrt{2}}(Y_{l6}+Y_{l-6})$

TABLE VII

Cubic Groups: Lattice Harmonics

28. Point group T (23)

Harmonic	
1	Y_{00}
2	$\frac{i}{\sqrt{2}}(Y_{32}-Y_{3-2})$
3	$\frac{1}{\sqrt{12}}\left\{\sqrt{7}\,Y_{40}+\sqrt{\frac{5}{2}}(Y_{44}+Y_{4-4})\right\}$
4	$\frac{1}{\sqrt{32}}\{\sqrt{5}(Y_{66}+Y_{6-6})-\sqrt{11}(Y_{62}+Y_{6-2})\}$
5	$\frac{1}{4}\{\sqrt{2}\,Y_{60}-\sqrt{7}(Y_{64}+Y_{6-4})\}$
6	$\frac{i}{\sqrt{48}}\{\sqrt{11}(Y_{76}-Y_{7-6})+\sqrt{13}(Y_{72}-Y_{7-2})\}$
7	$\frac{1}{8}\left\{\sqrt{33}\,Y_{80}+\sqrt{\frac{14}{3}}(Y_{84}+Y_{8-4})+\frac{1}{3}\sqrt{\frac{195}{2}}(Y_{88}+Y_{8-8})\right\}$
8	$\frac{i}{4}\left\{\sqrt{\frac{17}{3}}(Y_{94}-Y_{9-4})-\sqrt{\frac{7}{3}}(Y_{98}-Y_{9-8})\right\}$
9	$\frac{i}{4}\left\{\sqrt{\frac{13}{2}}(Y_{96}-Y_{9-6})-\sqrt{\frac{3}{2}}(Y_{92}-Y_{9-2})\right\}$
10	$\frac{1}{16}\left\{\sqrt{\frac{85}{2}}(Y_{1010}+Y_{10-10})-\sqrt{\frac{19}{6}}(Y_{106}+Y_{10-6})-\sqrt{\frac{247}{3}}(Y_{102}+Y_{10-2})\right\}$
11	$\frac{1}{8}\left\{-\sqrt{\frac{65}{6}}\,Y_{100}+\sqrt{11}(Y_{104}+Y_{10-4})+\frac{1}{2}\sqrt{\frac{187}{3}}(Y_{108}+Y_{10-8})\right\}$
12	$\frac{i}{8}\left\{\frac{1}{2}\sqrt{\frac{133}{3}}(Y_{1110}-Y_{11-10})+\frac{1}{2}\sqrt{27}(Y_{116}-Y_{11-6})+\sqrt{\frac{85}{6}}(Y_{112}-Y_{11-2})\right\}$

TABLE VII—*Continued*

13 $$\frac{1}{16}\left\{\frac{1}{5}\sqrt{\frac{676039}{246}}\,Y_{120}+\frac{1}{10}\sqrt{\frac{245157}{82}}\,(Y_{124}+Y_{12-4}) +\frac{1}{10}\sqrt{\frac{1771}{41}}\,(Y_{128}+Y_{12-8})+\frac{5}{2}\sqrt{\frac{41}{6}}\,(Y_{1212}+Y_{12-12})\right\}$$

14 $$\frac{1}{5\sqrt{41}}\left\{\frac{1}{4}\sqrt{891}\,Y_{120}-\sqrt{91}\,(Y_{124}+Y_{12-4}) +\frac{1}{4}\sqrt{\frac{12597}{2}}\,(Y_{128}+Y_{12-8})\right\}$$

15 $$\frac{1}{16}\left\{\sqrt{\frac{209}{6}}\,(Y_{1210}+Y_{12-10})-\sqrt{\frac{175}{2}}\,(Y_{126}+Y_{12-6}) +\sqrt{\frac{17}{3}}\,(Y_{122}+Y_{12-2})\right\}$$

16 $$\frac{i}{8\sqrt{3}}\left\{\frac{1}{2}\sqrt{\frac{253}{2}}\,(Y_{1312}-Y_{13-12})-\sqrt{5}\,(Y_{138}-Y_{13-8}) -\frac{5}{2}\sqrt{\frac{19}{2}}\,(Y_{134}-Y_{13-4})\right\}$$

17 $$\frac{i}{16\sqrt{3}}\left\{\sqrt{\frac{391}{2}}\,(Y_{1310}-Y_{13-10})+\sqrt{\frac{187}{2}}\,(Y_{136}-Y_{13-6}) -\sqrt{95}\,(Y_{132}-Y_{13-2})\right\}$$

18 $$\frac{1}{32}\left\{-\sqrt{\frac{595}{3}}\,Y_{140}+\frac{1}{2}\sqrt{429}\,(Y_{144}+Y_{14-4}) +\sqrt{\frac{247}{2}}\,(Y_{148}+Y_{14-8})+\frac{1}{2}\sqrt{\frac{2185}{3}}\,(Y_{1412}+Y_{14-12})\right\}$$

19 $$\frac{1}{64}\left\{\sqrt{\frac{1365}{2}}\,(Y_{1414}+Y_{14-14})-\sqrt{\frac{5}{6}}\,(Y_{1410}+Y_{14-10}) -\sqrt{\frac{253}{2}}\,(Y_{146}+Y_{14-6})-\sqrt{\frac{7429}{6}}\,(Y_{142}+Y_{14-2})\right\}$$

20 $$\frac{i}{8}\left\{\frac{1}{2}\sqrt{\frac{65}{2}}\,(Y_{1512}-Y_{15-12})-\sqrt{21}\,(Y_{158}-Y_{15-8}) +\frac{1}{2}\sqrt{\frac{23}{2}}\,(Y_{154}-Y_{15-4})\right\}$$

21 $$\frac{i}{64}\left\{\sqrt{685}\,(Y_{1514}-Y_{15-14})+\sqrt{\frac{2639}{137}}\,(Y_{1510}-Y_{15-10}) +\sqrt{\frac{95381}{137}}\,(Y_{156}-Y_{15-6})+\sqrt{\frac{88711}{137}}\,(Y_{152}-Y_{15-2})\right\}$$

22 $$\frac{i}{2\sqrt{274}}\left\{\sqrt{\frac{4807}{12}}\,(Y_{1510}-Y_{15-10})-\frac{1}{2}\sqrt{399}\,(Y_{156}-Y_{15-6}) +\sqrt{\frac{143}{3}}\,(Y_{152}-Y_{15-2})\right\}$$

29. Point group T_h ($m3$)

Harmonic

1 Y_{00}

2 $$\frac{1}{\sqrt{12}}\left\{\sqrt{7}\,Y_{40}+\sqrt{\frac{5}{2}}\,(Y_{44}+Y_{4-4})\right\}$$

3 $$\frac{1}{\sqrt{32}}\{\sqrt{5}\,(Y_{66}+Y_{6-6})-\sqrt{11}\,(Y_{62}+Y_{6-2})\}$$

4 $$\frac{1}{4}\{\sqrt{2}\,Y_{60}-\sqrt{7}\,(Y_{64}+Y_{6-4})\}$$

5 $$\frac{1}{8}\left\{\sqrt{33}\,Y_{80}+\sqrt{\frac{14}{3}}\,(Y_{84}+Y_{8-4})+\frac{1}{3}\sqrt{\frac{195}{2}}\,(Y_{88}+Y_{8-8})\right\}$$

6 $$\frac{1}{16}\left\{\sqrt{\frac{85}{2}}\,(Y_{1010}+Y_{10-10})-\sqrt{\frac{19}{6}}\,(Y_{106}+Y_{10-6}) -\sqrt{\frac{247}{3}}\,(Y_{102}+Y_{10-2})\right\}$$

7 $$\frac{1}{8}\left\{-\sqrt{\frac{65}{6}}\,Y_{100}+\sqrt{11}\,(Y_{104}+Y_{10-4})+\frac{1}{2}\sqrt{\frac{187}{3}}\,(Y_{108}+Y_{10-8})\right\}$$

8 $$\frac{1}{16}\left\{\frac{1}{5}\sqrt{\frac{676039}{246}}\,Y_{120}+\frac{1}{10}\sqrt{\frac{245157}{82}}\,(Y_{124}+Y_{12-4}) +\frac{1}{10}\sqrt{\frac{1771}{41}}\,(Y_{128}+Y_{12-8})+\frac{5}{2}\sqrt{\frac{41}{6}}\,(Y_{1212}+Y_{12-12})\right\}$$

9 $$\frac{1}{5\sqrt{41}}\left\{\frac{1}{4}\sqrt{891}\,Y_{120}-\sqrt{91}\,(Y_{124}+Y_{12-4}) +\frac{1}{4}\sqrt{\frac{12597}{2}}\,(Y_{128}+Y_{12-8})\right\}$$

10 $$\frac{1}{16}\left\{\sqrt{\frac{209}{6}}\,(Y_{1210}+Y_{12-10})-\sqrt{\frac{175}{2}}\,(Y_{126}+Y_{12-6}) +\sqrt{\frac{17}{3}}\,(Y_{122}+Y_{12-2})\right\}$$

11 $$\frac{1}{64}\left\{\sqrt{\frac{1365}{2}}\,(Y_{1414}+Y_{14-14})-\sqrt{\frac{5}{6}}\,(Y_{1410}+Y_{14-10}) -\sqrt{\frac{253}{2}}\,(Y_{146}+Y_{14-6})-\sqrt{\frac{7429}{6}}\,(Y_{142}+Y_{14-2})\right\}$$

12 $$\frac{1}{32}\left\{-\sqrt{\frac{595}{3}}\,Y_{140}+\frac{1}{2}\sqrt{429}\,(Y_{144}+Y_{14-4}) +\sqrt{\frac{247}{2}}\,(Y_{148}+Y_{14-8})+\frac{1}{2}\sqrt{\frac{2185}{3}}\,(Y_{1412}+Y_{14-12})\right\}$$

30. Point group O (432)

Harmonic

1 Y_{00}

2 $$\frac{1}{\sqrt{12}}\left\{\sqrt{7}\,Y_{40}+\sqrt{\frac{5}{2}}\,(Y_{44}+Y_{4-4})\right\}$$

TABLE VII—*Continued*

3 $\frac{1}{4}\{\sqrt{2}\,Y_{60}-\sqrt{7}\,(Y_{64}+Y_{6-4})\}$

4 $\frac{1}{8}\left\{\sqrt{33}\,Y_{80}+\sqrt{\frac{14}{3}}\,(Y_{84}+Y_{8-4})+\frac{1}{3}\sqrt{\frac{195}{2}}\,(Y_{88}+Y_{8-8})\right\}$

5 $\frac{i}{4}\left\{\sqrt{\frac{17}{3}}\,(Y_{94}-Y_{9-4})-\sqrt{\frac{7}{3}}\,(Y_{98}-Y_{9-8})\right\}$

6 $\frac{1}{8}\left\{-\sqrt{\frac{65}{6}}\,Y_{100}+\sqrt{11}\,(Y_{104}+Y_{10-4})+\frac{1}{2}\sqrt{\frac{187}{3}}\,(Y_{108}+Y_{10-8})\right\}$

7 $\frac{1}{16}\left\{\frac{1}{5}\sqrt{\frac{676039}{246}}\,Y_{120}+\frac{1}{10}\sqrt{\frac{245157}{82}}\,(Y_{124}+Y_{12-4}) +\frac{1}{10}\sqrt{\frac{1771}{41}}\,(Y_{128}+Y_{12-8})+\frac{5}{2}\sqrt{\frac{41}{6}}\,(Y_{1212}+Y_{12-12})\right\}$

8 $\frac{1}{5\sqrt{41}}\left\{\frac{1}{4}\sqrt{891}\,Y_{120}-\sqrt{91}\,(Y_{124}+Y_{12-4}) +\frac{1}{4}\sqrt{\frac{12597}{2}}\,(Y_{128}+Y_{12-8})\right\}$

9 $\frac{i}{8\sqrt{3}}\left\{\frac{1}{2}\sqrt{\frac{253}{2}}\,(Y_{1312}-Y_{13-12})-\sqrt{5}\,(Y_{138}-Y_{13-8}) -\frac{5}{2}\sqrt{\frac{19}{2}}\,(Y_{134}-Y_{13-4})\right\}$

10 $\frac{1}{32}\left\{-\sqrt{\frac{595}{3}}\,Y_{140}+\frac{1}{2}\sqrt{429}\,(Y_{144}+Y_{14-4}) +\sqrt{\frac{247}{2}}\,(Y_{148}+Y_{14-8})+\frac{1}{2}\sqrt{\frac{2185}{3}}\,(Y_{1412}+Y_{14-12})\right\}$

11 $\frac{i}{8}\left\{\frac{1}{2}\sqrt{\frac{65}{2}}\,(Y_{1512}-Y_{15-12})-\sqrt{21}\,(Y_{158}-Y_{15-8}) +\frac{1}{2}\sqrt{\frac{23}{2}}\,(Y_{154}-Y_{15-4})\right\}$

31. Point group $T_d\,(\bar{4}3m)$

Harmonic

1 Y_{00}

2 $\frac{i}{\sqrt{2}}\,(Y_{32}-Y_{3-2})$

3 $\frac{1}{\sqrt{12}}\left\{\sqrt{7}\,Y_{40}+\sqrt{\frac{5}{2}}\,(Y_{44}+Y_{4-4})\right\}$

4 $\frac{1}{4}\{\sqrt{2}\,Y_{60}-\sqrt{7}\,(Y_{64}+Y_{6-4})\}$

5 $\frac{i}{\sqrt{48}}\{\sqrt{11}\,(Y_{76}-Y_{7-6})+\sqrt{13}\,(Y_{72}-Y_{7-2})\}$

6 $\frac{1}{8}\left\{\sqrt{33}\,Y_{80}+\sqrt{\frac{14}{3}}\,(Y_{84}+Y_{8-4})+\frac{1}{3}\sqrt{\frac{195}{2}}\,(Y_{88}+Y_{8-8})\right\}$

7 $\frac{i}{4}\left\{\sqrt{\frac{13}{2}}\,(Y_{96}-Y_{9-6})-\sqrt{\frac{3}{2}}\,(Y_{92}-Y_{9-2})\right\}$

8 $\frac{1}{8}\left\{-\sqrt{\frac{65}{6}}\,Y_{100}+\sqrt{11}\,(Y_{104}+Y_{10-4})+\frac{1}{2}\sqrt{\frac{187}{3}}\,(Y_{108}+Y_{10-8})\right\}$

9 $\frac{i}{8}\left\{\frac{1}{2}\sqrt{\frac{133}{3}}\,(Y_{1110}-Y_{11-10})+\frac{1}{2}\sqrt{27}\,(Y_{116}-Y_{11-6}) +\sqrt{\frac{85}{6}}\,(Y_{112}-Y_{11-2})\right\}$

10 $\frac{1}{16}\left\{\frac{1}{5}\sqrt{\frac{676039}{246}}\,Y_{120}+\frac{1}{10}\sqrt{\frac{245157}{82}}\,(Y_{124}+Y_{12-4}) +\frac{1}{10}\sqrt{\frac{1771}{41}}\,(Y_{128}+Y_{12-8})+\frac{5}{2}\sqrt{\frac{41}{6}}\,(Y_{1212}+Y_{12-12})\right\}$

11 $\frac{1}{5\sqrt{41}}\left\{\frac{1}{4}\sqrt{891}\,Y_{120}-\sqrt{91}\,(Y_{124}+Y_{12-4}) +\frac{1}{4}\sqrt{\frac{12597}{2}}\,(Y_{128}+Y_{12-8})\right\}$

12 $\frac{i}{16\sqrt{3}}\left\{\sqrt{\frac{391}{2}}\,(Y_{1310}-Y_{13-10})+\sqrt{\frac{187}{2}}\,(Y_{136}-Y_{13-6}) -\sqrt{95}\,(Y_{132}-Y_{13-2})\right\}$

13 $\frac{1}{32}\left\{-\sqrt{\frac{595}{3}}\,Y_{140}+\frac{1}{2}\sqrt{429}\,(Y_{144}+Y_{14-4}) +\sqrt{\frac{247}{2}}\,(Y_{148}+Y_{14-8})+\frac{1}{2}\sqrt{\frac{2185}{3}}\,(Y_{1412}+Y_{14-12})\right\}$

14 $\frac{i}{64}\left\{\sqrt{685}\,(Y_{1514}-Y_{15-14})+\sqrt{\frac{2639}{137}}\,(Y_{1510}-Y_{15-10}) +\sqrt{\frac{95381}{137}}\,(Y_{156}-Y_{15-6})+\sqrt{\frac{88711}{137}}\,(Y_{152}-Y_{15-2})\right\}$

15 $\frac{i}{2\sqrt{274}}\left\{\sqrt{\frac{4807}{12}}\,(Y_{1510}-Y_{15-10})-\frac{1}{2}\sqrt{399}\,(Y_{156}-Y_{15-6}) +\sqrt{\frac{143}{3}}\,(Y_{152}-Y_{15-2})\right\}$

32. Point group $O_h\,(m3m)$

Harmonic

1 Y_{00}

2 $\frac{1}{\sqrt{12}}\left\{\sqrt{7}\,Y_{40}+\sqrt{\frac{5}{2}}\,(Y_{44}+Y_{4-4})\right\}$

3 $\frac{1}{4}\{\sqrt{2}\,Y_{60}-\sqrt{7}\,(Y_{64}+Y_{6-4})\}$

4 $\frac{1}{8}\left\{\sqrt{33}\,Y_{80}+\sqrt{\frac{14}{3}}\,(Y_{84}+Y_{8-4})+\frac{1}{3}\sqrt{\frac{195}{2}}\,(Y_{88}+Y_{8-8})\right\}$

TABLE VII—*Continued*

5	$\frac{1}{8}\left\{-\sqrt{\frac{65}{6}}\,Y_{100}+\sqrt{11}\,(Y_{104}+Y_{10-4})+\frac{1}{2}\sqrt{\frac{187}{3}}\,(Y_{108}+Y_{10-8})\right\}$
6	$\frac{1}{16}\left\{\frac{1}{5}\sqrt{\frac{676039}{246}}\,Y_{120}+\frac{1}{10}\sqrt{\frac{245157}{82}}\,(Y_{124}+Y_{12-4}) +\frac{1}{10}\sqrt{\frac{1771}{41}}\,(Y_{128}+Y_{12-8})+\frac{5}{2}\sqrt{\frac{41}{6}}\,(Y_{1212}+Y_{12-12})\right\}$
7	$\frac{1}{5\sqrt{41}}\left\{\frac{1}{4}\sqrt{891}\,Y_{120}-\sqrt{91}\,(Y_{124}+Y_{12-4}) +\frac{1}{4}\sqrt{\frac{12597}{2}}\,(Y_{128}+Y_{12-8})\right\}$
8	$\frac{1}{32}\left\{-\sqrt{\frac{595}{3}}\,Y_{140}+\frac{1}{2}\sqrt{429}\,(Y_{144}+Y_{14-4}) +\sqrt{\frac{247}{2}}\,(Y_{148}+Y_{14-8})+\frac{1}{2}\sqrt{\frac{2185}{3}}\,(Y_{1412}+Y_{14-12})\right\}$

this case, rather than using the set $\{Y_{l\mu}, \mu=-l, ..., l\}$, in Eq. (5), we use the set of real functions composed of the real and imaginary parts of the Y_{lm}'s, i.e., $\{\Re Y_{l\mu}, \Im Y_{l\mu}, \mu=0, ..., l\}$, which assures that each combination of (complex) spherical harmonics is real. The number and form of the completely symmetric harmonics up to $l=15$ are given, with the z axis choosen to be the special axis, if one exists. However, even with this choice, there may be an additional freedom for choosing the x and the y axes. For the tetragonal point group D_{2d}, we have provided such an example. In Table IV, symmetrized harmonics for D_{2d}, with respect to a standard set of axes are given, while in Table VIII, symmetrized harmonics for the same point group with respect to a nonstandard set of axes are shown. In the trigonal and hexagonal groups, in particular, there is also additional freedom to choose a setting. Although we have picked a given setting, this may not be the setting of interest in other cases—it is precisely because of such ambiguities in tables that a simple, computationally fast, and exact method for determining these coefficients is needed. In the tables we have converted the numerical values of the coefficients to analytic expressions (up to an arbitrary factor of ± 1) for ease of use; these values, however, were determined using the numerical algorithms described in this paper.

TABLE VIII

An example with Nonstandard Axes: D_{2d}

Harmonics 1–13

$m=0$, l even $\quad Y_{l0}$

Other harmonics are of the form $\{c(l, m)\,Y_{lm}+c^{*}(l, m)\,Y_{l-m}\}$ with

(l, m)	$c(l, m)$
3, 2	$\frac{1}{5}\left\{3\sqrt{\frac{1}{2}}+i\sqrt{8}\right\}$
4, 4	$\frac{1}{25}\left\{7\sqrt{\frac{1}{2}}-i12\sqrt{2}\right\}$
5, 2	$\frac{1}{5}\left\{3\sqrt{\frac{1}{2}}+i\sqrt{8}\right\}$
6, 4	$\frac{1}{25}\left\{7\sqrt{\frac{1}{2}}-i12\sqrt{2}\right\}$
7, 2	$\frac{1}{5}\left\{3\sqrt{\frac{1}{2}}+i\sqrt{8}\right\}$
7, 6	$\frac{1}{125}\left\{117\sqrt{\frac{1}{2}}-i22\sqrt{2}\right\}$
8, 4	$\frac{1}{25}\left\{7\sqrt{\frac{1}{2}}-i12\sqrt{2}\right\}$
8, 8	$\frac{1}{625}\left\{527\sqrt{\frac{1}{2}}-i168\sqrt{2}\right\}$

Note. The harmonics have been constructed (upto $l=8$) for the point group D_{2d} using a nonstandard set of axes. The mirror planes that contain the special z axis (for D_{2d}) in Table IV, have been rotated by an angle $\pi/4+\tan^{-1}(2)$ about z, to obtain a new set of x and y axes.

SUMMARY AND CONCLUSIONS

A method for the determination of symmetrized functions based on Gaussian integration has been presented. Given matrix representations of the rotation-translation operators of a (space) group, it is straightforward to obtain the lattice harmonics that transform according to the local point group, i.e., it is possible to do such group theory on the computer simply and exactly, even for situations where the local axes are rotated without having to deal explicitly with the Euler angles. This method and generalizations provide a way to deal with much of the necessary group theory needed in electronic structure calculations.

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