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Computation of Cubic Harmonics*†‡

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Symmetry-adapted functions (orthonormal linear combinations of angular-momentum eigenfunctions belonging to particular symmetry species) for the T_d and O_h point groups have been computed for $J \leqslant 100$ using an algorithm of Fox and Ozier, and Cholesky factorization of idempotent matrices. The results of Cholesky factorization are compared with those of both symmetric elimination with pivoting and an EISPACK diagonalization routine.

1. INTRODUCTION

The knowledge of linear combinations of angular-momentum eigenfunctions which transform according to the irreducible representations (irrep's) of the cubic (tetrahedral T_d and octahedral O_h) point groups is becoming increasingly important. These symmetry-adapted functions (SAF's) were constructed for T_d by Bethe [1], Jahn [2], Hecht [3], and Moret–Bailly *et al.* [4] for values of the angular-momentum quantum number $J \leqslant 21$. Fox and Ozier [5] developed an explicit algorithm for constructing T_d harmonics for arbitrary J. In that procedure the SAF's are among the eigenvectors of symmetric idempotent projection-operator matrices. Application of Cholesky factorization to construct a complete set of orthonormal eigenvectors was discussed by Householder and Fox [6]. The present work expands the theoretical developments of Fox and Ozier [5] to incorporate the O_h point group. The methods of [5, 6] are implemented to compute SAF's, or "cubic harmonics," for J up to 100 [7].

The group-theoretical approach here is in the same spirit as that used earlier [5]. Conventions for labeling coordinate systems, variables, group representations, etc., are identical to those in [5] unless explicitly stated otherwise.

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‡ Preliminary reports of portions of this work were given by K. Fox and B. J. Krohn at the 30th Symposium on Molecular Structure and Spectroscopy, Ohio State University, Columbus, Ohio, 16–20 June 1975, Abstract RA6; and at the SIAM–SIGNUM Meeting, San Francisco, California, 3–5 December 1975, Poster Session 3.

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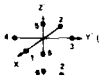
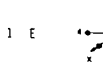
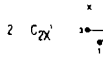
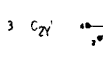
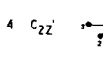
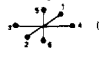
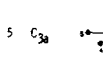
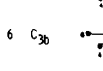
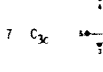
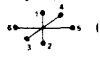
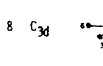
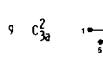
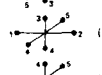
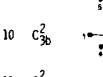
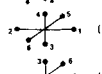
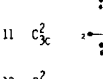
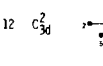
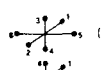
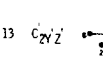
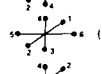
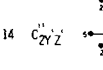
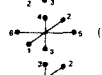
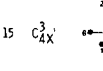
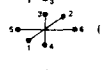
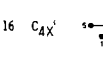
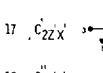
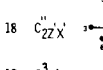
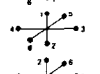
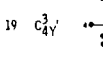
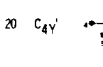
TABLE I

Symmetry Operations of the Point Group O_h with Corresponding Permutations of the Group $S(6)$ and Euler Angles

PROPER ROTATIONS				IMPROPER OPERATIONS				EULER ANGLES		
j	S_j	DIAGRAM	PERMUTATIONS	j	S_j	DIAGRAM	PERMUTATIONS	α'	β'	γ'
1	E		(1)(2)(3)(4)(5)(6)	25	I		(12)(34)(56)	0	0	0
2	$C_{2X'}$		(1)(2)(34)(56)	26	$\sigma_{Y'Z'}$		(12)(3)(4)(5)(6)	0	π	π
3	$C_{2Y'}$		(12)(3)(4)(56)	27	$\sigma_{Z'X'}$		(1)(2)(34)(5)(6)	0	π	0
4	$C_{2Z'}$		(12)(34)(5)(6)	28	$\sigma_{X'Y'}$		(1)(2)(3)(4)(56)	0	0	π
5	C_{3a}		(154)(263)	29	S^5_{6a}		(164253)	$3\pi/2$	$\pi/2$	π
6	C_{3b}		(164)(253)	30	S^5_{6b}		(154263)	$\pi/2$	$\pi/2$	0
7	C_{3c}		(163)(254)	31	S^5_{6c}		(153264)	$3\pi/2$	$\pi/2$	0
8	C_{3d}		(153)(264)	32	S^5_{6d}		(163254)	$\pi/2$	$\pi/2$	π
9	C^2_{3a}		(145)(236)	33	S_{6a}		(135246)	0	$\pi/2$	$3\pi/2$
10	C^2_{3b}		(146)(235)	34	S_{6b}		(136245)	π	$\pi/2$	$\pi/2$
11	C^2_{3c}		(136)(245)	35	S_{6c}		(146235)	π	$\pi/2$	$3\pi/2$
12	C^2_{3d}		(135)(246)	36	S_{6d}		(145236)	0	$\pi/2$	$\pi/2$
13	$C_{2Y'Z'}$		(12)(35)(46)	37	σ_{ac}		(1)(2)(36)(45)	$\pi/2$	$\pi/2$	$\pi/2$
14	$C''_{2Y'Z'}$		(12)(36)(45)	38	σ_{bd}		(1)(2)(35)(46)	$3\pi/2$	$\pi/2$	$3\pi/2$
15	$C^3_{4X'}$		(1)(2)(3645)	39	$S_{4X'}$		(12)(3546)	$\pi/2$	$\pi/2$	$3\pi/2$
16	$C_{4X'}$		(1)(2)(3546)	40	$S^3_{4X'}$		(12)(3645)	$3\pi/2$	$\pi/2$	$\pi/2$
17	$C'_{2Z'X'}$		(15)(26)(34)	41	σ_{bc}		(16)(25)(3)(4)	0	$\pi/2$	π
18	$C''_{2Z'X'}$		(16)(25)(34)	42	σ_{ad}		(15)(26)(3)(4)	0	$3\pi/2$	π
19	$C^3_{4Y'}$		(1526)(3)(4)	43	$S_{4Y'}$		(1625)(34)	0	$3\pi/2$	0
20	$C_{4Y'}$		(1625)(3)(4)	44	$S^3_{4Y'}$		(1526)(34)	0	$\pi/2$	0
21	$C'_{2X'Y'}$		(13)(24)(56)	45	σ_{ab}		(14)(23)(5)(6)	$3\pi/2$	π	0
22	$C''_{2X'Y'}$		(14)(23)(56)	46	σ_{cd}		(13)(24)(5)(6)	$\pi/2$	π	0
23	$C^3_{4Z'}$		(1423)(5)(6)	47	$S_{4Z'}$		(1324)(56)	0	0	$3\pi/2$
24	$C_{4Z'}$		(1324)(5)(6)	48	$S^3_{4Z'}$		(1423)(56)	0	0	$\pi/2$

O_h is the symmetry group for molecules like SF_6, just as T_d is for molecules like CH_4. The symmetry operations of O_h are listed in Table I, which corresponds to [5, Table I]. The proper rotations are numbered 1–24 and are denoted here by $\{S_j, 1 \leqslant j \leqslant 24\}$; the improper operations are numbered 25–48, and are $\{IS_j \equiv S_{j+24}, 1 \leqslant j \leqslant 24\}$, where I is the inversion. Those operations common to both O_h and T_d are $\{S_j, 1 \leqslant j \leqslant 12$ and $37 \leqslant j \leqslant 48\}$. In Table I all of these operations for O_h appear in the same order as those for T_d (in [5, Table I]), except S_{41} and S_{42} here are interchanged. The purpose of this interchange is to cause the three sequences of operations, 37–40 (where the x-direction is unique), 41–44 (where y is unique), and 45–48 (where z is unique) to be completely analogous to each other in both Tables I and III. (The sequences 13–16, 17–20, and 21–24 are also completely analogous.)

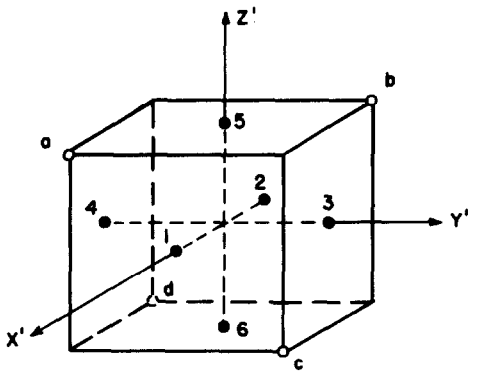


FIG. 1. Orientation of a regular tetrahedron with geometric center at the origin of Cartesian axes (X', Y', Z'), and vertices at positions a, b, c, and d (analogous to positions 1, 2, 3, and 4, respectively, in [5, Fig. 1]); labels 1–6 here refer to B positions in an octahedral AB_6 array, with A at the geometric center.

There is a slight change of notation between Fig. 1 and Table I here, and [5, Fig. 1, Table I]. Our labels a, b, c, d refer to the main diagonals passing through the vertices at positions 1, 2, 3, 4, respectively, in [5, Fig. 1]. The correspondence between the symbols for operations is as follows: $C_{31} \equiv C_{3a}$, $C_{32} \equiv C_{3b}$, etc., and $\sigma_{13} \equiv \sigma_{ac}$, $\sigma_{24} \equiv \sigma_{bd}$, etc. (In the σ-operations the subscripts define the plane of reflection.) A new notation for the C_2 operations $\{S_j; j = 13, 14, 17, 18, 21, 22\}$ has been introduced: the axis of rotation is in a plane specified by the two literal subscripts. For the symbols with a single-prime superscript, the axis of rotation is in the first and third quadrants of that plane; for those with a double-prime superscript the axis of rotation is in the second and fourth quadrants. The elements of the permutation group $S(6)$ corresponding to O_h are listed explicitly. The Euler angles measured in the molecule-fixed frame (MFF) are specified as in [5].

For completeness we tabulate the operations for the cubic subgroups of O_h. In Table II the sets of operations in each subgroup are indicated by a $\surd$.

Before turning to the actual calculation of SAF's for O_h, we wish to consider the matrix representations of T_d and O_h. In particular we demonstrate a generalization

TABLE II

Symmetry Operations in Cubic Point Groups; Presence is Denoted by √

Operations	T	T_h	T_d	O	O_h
$\mathscr{S}_1 \equiv \{S_1, \ldots, S_{12}\}$	√	√	√	√	√
$\mathscr{S}_2 \equiv \{S_{13}, \ldots, S_{24}\}$				√	√
$\mathscr{I}\mathscr{S}_1 \equiv \{S_{25}, \ldots, S_{36}\}$		√			√
$\mathscr{I}\mathscr{S}_2 \equiv \{S_{37}, \ldots, S_{48}\}$			√		√

TABLE III

Irreducible Representation Matrices[a,b] of O_h

	1	2	3	4	5	6	7	8	9	10	11	12
	25	26	27	28	29	30	31	32	33	34	35	36
A_{1g}	1				1				1			
A_{2g}	1				1				1			
E_g	$\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}$				$\begin{pmatrix}-\frac{1}{2} & (3)^{1/2}/2\\ -(3)^{1/2}/2 & -\frac{1}{2}\end{pmatrix}$				$\begin{pmatrix}-\frac{1}{2} & -(3)^{1/2}/2\\ (3)^{1/2}/2 & -\frac{1}{2}\end{pmatrix}$			
F_{1g}	XYZ	$X\bar{Y}\bar{Z}$	$\bar{X}YZ$	$\bar{X}\bar{Y}Z$	$\bar{Y}\bar{Z}X$	$\bar{Y}Z\bar{X}$	$YZ\bar{X}$	YZX	$Z\bar{X}\bar{Y}$	$Z\bar{X}Y$	$\bar{Z}X\bar{Y}$	ZXY
F_{2g}	XYZ	$X\bar{Y}\bar{Z}$	$\bar{X}YZ$	$\bar{X}\bar{Y}Z$	$\bar{Y}\bar{Z}X$	$\bar{Y}Z\bar{X}$	$YZ\bar{X}$	YZX	$Z\bar{X}\bar{Y}$	$Z\bar{X}Y$	$\bar{Z}X\bar{Y}$	ZXY
	13	14	15	16	17	18	19	20	12	22	23	24
	37	38	39	40	41	42	43	44	45	46	47	48
A_{1g}	1				1				1			
A_{2g}	−1				−1				1			
E_g	$\begin{pmatrix}\cos 2\epsilon_x & \sin 2\epsilon_x\\ \sin 2\epsilon_x & -\cos 2\epsilon_x\end{pmatrix}$				$\begin{pmatrix}\cos 2\epsilon_y & \sin 2\epsilon_y\\ \sin 2\epsilon_y & -\cos 2\epsilon_y\end{pmatrix}$				$\begin{pmatrix}\cos 2\epsilon_z & \sin 2\epsilon_z\\ \sin 2\epsilon_z & -\cos 2\epsilon_z\end{pmatrix}$			
F_{1g}	$\bar{X}ZY$	$\bar{X}\bar{Z}\bar{Y}$	$XZ\bar{Y}$	$X\bar{Z}Y$	$Z\bar{Y}X$	$Z\bar{Y}\bar{X}$	ZYX	$ZY\bar{X}$	YXZ	$\bar{Y}\bar{X}Z$	$Y\bar{X}\bar{Z}$	$\bar{Y}XZ$
F_{2g}	$X\bar{Z}\bar{Y}$	XZY	$\bar{X}\bar{Z}Y$	$\bar{X}Z\bar{Y}$	$\bar{Z}Y\bar{X}$	ZYX	$Z\bar{Y}\bar{X}$	$\bar{Z}\bar{Y}X$	$\bar{Y}\bar{X}Z$	YXZ	$\bar{Y}X\bar{Z}$	$Y\bar{X}\bar{Z}$

[a] Irrep's for the five u-species are given as follows. For proper operations (1–24) the representations are identical to these matrices. For inversion operations (25–48) the representations are the negatives of these matrices.

[b] Primes are eliminated from X, Y, and Z for convenience, but their meaning is the same as X', Y', and Z' in [5, Table II].

of [5, Table II]. These results will be useful, not only in the present work, but in future computations of vibration–rotation spectra of molecules with cubic symmetry. O_h has 10 irreducible representations: A_{1g}, A_{2g}, E_g, F_{1g}, F_{2g}, A_{1u}, A_{2u}, E_u, F_{1u}, and F_{2u}. The corresponding matrix realizations are presented in Table III. The enumeration of operations of the group is given in Table I. We have organized the operations of O_h into blocks of eight, instead of into classes, in analogy to [5, Table II]. These arrays, which consist of the invariant subgroup $\{S_j\,; j = 1, 2, 3, 4, 25, 26, 27, 28\}$ and its five cosets, form a compact display and facilitate the calculation of the cubic harmonics.

Table III contains the representations of type g explicitly. For the u-species the matrices are identical to those for g for proper operations $\{S_j, 1 \leqslant j \leqslant 24\}$, but are the negatives of those for g for the improper operations, $\{S_j, 25 \leqslant j \leqslant 48\}$. In the threefold representations the meaning of $X'Y'Z'$, etc., is the same as in [5, Table II]. For example,

$$S_{39} \equiv S_{4X'} \sim (\bar{X}'\bar{Z}'Y') \sim \begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix}, \tag{1}$$

as in [5, Eq. (9)].

In the present work we have introduced the parameters ϵ_α, with $\alpha = x, y$, or z, where ϵ_x is an arbitrary angle, $0 \leqslant \epsilon_x < 2\pi$, and where $\epsilon_y = \epsilon_x + \frac{2}{3}\pi$ and $\epsilon_z = \epsilon_x + \frac{4}{3}\pi$. The parameters ϵ_x, ϵ_y, and ϵ_z are identical, [8a] respectively, to ϵ_1, ϵ_2, and ϵ_3 given by Shaffer, Nielsen, and Thomas [8b] following their Eq. (7). We have used q_7 and q_8 defined there in terms of the ϵ's to generate our representation matrices of species E_g and E_u. The E_g rep transforms into the E rep of [5] for the choice $\epsilon_x = 30°$. In this case the roles of q_7 and q_8 in [8] are played by

$$\begin{aligned} f_e^{(E)} &= (\tfrac{2}{3})^{1/2}(X'^2 \cos \epsilon_x + Y'^2 \cos \epsilon_y + Z'^2 \cos \epsilon_z) \\ &= 2^{-1/2}(X'^2 - Y'^2) \end{aligned} \tag{2a}$$

and

$$\begin{aligned} f_f^{(E)} &= (\tfrac{2}{3})^{1/2}(X'^2 \sin \epsilon_x + Y'^2 \sin \epsilon_y + Z'^2 \sin \epsilon_z) \\ &= 6^{-1/2}(X'^2 + Y'^2 - 2Z'^2), \end{aligned} \tag{2b}$$

respectively, in [5]. The choices of basis functions for generating the E reps correspond to $\epsilon_x = 30°$ in [2, 3, 5], and to $\epsilon_x = 120°$ in [4]. It appears that $\epsilon_x = 30°$ is related to standard forms [9] of the spherical harmonics $Y_M{}^J$ for $J = 2$. The E rep in which ϵ_x remains arbitrary enjoys a certain amount of flexibility, which will be utilized in future applications.

We now turn to the correspondence between the projected functions in O_h and T_d. In [5] it was shown that the projected spherical harmonic,

$$f_\mu^{(k)} = \mathcal{O}_{\mu\mu}^{(k)} Y_K{}^J, \tag{3}$$

where k indicates the symmetry species and μ specifies a row of the representation, is given by the expression,

$$f_{\mu}^{(k)} = (l_k/h) \sum_{K'} \tau^{(k)} Y_{K'}^{J}, \tag{4a}$$

with

$$\tau^{(k)} = \sum_{S} \sigma(S)\, D^{(k)}(S)_{\mu\mu}^{*} \mathscr{D}_{K'K}^{J}(\alpha'\beta'\gamma'), \tag{4b}$$

where all symbols are defined in [5, Eqs. (1)–(7)] except that $\mathscr{D}_{K'K}^{J}(\alpha'\beta'\gamma')$ here replaces $D_{K'K}^{J}(\alpha'\beta'\gamma')$ for clarity.

Two properties of the T_d and O_h point groups are noted for the discussion which follows:

(i) Each operation in T_d corresponds to a pair of operations in O_h, such that one of the pair is identical to the operation in T_d while the other is equivalent to the first one followed by inversion.

(ii) For the operations common to T_d and O_h, the reps in T_d are identical to the reps in the g-type species of O_h, provided that the values of the phase ϵ_x for the reps of species E are coincident.

For the T_d point group, Eq. (4b) may be written in the form (see Table II)

$$\begin{aligned} {}^{(T_d)}\tau^{(k)} = & \sum_{S\in\mathscr{S}_1} D^{(k)}(S)_{\mu\mu}^{*} \mathscr{D}_{K'K}^{J}(\alpha'\beta'\gamma') \\ & + (-1)^{J} \sum_{S\in I\mathscr{S}_2} D^{(k)}(S)_{\mu\mu}^{*} \mathscr{D}_{K'K}^{J}(\alpha'\beta'\gamma'). \end{aligned} \tag{5a}$$

For the O_h point group, Eq. (4b) becomes (see Table II)

$$\begin{aligned} {}^{(O_h)}\tau^{(k_m')} = & \sum_{S\in\mathscr{S}_1} [D^{(k_m')}(S)_{\mu\mu}^{*} + (-1)^{J} D^{(k_m')}(IS)_{\mu\mu}^{*}]\, \mathscr{D}_{K'K}^{J}(\alpha'\beta'\gamma') \\ & + \sum_{S\in\mathscr{S}_2} [D^{(k_m')}(S)_{\mu\mu}^{*} + (-1)^{J} D^{(k_m')}(IS)_{\mu\mu}^{*}]\, \mathscr{D}_{K'K}^{J}(\alpha'\beta'\gamma'), \end{aligned} \tag{5b}$$

where k' represents one of the symbols A_1, A_2, E, F_1, or F_2 for O_h (as k does for T_d) and the subscript m in k_m' indicates g or u.

Defining

$$\xi(m) = \begin{cases} 0 & \text{if } m = g \\ +1 & \text{if } m = u, \end{cases} \tag{6}$$

we have, for each proper operation $\{S_j\,; j = 1, 2, \ldots, 24\}$ (see Table III)

$$D^{(k_m')}(S)_{\mu'\mu}^{*} = D^{(k_g')}(S)_{\mu'\mu}^{*} \tag{7a}$$

and

$$D^{(k_m')}(IS)_{\mu'\mu}^{*} = (-1)^{\xi(m)} D^{(k_g')}(S)_{\mu'\mu}^{*} \tag{7b}$$

where μ' need not equal μ. Substitution of Eqs. (7) into Eq. (5b) yields

$$
{}^{(O_h)}\tau^{(k_{m'})} = [1 + (-1)^{J+\xi(m)}] \Big[\sum_{S \in \mathscr{S}_1} D^{(k_{g'})}(S)^*_{\mu\mu} \mathscr{D}^J_{K'K}(\alpha'\beta'\gamma') + (-1)^{\xi(m)} \sum_{S \in I\mathscr{S}_2} D^{(k_{g'})}(S)^*_{\mu\mu} \mathscr{D}^J_{K'K}(\alpha'\beta'\gamma') \Big]. \tag{8}
$$

The factor $[1 + (-1)^{J+\xi(m)}]$ permits only projected functions of type g when J is even and only functions of type u when J is odd.

Comparison of Eqs. (5a) and (8) and use of property (ii) shows that, in either nonvanishing case (where one has $(-1)^J = (-1)^{\xi(m)}$) it follows that

$$
{}^{(O_h)}\tau^{(k_{m'})} = 2\,{}^{(T_d)}\tau^{(k)} \qquad \text{when} \quad k' = k. \tag{9}
$$

As there are twice as many operations in O_h as in T_d, the expressions for ${}^{(O_h)}f_\mu^{(k_{m'})}$ and ${}^{(T_d)}f_\mu^{(k)}$ become identical, as do the expressions for "partner" functions. Therefore, calculations of the SAF's for T_d simultaneously produce the SAF's for O_h. Henceforth we shall refer to these SAF's as "cubic harmonics," and omit the subscripts g and u in the irreps of O_h.

In Section 2 we give the techniques which we have employed in the numerical computation of the cubic harmonics. The results, their systematics, and comparisons with respect to different routines for matrix diagonalization are presented in Section 3 and Appendix A. New applications of high-J cubic harmonics are discussed in Section 4. Finally, some properties of the $d^J_{K'K}(\pi/2)$ which are useful in their numerical and algebraic [10] calculations, are given in Appendix B.

2. Techniques and Calculations

By means of the algorithm of [5], the normalized cubic harmonics have been constructed [7] to span the subspace $[J, k, \mu]$ [11] of each symmetry species k and partner irrep μ, for each integral value of J from 0 to 100.

It is appropriate to emphasize here the important consequences [5] of Jahn's use of restrictive elementary combinations of spherical harmonics $Y_K{}^J$. First, we have the definitions [2]

$$
U_K{}^J = 2^{-1/2}[Y^J_{-K} + (-1)^K Y_K{}^J], \tag{10a}
$$

$$
U_0{}^J \equiv W^J = Y_0{}^J, \tag{10b}
$$

and

$$
V_K{}^J \equiv -i(2)^{-1/2}[Y^J_{-K} - (-1)^K Y_K{}^J], \tag{10c}
$$

where $K \geqslant 1$. Then the molecular Hamiltonian of cubic symmetry does not connect U-type functions with V-type functions [5]. Second, we may consider separately

the two sets of functions with $K = 0, 4, 8,...$ and $K = 2, 6, 10,...$, as these are not mixed by the Hamiltonian [5].

Starting with one of the four restricted bases,

$$\begin{aligned} &\{U_K^J,\ K = 0, 4, 8,...\}, \qquad &&\{V_K^J,\ K = 4, 8, 12,...\}, \\ &\{U_K^J,\ K = 2, 6, 10,...\}, \qquad &&\{V_K^J,\ K = 2, 6, 10,...\}, \end{aligned} \tag{11}$$

one constructs [5] cubic harmonics which belong, not only to a unique symmetry species, but also to a particular row of the representation. Thus the SAF's of species E emerge in two sets denoted by the labels (E_e, E_f), and those of species F_1 and F_2 are produced in three sets, (F_{1z}, F_{1x}, F_{1y}) and (F_{2z}, F_{2x}, F_{2y}). Each SAF in the E_e-set has a unique partner in E_f; each SAF in the F_{1z}-set has a unique partner in each of F_{1x} and F_{1y} (similarly for F_{2z}). Furthermore, the two sets of SAF's for species E are mutually orthogonal, as are the three sets of SAF's for species F_1 and F_2, and each set forms an invariant subspace with respect to the Hamiltonian (e.g., wavefunctions belonging to F_{2z} do not mix with those belonging to F_{2x}). Finally, in the present procedure, the SAF's belonging to the subspaces F_{1x}, F_{1y} (F_{2x}, F_{2y}) are constructed from either U_K^J's or V_K^J's with odd values of K as determined by application of the transfer operator [5] to the even-K SAF's from the subspace F_{1z} (F_{2z}).

All of the cubic harmonics calculated here, except those belonging to irreps F_{1z} and F_{2z}, require [5] knowledge of the functions $d^J_{K'K}(\beta)$ evaluated at $\beta = \pi/2$; their computation is discussed in Appendix B. In particular, for irreps A_1, A_2, and E_e[11] one constructs symmetric idempotent matrices of the projection operators according to [5, Eqs. (53)–(58)]. The eigenvalues of these matrices are either $+1$ or 0 (because of idempotence). The eigenvectors belonging to the subspace of the degenerate eigenvalue $+1$ consist of the coefficients c_{iK} which define the SAF's that span the subspace $[J, k, \mu]$:

$$\Phi_i^{Jk\mu} = \sum_K c_{iK}^{Jk\mu} U_K^J \qquad \text{or} \qquad \Phi_i^{Jk\mu} = \sum_K c_{iK}^{Jk\mu} V_K^J. \tag{12}$$

In general, when the SAF's are not subjected to further conditions, they are not unique. However, any two sets of orthonormal SAF's that span the same space $[J, k, \mu]$ are related by a unitary transformation.

In the present work, the idempotent matrices were decomposed by Cholesky factorization [6, 12]. If A is a real symmetric positive definite matrix, then its Cholesky factors [12] determined without pivoting are triangular matrices which satisfy the equation

$$A = A^T = LL^T, \tag{13}$$

where L is a lower triangular matrix. If A is $\mathbf{n} \times \mathbf{n}$ and, e.g., $\mathbf{n} = 4$ with

$$A = \begin{pmatrix} a_{11} & a_{21} & a_{31} & a_{41} \\ a_{21} & a_{22} & a_{32} & a_{42} \\ a_{31} & a_{32} & a_{33} & a_{43} \\ a_{41} & a_{42} & a_{43} & a_{44} \end{pmatrix} \qquad \text{and} \qquad L = \begin{pmatrix} l_{11} & 0 & 0 & 0 \\ l_{21} & l_{22} & 0 & 0 \\ l_{31} & l_{32} & l_{33} & 0 \\ l_{41} & l_{42} & l_{43} & l_{44} \end{pmatrix} \tag{14}$$

then one has [12]

$$
\begin{aligned}
&l_{11} = (a_{11})^{1/2} \\
&l_{21} = a_{21}/l_{11} \qquad l_{22} = (a_{22} - l_{21}^2)^{1/2} \\
&l_{31} = a_{31}/l_{11} \qquad l_{32} = (a_{32} - l_{31}l_{21})/l_{22} \qquad l_{33} = (a_{33} - l_{31}^2 - l_{32}^2) \\
&l_{41} = a_{41}/l_{11} \qquad l_{42} = (a_{42} - l_{41}l_{21})/l_{22} \qquad l_{43} = (a_{43} - l_{41}l_{31} - l_{42}l_{32})/l_{33} \\
&\qquad\qquad l_{44} = (a_{44} - l_{41}^2 - l_{42}^2 - l_{43}^2)^{1/2}.
\end{aligned} \tag{15}
$$

In our work, however, each matrix is not positive definite, but idempotent (and, therefore, positive semidefinite), whose rank $\mathbf{r}$ is the multiplicity of the eigenvalue $+1$. Consequently [13, 14] one expects the above procedure to be inapplicable because it does not involve a search for the largest diagonal element and an interchange of appropriate rows and columns before each step: one might encounter a singularity due to a zero diagonal element in L or a column that is linearly dependent on previous columns (or nearly so), before reaching the end of $\mathbf{r}$ "good columns." However, the difficulty appears to be avoidable in this problem if we arrange our matrices in a particular way (see Section 3), so that we are able to perform the above Cholesky factorization without pivoting. We have not fully investigated the reasons why pivoting is not necessary. Moler and Stewart [14] have analyzed the effects of roundoff error in this algorithm, and have shown that if the diagonal elements of the computed L are not too small, then the columns of L must be close to orthogonal and AL must be close to L. (Specific examples and further discussion are given in Section 3.)

The above procedure yields a trapezoidal matrix L of $\mathbf{r}$ columns with $\mathbf{r} \leqslant \mathbf{n}$, because $l_{\mathbf{r}+1,\mathbf{r}+1} \equiv 0$. The $\mathbf{r}$ columns thus determined comprise *all* of the eigenvectors of A with eigenvalue $+1$, and they are orthonormal [6]. Four equations which apply to A and its eigenvectors are

$$A^2 = A, \tag{16a}$$

$$A = LL^T, \tag{16b}$$

$$AL = L, \tag{16c}$$

and

$$L^TL = I, \tag{16d}$$

where Eqs. (16c) and (16d) are implied by Eqs. (16a) and (16b); here I is the $\mathbf{r} \times \mathbf{r}$ identity matrix.

The following symmetric idempotent matrices have been constructed from [5, Eqs. (53)–(58)]; their eigenvectors, given below, corresponding to the eigenvalue $+1$, are SAF's for their respective subspaces [11]:

$$
K = \begin{matrix} \\ 2 \\ 6 \end{matrix}
\begin{matrix} \begin{matrix} 2 & \quad 6 \end{matrix} \\ \begin{pmatrix} 5/16 & 55^{1/2}/16 \\ 55^{1/2}/16 & 11/16 \end{pmatrix} \end{matrix}
\qquad [J = 6, E_e], \tag{17a}
$$

$$K' = \begin{matrix} \\ 4 \\ 8 \end{matrix} \begin{matrix} K = \\ \begin{pmatrix} 17/24 & -(7 \cdot 17)^{1/2}/24 \\ -(7 \cdot 17)^{1/2}/24 & 7/24 \end{pmatrix} \end{matrix} \quad [J = 9, A_2], \tag{17b}$$

$$K' = \begin{matrix} \\ 0 \\ 4 \\ 8 \end{matrix} \begin{matrix} K = \\ \begin{pmatrix} 33/64 & (7 \cdot 11)^{1/2}/32 & (5 \cdot 11 \cdot 13)^{1/2}/64 \\ (7 \cdot 11)^{1/2}/32 & 7/48 & (5 \cdot 7 \cdot 13)^{1/2}/96 \\ (5 \cdot 11 \cdot 13)^{1/2}/64 & (5 \cdot 7 \cdot 13)^{1/2}/96 & 65/192 \end{pmatrix} \end{matrix} \quad [J = 8, A_1], \tag{17c}$$

$$K' = \begin{matrix} \\ 4 \\ 8 \\ 12 \\ 16 \\ 20 \end{matrix} \begin{matrix} K = \\ \begin{pmatrix} 0.507050 & -0.240371 & -0.175644 & 0.066790 & 0.396056 \\ -0.240371 & 0.662923 & 0.263113 & -0.183236 & 0.250746 \\ -0.175644 & 0.263113 & 0.384201 & 0.366114 & 0.049718 \\ 0.066790 & -0.183236 & 0.366114 & 0.779134 & 0.002895 \\ 0.396056 & 0.250746 & 0.049718 & 0.002895 & 0.666692 \end{pmatrix} \end{matrix}$$

$$[J = 21, E_e]; \tag{17d}$$

Example	Subspace	Order	Rank = No. of SAF's	SAF's
(17a)	$[6, E_e]$	2	1	$(5/16)^{1/2}\, U_2^6 + (11/16)^{1/2}\, U_6^6$
(17b)	$[9, A_2]$	2	1	$-(17/24)^{1/2}\, V_4^8 + (7/24)^{1/2}\, V_8^8$
(17c)	$[8, A_1]$	3	1	$(33/64)^{1/2} U_0^8 + (7/48)^{1/2} U_4^8 + (65/192)^{1/2} U_8^8$
(17d)	$[21, E_e]$	5	3	See Eqs. (18) and (19)

In examples (17a)–(17c) where the rank is 1, each SAF is unique and is in agreement with the results of Jahn [2] and Moret-Bailly [4], except possibly for an overall phase factor. When the rank exceeds 1, the eigenvectors are not unique. In example (17d), Cholesky factorization yields the (orthonormal) eigenvectors

$$\Phi_1^{21,E_e} = 0.712074\, V_4^{21} - 0.337565\, V_8^{21} - 0.246666\, V_{12}^{21} + 0.093797\, V_{16}^{21} + 0.556200\, V_{20}^{21}, \tag{18a}$$

$$\Phi_2^{21,E_e} = 0.740927\, V_8^{21} + 0.242733\, V_{12}^{21} - 0.204573\, V_{16}^{21} + 0.591826\, V_{20}^{21}, \tag{18b}$$

$$\Phi_3^{21,E_e} = 0.514235\, V_{12}^{21} + 0.853514\, V_{16}^{21} + 0.084120\, V_{20}^{21}. \tag{18c}$$

On the other hand, reflection of the matrix (17d) about the second main diagonal (i.e., the diagonal running from the lower left to the upper right), and Cholesky

factorization of the result yields the following set of orthonormal eigenvectors:

$$\Theta_1^{21,E_e} = 0.816512\ V_{20}^{21} + 0.003546\ V_{16}^{21} + 0.060890\ V_{12}^{21} + 0.307094\ V_8^{21} + 0.485058\ V_4^{21}, \tag{19a}$$

$$\Theta_2^{21,E_e} = 0.882679\ V_{16}^{21} + 0.414531\ V_{12}^{21} - 0.208825\ V_8^{21} + 0.073719\ V_4^{21}, \tag{19b}$$

$$\Theta_3^{21,E_e} = 0.456790\ V_{12}^{21} + 0.724575\ V_8^{21} - 0.516076\ V_4^{21}. \tag{19c}$$

As these two sets of orthonormal basis vectors in Eqs. (18) and (19) span the same subspace, they must be related by a unitary transformation. In fact, we have explicitly that

$$\begin{pmatrix} \Phi_1 \\ \Phi_2 \\ \Phi_3 \end{pmatrix} = \begin{pmatrix} 0.681190 & 0.724822 & 0.103023 \\ 0.103527 & -0.234676 & 0.966545 \\ -0.724751 & 0.647735 & 0.234898 \end{pmatrix} \begin{pmatrix} \Theta_1 \\ \Theta_2 \\ \Theta_3 \end{pmatrix}. \tag{20}$$

We also have verified that all of the matrices and SAF's of examples (17a)–(17d) satisfy the matrix equations (16a)–(16d).

3. Results, Systematics, and Comparisons with Other Methods

A computer program is available [7] which calculates SAF's for arbitrary values of J, symmetry species, and partners. It incorporates the recursion formula for $d^J_{K',K}(\pi/2)$ and the algorithm for cubic harmonics of Fox and Ozier [5], and Cholesky decomposition [6] (as discussed above) of the idempotent matrices generated by the algorithm for species A_1, A_2, and E_e. Presented as an example in Table IV are all of the SAF's computed for each subspace associated with $J = 14$, and in Table V are two sets of SAF's belonging to the subspace $[J = 100, A_2]$, as determined in double precision (relative accuracy $= 5.0 \times 10^{-29}$) on the CDC 6600 and 7600 computers at Los Alamos. Table V gives the SAF's for the two "arrangements" of the same idempotent matrix, one with the lowest value of K in the first column and the other with the highest value of K in the first column; the two sets are analogous, respectively, to the Φ_i and the Θ_i of the previous Section.

It is evident that at high J the coefficients c_{iK} in a particular SAF generally do not all have the same magnitude, but suffer extreme variations, especially when the "high-K" SAF's are determined first; solutions with such peculiarities are found to obey Eqs. (16c,d) satisfactorily in double precision. However, the "arrangement" of the matrix (with respect to reflection across the second main diagonal as discussed in Section 2)

does affect crucially, as follows, the accuracy of the calculated SAF's with J near 100 (for J even or odd):

Spec. \ Arr.	High K in upper left	Low K in upper left
A_1, A_2	26 significant figures	Poor
E_e	Poor	26 significant figures

This diagram indicates several facts. First, one can use Cholesky factorization without pivoting to obtain a set of SAF's for each value of J, and symmetry species A_1, A_2, and E_e, because at least one arrangement of each idempotent matrix always yields a basis set of SAF's with very little loss of accuracy. Second, despite the fact that Cholesky factorization without pivoting cannot be applied *generally* to positive semidefinite matrices [13], we have found specific examples of such matrices that can be so decomposed. Our matrices are idempotent, constructed from known formulas [5], and "arranged" as specified above. Third, the deficiency due to the absence of pivoting is manifest in the excessive losses of accuracy that occur during decomposition of our matrices in their "poor arrangements." More specifically, we calculated the inner product $(\mathbf{\Phi}_i \cdot \mathbf{\Phi}_j)$ for each pair of SAF's to test their orthonormality (Eq. (16d)), and the vector difference $\mathbf{X}_i = (A\mathbf{\Phi}_i - \mathbf{\Phi}_i)$ to verify that each SAF is an eigenvector of A corresponding to the eigenvalue $+1$ (Eq. (16c)). For the "poorly arranged" matrices we found that, as $\mathbf{\Phi}_i$ and $\mathbf{\Phi}_j$ were generated *progressively later during the Cholesky factorization* (i.e., as i and j approached $\mathbf{r}$, the rank of the matrix), the values of $(\mathbf{\Phi}_i \cdot \mathbf{\Phi}_j)$ (for $i \neq j$), and of the components of $\mathbf{X}_i$, increased rapidly in size and indicated unacceptable magnifications of round-off error. For $J = 100$, in a "poorly arranged" matrix, typical indications for the SAF's $\mathbf{\Phi}_{r-1}$ and $\mathbf{\Phi}_r$, determined last, are that $|(\mathbf{\Phi}_{r-1} \cdot \mathbf{\Phi}_r)|$ is about 10^{-18}–10^{-17}, that $1 - \mathbf{\Phi}_r \cdot \mathbf{\Phi}_r$ is about 10^{-16}, and that components of $\mathbf{X}_r$ can be as large as 10^{-21} in magnitude. (This to be compared with the observations that $|(\mathbf{\Phi}_{r-1} \cdot \mathbf{\Phi}_r)|$ and components of $\mathbf{X}_r$ are about 10^{-26} for the "good arrangements.") Although such losses of accuracy are not critical to double-precision computations, they can alter most, if not all, of the significant figures in single precision.

Other methods of decomposition of the idempotent matrices were tested to compare Cholesky factorization. A routine employing symmetric elimination of rows and columns, including a search for the largest diagonal element and pivoting before each elimination, was written by Moler [15] for our use. We also have employed the EISPACK routines [16] "TRED2" and "IMTQL2" which contain the intermediate step of tridiagonalization before diagonalization. These methods are discussed in Appendix A, and the results are compared in Table VI. We attribute the short execution times for Cholesky factorization to the absence of pivoting; because this absence does not cause appreciable extra losses in accuracy, we surmise that the

TABLE IV

Cubic Harmonics for $J = 14$[a]

$$\Phi_{K=12}(A_1) = 0.596348U_{12}^{14} + 0.491132U_{8}^{14} + 0.457682U_{4}^{14} - 0.440096U_{0}^{14}$$

$$\Phi_{K=14}(A_2) = 0.577280U_{14}^{14} - 0.020172U_{10}^{14} - 0.248531U_{6}^{14} - 0.777543U_{2}^{14}$$

$$\begin{cases} \Phi_{K=2}(E_e) = 0.628829U_{2}^{14} - 0.307307U_{6}^{14} - 0.024942U_{10}^{14} + 0.713803U_{14}^{14} \\ \Phi_{K=2}(E_f) = -0.546584U_{0}^{14} - 0.668241U_{4}^{14} - 0.330340U_{8}^{14} + 0.381543U_{12}^{14} \end{cases}$$

$$\begin{cases} \Phi_{K=6}(E_e) = 0.918583U_{6}^{14} - 0.013802U_{10}^{14} + 0.394987U_{14}^{14} \\ \Phi_{K=6}(E_f) = -0.573063U_{0}^{14} - 0.135586U_{4}^{14} + 0.437774U_{8}^{14} - 0.679389U_{12}^{14} \end{cases}$$

$$\begin{cases} \Phi_{K=10}(E_e) = 0.999390U_{10}^{14} + 0.034922U_{14}^{14} \\ \Phi_{K=10}(E_f) = -0.423273U_{0}^{14} + 0.570612U_{4}^{14} - 0.676770U_{8}^{14} - 0.192934U_{12}^{14} \end{cases}$$

$$\begin{cases} \Phi_{K=4}(F_{1z}) = V_{4}^{14} \\ \Phi_{K=4}(F_{1x}) = 0.117942V_{1}^{14} - 0.322924V_{3}^{14} + 0.437482V_{5}^{14} - 0.409643V_{7}^{14} + 0.203123V_{9}^{14} + 0.185425V_{11}^{14} - 0.668558V_{13}^{14} \\ \Phi_{K=4}(F_{1y}) = 0.117942U_{1}^{14} + 0.322924U_{3}^{14} + 0.437482U_{5}^{14} + 0.409643U_{7}^{14} + 0.203123U_{9}^{14} - 0.185425U_{11}^{14} - 0.668558U_{13}^{14} \end{cases}$$

$$\begin{cases} \Phi_{K=8}(F_{1z}) = V_{8}^{14} \\ \Phi_{K=8}(F_{1x}) = 0.253124V_{1}^{14} - 0.457119V_{3}^{14} + 0.075265V_{5}^{14} + 0.460515V_{7}^{14} - 0.298272V_{9}^{14} - 0.607403V_{11}^{14} - 0.226554V_{13}^{14} \\ \Phi_{K=8}(F_{1y}) = 0.253124U_{1}^{14} + 0.457119U_{3}^{14} + 0.075265U_{5}^{14} - 0.460515U_{7}^{14} - 0.298272U_{9}^{14} + 0.607403U_{11}^{14} - 0.226554U_{13}^{14} \end{cases}$$

$$\begin{cases} \Phi_{K=12}(F_{1z}) = V_{12}^{14} \\ \Phi_{K=12}(F_{1x}) = 0.461026V_{1}^{14} - 0.116381V_{3}^{14} - 0.594030V_{5}^{14} - 0.573887V_{7}^{14} - 0.291312V_{9}^{14} - 0.081935V_{11}^{14} - 0.010764V_{13}^{14} \\ \Phi_{K=12}(F_{1y}) = 0.461026U_{1}^{14} + 0.116381U_{3}^{14} - 0.594030U_{5}^{14} + 0.573887U_{7}^{14} - 0.291312U_{9}^{14} + 0.081935U_{11}^{14} - 0.010764U_{13}^{14} \end{cases}$$

$$
\begin{cases}
\Phi_{K=2}(F_{2z}) = V_2^{14} \\
\Phi_{K=2}(F_{2x}) = 0.058097V_1^{14} - 0.172608V_3^{14} + 0.281808V_5^{14} - 0.381153V_7^{14} + 0.463899V_9^{14} - 0.517586V_{11}^{14} + 0.508959V_{13}^{14} \\
\Phi_{K=2}(F_{2y}) = -0.058097U_1^{14} - 0.172608U_3^{14} - 0.281808U_5^{14} - 0.381153U_7^{14} - 0.463899U_9^{14} - 0.517586U_{11}^{14} - 0.508959U_{13}^{14}
\end{cases}
$$

$$
\begin{cases}
\Phi_{K=6}(F_{2z}) = V_6^{14} \\
\Phi_{K=6}(F_{2x}) = 0.181761V_1^{14} - 0.427070V_3^{14} + 0.375044V_5^{14} - 0.011075V_7^{14} - 0.433853V_9^{14} + 0.466238V_{11}^{14} + 0.488045V_{13}^{14} \\
\Phi_{K=6}(F_{2y}) = -0.181761U_1^{14} - 0.427070U_3^{14} - 0.375044U_5^{14} - 0.011075U_7^{14} + 0.433853U_9^{14} + 0.466238U_{11}^{14} - 0.488045U_{13}^{14}
\end{cases}
$$

$$
\begin{cases}
\Phi_{K=10}(F_{2z}) = V_{10}^{14} \\
\Phi_{K=10}(F_{2x}) = 0.339306V_1^{14} - 0.375561V_3^{14} - 0.356481V_5^{14} + 0.357390V_7^{14} + 0.616455V_9^{14} + 0.323486V_{11}^{14} + 0.066020V_{13}^{14} \\
\Phi_{K=10}(F_{2y}) = -0.339306U_1^{14} - 0.375561U_3^{14} + 0.356481U_5^{14} + 0.357390U_7^{14} - 0.616455U_9^{14} + 0.323486U_{11}^{14} - 0.066020U_{13}^{14}
\end{cases}
$$

$$
\begin{cases}
\Phi_{K=14}(F_{2z}) = V_{14}^{14} \\
\Phi_{K=14}(F_{2x}) = 0.746948V_1^{14} + 0.565677V_3^{14} + 0.320813V_5^{14} + 0.132829V_7^{14} + 0.038269V_9^{14} + 0.006987V_{11}^{14} + 0.000646V_{13}^{14} \\
\Phi_{K=14}(F_{2y}) = -0.746948U_1^{14} + 0.565677U_3^{14} - 0.320813U_5^{14} + 0.132829U_7^{14} - 0.038269U_9^{14} + 0.006987U_{11}^{14} - 0.000646U_{13}^{14}
\end{cases}
$$

[a] See [11] for notation of the symmetry species. For SAF's of irrep's A_1, A_2, and E_e the "good arrangement" of each idempotent matrix was decomposed by Cholesky factorization. This use of K to label SAF's is consistent with the notation of [5, Eqs. (36)–(42)].

TABLE V — SAF's[a] for [$J = 100, A_2$]

	K = 98	94	90	86	82	78	74	70
K'=98	5.773502690D-01	0.	0.	0.	0.	0.	0.	0.
94	-6.514495540-23	5.773502690-01	0.	0.	0.	0.	0.	0.
90	-3.115423000-20	-4.089072540-17	5.773502690-01	0.	0.	0.	0.	0.
86	-6.517136790-18	-7.070284710-15	-1.904786380-12	5.773502690-01	0.	0.	0.	0.
82	-7.437082060-16	-6.602411470-13	-1.436850360-10	-1.304715460-08	5.773499630-01	0.	0.	0.
78	-5.228133160-14	-3.755824090-11	-6.513200680-09	-4.627140480-07	-1.660934330-05	5.771826470-01	0.	0.
74	-2.444932640-12	-1.403505400-09	-1.909232330-07	-1.040047410-05	-2.781085470-04	-4.024544330-03	5.607059450-01	0.
70	-8.018041110-11	-3.625740870-08	-3.798563460-06	-1.548344830-04	-2.980607470-03	-2.937495870-02	-1.536675810-01	5.237285030-01
66	-1.915706580-09	-6.713123640-07	-5.299596490-05	-1.567702400-03	-2.074801100-02	-1.288233970-01	-3.568077940-01	-5.894522010-01
62	-3.431516580-08	-9.143221040-06	-5.296664870-04	-1.092820960-02	-9.302110500-02	-3.168866490-01	-2.834509410-01	3.023706300-01
58	-4.710764620-07	-9.133954370-05	-3.838407580-03	-5.231151680-02	-2.569343240-01	-3.402034340-01	2.098456170-01	7.533827410-02
54	-5.041686830-06	-7.231128030-04	-2.023007640-02	-1.679768130-01	-3.816988100-01	7.150203180-02	1.367587810-01	-2.906773680-01
50	-4.263139240-05	-4.284071000-03	-7.691817880-02	-3.390965520-01	-1.488024330-01	2.714207460-01	-2.763217270-01	3.469759270-01
46	-2.877401490-04	-1.944208620-02	-2.056476000-01	-3.526542090-01	2.707808360-01	-1.970396550-01	1.959206760-01	-3.166135850-01
42	-1.561938310-03	-6.723903480-02	-3.630667030-01	-5.067824070-03	9.462639250-02	-6.335018180-02	-3.416599700-02	2.561766390-01
38	-6.852966130-03	-1.744501950-01	-3.515949910-01	3.069259920-01	-2.777260370-01	2.340657850-01	-1.093241260-01	-1.947811630-01
34	-2.435668590-02	-3.276029900-01	-2.097985380-02	7.262896540-03	1.189675620-01	-2.572581610-01	1.990187240-01	1.432811640-01
30	-7.005149450-02	-4.080063510-01	3.059984140-01	-2.776783260-01	1.353815640-01	1.252007460-01	-2.366833420-01	-1.035917070-01
26	-1.820964400-01	-2.444096370-01	1.120550650-01	1.318255350-01	-2.540923930-01	2.169816580-02	2.368374720-01	7.420349860-02
22	-2.976887750-01	1.288873720-01	-2.765012270-01	1.667085750-01	1.852271070-01	-1.450716730-01	-2.142768640-01	-5.277105770-02
18	-4.211647560-01	3.318761270-01	-7.196031840-02	-2.582589540-01	-8.901867510-03	2.173700420-01	1.799415110-01	3.710993110-02
14	-4.266077940-01	7.528283900-02	2.815929090-01	8.034137930-02	-1.605755840-01	-2.338203870-01	-1.406405260-01	-2.547041060-02
10	-2.360972140-01	-2.656168530-01	-3.651494680-02	1.661973410-01	2.411210640-01	2.021575280-01	1.000165530-01	1.652910070-02
6	9.095828020-02	-1.737388660-01	-2.569555510-01	-2.545986600-01	-2.062464200-01	-1.352895700-01	-5.962613860-02	-9.294142760-03
2	3.504762360-01	2.315241940-01	1.663784340-01	1.186977810-01	8.013054760-02	4.741080430-02	1.979226740-02	2.998272810-03

	K = 2	6	10	14	18	22	26	30
K'= 2	4.767361990-01	0.	0.	0.	0.	0.	0.	0.
6	-2.212272160-01	4.299375130-01	0.	0.	0.	0.	0.	0.
10	-2.187519890-01	-3.171959310-01	3.564991490-01	0.	0.	0.	0.	0.
14	-2.150274070-01	-2.765296590-01	-4.289962800-01	2.599091460-01	0.	0.	0.	0.
18	-2.100390170-01	-2.252364690-01	-2.598361670-01	-5.037202830-01	1.561593760-01	0.	0.	0.
22	-2.037669090-01	-1.657283280-01	-9.211073530-02	-8.183392590-02	-4.737923160-01	6.987344350-02	0.	0.
26	-1.961851270-01	-1.008962350-01	5.332197880-02	1.778093690-01	2.362014370-01	-3.213771150-01	1.936776940-02	0.
30	-1.872608350-01	-3.402556230-02	1.586600640-01	2.551975670-01	2.954869730-01	4.603043740-01	-1.309585960-01	2.078971690-03
34	-1.769532080-01	3.130770640-02	2.118097100-01	1.793314370-01	3.149906410-02	-4.968206590-02	3.546996930-01	-2.011044750-02
38	-1.652119230-01	9.136130200-02	2.085009690-01	1.856729860-02	-2.120166030-01	-3.149145030-01	-4.457026500-01	8.876598360-02
42	-1.519751350-01	1.423734820-01	1.535229590-01	-1.407770800-01	-2.327776890-01	-4.547477710-02	1.541094770-01	-2.348082880-01
46	-1.371666940-01	1.807349610-01	6.076518040-02	-2.228837740-01	-4.339901060-02	2.564229760-01	2.824311580-01	4.088869330-01
50	-1.206923060-01	2.031895660-01	-4.818130150-02	-1.892449480-01	1.777264910-01	1.648910580-01	-2.173537200-01	-4.620508230-01
54	-1.024340880-01	2.070686970-01	-1.469979140-01	-5.512987560-02	2.338640930-01	-1.623522970-01	-1.989140600-01	2.898162230-01
58	-8.224268180-02	1.905669180-01	-2.091574720-01	1.129891240-01	6.957594900-02	-2.444441950-01	2.608388030-01	4.465452120-02
62	-5.992546490-02	1.530696570-01	-2.137235460-01	2.228583660-01	-1.688306030-01	5.099109350-02	1.182607830-01	-3.369091140-01
66	-3.522828860-02	9.555016820-02	-1.518425970-01	2.008969710-01	-2.409365560-01	2.736001630-01	-3.117378650-01	4.334968350-01
70	-7.805890430-03	2.106403380-02	-3.289525160-02	4.130045370-02	-4.223083800-02	2.533133750-02	4.372709760-02	-3.487922520-01
74	2.288873320-02	-6.460905930-02	1.113539960-01	-1.656742710-01	2.289170740-01	-2.935764400-01	3.015065110-01	2.009180540-01
78	5.739710560-02	-1.520812440-01	2.271924860-01	-2.585623570-01	2.052621390-01	-3.223157710-03	-3.726052760-01	-8.568918490-02
82	9.704185920-02	-2.270284780-01	2.480421780-01	-1.085478730-01	-1.672614400-01	3.407159170-01	2.329661520-01	2.700761820-02
86	1.437486720-01	-2.679261120-01	1.189745200-01	2.087080520-01	-2.767391700-01	-3.140126530-01	-8.915623630-02	-6.122152060-03
90	2.014922170-01	-2.413787850-01	-1.502653230-01	2.873790130-01	3.337736490-01	1.321214270-01	2.103175990-02	9.597704210-04
94	2.803868380-01	-8.903382520-02	-3.697258640-01	-3.057841270-01	-1.258464110-01	-2.731037360-02	-2.778348830-03	-8.594714110-05
98	4.244434340-01	3.405453640-01	1.810850300-01	6.471701470-02	1.501699460-02	2.085279820-03	1.462544730-04	5.275669380-06

[a] This scheme of labeling the SAF's with K and the components with K' is consistent with the notation of [5, Eqs. (36)–(42)]. Both the upper and lower sets of SAF's are derived by Cholesky factorization of the same symmetric idempotent matrix taken, respectively, in its "good" and "poor" arrangements. All of the digits shown are probably correct, except several figures in the second and third components of the first SAF in the upper set, which are extremely small. In this table the notation D, followed by a negative integer, indicates that the associated

"good arrangements" of the idempotent matrices are already nearly optimally pivoted. The iterative procedure of "IMTQL2" gains still more accuracy, but requires considerably more time.

TABLE VI

Comparative Statistics for Three Methods of Decomposition of Symmetric Idempotent Matrices during Computation of SAF's for $J = 100$

Test	Cholesky factorization without pivoting[a]			Symmetric elimination with pivoting			Tridiagonalization (QR) and diagonalization		
	A_1	A_2	E_e	A_1	A_2	E_e	A_1	A_2	E_e
Time of execution[b] (msec)	7.1	6.1	9.7	22.0	19.2	25.8	248.9	218.2	169.3
Max$[1 - \Phi_i \cdot \Phi_i] \times 10^{28}$ [c]	140.	170.	320.	200.	270.	190.	23.	19.	40.
Max$[\lvert \Phi_i \cdot \Phi_j \rvert] \times 10^{28}$ [c]	19.	17.	50.	58.	76.	72.	2.3	1.8	2.9
Max$[\lvert A\Phi_i - \Phi_i \rvert] \times 10^{28}$ [c,d]	79.	63.	80.	73.	88.	61.	43.	35.	25.

[a] The "good arrangement" of each idempotent matrix, as discussed in Section 3, is always taken.

[b] Each time interval represents an average value for 10 runs through the routine that decomposes the matrix; all tests of the time were made on the same CDC 7600 computer at LASL.

[c] It is important to note that these entries indicate roundoff errors that accumulate both during computation of the eigenvectors Φ_i and during the arithmetic required to conduct the tests.

[d] These values indicate the absolute value of the largest *component* that occurs in all of the vector differences in each subspace.

4. Applications of High-J SAF'S

Methane is a significant constituent of the atmospheres of the outer planets (AOP), and the stratosphere of the Earth [17]. Enormous quantities of CH_4 present in AOP suggest that absorption features arising from vibration–rotation transitions in the infrared will be important [18] out to J near 30 for the strong fundamentals ν_3 and ν_4. Appropriate laboratory spectra, requiring very long effective absorption paths and low temperatures, are not yet available. Consequently, spectral line positions and intensities have been calculated, and corresponding planetary spectra have been synthesized [18] for $0 \leqslant J \leqslant 30$ in ν_3 and ν_4 of CH_4. In that work, the theoretical formulation of Moret-Bailly *et al.* [4, 19] was applied, and tetrahedral splittings were computed using Dang-Nhu's program [20] for F-coefficients.

Vibration–rotation spectra of molecules like SF_6 with octahedral symmetry appear to be similar to corresponding spectra of tetrahedral molecules like CH_4. The theoretical bases for these similarities are well established [4, 19]. Recently, an ultra-high resolution spectrum of the infrared-active fundamental ν_3 of SF_6 was

obtained [21], and a preliminary analysis was made [21] for $0 \leqslant J \leqslant 20$. Similar spectra, of even higher resolution [22], were unraveled [23, 24] to determine the quantum numbers of absorption transitions in SF_6 which corresponds to emission in the 10.6-μm region by a CO_2 laser. Infrared transitions involving $J \leqslant 60$ in SF_6 were identified in this application.

From a purely abstract viewpoint, it is intriguing to study the systematics of the coefficients [4] $F_{A_1 pp}^{(4,J,J)}$ used in analyses of high-resolution vibration–rotation spectra of spherical-top molecules. These coefficients have been calculated for $2 \leqslant J \leqslant 100$ [25] and remarkable regularities have been found [26]. This problem is part of an extensive theoretical program to analyze ultra-high resolution infrared spectra of molecules like SF_6 and CH_4 [27].

APPENDIX A: Methods, Other than Cholesky Factorization, for Determining the Eigenvectors of a Symmetric Idempotent Matrix

1. *Symmetric Elimination with Pivoting*

The following procedure (and its implementation), written by Moler [15], permits a search for the largest diagonal element of A (and an interchange of rows and columns) before each elimination of a row and column, so that round-off error [14] is acceptably small. The matrix remains symmetric after each complete elimination.

Let A be a symmetric idempotent matrix and let Y be a nonsingular matrix such that

$$Y^T A Y = D, \tag{A.1}$$

where D is a diagonal matrix with no negative elements. Then

$$A = (Y^T)^{-1} D Y^{-1} = (Y^{-1})^T D Y^{-1} \tag{A.2}$$

or

$$A = \mathscr{L}\mathscr{L}^T, \tag{A.3}$$

where

$$\mathscr{L} = (Y^{-1})^T D^{1/2}. \tag{A.4}$$

As Eq. (A.3) is of the form

$$PAP^T = LL^T \tag{A.5}$$

[6, Eq. (2)], with $P = I$, it follows that

$$\mathscr{L}^T \mathscr{L} = I \tag{A.6}$$

(i.e., the nonvanishing columns of $\mathscr{L}$ are orthonormal) and that

$$A\mathscr{L} = 1 \cdot \mathscr{L} \tag{A.7}$$

(i.e., the nonvanishing columns of $\mathscr{L}$ are eigenvectors of A corresponding to the eigenvalue $+1$).

We determine Y^T by a succession of **r** eliminations of a row and a column (where **r** is the rank of A and **n** is the order of A). In matrix notation this is written

$$A_0 \equiv A, \tag{A.8}$$

$$A_1 = M_1 A_0 M_1^{-1}, \tag{A.9}$$

$$A_2 = M_2 A_1 M_2^{-1}, \tag{A.10}$$

$$\vdots$$

$$D = A_r = M_r A_{r-1} M_r^{-1}, \tag{A.11}$$

and

$$Y^T = M_r M_{r-1} \cdots M_1, \tag{A.12}$$

where each M_j, $1 \leqslant j \leqslant \mathbf{r}$, is selected to eliminate the row and column corresponding to the largest diagonal element a_{mm} in A_{j-1}. M_j is $\mathbf{n} \times \mathbf{n}$ and has the form

$$\begin{pmatrix} 1 & 0 & \cdots & -a_{1m}/a_{mm} & \cdots & 0 \\ 0 & 1 & \cdots & -a_{2m}/a_{mm} & \cdots & 0 \\ \vdots & \vdots & & \vdots & & \vdots \\ 0 & 0 & \cdots & 1 & \cdots & 0 \\ \vdots & \vdots & & \vdots & & \vdots \\ 0 & 0 & \cdots & -a_{nm}/a_{mm} & \cdots & 1 \end{pmatrix} \tag{A.13}$$

and M_j^{-1} has the form

$$\begin{pmatrix} 1 & 0 & \cdots & a_{1m}/a_{mm} & \cdots & 0 \\ 0 & 1 & \cdots & a_{2m}/a_{mm} & \cdots & 0 \\ \vdots & \vdots & & \vdots & & \vdots \\ 0 & 0 & \cdots & 1 & \cdots & 0 \\ \vdots & \vdots & & \vdots & & \vdots \\ 0 & 0 & \cdots & a_{nm}/a_{mm} & \cdots & 1 \end{pmatrix}. \tag{A.14}$$

Finally, Eq. (A.4) becomes

$$\mathscr{L} = M_1^{-1} M_2^{-1} \cdots M_r^{-1} D^{1/2}. \tag{A.15}$$

For example, applying this procedure to matrix (17d) of Section 2 we find successively

$$A_1 = \begin{pmatrix} 0.501325 & -0.224663 & -0.207029 & 0 & 0.395808 \\ -0.224663 & 0.619830 & 0.349215 & 0 & 0.251427 \\ -0.207029 & 0.349215 & 0.212165 & 0 & 0.048357 \\ 0 & 0 & 0 & 0.779134 & 0 \\ 0.395808 & 0.251427 & 0.048357 & 0 & 0.666681 \end{pmatrix}, \tag{A.16}$$

$$A_2 = \begin{pmatrix} 0.266334 & -0.373935 & -0.235739 & 0 & 0 \\ -0.373935 & 0.525009 & 0.330978 & 0 & 0 \\ -0.235739 & 0.330978 & 0.208657 & 0 & 0 \\ 0 & 0 & 0 & 0.779134 & 0 \\ 0 & 0 & 0 & 0 & 0.666681 \end{pmatrix}, \tag{A.17}$$

and

$$A_3 = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0.525009 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0.779134 & 0 \\ 0 & 0 & 0 & 0 & 0.666681 \end{pmatrix}, \tag{A.18}$$

with

$$M_1 = \begin{pmatrix} 1 & 0 & 0 & -0.085724 & 0 \\ 0 & 1 & 0 & 0.235179 & 0 \\ 0 & 0 & 1 & -0.469899 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -0.003716 & 1 \end{pmatrix}, \tag{A.19}$$

$$M_2 = \begin{pmatrix} 1 & 0 & 0 & 0 & -0.593699 \\ 0 & 1 & 0 & 0 & -0.377132 \\ 0 & 0 & 1 & 0 & -0.072534 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix}, \tag{A.20}$$

$$M_3 = \begin{pmatrix} 1 & 0.712245 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & -0.630423 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix}, \tag{A.21}$$

and

$$\mathscr{L} = \begin{matrix} (K' = 4) \\ (8) \\ (12) \\ (16) \\ (20) \end{matrix} \begin{pmatrix} 0 & -0.516075 & 0 & 0.075667 & 0.484758 \\ 0 & 0.724575 & 0 & -0.207589 & 0.307930 \\ 0 & 0.456789 & 0 & 0.414773 & 0.059224 \\ 0 & 0 & 0 & 0.882686 & 0 \\ 0 & 0 & 0 & 0.003280 & 0.816505 \end{pmatrix}. \tag{A.22}$$

The three nonvanishing columns of $\mathscr{L}$ must be related to $\{\Phi_i\,;\, i = 1, 2, 3\}$ and to $\{\Theta_i\,;\, i = 1, 2, 3\}$ of Section 2 by unitary transformations.

2. *Tridiagonalization followed by Diagonalization*

The program TRED2 [16] which incorporates a series of orthogonal transformations according to Householder [16], has been employed to reduce our symmetric idempotent matrices to symmetric tridiagonal form. Because the eigenvalues $+1$ and 0 occur with respective multiplicities **r** and **(n − r)** that generally exceed 1, we expect [13] the tridiagonal matrix to be fractured by a number of zeros that occur on the subdiagonal: if the multiplicity of an eigenvalue is p, then there must be at least $(p-1)$ vanishing subdiagonal elements, so that at least p separated matrices occur along the diagonal. The following tridiagonal matrix emerges after application of TRED2 to matrix (17d) of Section 2:

$$\left(\begin{array}{cc|cc|c} 0.666692 & -0.471396 & 0 & 0 & 0 \\ -0.471396 & 0.333308 & 0 & 0 & 0 \\ \hline 0 & 0 & 0.955602 & 0.205977 & 0 \\ 0 & 0 & 0.205977 & 0.044398 & 0 \\ \hline & & 0 & 0 & 1 \end{array}\right). \tag{A.23}$$

In all of the examples that we have seen, the number of subdiagonal zeros is $(p-1)$, where $p = \max[\mathbf{r}, (\mathbf{n}-\mathbf{r})]$; the separated matrices are always 2×2 or 1×1, and the number of 2×2 matrices is $\min[\mathbf{r}, (\mathbf{n}-\mathbf{r})]$.

These tridiagonal matrices are diagonalized by the routine IMTQL2 [16], which is based on the QR algorithm [13]. Each 2×2 matrix is reduced to the form

$$\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}. \tag{A.24}$$

Final eigenvectors are columns of the accumulated product of the successive orthogonal transformations performed in TRED2 and IMTQL2. The combined package yields a complete set of orthonormal eigenvectors for the subspaces corresponding to both eigenvalues $+1$ and 0, but only those belonging to the subspace of $+1$ relate to the present problem.

APPENDIX B: Properties of $d^J_{K'K}(\pi/2)$

In the construction of "cubic harmonics" or SAF's, the matrix elements of the finite rotations [9, 28] for an angle $\pi/2$ play an essential role. In the present work, as in [5], we follow the phase convention of [28], namely,

$$d^J_{K'K}(\beta) \text{ (here and in [28])} = (-1)^{K+K'} d^J_{K'K}(\beta) \qquad [9]. \tag{B.1}$$

From known recursion formulas for the hypergeometric functions [29], a variety of useful recursion relations can be found [5, 30–35] for the $d^J_{K'K}(\beta)$, because these are

simply related to the Jacobi polynomials [9]. For $\beta = \pi/2$, [5, Eq. (64)] (also, see [32, Eq. (A.5.10)]) reduces to a particularly convenient recursion for numerical calculation of $d^J_{K'K}$ with J fixed [36]:

$$(J + K + 1)^{1/2}(J - K)^{1/2}d^J_{K'(K+1)} = -2K'd^J_{K'K} - (J - K + 1)^{1/2}(J + K)^{1/2}d^J_{K'(K-1)} . \tag{B.2}$$

With this recursion, it is not difficult to calculate the $d^J_{K'K}$ for high J. For example, we have calculated all the values of $d^J_{K'K}(\pi/2)$ for $0 \leqslant J \leqslant 100$ in 4.6 and 8.8 sec using single- and double-precision arithmetic, respectively, on a CDC 7600 computer. The values in these two calculations agreed to at least 11 significant figures.

In order to implement Eq. (B.2), certain starting values and symmetry relations are important:

$$d^J_{JJ} = 1/2^J, \tag{B.3}$$

$$d^J_{J-1,J} = (2J)^{1/2}/2^J, \tag{B.4}$$

$$d^J_{J-1,J-1} = -(J - 1)/2^{J-1}, \tag{B.5}$$

and

$$d^J_{K'K}(\beta) = (-1)^{K-K'}d^J_{KK'}(\beta), \tag{B.6}$$

together with Eq. (B.2) are sufficient to generate all the $d^J_{K'K}$ for a given J. The number of explicit calculations may be reduced further by means of the relations

$$d^J_{-K'K} = (-1)^{J-K}d^J_{K'K} \tag{B.7}$$

and

$$d^J_{-K'-K}(\beta) = (-1)^{K'-K}d^J_{K'K}(\beta). \tag{B.8}$$

Equations (B.6) and (B.8) are from [28], Eq. (B.7) is from [9], and Eqs. (B.3)–(B.5) follow readily from formulas in [9].

In our study of the numerical algebra of the Cholesky factorization, we have found that certain inequalities for the d's must exist. These inequalities will be presented and discussed in future work.

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	Moret-Bailly	
Jahn	Even J	Odd J
A_1	A_1	A_2
A_2	A_2	A_1
E_e	E^*	E
E_f	E	E^*
F_{1z}	F_{1z}	F_{2z}
F_{2z}	F_{2z}	F_{1z}

The results of [5], which gives SAF's for both the E_e and E_f subspaces, together with the notation of [4] for E alone, imply that the SAF's for species A_1, E, and F_1 are linear combinations of $Y_K{}^J$ with $K = 0, \pm 4, \pm 8, \ldots$; for A_2, E^*, and F_2, with $K = \pm 2, \pm 6, \pm 10, \ldots$.

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