Analysis of nearly degenerate bands of spherical top molecules: Matrix elements of the vibrational-rotational Hamiltonian[a)][b)]

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We formulate a general method for calculating energy eigenvalues and eigenfunctions in a simultaneous analysis of nearly degenerate vibrational-rotational bands of spherical top molecules. The basis functions are products of rigid rotor and N-dimensional harmonic oscillator eigenfunctions. General explicit expressions are derived for the matrix elements of vibrational operators in the basis of N-dimensional harmonic oscillator eigenfunctions. Using these general expressions, the matrix elements of vibrational operators in the basis of five-dimensional harmonic oscillator eigenfunctions applicable, for example, in the analysis of the nearly degenerate ν_2 and ν_4 fundamental vibrational-rotational bands of tetrahedral XY_4 molecules like CH_4, are calculated explicitly.

I. INTRODUCTION

Nearly degenerate vibrational-rotational bands of spherical top molecules are often close enough in spectral frequency to produce significant perturbations. The ν_2 and ν_4 fundamentals of CH_4 comprise an example, as had been shown earlier.[1-3] Various theoretical approaches to a simultaneous analysis of such nearly degenerate vibrational-rotational bands have been formulated. In the case of ν_2 and ν_4 of CH_4, Gray and Robiette[4] combined the ν_2 Hamiltonian of Herranz and Thyagarajan[5]; the ν_4 Hamiltonian of Robiette, Gray, and Birss[6]; and the Coriolis coupling term of Jahn[1] to produce a $\{\nu_2, \nu_4\}$ Hamiltonian. This was diagonalized in a basis consisting of rigid-rotor eigenfunctions and two and threefold harmonic oscillator eigenfunctions for ν_2 and ν_4, respectively. In contrast, Berger[7,8] treated the ν_2 and ν_4 states as substates of a hypothetical fivefold harmonic oscillator. This approach eliminated the difficulty of applying the spherical tensor formalism to ν_2 alone.[9] Another formalism, using an unsymmetrized coupling scheme, has been developed and applied by Champion[10] to ν_2 and ν_4 of CH_4.

In this paper, we develop a completely general formalism for calculating the matrix elements of a Hamiltonian for an arbitrary number of nearly degenerate vibrational-rotational bands. The Hamiltonian of a $\{\nu_1, \nu_2, \ldots, \nu_m\}$ manifold of such bands with respective degeneracies $n_1, n_2, \ldots, n_m$ can be expressed as

$$\mathcal{H} = BJ^2 + h\nu_1 \sum_{i=1}^{n1} (a_i^\dagger a_i + \tfrac{1}{2}) + h\nu_2 \sum_{i=n_1+1}^{n_1+n_2} (a_i^\dagger a_i + \tfrac{1}{2}) + \cdots + h\nu_m \sum_{i=N-n_m+1}^{N} (a_i^\dagger a_i + \tfrac{1}{2}) + \cdots, \tag{1}$$

which can be written in the form

$$\mathcal{H} = BJ^2 + h\nu_0 \sum_{i=1}^{N} (a_i^\dagger a_i + \tfrac{1}{2}) + \cdots. \tag{2}$$

The first and second terms represent, respectively, a rigid rotor and a harmonic oscillator of degeneracy $N = n_1 + n_2 + \cdots + n_m$. Using as our basis functions the products of eigenfunctions of these operators, we show explicitly how to calculate matrix elements of the remaining terms. The calculation of matrix elements of rotational operators in the basis of rigid-rotor eigenfunctions is well developed.[11] The calculation of matrix elements of vibrational operators in the basis of N-degenerate harmonic oscillator eigenfunctions is simplified by Louck's[12] formalism. Explicit expressions will be given below for the latter calculation. It is important to note that the Coriolis coupling term will be introduced explicitly in connection with Eqs. (2′) and Eqs. (20)–(22).

The nearly degenerate $2\nu_2$, $2\nu_4$, and $\nu_2+\nu_4$ overtone and combination bands[13,14] of CH_4 can be treated as components of the $\{\nu_2, \nu_4\}$ manifold and, using the above formalism with $N=2+3=5$, analyzed on the basis of a fivefold oscillator. The $2\nu_1$, $2\nu_3$, and $\nu_1+\nu_3$ bands can be analyzed on the basis of a fourfold harmonic oscillator, i.e., $N=1+3=4$. Any pure overtone of ν_3 can also be analyzed using this formalism, of course, on the basis of a threefold oscillator.

As a more detailed example, consider the ν_2 and ν_4 bands of a tetrahedral XY_4 molecule like CH_4. We express[15] the rotational-vibrational Hamiltonian for the $\{\nu_2, \nu_4\}$ manifold as

$$\mathcal{H} = BJ^2 + h\nu_4 \sum_{i=1}^{3} (a_i^\dagger a_i + \tfrac{1}{2}) + h\nu_2 \sum_{i=4}^{5} (a_i^\dagger a_i + \tfrac{1}{2}) + \cdots. \tag{1′}$$

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$a_i^\dagger$ and a_i are creation and annihilation operators, respectively, for the triply-degenerate ν_4 ($i=1, 2, 3$) and doubly degenerate ν_2($i=4, 5$) harmonic oscillators. $\mathcal{H}$ can be written in the form

$$\mathcal{H} = BJ^2 + h\nu_0 \sum_{i=1}^{5} (a_i^\dagger a_i + \tfrac{1}{2}) + h(\nu_4 - \nu_2)/4$$
$$+ \tfrac{1}{2} h(\nu_4 - \nu_2) \left[\sum_{i=1}^{3} a_i^\dagger a_i - \sum_{i=4}^{5} a_i^\dagger a_i \right] + \mathcal{H}' , \tag{2'}$$

where $\nu_0 \equiv \frac{1}{2}(\nu_2 + \nu_4)$ and $\mathcal{H}'$ contains the Coriolis coupling term together with higher-order vibrational, rotational, and vibrational–rotational terms as indicated in Eqs. (20) and (21) and the accompanying text. The first two terms in Eq. (2′) represent a rigid rotor and a quintuply degenerate harmonic oscillator.

In the next section, results concerning N-dimensional harmonic oscillator eigenfunctions and matrix elements of vibrational operators[12] are reviewed. Explicit expressions for the calculation of the matrix elements of vibrational operators in the basis of N-dimensional harmonic oscillator eigenfunctions are then given.[14] In Sec. III, we show how these expressions can be used to deduce the matrix elements of the vibrational operators of the Hamiltonian for the purpose of analyzing the $\{\nu_2, \nu_4\}$ manifold. These matrix elements are derived explicitly and tabulated.

II. THEORY

The Hamiltonian for an N-dimensional (isotropic) harmonic oscillator is

$$H = \tfrac{1}{2} h\nu \sum_{j=1}^{N} [(p_j/\hbar)^2 + x_j^2] , \tag{3}$$

where $\hbar \equiv h/2\pi$ and the commutator $[x_i, p_j] = i\hbar\delta_{ij}$. With creation and annihilation operators defined, respectively, by

$$a_j^\dagger = (1/\sqrt{2})(x_j - p_j/\hbar) , \tag{4}$$

$$a_j = (1/\sqrt{2})(x_j + p_j/\hbar) , \tag{5}$$

with $[a_i, a_j] = [a_i^\dagger, a_j^\dagger] = 0$ and $[a_i, a_j^\dagger] = \delta_{ij}$ the Hamiltonian H can be rewritten as

$$H = h\nu \sum_{j=1}^{N} (a_j^\dagger a_j + \tfrac{1}{2}) . \tag{6}$$

The $\frac{1}{2}N(N-1)$ components of the vibrational angular momentum are defined by

$$L(i, j) = x_i p_j - x_j p_i , \tag{7}$$

with $i<j$; this can be written as

$$L(i, j) = i\hbar(a_i a_j^\dagger - a_j a_i^\dagger) . \tag{8}$$

The vibrational angular momentum analogs of J^2 are defined by

$$L_K^2 = \sum_{i<j=1}^{K} [L(i, j)]^2 , \tag{9}$$

where $K = N, N-1, \ldots, 2$ is an index labeling the $N-1$ vibrational angular momenta and $L_2 \equiv L(1, 2)$.

Louck[12] has shown that $\{H, L_N^2, L_{N-1}^2, \ldots, L_3^2, L(1, 2)\}$ constitute a complete set of commuting operators. The eigenfunctions and eigenvalues of this set of operators are given by

$$H\Psi(v, l_N, l_{N-1}, \ldots, l_3, l_2)$$
$$= h\nu(v + \tfrac{1}{2}N)\Psi(v, l_N, l_{N-1}, \ldots, l_3, l_2) , \tag{10}$$

$$L_K^2\Psi(v, l_N, l_{N-1}, \ldots, l_3, l_2)$$
$$= l_K(l_K + K - 2)\hbar^2\Psi(v, l_N, l_{N-1}, \ldots, l_3, l_2) , \tag{11}$$

with $K = N, N-1, \ldots, 3$ and

$$L(1, 2)\Psi(v, l_N, l_{N-1}, \ldots, l_3, l_2)$$
$$= l_2\hbar\Psi(v, l_N, l_{N-1}, \ldots, l_3, l_2) , \tag{12}$$

where $v = 0, 1, 2, \ldots$; $l_N = v, v-2, v-4, \ldots, 0$ or 1; $l_{N-1} = 0, 1, 2, \ldots, l_N; \ldots$; $l_3 = 0, 1, 2, \ldots, l_4$; and $l_2 = 0, \pm 1, \pm 2, \ldots, \pm l_3$. For example, in the familiar three-dimensional case, $N = 3$ and $H\Psi(v, l_3, l_2) = h\nu(v + \frac{3}{2})\Psi(v, l_3, l_2)$, $L_3^2\Psi(v, l_3, l_2) = l_3(l_3+1)\hbar^2\Psi(v, l_3, l_2)$, and $L(1, 2)\Psi(v, l_3, l_2) = l_2\hbar\Psi(v, l_3, l_2)$.

The set of eigenfunctions $\Psi(v, l_N, l_{N-1}, \ldots, l_3, l_2)$ provides a convenient basis in which to calculate the matrix elements of an arbitrary vibrational operator of a vibrational-rotational Hamiltonian. Such an operator can be written, as exemplified in Eqs. (22)–(24) below, in terms of the following set of vibrational operators:

$$L(i, j) \equiv i\hbar(a_i a_j^\dagger - a_j a_i^\dagger) , \quad i<j = 1, 2, \ldots, N , \tag{13a}$$

$$M(i, j) \equiv i\hbar(a_i a_j^\dagger + a_j a_i^\dagger) , \quad i<j = 1, 2, \ldots, N , \tag{13b}$$

$$a_i^\dagger a_i , \quad i = 1, 2, \ldots, N . \tag{13c}$$

The calculation of their matrix elements is simplified by Louck's[12] formalism. The matrix elements of $L(1, 2)$ are given by

$$\langle v', l'_N, l'_{N-1}, \ldots, l'_3, l'_2 | L(1, 2) | v, l_N, l_{N-1}, \ldots, l_3, l_2\rangle$$
$$= \delta(v, v') \prod_{K=2}^{N} \delta(l_K, l'_K) , \tag{14}$$

and those of $L(K-1, K)$ by

$$\langle v', l'_N, l'_{N-1}, \ldots, l'_3, l'_2 | L(K-1, K) | v, l_N, l_{N-1}, \ldots, l_3, l_2\rangle = \delta(v', v) \prod_{\substack{r=1 \\ r\neq K-1}}^{N} \delta(l'_r, l_r) \Biggl\{ \delta(l'_{K-1}, l_{K-1}+1)\hbar$$
$$\times \left[\frac{(l_K - l_{K-1})(l_K + l_{K-1} + K - 2)(l_{K-1} - l_{K-2} + 1)(l_{K-1} + l_{K-2} + K - 3)}{(2l_{K-1} + K - 3)(2l_{K-1} + K - 1)} \right]^{1/2} + \delta(l'_{K-1}, l_{K-1} - 1)\hbar$$
$$\times \left[\frac{(l_K - l_{K-1} + 1)(l_K + l_{K-1} + K - 3)(l_{K-1} - l_{K-2})(l_{K-1} + l_{K-2} + K - 4)}{(2l_{K-1} + K - 5)(2l_{K-1} + K - 3)} \right]^{1/2} \Biggr\} , \tag{15}$$

where $K=3,4,\ldots,N$; and $l_1\equiv 0$ by definition. The matrix elements of the remaining operators $L(i,j)$ are calculated using the commutation relations

$$i\hbar L(i,j)=[L(i,j-1),L(j-1,j)]\ . \tag{16}$$

The matrix elements of $M(i,j)$ and $a_i^\dagger a_i$ are simply calculated from the matrix elements of the creation and annihilation operators $a_i^\dagger$ and a_i, $i=1,2,\ldots,N$. The operators $a_N^\dagger$ and a_N have matrix elements

$$\begin{aligned}\langle v', l_N', l_{N-1}', \ldots, l_3', l_2' | a_N | v, l_N, l_{N-1}, \ldots, l_3, l_2\rangle \\ = \prod_{K=2}^{N-1} \delta(l_K', l_K)\Bigg\{\delta(v', v-1)\,\delta(l_N', l_{N+1})\left[\frac{(v-l_N)(l_N-l_{N-1}+1)(l_N+l_{N-1}+N-2)}{(2l_N+N-2)(2l_N+N)}\right]^{1/2} \\ -\delta(v', v-1)\,\delta(l_N', l_N-1)\left[\frac{(v+l_N+N-2)(l_N-l_{N-1})(l_N+l_{N-1}+N-3)}{(2l_N+N-4)(2l_N+N-2)}\right]^{1/2}\Bigg\}\ ,\end{aligned} \tag{17}$$

and

$$\begin{aligned}\langle v', l_N', l_{N-1}', \ldots, l_3', l_2' | a_N^\dagger | v, l_N, l_{N-1}, \ldots, l_3, l_2\rangle \\ = \prod_{K=2}^{N-1} \delta(l_K', l_K)\Bigg\{-\delta(v', v+1)\,\delta(l'_N, l_N+1)\left[\frac{(v+l_N+N)(l_N-l_{N-1}+1)(l_N+l_{N-1}+N-2)}{(2l_N+N-2)(2l_N+N)}\right]^{1/2} \\ +\delta(v', v+1)\,\delta(l'_N, l_N-1)\left[\frac{(v-l_N+2)(l_N-l_{N-1})(l_N+l_{N-1}+N-3)}{(2l_N+N-4)(2l_N+N-2)}\right]^{1/2}\Bigg\}\ .\end{aligned} \tag{18}$$

The matrix elements of the remaining creation and annihilation operators are calculated using the commutation relations

$$\begin{aligned} i\hbar a_i^\dagger &= [a_N^\dagger, L(i, N)]\ , \\ i\hbar a_i &= [a_N, L(i, N)]\ . \end{aligned} \tag{19}$$

III. MATRIX ELEMENTS OF $\{\nu_2,\nu_4\}$ HAMILTONIAN

In the simultaneous analysis of the $\{\nu_2, \nu_4\}$ bands of spherical top molecules like methane, we consider the special case of the above formalism for $N=5$. To calculate the matrix elements of the Hamiltonian $\mathcal{H}$ in Eq. (2′), we use the basis functions $\Psi(v, l_5, l_4, l_3, l_2)\Psi(J, K)$, where $\Psi(J, K)$ is a rigid-rotor eigenfunction and $\Psi(v, l_5, l_4, l_3, l_2)$ is a five-dimensional harmonic oscillator eigenfunction. The relationship between the $\Psi(v, l_5, l_4, l_3, l_2)$ of the $\{\nu_2, \nu_4\}$ manifold and the ν_2 and ν_4 harmonic oscillator eigenfunctions is given in Eq. (A3) of Appendix A.

The fundamental $\{\nu_2, \nu_4\}$ Hamiltonian of Eq. (2′) can be written as

$$\begin{aligned}\mathcal{H} &= h\nu_2+\tfrac{3}{2}h\nu_4+h\nu_0+\mathcal{H}(\nu_2\nu_4 \text{ split}) \\ &\quad +\mathcal{H}_R+kJ\cdot S^{(24)}+\mathcal{H}_{R\nu_2}+\mathcal{H}_{R\nu_4}+\mathcal{H}_{\nu_2\nu_4}\ ,\end{aligned} \tag{20}$$

where $h\nu_2+\frac{3}{2}\nu_4$ and $h\nu_0=\frac{1}{2}h(\nu_2+\nu_4)$ are the $\{\nu_2, \nu_4\}$ vibrational energies for the ground state and "average" fundamental, respectively. The eigenvalues of

$$\mathcal{H}(\nu_2\,\nu_4 \text{ split})\equiv\tfrac{1}{2}h(\nu_4-\nu_2)\left[\sum_{i=1}^{3}a_i^\dagger a_i-\sum_{i=4}^{5}a_i^\dagger a_i\right] \tag{21}$$

represent the difference between the average fundamental energy $h\nu_0$ and the energies $h\nu_2$ and $h\nu_4$ of their respective harmonic oscillators. And $kJ\cdot S^{(24)}$ is the Coriolis coupling term.[1] The remaining terms $\mathcal{H}_R$, $\mathcal{H}_{R\nu_2}$, $\mathcal{H}_{R\nu_4}$, and $\mathcal{H}_{\nu_2\nu_4}$ are pure rotational, vibrational-rotation, and pure vibrational, respectively. Note that $\mathcal{H}'$ of Eq. (2′) is now more explicitly specified as $\mathcal{H}_R-BJ^2+kJ\cdot S^{(24)}+\mathcal{H}_{R\nu_2}+\mathcal{H}_{R\nu_4}+\mathcal{H}_{\nu_2\nu_4}$. Matrix elements of all vibrational operators in the $\{\nu_2, \nu_4\}$ Hamiltonian of Eq. (20) can be calculated using the basis functions $\Psi(v=1, l_5, l_4, l_3, l_2)$ and the formalism of the previous section.

All vibrational operators in the $\{\nu_2, \nu_4\}$ Hamiltonian considered by Gray and Robiette,[4] together with higher-order vibrational terms considered by Hecht,[9] can be related to the $N=5$ operators $L(i, j)$, $M(i, j)$, and $a_i^\dagger a_i$ in Eqs. (13a)–(13c). For example, the Cartesian components of the vibrational part $S^{(24)}$ of Jahn's Coriolis coupling term[1] can be expressed as

$$S_x^{(24)}=-\tfrac{1}{2}L(1, 4)+\tfrac{1}{2}\sqrt{3}L(1, 5)\ , \tag{22a}$$

$$S_y^{(24)}=-\tfrac{1}{2}L(1, 4)-\tfrac{1}{2}\sqrt{3}L(1, 5)\ , \tag{22b}$$

$$S_z^{(24)}=L(3, 4)\ . \tag{22c}$$

The two vibrational-rotational operators of $H_{R\nu_2}$, denoted[4] by T and N, can be written as

$$T=-(12)^{1/2}L(4, 5)(J_xJ_yJ_z+J_zJ_yJ_x)\ , \tag{23}$$

$$\begin{aligned}N &= (a_4^\dagger a_4-a_5^\dagger a_5)(J_x^2+J_y^2-2J_z^2) \\ &\quad +iM(4, 5)\sqrt{3}(J_x^2-J_y^2)\ .\end{aligned} \tag{24}$$

The matrix elements of all vibrational operators $L(i, j)$, $M(i, j)$, and $a_i^\dagger a_i$ in the fundamental state of a five-dimensional isotropic harmonic oscillator have been calculated and are tabulated in Appendix B.

In the general case of $\{\nu_2, \nu_4\}$ and other manifolds, the analytical results developed in the present work will be helpful in calculations related to the spectra of nearly-degenerate vibrational-rotational bands of spherical-top molecules like methane. The general formalism will facilitate simultaneous analysis of these bands. Combination and overtone bands can be handled in a routine manner, and entire computations can be dealt with systematically.

APPENDIX A: RELATIONSHIP BETWEEN FIVE-DIMENSIONAL AND ν_2 AND ν_4 HARMONIC OSCILLATOR EIGENFUNCTIONS

The five-dimensional harmonic oscillator eigenfunction $\Psi(v, l_5, l_4, l_3, l_2)$ can be written as a linear combination of occupancy states $|\mu_1, \mu_2, \mu_3, \mu_4, \mu_5\rangle$, where [see Eq. (1′)] μ_1, μ_2, and μ_3 refer to the triply-degenerate ν_4; and μ_4 and μ_5 refer to the doubly-degenerate ν_2.

$$\Psi(v, l_5, l_4, l_3, l_2) = \sum_{\mu_i}{}' C(v, l_5, l_4, l_3, l_2; \mu_1, \mu_2, \mu_3, \mu_4, \mu_5)|\mu_1, \mu_2, \mu_3, \mu_4, \mu_5\rangle . \tag{A1}$$

The prime on the sum over all μ_i denotes the restriction $\sum_{i=1}^{5} \mu_i = v$. Conditions on the coefficients $C(v, l_5, l_4, l_3, l_2; \mu_1, \mu_2, \mu_3, \mu_4, \mu_5)$ are derived by substituting Eq. (A1) into Eqs. (11) and (12), and expressing the operators L_K^2 in terms of creation and annihilation operators by means of Eqs. (8) and (9). For $v=0$, 1, and 2, then

$$\Psi(0, 0, 0, 0, 0) = |0, 0, 0, 0, 0\rangle , \tag{A2}$$

$$\begin{aligned}
&\Psi(1, 1, 0, 0, 0) = -|0, 0, 0, 0, 1\rangle ,\\
&\Psi(1, 2, 2, 0, 0) = i|0, 0, 0, 1, 0\rangle ,\\
&\Psi(1, 1, 1, 1, 1) = -(1/\sqrt{2})(|1, 0, 0, 0, 0\rangle + i|0, 1, 0, 0, 0\rangle) ,\\
&\Psi(1, 1, 1, 1, 0) = |0, 0, 1, 0, 0\rangle ,\\
&\Psi(1, 1, 1, 1, -1) = (1/\sqrt{2})(|1, 0, 0, 0, 0\rangle - i|0, 1, 0, 0, 0\rangle) ,
\end{aligned} \tag{A3}$$

$$\begin{aligned}
&\Psi(2, 0, 0, 0, 0) = (1/\sqrt{5})(|2, 0, 0, 0, 0\rangle + |0, 2, 0, 0, 0\rangle + |0, 0, 2, 0, 0\rangle + |0, 0, 0, 2, 0\rangle + |0, 0, 0, 0, 2\rangle) ,\\
&\Psi(2, 2, 0, 0, 0) = (1/\sqrt{20})(|2, 0, 0, 0, 0\rangle + |0, 2, 0, 0, 0\rangle + |0, 0, 2, 0, 0\rangle + |0, 0, 0, 2, 0\rangle - 4|0, 0, 0, 0, 2\rangle) ,\\
&\Psi(2, 2, 1, 0, 0) = i|0, 0, 0, 1, 1\rangle ,\\
&\Psi(2, 2, 1, 1, 1) = -(1/\sqrt{2})(|1, 0, 0, 0, 1\rangle + i|0, 1, 0, 0, 1\rangle) ,\\
&\Psi(2, 2, 1, 1, 0) = |0, 0, 1, 0, 1\rangle ,\\
&\Psi(2, 2, 1, 1, -1) = (1/\sqrt{2})(|1, 0, 0, 0, 1\rangle - i|0, 1, 0, 0, 1\rangle) ,\\
&\Psi(2, 2, 2, 0, 0) = -(1/\sqrt{12})(|2, 0, 0, 0, 0\rangle + |0, 2, 0, 0, 0\rangle + |0, 0, 2, 0, 0\rangle - 3|0, 0, 0, 2, 0\rangle) ,\\
&\Psi(2, 2, 2, 1, 1) = (i/\sqrt{2})(|1, 0, 0, 1, 0\rangle + i|0, 1, 0, 1, 0\rangle) ,\\
&\Psi(2, 2, 2, 1, 0) = -i|0, 0, 1, 1, 0\rangle ,\\
&\Psi(2, 2, 2, 1, -1) = -(i/\sqrt{2})(|1, 0, 0, 1, 0\rangle - i|0, 1, 0, 1, 0\rangle) ,\\
&\Psi(2, 2, 2, 2, 2) = -\tfrac{1}{2}(|2, 0, 0, 0, 0\rangle - |0, 2, 0, 0, 0\rangle + i\sqrt{2}|1, 1, 0, 0, 0\rangle) ,\\
&\Psi(2, 2, 2, 2, 1) = (1/\sqrt{2})(|1, 0, 1, 0, 0\rangle + i|0, 1, 1, 0, 0\rangle) ,\\
&\Psi(2, 2, 2, 2, 0) = (1/\sqrt{6})(|2, 0, 0, 0, 0\rangle + |0, 2, 0, 0, 0\rangle - 2|0, 0, 2, 0, 0\rangle) ,\\
&\Psi(2, 2, 2, 2, -1) = -(1/\sqrt{2})(|1, 0, 1, 0, 0\rangle - i|0, 1, 1, 0, 0\rangle) ,\\
&\Psi(2, 2, 2, 2, -2) = -\tfrac{1}{2}(|2, 0, 0, 0, 0\rangle - |0, 2, 0, 0, 0\rangle - i\sqrt{2}|1, 1, 0, 0, 0\rangle) ,
\end{aligned} \tag{A4}$$

For the $v=1$ fundamental, the five-dimensional harmonic oscillator eigenfunctions $\Psi(1, 1, 0, 0, 0)$ and $\Psi(1, 1, 1, 0, 0)$ correspond to ν_2; and $\Psi(1, 1, 1, 1, l_2)$ with $l_2=0$ and ± 1, to ν_4.

APPENDIX B: MATRIX ELEMENTS OF $L(i,j)$, $M(i,j)$, AND $a_j^\dagger a_i$ IN FUNDAMENTAL FIVE-DIMENSIONAL ISOTROPIC HARMONIC OSCILLATOR

Matrix elements of the vibrational operators defined in Eqs. (13a)–(13c) can be expressed in a five-by-five array whose rows and columns are labeled by the ordered states $|1, 1, 0, 0, 0\rangle$, $|1, 1, 1, 0, 0\rangle$, $|1, 1, 1, 1, 1\rangle$, $|1, 1, 1, 1, 0\rangle$, and $|1, 1, 1, 1, -1\rangle$, corresponding to row and column labels α, β, γ, δ, and ϵ, respectively. The following nonzero matrix elements result:

$$\langle\gamma|L(1, 2)|\gamma\rangle = -\langle\epsilon|L(1, 2)|\epsilon\rangle = \hbar , \tag{B1a}$$

$$\langle\gamma|L(1, 3)|\delta\rangle = -\langle\delta|L(1, 3)|\gamma\rangle = \langle\delta|L(1, 3)|\epsilon\rangle = -\langle\epsilon|L(1, 3)|\delta\rangle = i\hbar/\sqrt{2} , \tag{B1b}$$

$$\langle\beta|L(1, 4)|\epsilon\rangle = -\langle\beta|L(1, 4)|\gamma\rangle = -\langle\gamma|L(1, 4)|\beta\rangle = \langle\epsilon|L(1, 4)|\beta\rangle = \hbar/\sqrt{2} , \tag{B1c}$$

$$\langle\alpha|L(1, 5)|\gamma\rangle = -\langle\alpha|L(1, 5)|\epsilon\rangle = -\langle\gamma|L(1, 5)|\alpha\rangle = \langle\epsilon|L(1, 5)|\alpha\rangle = i\hbar/\sqrt{2} , \tag{B1d}$$

$$\langle\gamma|L(2, 3)|\delta\rangle = \langle\delta|L(2, 3)|\gamma\rangle = \langle\delta|L(2, 3)|\epsilon\rangle = \langle\epsilon|L(2, 3)|\delta\rangle = \hbar/\sqrt{2} , \tag{B1e}$$

$$\langle\gamma|L(2, 4)|\beta\rangle = \langle\epsilon|L(2, 4)|\beta\rangle = -\langle\beta|L(2, 4)|\gamma\rangle = -\langle\beta|L(2, 4)|\epsilon\rangle = i\hbar/\sqrt{2} , \tag{B1f}$$

$$\langle\alpha|L(2,5)|\gamma\rangle=\langle\alpha|L(2,5)|\epsilon\rangle=\langle\gamma|L(2,5)|\alpha\rangle=\langle\epsilon|L(2,5)|\alpha\rangle=-\hbar/\sqrt{2}\,, \tag{B1g}$$

$$\langle\beta|L(3,4)|\delta\rangle=\langle\delta|L(3,4)|\beta\rangle=\hbar\,, \tag{B1h}$$

$$\langle\delta|L(3,5)|\alpha\rangle=-\langle\alpha|L(3,5)|\delta\rangle=i\hbar\,, \tag{B1i}$$

$$\langle\alpha|L(4,5)|\beta\rangle=\langle\beta|L(4,5)|\alpha\rangle=\hbar\,, \tag{B1j}$$

$$\langle\gamma|M(1,2)|\epsilon\rangle=-\langle\epsilon|M(1,2)|\gamma\rangle=-\hbar\,, \tag{B2a}$$

$$\langle\delta|M(1,3)|\epsilon\rangle=\langle\epsilon|M(1,3)|\delta\rangle=-\langle\gamma|M(1,3)|\delta\rangle=-\langle\delta|M(1,3)|\gamma\rangle=i\hbar/\sqrt{2}\,, \tag{B2b}$$

$$\langle\beta|M(1,4)|\gamma\rangle=-\langle\beta|M(1,4)|\epsilon\rangle=-\langle\gamma|M(1,4)|\beta\rangle=\langle\epsilon|M(1,4)|\beta\rangle=-\hbar/\sqrt{2}\,, \tag{B2c}$$

$$\langle\alpha|M(1,5)|\gamma\rangle=-\langle\alpha|M(1,5)|\epsilon\rangle=\langle\gamma|M(1,5)|\alpha\rangle=-\langle\epsilon|M(1,5)|\alpha\rangle=i\hbar/\sqrt{2}\,, \tag{B2d}$$

$$\langle\gamma|M(2,3)|\delta\rangle=-\langle\delta|M(2,3)|\gamma\rangle=-\langle\delta|M(2,3)|\epsilon\rangle=\langle\epsilon|M(2,3)|\delta\rangle=-\hbar/\sqrt{2}\,, \tag{B2e}$$

$$\langle\beta|M(2,4)|\gamma\rangle=\langle\beta|M(2,4)|\epsilon\rangle=\langle\gamma|M(2,4)|\beta\rangle=\langle\epsilon|M(2,4)|\beta\rangle=-i\hbar\,, \tag{B2f}$$

$$\langle\alpha|M(2,5)|\gamma\rangle=\langle\alpha|M(2,5)|\epsilon\rangle=-\langle\gamma|M(2,5)|\alpha\rangle=-\langle\epsilon|M(2,5)|\alpha\rangle=-\hbar/\sqrt{2}\,, \tag{B2g}$$

$$\langle\beta|M(3,4)|\delta\rangle=-\langle\delta|M(2,4)|\beta\rangle=\hbar\,, \tag{B2h}$$

$$\langle\alpha|M(3,5)|\delta\rangle=\langle\delta|M(3,5)|\alpha\rangle=-i\hbar\,, \tag{B2i}$$

$$\langle\alpha|M(4,5)|\beta\rangle=-\langle\beta|M(4,5)|\alpha\rangle=\hbar\,, \tag{B2j}$$

$$\langle\gamma|a_1^\dagger a_1|\gamma\rangle=-\langle\gamma|a_1^\dagger a_1|\epsilon\rangle=-\langle\epsilon|a_1^\dagger a_1|\gamma\rangle=\langle\epsilon|a_1^\dagger a_1|\epsilon\rangle=\tfrac{1}{2}\,, \tag{B3a}$$

$$\langle\gamma|a_2^\dagger a_2|\gamma\rangle=\langle\gamma|a_2^\dagger a_2|\epsilon\rangle=\langle\epsilon|a_2^\dagger a_2|\gamma\rangle=\langle\epsilon|a_2^\dagger a_2|\epsilon\rangle=\tfrac{1}{2}\,, \tag{B3b}$$

$$\langle\delta|a_3^\dagger a_3|\delta\rangle=\langle\beta|a_4^\dagger a_4|\beta\rangle=\langle\alpha|a_5^\dagger a_5|\alpha\rangle=1\,. \tag{B3c}$$

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[14] The normal vibrations of a tetrahedral XY_4 molecule like methane are depicted, for example, by G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (Van Nostrand, Princeton, 1945). The respective degeneracies of ν_1, ν_2, ν_3, and ν_4 are 1, 2, 3, and 3.

[15] While our starting point in treating the $\{\nu_1, \nu_4\}$ manifold as a five-dimensional isotropic harmonic oscillator is the same as that of Refs. 7 and 8, the approach presented in this paper is immediately applicable to an arbitrary N-dimensional manifold, the $\{\nu_2, \nu_4\}$ manifold being only an example of the special case of $N = 5$.

[16] L. Weiss, D. B. Litvin, and K. Fox (in preparation), in which a computer program has been written to calculate matrix elements of vibrational operators in N-dimensional space.