

Calculation of High-Order Rotational Centrifugal-Distortion Matrix Elements for a Hund's Case (a) Basis Set

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The derivation of explicit expressions for the Hund's case (a) matrix elements of \mathbf{R}^{2k} is discussed, where \mathbf{R} is the mechanical rotational angular momentum operator of the molecule. A recursion relation is developed that permits matrix elements of \mathbf{R}^{2k} to be expressed in terms of those of $\mathbf{R}^{2(k-1)}$, thus affording a straightforward means of calculating the case (a) matrix elements of rotational centrifugal-distortion constants D_v , H_v , L_v , M_v , etc., to an arbitrarily high order. The explicit matrix elements of L_v are listed.

INTRODUCTION

The rotational motion of a diatomic molecule is described by the Hamiltonian

$$\mathbf{H}_{\text{rot}} = B(r)\mathbf{R}^2. \quad (1)$$

Here

$$B(r) = h/8\pi^2\mu cr^2 \quad (2)$$

is proportional to the reciprocal of the instantaneous moment of inertia $I(r) = \mu r^2$ of the molecule, where μ is the reduced mass and r is the internuclear separation. In Eq. (1), \mathbf{R} is the rotational angular momentum operator of the nuclei, which is related to the total angular momentum operator \mathbf{J} , the total electronic orbital angular momentum operator \mathbf{L} , and the total electronic spin angular momentum operator \mathbf{S} by

$$\mathbf{R} = \mathbf{J} - \mathbf{L} - \mathbf{S}. \quad (3)$$

As the molecule rotates, it swells in size and the effect of the rotational stretching may be represented by replacing \mathbf{H}_{rot} by an effective rotational Hamiltonian of the form (1)

$$\mathbf{H}_{\text{rot}}^{\text{eff}} = B_v\mathbf{R}^2 - D_v\mathbf{R}^4 + H_v\mathbf{R}^6 + L_v\mathbf{R}^8 + M_v\mathbf{R}^{10} + \dots, \quad (4)$$

where the rotational constants B_v , D_v , H_v , L_v , M_v , etc., associated with the vibrational level v are to be determined from a least-squares fit of the observed line positions to

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calculated line positions constructed from appropriate energy levels found by diagonalizing the secular determinants of the upper and lower vibrational levels (2).

For this purpose it is necessary to develop explicit expressions for the matrix elements of $\mathbf{H}_{\text{rot}}^{\text{eff}}$. If the basis set is chosen to be the Hund's case (b) wavefunctions, then this presents no difficulty, since \mathbf{R}^2 is diagonal in this representation, provided the interaction with other electronic states caused by rotation is neglected. With this proviso, \mathbf{R}^2 may be replaced by $\mathbf{N}^2 - L_z^2$, where $\mathbf{N} = \mathbf{J} - \mathbf{S}$ and L_z is the component of \mathbf{L} along the internuclear axis chosen to coincide with the z axis. Thus,

$$\langle N\Lambda\Sigma | \mathbf{H}_{\text{rot}}^{\text{eff}} | N\Lambda\Sigma \rangle = B_v [N(N+1) - \Lambda^2] - D_v [N(N+1) - \Lambda^2]^2 + H_v [N(N+1) - \Lambda^2]^3 + L_v [N(N+1) - \Lambda^2]^4 + M_v [N(N+1) - \Lambda^2]^5 + \dots \quad (5)$$

However, for many purposes the Hund's case (a) wavefunctions are a more convenient basis set (1, 2) and we are confronted with the more difficult task of finding the matrix elements of \mathbf{R}^{2k} for $k = 1, 2, 3, \dots$, where $\mathbf{R}^2 = \mathbf{N}^2 - L_z^2 = (\mathbf{J} - \mathbf{S})^2 - L_z^2$ is no longer diagonal in this representation.

Matrix Multiplication Method

This computation can be carried out in a straightforward manner by the use of matrix multiplication, where, for example, the matrix elements of \mathbf{R}^4 are formed from products of the matrix elements of \mathbf{R}^2 . Let us write

$$\mathbf{R}^2 = \mathbf{x} - \mathbf{y}, \quad (6)$$

where

$$\mathbf{x} = \mathbf{J}^2 - 2J_z S_z + \mathbf{S}^2 - \Lambda^2 \quad (7)$$

and

$$\mathbf{y} = J_+ S_- + J_- S_+ = 2(J_x S_x + J_y S_y). \quad (8)$$

Then with the help of the matrix elements²

and

$$\langle S\Sigma \pm 1 | S_{\pm} | S\Sigma \rangle = - [S(S+1) - \Sigma(\Sigma \pm 1)]^{\frac{1}{2}},$$

or equivalently

$$\langle \Omega\Sigma | J_{\pm} | \Omega \pm 1, \Sigma \pm 1 \rangle = [J(J+1) - \Omega(\Omega \pm 1)]^{\frac{1}{2}}$$

and

$$\langle \Omega\Sigma | S_{\mp} | \Omega \pm 1, \Sigma \pm 1 \rangle = - [S(S+1) - \Sigma(\Sigma \pm 1)]^{\frac{1}{2}}.$$

$$\langle J\Omega\Sigma | \mathbf{x} | J\Omega\Sigma \rangle = f(\Omega\Sigma) \quad (9)$$

and

$$\langle J\Omega\Sigma | \mathbf{y} | J\Omega \pm 1, \Sigma \pm 1 \rangle = - g(\Omega\Sigma), \quad (10)$$

where

$$f(\Omega\Sigma) = J(J+1) - \Omega^2 + S(S+1) - \Sigma^2 \quad (11)$$

and

$$g(\Omega\Sigma) = [J(J+1) - \Omega(\Omega \pm 1)]^{\frac{1}{2}} [S(S+1) - \Sigma(\Sigma \pm 1)]^{\frac{1}{2}}, \quad (12)$$

the matrix elements of \mathbf{R}^{2k} for $k > 1$ may be found from the above $k = 1$ elements by matrix multiplication. For example, $\mathbf{R}^4 = (\mathbf{x} - \mathbf{y})^2 = \mathbf{x}^2 - \mathbf{xy} - \mathbf{yx} + \mathbf{y}^2$. The diagonal

² We follow the phase convention of Ref. (2), Eqs. (12)-(13), namely

$$\langle J\Omega \pm 1 | J_{\mp} | J\Omega \rangle = [J(J+1) - \Omega(\Omega \pm 1)]^{\frac{1}{2}}$$

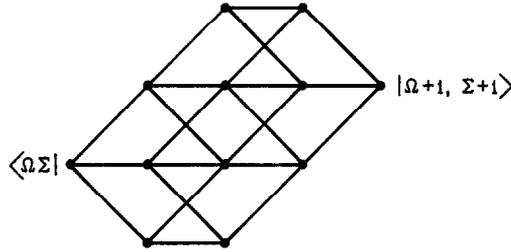


FIG. 1. Diagram of the matrix element $\langle \Omega \Sigma | \mathbf{R}^8 | \Omega + 1, \Sigma + 1 \rangle$.

matrix element of \mathbf{R}^4 is given by

$$\begin{aligned} \langle \Omega \Sigma | \mathbf{R}^4 | \Omega \Sigma \rangle &= \langle \Omega \Sigma | x^2 + y^2 | \Omega \Sigma \rangle, \\ &= \sum_{\Omega', \Sigma'} [\langle \Omega \Sigma | x | \Omega' \Sigma' \rangle \langle \Omega' \Sigma' | x | \Omega \Sigma \rangle + \langle \Omega \Sigma | y | \Omega' \Sigma' \rangle \langle \Omega' \Sigma' | y | \Omega \Sigma \rangle], \\ &= f(\Omega \Sigma) f(\Omega \Sigma) + g(\Omega \Sigma) g(\Omega \Sigma) + g(\Omega \mp 1, \Sigma \mp 1) g(\Omega \mp 1, \Sigma \mp 1), \end{aligned} \quad (13)$$

the first off-diagonal matrix element by

$$\begin{aligned} \langle \Omega \Sigma | \mathbf{R}^4 | \Omega \pm 1, \Sigma \pm 1 \rangle &= \langle \Omega \Sigma | -xy - yx | \Omega \pm 1, \Sigma \pm 1 \rangle, \\ &= - \sum_{\Omega', \Sigma'} [\langle \Omega \Sigma | x | \Omega' \Sigma' \rangle \langle \Omega' \Sigma' | y | \Omega \pm 1, \Sigma \pm 1 \rangle \\ &\quad + \langle \Omega \Sigma | y | \Omega' \Sigma' \rangle \langle \Omega' \Sigma' | x | \Omega \pm 1, \Sigma \pm 1 \rangle], \\ &= f(\Omega \Sigma) g(\Omega \Sigma) + g(\Omega \Sigma) f(\Omega \pm 1, \Sigma \pm 1), \end{aligned} \quad (14)$$

and the second (last) off-diagonal matrix element by

$$\begin{aligned} \langle \Omega \Sigma | \mathbf{R}^4 | \Omega \pm 2, \Sigma \pm 2 \rangle &= \langle \Omega \Sigma | y^2 | \Omega \pm 2, \Sigma \pm 2 \rangle, \\ &= \sum_{\Omega', \Sigma'} \langle \Omega \Sigma | y | \Omega' \Sigma' \rangle \langle \Omega' \Sigma' | y | \Omega \pm 2, \Sigma \pm 2 \rangle, \\ &= g(\Omega \Sigma) g(\Omega \pm 1, \Sigma \pm 1). \end{aligned} \quad (15)$$

This agrees with the results found previously by Kovács (3). The method may be extended to H_v and high-order rotational centrifugal-distortion matrix elements but the computation becomes tedious very rapidly. Explicit expressions for H_v have been presented elsewhere, (2, 4) and we list in Table I the results for L_v . We have also derived in the same manner explicit expressions for M_v , but they are too cumbersome and space-consuming to tabulate.

It is interesting to consider a diagrammatic description for the matrix elements of \mathbf{R}^{2k} . The general matrix element $\langle \Omega \Sigma | \mathbf{R}^{2k} | \Omega \pm q, \Sigma \pm q \rangle$ may be written as a sum of all the intermediate matrix elements of \mathbf{R}^2 that carries one from the initial state $\langle \Omega \Sigma |$ to the final state $| \Omega \pm q, \Sigma \pm q \rangle$ in k steps. For example, the matrix element $\langle \Omega \Sigma | \mathbf{R}^8 | \Omega + 1, \Sigma + 1 \rangle$ is diagrammed in this manner in Fig. 1. Here each step can connect $\langle \Omega' \Sigma' |$ to $| \Omega' \Sigma' \rangle$ (matrix element of x) or can connect $\langle \Omega' \Sigma' |$ to $| \Omega' \pm 1, \Sigma' \pm 1 \rangle$ (matrix element of y). The former type of step introduces a multiplicative factor $f(\Omega' \Sigma')$; the latter type of step introduces a multiplicative factor $g(\Omega' \Sigma')$ for $\langle \Omega' \Sigma' |$ to $| \Omega' + 1, \Sigma' + 1 \rangle$ or $g(\Omega' \mp 1,$

TABLE I
Case (a) Matrix Elements of \underline{R}^3

$$\begin{aligned} \langle \Omega \Sigma | \underline{R}^3 | \Omega \Sigma \rangle = & \\ & f^3(\Omega \Sigma) + g^2(\Omega \Sigma) [3f^2(\Omega \Sigma) + 2f(\Omega \Sigma) f(\Omega \pm 1, \Sigma \pm 1) + f^2(\Omega \pm 1, \Sigma \pm 1) + g^2(\Omega \pm 1, \Sigma \pm 1) \\ & + g^2(\Omega \Sigma) + g^2(\Omega \mp 1, \Sigma \mp 1)] \\ & + g^2(\Omega \mp 1, \Sigma \mp 1) [3f^2(\Omega \Sigma) + 2f(\Omega \Sigma) f(\Omega \mp 1, \Sigma \mp 1) + f^2(\Omega \mp 1, \Sigma \mp 1) + g^2(\Omega \Sigma) \\ & + g^2(\Omega \mp 1, \Sigma \mp 1) + g^2(\Omega \mp 2, \Sigma \mp 2)] \quad . \end{aligned}$$

$$\begin{aligned} \langle \Omega \Sigma | \underline{R}^3 | \Omega \pm 1, \Sigma \pm 1 \rangle = & \\ & g(\Omega \Sigma) \{ [f^3(\Omega \Sigma) + f^3(\Omega \pm 1, \Sigma \pm 1) + f(\Omega \Sigma) f^2(\Omega \pm 1, \Sigma \pm 1) + f^2(\Omega \Sigma) f(\Omega \pm 1, \Sigma \pm 1)] \\ & + g^2(\Omega \Sigma) [2f(\Omega \Sigma) + 2f(\Omega \pm 1, \Sigma \pm 1)] \\ & + g^2(\Omega \pm 1, \Sigma \pm 1) [f(\Omega \Sigma) + 2f(\Omega \pm 1, \Sigma \pm 1) + f(\Omega \pm 2, \Sigma \pm 2)] \\ & + g^2(\Omega \mp 1, \Sigma \mp 1) [2f(\Omega \Sigma) + f(\Omega \mp 1, \Sigma \mp 1) + f(\Omega \pm 1, \Sigma \pm 1)] \} \quad . \end{aligned}$$

$$\begin{aligned} \langle \Omega \Sigma | \underline{R}^3 | \Omega \pm 2, \Sigma \pm 2 \rangle = & \\ & g(\Omega \Sigma) g(\Omega \pm 1, \Sigma \pm 1) [f^2(\Omega \Sigma) + f^2(\Omega \pm 1, \Sigma \pm 1) + f^2(\Omega \pm 2, \Sigma \pm 2) + f(\Omega \Sigma) f(\Omega \pm 1, \Sigma \pm 1) \\ & + f(\Omega \pm 1, \Sigma \pm 1) f(\Omega \pm 2, \Sigma \pm 2) + f(\Omega \Sigma) f(\Omega \pm 2, \Sigma \pm 2) + g^2(\Omega \mp 1, \Sigma \mp 1) + g^2(\Omega \Sigma) \\ & + g^2(\Omega \pm 1, \Sigma \pm 1) + g^2(\Omega \pm 2, \Sigma \pm 2)] \quad . \end{aligned}$$

$$\begin{aligned} \langle \Omega \Sigma | \underline{R}^3 | \Omega \pm 3, \Sigma \pm 3 \rangle = & \\ & g(\Omega \Sigma) g(\Omega \pm 1, \Sigma \pm 1) g(\Omega \pm 2, \Sigma \pm 2) [f(\Omega \Sigma) + f(\Omega \pm 1, \Sigma \pm 1) + f(\Omega \pm 2, \Sigma \pm 2) \\ & + f(\Omega \pm 3, \Sigma \pm 3)] \quad . \end{aligned}$$

$$\begin{aligned} \langle \Omega \Sigma | \underline{R}^3 | \Omega \pm 4, \Sigma \pm 4 \rangle = & \\ & g(\Omega \Sigma) g(\Omega \pm 1, \Sigma \pm 1) g(\Omega \pm 2, \Sigma \pm 2) g(\Omega \pm 3, \Sigma \pm 3) \quad . \end{aligned}$$

$\Sigma' \mp 1$) for $\langle \Omega' \Sigma' |$ to $|\Omega' - 1, \Sigma' - 1\rangle$. The matrix element $\langle \Omega \Sigma | \underline{R}^{2k} | \Omega \pm q, \Sigma \pm q \rangle$ is then given by the sum of all k -fold products of f and g that represent the distinct k -step paths from $\langle \Omega \Sigma |$ to $|\Omega \pm q, \Sigma \pm q\rangle$. Although it is a simple matter to determine the number of distinct k -step paths for the general matrix element $\langle \Omega \Sigma | \underline{R}^{2k} | \Omega \pm q, \Sigma \pm q \rangle$, we were unable to find a general means of explicitly enumerating these paths in terms of products of f and g functions.

General Recursion Relations

Instead of using these increasingly complex explicit expressions for the high-order centrifugal-distortion matrix elements in the reduction of measured line positions to molecular constants, we have found it preferable to derive and employ a recursion relation that expresses the matrix elements of \mathbf{R}^{2k} in terms of the matrix elements of $\mathbf{R}^{2(k-1)}$ for $k = 2, 3, 4, \dots$. By use of the matrix multiplication technique, we may write

$$\begin{aligned} \langle \Omega \Sigma | \mathbf{R}^{2k} | \Omega \pm q, \Sigma \pm q \rangle &= \sum_{\Omega' \Sigma'} \langle \Omega \Sigma | \mathbf{R}^2 | \Omega' \Sigma' \rangle \langle \Omega' \Sigma' | \mathbf{R}^{2(k-1)} | \Omega \pm q, \Sigma \pm q \rangle, \\ &= f(\Omega \Sigma) \langle \Omega \Sigma | \mathbf{R}^{2(k-1)} | \Omega \pm q, \Sigma \pm q \rangle \\ &\quad + g(\Omega \Sigma) \langle \Omega \pm 1, \Sigma \pm 1 | \mathbf{R}^{2(k-1)} | \Omega \pm q, \Sigma \pm q \rangle \\ &\quad + g(\Omega \mp 1, \Sigma \mp 1) \langle \Omega \mp 1, \Sigma \mp 1 | \mathbf{R}^{2(k-1)} | \Omega \pm q, \Sigma \pm q \rangle, \end{aligned} \quad (16)$$

where $q = 0, 1, 2, \dots, k$ and $q \leq 2S$. Thus, the application of the rotational centrifugal-distortion correction of order $2k$ requires only the elements $\langle \Omega \Sigma | \mathbf{R}^2 | \Omega' \Sigma' \rangle$ and $\langle \Omega \Sigma | \mathbf{R}^{2(k-1)} | \Omega' \Sigma' \rangle$, where the former are evaluated using Eqs. (9-12) and the latter are generated from the former by repeated applications of the recursion relation, Eq. (16). Or, in other words, one forms the $2S + 1$ by $2S + 1$ matrix for \mathbf{R}^2 using Eqs. (9-12) and then uses these matrix elements, along with the recursion relation Eq. (16), to generate the $2S + 1$ by $2S + 1$ matrix of \mathbf{R}^4 , and so on. Since one does not apply rotational centrifugal-distortion corrections of order $2k$ without first, or simultaneously, applying all lower orders, this recursion relation does not require the calculation of any quantities that are not used in the analysis. This technique for calculating the matrix elements of high-order rotational centrifugal-distortion corrections has the advantages that: (a) it is easily extended to the next higher order without new algebra or programming, (b) it is readily programmed and checked, in contrast to the use of explicit expressions for $\langle \Omega \Sigma | \mathbf{R}^{2k} | \Omega' \Sigma' \rangle$, and (c) it is approximately as fast as the use of explicit expressions.

DISCUSSION

At first glance, a study of high-order rotational centrifugal-distortion corrections might appear to be an elaboration of minutia. Indeed, this impression is reinforced by the fact that most spectroscopic studies fail to consider rotational centrifugal-distortion corrections beyond the D_v term. However, this may be explained, in part, by the past difficulty of correctly including centrifugal distortion in the calculation of the rotational energy levels. The severity of this limitation may be appreciated by realizing that in the past the D_v centrifugal-distortion term has often been tacked on to the energy level expressions in an incorrect, ad hoc manner, and, more often than not, D_v has not been determined from the line positions, but rather its value has been fixed in the analysis to the estimate given by the Dunham relations (5). It is not surprising, therefore, to find that the application of high-order rotational centrifugal distortion coefficients has been rather neglected in practice.

In reducing diatomic spectra to molecular constants, it is necessary to include a sufficient number of rotational centrifugal-distortion constants D_v, H_v, L_v, M_v , etc.,

to represent the measured line positions within their uncertainties. The number of high-order rotational centrifugal-distortion corrections required will depend on the accuracy of the individual line position measurements, on the rotational extent of the data, and on the reduced mass of the molecule. For example, the inclusion of rotational centrifugal-distortion constants beyond the D_v term in Eq. (4) is seldom statistically significant in optical studies of nonhydride molecules with low to moderate J values. On the other hand, microwave measurements involving only energy levels with low J values may warrant the use of the higher-order corrections because of the much higher accuracy inherent in this technique. Moreover, the need to apply extensive high-order rotational centrifugal-distortion corrections may be essential even for optical studies if the molecular spectra are obtained from high-temperature sources, such as in arc, flame, or solar spectra or for hydrides.

Thus, it is of practical importance, both in optical and in microwave studies, to find a general means of including rotational centrifugal-distortion corrections to high order in the calculation of the energy levels of a diatomic molecule. For example, we find that a fit of Dieke and Crosswhite's (δ) line positions for the OH $A^2\Sigma^+ \rightarrow X^2\Pi_i$ bands within their experimental uncertainty ($\sim 0.03 \text{ cm}^{-1}$) requires rotational centrifugal-distortion constants through L_v (7). Furthermore, this need for a general and practical procedure becomes all the more apparent when it is realized that (a) the higher-order rotational centrifugal-distortion corrections are a slowly convergent series³ whose convergence rate decreases with increasing J , and (b) the decision to truncate Eq. (4) at a certain order requires one to perform a calculation that includes the next higher-order rotational centrifugal distortion term in order to show that the resultant set of molecular constants are not statistically meaningful. The above recursion relation for the Hund's case (a) matrix elements of \mathbf{R}^{2k} should facilitate the more accurate determination of molecular constants from measured line positions when high-order rotational centrifugal-distortion corrections must be considered.

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³ In the $A^2\Sigma^+$ and $X^2\Pi_i$ states of OH, for example, the Dunham relations predict that at $J = 30.5$, which is a commonly observed level, the contribution from each successive centrifugal distortion coefficient decreases only by a factor of approximately ten from the preceding coefficient. Of course, at higher rotational levels the convergence is even slower.

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