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Anharmonic Potential Functions of Simple Molecules. III. Computation of Vibration-Rotation Energies of XYZ and X_2Y_2 Type Linear Molecules through Direct Numerical Diagonalization: Application to the N_2O Molecule

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A formalism has been developed for the calulation of vibration-rotation energy levels of linear XYZ and X_2Y_2 type molecules through direct numerical diagonalization of vibration hamiltonian matrix. The procedure of evaluating vibration as well as vibration-rotation energies can be described mostly in matrix algebra and thus easily converted to computer languages. The N_2O molecule was chosen as an example of numerical treatment. Several approaches have been checked in evaluating B_v and D_v and they are discussed from the view point of accuracy and efficiency in computations. It is found that the variational approach of computing $B_v{}^r$, contribution of rotational hamiltonian to B_v, is very efficient and accurate. Some peculiar features of the molecular potential of the X_2Y_2 type molecule are discussed in connection with their adaptation on the direct numerical diagonalization method.

There has been an increasing number of studies on the direct numerical diagonalization method of vibrational hamiltonian matrix in terms of a large number of harmonic oscillator basis wave functions.[1-7] The major advantages of reducing the vibrational hamiltonian numerically to fit the observed spectroscopic quantities are threefold. (1) Accidental degeneracies, which require special and somewhat cumbersome treatments in conventional perturbation method, are automatically taken care of. (2) Higher order terms in vibrational potential as well as in expansions of moment of inertial tensor are incorporated without changing the general scheme of computations. (3) Orthonormal vibrational wave functions are readily available through diagonalization as linear combinations of basis harmonic oscillator wave functions. These wave functions may be used to compute any average molecular properties in a given vibrational state.

It is also possible, at least in principle, to apply this method to individual vibration-rotation energy levels. The Coriolis coupling terms in the hamiltonian, however, interact the ro-vibrational states with $\Delta l = \pm 1$ in linear polyatomic molecules, and the factorization is no longer possible for the vibration-rotation states with $J \neq 0$. Therefore, an entire vibration-rotation hamiltonian matrix (unfactorized) must be solved at a time, which forces to use a huge number of basis wave functions (usually products of harmonic oscillator wave function and symmetric rotor type wave function). Since the vibration-rotation coupling constants are as important as the vibrational wavenumbers themselves in the determination of molecular force field, several less rigorous methods have been proposed to calculate vibration-rotation levels. Recent studies of Whiffen *et al.*[6,7] on the OCS molecule have made a significant contribution to this field.

This is our third report on the above subject and the method previously reported (hereafter referred to as I and II) has been extended to include the XYZ and X_2Y_2 type linear molecules. It is shown that the rotational and Coriolis parts of the vibration-rotation hamiltonian are reduced to almost identical forms for these two types of molecule. Several methods have been tested for the evaluation of vibration rotation levels and in each case these levels are converted to the corresponding rotational constant (B_v) and the centrifugal distortion constant (D_v). The results are compared from the view point of accuracy and efficiency in computations.

Extensive numerical calculations have been made on the N_2O molecule and the results are given in the present paper. This molecule is of particular interest, for we plan to apply the resultant vibrational wave functions to the intensity problem for N_2O. In some cases we also used the OCS molecule so that the direct comparison is possible for the results of Whiffen *et al.*[6,7]

The X_2Y_2 type molecule requires some extra handling since it has two degenerate modes and individual l_4 and l_5 are no longer "good" quantum numbers. The proper treatment in direct diagonalization procedure has also been discussed.

Hamiltonian

The general form of the vibration-rotation hamiltonian of a polyatomic molecule given by Goldsmith, Amat, and Nielsen[8] is reduced to a much simpler form for a linear molecule.[9,10] It is conveniently expressed as the sum of the vibrational, rotational, and Coriolis hamiltonians:

$$\mathbf{H} = \mathbf{H}_{\mathrm{vib}} + \mathbf{H}_{\mathrm{rot}} + \mathbf{H}_{\mathrm{Cor}}, \tag{1}$$

$$\mathbf{H}_{\mathrm{vib}} = V_{\mathrm{h}}(q_s{}^2, j_s{}^2) + V_{\mathrm{anh}}(q_s) + \mathbf{H}'_{\mathrm{vib}}, \tag{2}$$

$$\mathbf{H}'_{\mathrm{vib}} = B(j_x{}^2 + j_y{}^2) = (B/2)(j_+j_- + j_-j_+), \tag{3}$$

$$\mathbf{H}_{\mathrm{rot}} = B(J_x{}^2 + J_y{}^2) = (B/2)(J_+J_- + J_-J_+), \tag{4}$$

$$\mathbf{H}_{\mathrm{Cor}} = -2B(j_xJ_x + j_yJ_y) = -B(j_+J_- + j_-J_+). \tag{5}$$

The definitions for symbols appearing in Eqs. 1—5 are summarized in Table 1. All the operators are dimensionless, hamiltonains and other constants are given in cm^{-1} as in I and II. The reduced moment of inertia, I', can be expressed in the following form.[9,10]

$$I' = I_e[1 + \gamma_1 q_1 + \gamma_s q_s]^2. \tag{6}$$

For the molecules of current interest, the expansion coefficients, γ's, are given as

TABLE 1. LISTINGS OF SYMBOLS TO DESCRIBE VIBRATION-ROTATION HAMILTONIANS

q_s	Dimensionless normal coordinate
j_s	Dimensionless vibrational momentum conjugated to q_s $[j_s=p_s/\hbar=\hbar^{-1}(\partial T/\partial \dot{q}_s)]$
V_h	Harmonic part of vibrational potential
V_{anh}	Anharmonic part of vibrational potential
j_x, j_y	x,y-Components of vibrational angular momenta $(j_x=p_x/\hbar, j_y=p_y/\hbar)$
j_+, j_-	Ladder operators for vibrational angular momenta $(j_\pm=j_x\pm ij_y)$
J_x, J_y	Dimensionless total angular momenta $(J_x=P_x/\hbar, J_y=P_y/\hbar)$
J_+, J_-	Ladder operators for total angular momenta $(J_\pm=J_x\pm iJ_y)$
I_e	Equilibrium moment of inertia
B_e	Equilibrium rotational constant $\hbar=/(4\pi c I_e)$
I'	Instantaneous moment of inertia with correction of Coriolis effect
B	Instantaneous rotational constant defined as $\hbar/(4\pi c I')$

a) The molecular axis coincides with the z-axis.

$$\mathrm{XY_2}:\ \gamma_1 = (2B_e/\omega_1)^{1/2} \qquad s = 3 \quad \gamma_3 = 0$$

$$\mathrm{XYZ}:\ \gamma_1 = (2B_e/\omega_1)^{1/2}|\zeta_{23}{}^x| \quad s = 3 \quad \gamma_3 = (2B_e/\omega_3)^{1/2}|\zeta_{21}{}^x|$$

$$\mathrm{X_2Y_2}:\ \gamma_1 = (2B_e/\omega_1)^{1/2}|\zeta_{42}{}^x| \quad s = 2 \quad \gamma_2 = (2B_e/\omega_2)^{1/2}|\zeta_{41}{}^x|$$

This is the results from the fact that only $a_1{}^{xx}=a_1{}^{yy}$ and $a_s{}^{xx}=a_s{}^{yy}$ are nonvanishing among the derivatives of moment of inertia with respect to normal coordinate: *i.e.* $a_{s\sigma}^{\alpha\beta}=(\partial I^{\alpha\beta}/\partial Q_{s\sigma})$. See, for example, Eq. 17 of Ref. 10. The phases of normal coordinates q_1 and q_s are taken so that the coefficients $a_1{}^{xx}$ and $a_s{}^{xx}$, and thus γ_1 and γ_s, are positive. Taking the reciprocal of I' and expanding it in terms of the related normal coordinates, B is given as

$$\begin{aligned} B &= B_e\sum_{k=0}(-1)^k(k+1)(\gamma_1 q_1+\gamma_s q_s)^k \\ &= B_e[1+\sum_{k=1}(-1)^k(k+1)(\gamma_1 q_1+\gamma_s q_s)^k]. \end{aligned} \tag{7}$$

Equation 7 reflects the vibrational effects on rotational constants through the changes in moment of inertia. Coupling between the vibrational and rotational angular momenta also affects vibration-rotation energies. Vibrational angular momentum operators $j_\pm$ are given as the sum of

$$j_\pm = \sum_{i=1}^{m} j_\pm^{(s_i, d_i)}, \tag{8}$$

where m is a number of nonvanishing Coriolis coupling constants, s_i and d_i denote nondegenerate and degenerate dimensionless normal coordinates associated with the Coriolis coupling constant. Each term in summation is given as

$$j_\pm^{(s,d)} = \pm i\cdot\zeta_{ds}{}^x[(\omega_d/\omega_s)q_s p_\pm - (\omega_s/\omega_d)j_s q_\pm], \tag{9}$$

where $q_\pm=q_{dx}\pm iq_{dy}$ and $p_\pm=j_{dx}\pm ij_{dy}$ and the suffix i for the coordinate is dropped in Eq. 9. For the present case, the relevant indeces are:

$\mathrm{XY_2}$: $m = 1$ $(s_1=3,\ d_1=2)$,
XYZ: $m = 2$ $(s_1=1,\ d_1=2)$ and $(s_2=3,\ d_2=2)$,
$\mathrm{X_2Y_2}$: $m = 3$ $(s_1=1,\ d_1=4)$, $(s_2=2,\ d_2=4)$, and $(s_3=3,\ d_3=5)$

Substitutions of $j_\pm$ into Eqs. 3 and 5 yield the final forms of hamiltonians in terms of dimensionless normal coordinates and their conjugate momenta.

Energy Levels

Vibrational Energy and Its Matrix Representation. Pure vibrational energies are determined from harmonic and anharmonic potential as well as from squared angular vibrational momenta designated as $\mathbf{H}'_{vib}$ in Eq. 3. The number of nonvanishing force constants are tabulated in Table 2 for the three types of linear molecules. As in II, the force constants in curvilinear internal coordinates are transformed into normal coordinate space. It is also convenient to set up the vibrational hamiltonian matrix as the sum of its component matrices for individual force constants.

TABLE 2. NON-VANISHING FORCE CONSTANTS IN GENERAL QUARTIC FORCE FIELD

	Quadratic[a]	Cubic	Quartic	Total
XY_2	3	3	6	12
XYZ	4	6	9	19
X_2Y_2	6	11	23	40

a) This column corresponds to the sum of harmonic frequencies and independent Coriolis coupling constant(s) in normal coordinate space. Because of the Coriolis sum rule, only one Coriolis coupling constant is independent in XYZ and X_2Y_2 type molecules. (None in XY_2 type)

$$\boldsymbol{H}_v = \sum_{i=1}^{f+1} k^{(i)}\boldsymbol{Z}^{(i)}, \tag{10}$$

where f is a total number of force constants, $k^{(i)}$ could be either ω_s, $k_{ss's''}$ or $k_{ss's''s'''}$. The matrix element $Z_{nn'}^{(i)}$ is defined as

$$Z_{nn'}^{(i)} = \langle n|U^{(i)}(q)|n'\rangle \tag{11}$$

If $k^{(a)}=k_{111}$, for example, $U^{(a)}=q_1{}^3$, and if $k^{(b)}=k_{1122}$, then $U^{(b)}=q_1{}^2q_2{}^2$, $|n>$ represents harmonic oscillator wave function. To be more precise it is either $|n>=|n_1, n_2, l_2, n_3>$ or $|n_1, n_2, n_3, n_4, l_4, n_5, l_5>$. It is convenient to include the term arising from $\mathbf{H}'_{vib}$ in $\boldsymbol{Z}^{(i)}$ and treat as if it were the $(f+1)$th force constant, *i.e.* $k^{(f+1)}=B_e$ and $Z_{nn'}^{(f+1)}=(1/2)<n|j_+j_-+j_-j_+|n'>+$higher terms. By selecting a proper set of basis functions, $\boldsymbol{H}_v$ is divided into a desired number of symmetry manifolds (σ, π, δ, $\cdots$), each of which may be treated seperately. Then the eigenvalue problem is solved which yields a diagonal eigen value matrix $\boldsymbol{W}_v$ and the eigen vector matrix $\boldsymbol{A}_v$, the n-th column corresponds to the eigenvector of the n-th eigenvalue.

$$\boldsymbol{H}_v\boldsymbol{A}_v = \boldsymbol{A}_v\boldsymbol{W}_v \tag{12}$$

As described in I and II, only a limited number of lower eigenvalues, which is of immediate interest to us, is usually obtained by a modified Givens-Housholder method for symmetric matrices.[11] Therefore, $\boldsymbol{A}_v$ is not necessarily a square matrix but may be considered as a rectangular matrix. A set of orthonormal vibrational wave functions is readily obtained as a linear combination of the harmonic oscillator wave functions:

$$|v\rangle = \sum_{n} a_{vn}|n\rangle, \tag{13}$$

where a_{vn} is a corresponding element of $\boldsymbol{A}_v$.

Vibration-rotation Energy. The contributions from $\mathbf{H}_{\rm rot}$ as well as from $\mathbf{H}_{\rm Cor}$ must be considered to obtain the rotational energies of a given vibrational state. The basis function is usually in the form of $|n,J\rangle=|n\rangle\cdot|J\rangle$, the latter being a symmetric rotor type wave function. Since the matrix elements are diagonal with respect to J, the vibration-rotation hamiltonian matrix may be set for any required value of J. Since the operators $J_x^2+J_y^2$ can be replaced by $[J(J+1)-l^2]$ for practical purposes, the effect of $\mathbf{H}_{\rm rot}$ is most conveniently treated as the $(f+2)$th component of $\boldsymbol{Z}$:

$$\boldsymbol{H}_r(J) = k^{(f+2)}\boldsymbol{Z}^{(f+2)}, \tag{14}$$

$$k^{(f+2)} = B_e[J(J+1)-l^2], \tag{15}$$

$$Z_{nn'}^{(f+2)} = \sum_{k=0}(-1)^k(k+1)[\sum_{m=0}^{k} {}_kC_m\gamma_1{}^{k-m}\gamma_s{}^m \times\langle n|q_1{}^{k-m}q_s{}^m|n'\rangle| \tag{16}$$

The γ's are given in Eq. 6 and ${}_kC_m=k!/[m!(k-m)!]$. The contribution from $\mathbf{H}_{\rm rot}$ may be obtained either by diagonalizing directly $\boldsymbol{H}_{\rm vr}(J)$

$$\boldsymbol{H}_{\rm vr}(J) = \boldsymbol{H}_v + \boldsymbol{H}_r(J) = \sum_{i=1}^{f+2} k^{(i)}\boldsymbol{Z}^{(i)},$$

$$\boldsymbol{H}_{\rm vr}(J)\boldsymbol{A}_{\rm vr}(J) = \boldsymbol{A}_{\rm vr}(J)\boldsymbol{W}_{\rm vr}(J) \tag{17}$$

or by using a variation method: $\boldsymbol{Z}^{(f+2)}$ is transformed by $\boldsymbol{A}_v$ in Eq. 12 and the diagonal elements are taken to represent the rotational contribution.

$$\boldsymbol{W}_{\rm vr}(J) \cong \boldsymbol{W}_v + k^{(f+2)}[\widetilde{\boldsymbol{A}}_v\boldsymbol{Z}^{(f+2)}\boldsymbol{A}_v]_{\rm diagonal} \tag{18}$$

In either case we define $\boldsymbol{W}_v{}^r(J)$ as the contribution from $\mathbf{H}_{\rm rot}$ to the energy specified by J and v.

$$\boldsymbol{W}_v{}^r(J) = \boldsymbol{W}_{\rm vr}(J) - \boldsymbol{W}_v = \boldsymbol{W}_{\rm vr}(J) - \boldsymbol{W}_{\rm vr}(0) \tag{19}$$

The Coriolis hamiltonian, $\mathbf{H}_{\rm Cor}$, consists essentially of the products of the total and vibrational angular momentum operators and thus has no diagonal matrix elements with respect to vibrational quantum numbers. The total hamiltonian matrix with an arbitary nonzero J is schematically shown in Fig. 1, where each small square represents the submatrix of the size up to 200 by 200 and a superscript l specifies symmetry manifold. Let this total hamiltonian matrix be $\boldsymbol{H}(J)=\boldsymbol{H}_{\rm vrc}(J)$, then the ultimate purpose of our calculation is to obtain $\boldsymbol{W}(J)$ in Eq. 20,

$$\boldsymbol{H}(J)\boldsymbol{A}(J) = \boldsymbol{A}(J)\boldsymbol{W}(J) \tag{20}$$

We may also define $\boldsymbol{W}_v{}^c(J)$ as the contribution from $\mathbf{H}_{\rm Cor}$,

$$\boldsymbol{W}_v{}^c(J) = \boldsymbol{W}(J) - \boldsymbol{W}_{\rm vr}(J) = \boldsymbol{W}_{\rm vrc}(J) - \boldsymbol{W}_{\rm vr}(J) \tag{21}$$

However, the total hamiltonian matrix for the states with $|l|\leq3$ is well over one thousand. This total hamiltonian matrix may be divided into two blocks (so called c- and d-states) by taking symmetric and antisymmetric combinations of the basis functions with respect to $\pm l$, which seperates the l-type doublets (see Fig. 2). Still the size of the matrices is beyond the present practical limit and introduction of a certain approximation is inevitable. The second-order perturbation theory was used in II to calculate the Coriolis effects, however, this method requires summation over the third vibrational states and takes considerable computing time. A double diagonalization method is employed in the present case, which is almost equivalent to the perturbation method, but is much simpler to handle in computer since each step is described by matrix algebra. First, we start with $\boldsymbol{A}_{\rm vr}{}^l(J)$ in Eq. 17, which is rectangular in most cases, a superscript being added again to specify the symmetry manifold. The original $\boldsymbol{H}_C{}^{ll'}$ matrices are successively transformed by using the related $\boldsymbol{A}_{\rm vr}{}^l$ and $\boldsymbol{A}_{\rm vr}{}^{l'}$, where $l'=l\pm1$. Finally an assembly of the transformed matrices is diagonalized again to yield (approximate) solutions, $\boldsymbol{W}(J)$. The total process is schematically shown in Fig. 3.

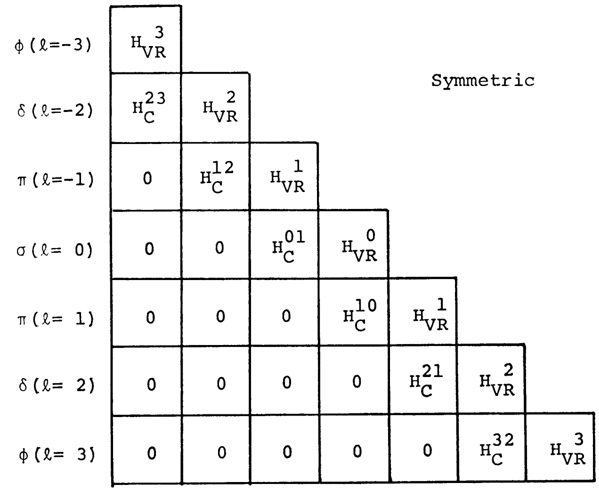

Fig. 1. A full vibration-rotation hamiltonian matrix with $|l|\leq3$. Each square represents the matrix of size up to 200 by 200. The Coriolis hamiltoniam matrix $\boldsymbol{H}_C$ is off-diagonal with respect to l. For rotationless state ($J=0$), $\boldsymbol{H}_C$ vanishes and each $\boldsymbol{H}_{\rm VR}$ matrix can be treated separately.

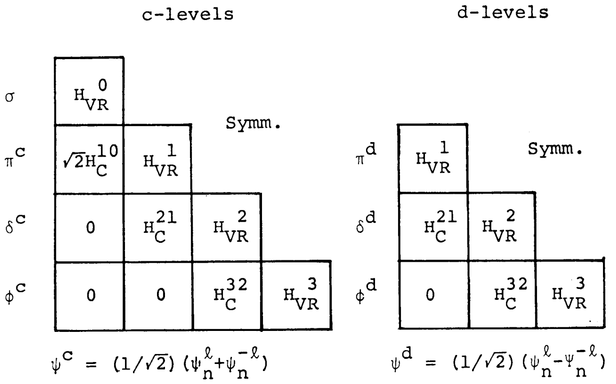

Fig. 2. The seperation of c- and d-states which causes l-type doubling. It is easily seen from the figure that π-states are most strongly affected.

The rotational levels in the n-th vibrational state are given for linear molecules as

$$E_v(J) = \nu_0(v) + B_v[J(J+1)-l^2] - D_v[J(J+1)-l^2]^2 + \cdots \tag{22}$$

where B_v and D_v are the rotational and centrifugal

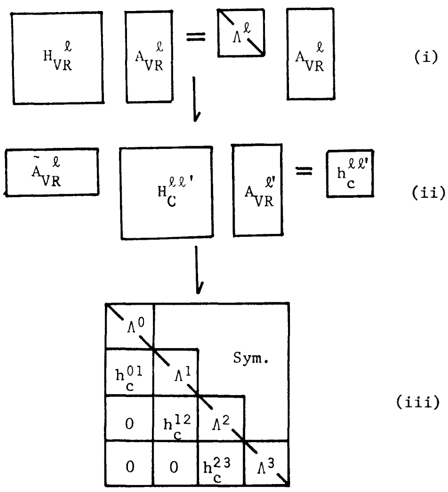

Fig. 3. Schematic representation of double diagonalization procedure. (i) The first diagonalization of $\boldsymbol{H}^{l}_{VR}$ (The matrix size is usually 200 by 200, and l=0, 1, 2,⋯) The lowest fortv eigenvalues are obtained: $\boldsymbol{\Lambda}^{l}$ is a diagonal matrix of 40 by 40 and $\boldsymbol{A}^{l}_{VR}$ is an eigen vector matrix of 40 by 200. (ii) Transformation of $\boldsymbol{H}^{ll'}_{C}$ matrix (iii) Reassembled matrix which is subjected to the second diagonalization to yield (approximate) solutions to $\boldsymbol{W}(J)$ in Eq. 20.

distortion constants, respectively. They are usually determined from the observed transitions experimentally. Theoretical values of B_v and D_v are obtained by solving Eq. 12 first, then Eq. 20 for two different nonzero J's, say 5 and 10. The contributions from $\mathbf{H}_{rot}$ and $\mathbf{H}_{Cor}$ to B_v and D_v may be written as

$$B_v = B_e + B_v{}^r + B_v{}^c \tag{23}$$

and

$$D_v = D_e + D_v{}^r + D_v{}^c \tag{24}$$

Each term in Eqs. 23 and 24 gives a good measure for the effect of $\mathbf{H}_{rot}$ or $\mathbf{H}_{Cor}$ and can easily be obtained from $\boldsymbol{W}_v{}^r(J)$ and $\boldsymbol{W}_v{}^c(J)$. The calculated values of $B_v{}^r$ and $B_v{}^c$ are used to compare the results of different approaches and approximations.

The variational method given in Eq. 18 for evaluation of $B_v{}^r$ and the analytical method of Foord, Smith, and Whiffen (hereafter referred to as FSW method⁶⁾) have also been tested. The latter uses the analytical expressions derived from the second-order perturbation theory, however, the vibrational quantum numbers in the expression are replaced by the "averaged" quantum numbers obtained from the perturbed wave functions. Their formula can easily be extended to cover X_2Y_2 type molecules and it is in the following form,

$$B_v{}^c = \sum_{i=1}^{m} (\zeta_{ds}{}^x)^2 \left[2f(\omega_s, \omega_d)\left(\hat{n}_s + \frac{1}{2}\right) + f(\omega_d, \omega_s)(\hat{n}_d + 1) \right], \tag{25}$$

where $f(x,y) = (3x^2+y^2)/[x(x^2-y^2)]$, $\hat{n}_s$ and $\hat{n}_d$ are averaged contributions of n_s and n_d to a particular vibrational level. Their values are readily obtained from the corresponding a_{vn}'s. Although this treatment ignores certain off-diagonal effects, it is nonetheless an attractive approximation if it works reasonably well, since this approach requires only A_v in Eq. 12 and the second diagonalization process may be skipped altogether.

Computational Procedures

Most of numerical computations have been carried out by a Hitac 8800/8700 system in Computer Centre in the University of Tokyo. As described in II the harmonic oscillator basis functions are specified either by a set of four integers corresponding to n_1, n_2, n_3, and l_2 for XYZ or by a set of seven integers corresponding to n_1 through n_5, l_4 and l_5 for X_2Y_2. A desired number of basis functions is systematically generated with the condition $\sum_s n_s \leq n_{max}$ ($l_t = n_t$, $n_t - 2$, ⋯1 or 0). For the case of N_2O, l_2 uniquely specifies the symmetry species, while the following simple rule applies for X_2Y_2.

(1) $n_3 + n_5$ (even, odd) (g, u)
(2) $l = l_4 + l_5$ (0, 1, 2, 3, ⋯) (σ, π, δ, ϕ, ⋯)

The generation of matrix elements was described in II in detail and it is not repeated here. As indicated in Eq. 8, the vibrational angular momentum operators $j_{\pm}$ have more than one term in the present case. The evaluation of $Z_{nn'}{}^{(f+1)}$ involves the product of operator $j_+{}^{(s_i, d_i)} \cdot j_-{}^{(s_j, d_j)}$ with $i \neq j$. Therefore, the treatment of $\mathbf{H}'_{vib}$ has been modified to incorporate the cases mentioned above. A modified version of the Givens-Housholder method for real symmetric matrices, which allows to compute a limited number of either lowest or highest eigenvalues has been used as in II. Usually 200 basis functions are used for each symmetry species and the lowest 40 eigenvalues and eigenvectors are obtained; This saves considerable computing time and memories as compared with the case where a full set of eigenvalues and eigenvectors is forced to acquire.

Results and Discussion

The general quartic force field previously determined for the nitrous oxide molecule¹²⁾ has been used in the present calculation. These force constants are transformed into dimensionless normal coordinate space and their values are listed in Table 3. Within the framework of the second-order perturbation scheme three quartic force constants, k_{1113}, k_{1333}, and k_{1223} do not contribute to the vibrational energy and thus their values were not listed in the original paper,¹²⁾ however, they are all included in the present calculation. The bond lengths initially used were the same as those

Table 3. Force constants of N_2O in dimensionless normal coordinates (cm^{-1})

ω_1	1300.44	k_{1111}	2.96
ω_2	596.49	k_{1113}	−8.59
ω_3	2281.57	k_{1122}	−10.15
		k_{1133}	20.10
k_{111}	−59.72	k_{1223}	2.76
k_{113}	80.76	k_{1333}	1.66
k_{122}	54.40	k_{2222}	2.13
k_{133}	−226.60	k_{2233}	−30.40
k_{223}	51.06	k_{3333}	7.14
k_{333}	−64.82		

previously given.[12] Later the more recent values of r_e(NN)=1.1282 and r_e(NO)=1.1843 Å are used, which yield B_e=0.4211312 cm^{-1}.[13]

The requirement of $a_1^{xx}>0$ and $a_3^{xx}>0$ determines the phases of q_1 and q_3 uniquely. The transformation coefficients from mass-adjusted Cartesian to dimensionless normal coordinates (Nielsen's $l_{is\sigma}$[14]) are as follows.

$l_{is\sigma}$	z_1 (N)	z_2 (N)	z_3 (O)
q_1	−0.6184	−0.1952	0.7612
q_3	−0.5471	0.8023	−0.2387
	x_1 (y_1)	x_2 (y_2)	x_3 (y_3)
q_{2x}(q_{2y})	−0.4228	0.8247	−0.3760

Table 4. Calculated vibrational levels of N_2O and their convergence test.
The major components of eigenvector coefficients a_{vn}'s are also given.

v	$\nu(200)$[a]	$\Delta\nu(150)$[b]	Major components of a_{vn}[c]
(1) σ-state (l_2=0)			
1	0.00	0	0.996(000)[d]
2	1167.51	1	0.944(020) 0.316*(100)
3	1284.08	2	0.925(100) 0.320(020)
4	2223.41	5	0.967(001)
5	2316.40	2	0.828(040) 0.533*(120)
6	2460.88	4	0.706(120) 0.520(040) 0.430*(200)
7	2559.20	10	0.807(200) 0.437(120) 0.263(300)
8	3362.60	8	0.935(021) 0.253*(101)
9	3446.60	8	0.695(060) 0.636*(140) 0.262(220)
10	3479.67	34	0.850(101) 0.313(021)
15	4489.16	38	0.829(041) 0.472*(121)
20	4899.29	155	0.590(320) 0.499*(160) 0.409*(080) 0.223*(400)
(2) π-state (l_2=1)			
1	588.67	0	0.998(010)
2	1746.84	0	0.901(030) 0.420*(110)
3	1878.23	2	0.890(110) 0.422(030)
4	2795.99	7	0.971(011)
5	2886.33	2	0.769(050) 0.592*(130)
6	3043.30	6	0.569(130) 0.566(050) 0.551*(210)
7	3158.18	14	0.738(210) 0.546(130) 0.237(050) 0.211(310)
8	3929.43	12	0.897(031) 0.355*(111)
9	4006.93	11	0.652(150) 0.634*(070) 0.324*(230)
10	4054.22	49	0.826(111) 0.359(031) 0.276(211)
15	5048.57	48	0.767(051) 0.542*(131)
20	5470.11	215	0.547(330) 0.432*(171) 0.430*(090) 0.327*(410)

a) $\nu(n)$ in cm^{-1}: obtained by solving $n\times n$ eigenvalue problem. b) $\Delta\nu(m)$ in 10^{-2} cm^{-1}: $\Delta\nu(m)=\nu(m)-\nu(200)$. c) Asterisks indicate negative coefficients. d) The basis functions are given as a set of three integers ($n_1n_2n_3$), l_2 is omitted since it is constant in a given symmetry block.

The molecular axis coincides with z-axis, the phases of q_{2x} and q_{2y} are chosen so that they go smoothly to the case of the XY_2 type molecules where ζ_{23}^x is taken to be +1.0.

Convergence Test. As described in I and II, the accuracy of the present treatment depends on the number of the basis functions used. Ten lowest wavenumbers of the σ- and π-species with 200 basis functions are listed in Table 4 along with the 15 and 20th wavenumbers for comparison. In this case n_{max} is about 13 which is smaller than the corresponding value of 19 for XY_2, because of lower symmetry. Calculation has also been made with 150 basis functions and the differences in wavenumbers are entered in the second column of Table 4. Also listed are some coefficients a_{vn}'s which contribute significantly to the vibrational levels in Table 4. Similar treatment has been done for the calculated values of B_v^r and the results are given in Table 5. The terms up to $k=4$ in Eq. 7 are retained in $\mathbf{H}_{rot}$. The accuracy of the computed B_v^c depends on the second factor, namely the number of eigenvalues and eigen-

Table 5. Calculated rotational constants of N_2O and their convergence test
All Units are given in 10^{-6} cm^{-1}.

v	B_v-B_0	B_v^r	ΔB_v^r	B_v^c	ΔB_v^c (I)	ΔB_v^c (II)	ΔB_v^c (III)
(1) σ-state (l_2=0)							
1	0	−2030	0	−127	0	0	2
2	928	−378	0	−851	0	0	26
3	−1872	−3881	1	−148	0	0	22
4	−3363	−5930	2	410	0	2	−46
5	1787	1144	1	−1513	1	3	85
6	−1010	−2237	3	−929	−1	2	13
7	−3692	−5648	8	−201	0	1	−40
8	−2458	−4310	5	−305	−1	13	63
9	2708	2715	0	−2163	0	25	166
10	−5185	−7799	24	457	1	0	−125
15	−1555	−2793	27	−918	−6	749	81
20	−2161	−2943	101	−1375	−11	108	−212
(2) π-state (l_2=1)							
1	511	−1110	0	−536	0	0	18
2	1370	427	1	−1213	−1	0	61
3	−1335	−2869	2	−622	0	0	2
4	−2933	−5079	3	−10	−1	5	23
5	2241	1948	0	−1863	0	11	133
6	−650	−1501	5	−1305	0	10	58
7	−3114	−4517	12	−754	−1	6	−19
8	−2036	−3523	8	−669	−5	287	38
9	3232	3572	1	−2495	−1	307	208
10	−4750	−6898	29	−9	4	125	−115
15	−739	−2020	29	−876	10	*	443
20	−1047	−2312	137	−892	−47	*	*

$B_v=B_v(40/200)$, $B_v^r=B_v^r(40/200)$, and $B_v^c=B_v^c(40/200)$. (m/n) means that the value is calculated from an n by n eigenvalue problem, and the lowest m eigenvalues are obtained.
$\Delta B_v^r=B_v^r(40/150)-B_v^r$, $\Delta B_v^c(\mathrm{I})=B_v^c(40/150)-B_v^c$, $\Delta B_v^c(\mathrm{II})=B_v^c(30/200)-B_v^c$, and $\Delta B_v^c(\mathrm{III})=B_v^c(\mathrm{FSW})-B_v^c$, where B_v^c(FSW) is estimated from Eq. 25.

vectors actually obtained. By varying this number with the fixed basis functions, another convergence test is performed for B_v^c. Only a leading term is retained in $\mathbf{H}_{\mathrm{Cor}}$ so that direct comparison is possible for the FSW method in dealing $\mathbf{H}_{\mathrm{Cor}}$. The last column in Table 5 shows the differences of B_v^c's computed by the two different methods.

The convergence test for wavenumbers and rotational constants has a markedly similar trend to that of CO_2. This result is in accordance with the earlier conclusion (II) that γ_s is a good measure for the convergence. The value $\gamma_1(N_2O)=0.025$ is very close to that of $\gamma_1(CO_2)=0.024$. The value of γ_3, which is zero for XY_2, is still very small (0.0036). It is gratifying to know that for most low-lying vibrational levels, the present method of the 200 basis functions with the 40 eigenvalues yields the wavenumbers and rotational constants free from the truncation effect of matrix sizes. It must be pointed out here, however, that the 10th lowest wavenumber of N_2O in the π-species, for example, is around 4000 cm^{-1} which is much lower than the corresponding value of 7000 cm^{-1} for the π_g-species of CO_2. A test run for the OCS molecule, of which γ_1 value is 0.021, has been attempted. This molecule shows much quicker convergence than N_2O.

As mentioned earlier, the quartic force constants k_{1333}, k_{1223}, and k_{1113}, do not contribute to the vibrational energies within the second-order perturbation theory. To see the actual effects of these force constants, the calculation is proceeded to drop these force constants one at a time. The results are summarized in Table 6, where only differences in 10^{-2} cm^{-1} are given. Table 6 shows in a way a limitation of the second order perturbation theory. The effect of k_{1113} is the largest, but this may be due to its relatively large value.

If we compare the present results with those calculated earlier by perturbation theory, discrepancies as large as 20 cm^{-1} are found for some levels involved in Fermi resonance. This has also been observed for the CO_2 molecule. More strictly, the quintic force constants, k_{11122}, k_{12222}, and k_{12233} must be considered to make the present calculation directly comparable with that of perturbation theory, since these quintic force constants were implicitly included as the parts of the third-order parameters in Fermi resonance.[12] This has not been tested, although the values of these force constants have become available recently.[15] The agreements of wavenumbers and rotational constants are much better for the levels which are relatively free from the effect of Fermi resonance. For example, discrepancies are within 0.6 cm^{-1} for the 001 and 002 levels located at 2223.7 and 4417.3 cm^{-1}, respectively.

Variational Method in Computing B_v^r. Off-diagonal matrix elements of transformed $\boldsymbol{Z}$ matrix were ignored in Eq. 18. This may be justified since the off-diagonal elements contribute mostly to higher order rotational terms: $[J(J+1)-l^2]^n$, where n is greater than one. The equation may be rewritten so as to give the explicit expression for B_v^r,

$$B_v^r = B_e[\tilde{\boldsymbol{A}}_v \boldsymbol{Z}^{(J+2)} \boldsymbol{A}_v]_{\text{diagonal}} \tag{26}$$

The B_v^r values computed from Eq. 26 are found to agree almost exactly with those obtained by solving Eq. 17 successively with three J's (0, 5, 10) and then fitting the energies to Eq. 22. Discrepancies are less than 10^{-8} cm^{-1}. The agreements are less perfect ($\simeq 5\times10^{-6}$ cm^{-1}) if we drop the centrifugal term in Eq. 22 and fit the remaining two parameters from the results of $J=0$ and $J=5$, as has been done in II. In a way this is a numerical verification that Eq. 26 holds rigorously since B_v^r is a coefficient of $[J(J+1)-l^2]$, which is the leading term in the rotational energy expansion. It also implies that the consideration of centrifugal distortions is required to obtain an accurate value of rotational constant.

FSW Method in Evaluating B_v^c. Although the Coriolis coupling is considered as the second-order effect, the B_v^c values are far from negligible. On the average the $|B_v^c|$ value is smaller than the $|B_v^c|$ value, however, in some vibrational levels this tendency is reversed. The treatment of $\mathbf{H}_{\mathrm{Cor}}$ may be the most cumbersome and time-consuming in the direct diagonalization procedure and this makes the FSW method mentioned earlier quite attractive. In the last column of Table 5 entered the calculated differences of B_v^c. The discrepancies are in the order of 10 to 15%. This was rather expected since Eq. 25 was derived by dropping some off-diagonal terms: Eq. 25 is independent of the sign of

TABLE 6. EFFECTS OF "Off-Diagonal" FORCE CONSTANTS TO VIBRATIONAL FREQUENCIES[a)]

σ-species	k_{1333} (1.66)	k_{1223} (2.76)	k_{1113} (−8.59)	π-species	k_{1333} (1.66)	k_{1223} (2.76)	k_{1113} (−8.59)
1	0	0	0	1	1	1	−2
2	−2	−9	9	2	−4	−33	21
3	11	21	−135	3	18	58	−165
4	−9	−3	−133	4	−3	−1	−126
5	−10	−86	50	5	−16	−160	−85
6	18	85	−163	6	19	95	−191
7	28	60	502	7	45	161	−624
8	−6	−4	119	8	−9	−16	−116
9	−25	−273	149	9	−34	−420	224
10	13	35	788	10	57	86	−779
15	−22	43	−94	15	−34	94	−69
20	54	301	835	20	−25	306	−880

a) Only the differences are listed in 10^{-2} cm^{-1}: $\Delta\nu=\nu$(without k listed in column head) $-\nu(200)$.

ζ's, while sign dependent terms are expected as off-diagonal contribution.[7] However, the overall errors due to this are relatively small for the total computed value of B_v. In addition, this method is not affected by the second truncation problem discussed earlier. It is more robust and may give better approximation for higher vibrational levels.

If only wavenumbers and rotational constants are to be computed, the logical approach is to solve pure vibrational hamiltonian, Eq. 12, and then to apply Eqs. 25 and 26 to obtain $B_v{}^r$ and $B_v{}^c$, respectively. This is particularly useful in the refinement process in which a number of cycles of calculations should be carried out. The more exact method may be applied in the final stage of refinement.

Centrifugal Distortion and l-Type Doubling Constants. If the centrifugal distortion constants are also to be computed, the procedure given in Eq. 12 through Eq. 21 cannot be avoided. To obtain an accurate D_J value the third-order term $H_J[J(J+1)-l^2]^3$ should be added to Eq. 22 and the four parameters must be fit from four sets of calculations ($J=0$ and three nonzero J's). This has already been done by Whiffen for the OCS molecule.[7] The present calculation shows that the $D_v{}^r$ values are almost constant and in the range of 35—40 (10^{-8} cm^{-1}). The variations of the D_v values seem to arise mostly from $D_v{}^c$, the contribution of $\mathbf{H}_{\mathrm{Cor}}$ to D_v.

Table 7. Observed and calculated l-type doubling constants (q_v) for the π-species of N_2O in the unit of 10^{-6} cm^{-1}

Level	Obsd	Ref	Calcd
1	792	a	834
2			1556
3	909	a	988
4	777	a	819
5			2252
6			1724
7	1075	a	1190
8	1459	b	1518
9			2918
10	883	b	928

a) Ref. 16. b) Ref. 17.

The l-type doubling constants are obtained by a procedure analogous to that given in II (see also Fig. 2). The comparison of experimental and calculated constants are listed in Table 7. Just in the cases of CO_2 and CS_2, the calculated values slightly exceed the observed values, but overall profile is well represented by the calculation.

The X_2Y_2 Type Molecule. Acetylene may be an only X_2Y_2 type molecule on which the general quartic force field has been studied in some detail.[18–20] Numerical computations were carried out by using a modified GVFF[19] to test an extended portion of the direct diagonalization procedure. However, the details of numerical computations are not given here. Acetylene has two CH stretching fundamentals over 3000 cm^{-1}, it seems necessary to use more than 200 basis functions because of slower convergence. Rotational expansion is also slow in convergence with $\gamma_2=0.033$. Peculiar features of the X_2Y_2 molecular potential and their treatment in the direct diagonalization method are briefly described here. This type of molecule has non-vanishing force constants k_{345} (k_{1345} and k_{2345} as well) and k'_{4455} which appear in V_{anh} as[21)

$$k_{345}q_3r_4r_5\cos(\chi_4-\chi_5) \text{ and } k'_{4455}r_4{}^2r_5{}^2\cos(2\chi_4-2\chi_5).$$

They have off-diagonal matrix elements with respect to individual l_s, although the final matrix elements are always diagonal with respect to $l=l_4+l_5$. These force constants cause the well-known vibrational l-type doubling or resonance. In the σ_g- and σ_u-species, it is possible to reduce the size of hamiltonian matrices by taking linear combinations such as $|1^11^{-1}\rangle\pm|1^{-1}1^1\rangle$. However, the merit of taking similar combinations diminishes in the states with $l\neq 0$. In the present calculation no attempts have been made to separate $+$ and $-$states. They are mixed in the σ_g- or σ_u-species, but their symmetries are obvious from the corresponding signs of a_{vn}'s.

The angular parts as well as the radial parts of degenerate normal coordinates have to be considered in evaluating the matrix elements associated with the above force constants, the subroutine OPERR is modified to allow this type of operations.

Concluding Remarks. A general algorithm for the direct diagonalization method of vibrational hamiltonian matrix has been extended to the XYZ and X_2Y_2 type linear molecules. The use of matrix algebra makes it easily adaptable to the computer programs. Some improvements have been made on the treatment of vibration-rotation energies. As pointed out in II, the present method yields an improved set of orthonormal vibrational wave functions, which may be used to evaluate an expectation value of any physical property P for a given vibrational level, where P is a function of normal coordinates.

$$\bar{P}_v = \langle v|P(q)|v\rangle = \sum_{n,m} a_{vn}a_{vm}\langle n|P(q)|m\rangle \tag{27}$$

Formula for the transition moment has been given in II and extensive studies have been done on the dipole moment functions of the CO_2 and N_2O molecules and the vibrational wave functions obtained here are very useful, the details will be given elsewhere.[22)

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