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Anharmonic Potential Functions of Simple Molecules. I. Direct Numerical Diagonalization of Vibrational Hamiltonian Matrix and Its Application to CO and HCl

Isao Suzuki

Department of Chemistry, Faculty of Science, The University of Tokyo, Bunkyo-ku, Tokyo

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The vibrational energy levels of diatomic molecules are related with the harmonic and anharmonic force constants by solving the vibrational Hamiltonian matrix numerically. The associated rotational levels are computed by two different methods; (1) perturbation treatment which utilizes the wave functions obtained, and (2) direct numerical diagonalization of the vibration-rotation submatrices. This approach, combined with the least-squares procedure, is applied to the determination of anharmonic force constants for CO and HCl molecules. Special attention is paid to the truncation effect of potential functions upon the calculated energy levels. Limitations in the usual perturbation method as well as the applicability of the present method to triatomic molecules are discussed.

The least-squares determination of the harmonic and anharmonic force constants from available spectroscopic data has been attempted for a few simple polyatomic molecules such as CO_2, HCN, OCS, N_2O, H_2O, and HCCH.[1-9] In the above determination, the potential function is expressed in terms of an appropriate coordinate system and is expanded in a power series, the terms quadratic through quartic being retained. The relationships between these force constants and the vibration and vibration-rotation energies are rather complicated; the perturbation technique is usually employed, and the vibration-rotation Hamiltonian of a polyatomic molecule is solved by the successive application of the contact transformations.[10,11] This may be an only approach to finding analytical expressions relating these force constants with energy levels, but some problems concerning its direct use in the least-squares determination of anharmonic force constants remain unsolved: (a) validity of the approximation used, (b) the truncation effect upon the higher order terms, and (c) treatment of anharmonic resonances, especially the handling of weak resonances. If, on the other hand, a proper set of basis wave functions (usually harmonic oscillator wave functions) is chosen, the vibrational Hamiltonian can readily be written down in matrix form, and the vibrational energy levels are obtained through numerical diagonalization. In addition, an orthogonal and normalized wave function can be obtained for each vibrational state as a linear combination of the original basis functions. The components of the eigen vector correspond to the coefficients of the linear combination, from which the rotational energy levels in a given vibrational state are derived by the standard pertur-

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[4] T. Nakagawa and Y. Morino, This Bulletin, **42**, 2212 (1969).

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[10] H. H Nielsen, *Rev. Mod. Phys.*, **23**, 90 (1951); "*Handbuch* der Physik," S. Flügge, ed. Vol. 37, Springer-Verlag, Berlin (1959).

[11] M. Goldsmith, G. Amat, and H. H. Nielsen, *J. Chem. Phys.*, **24**, 1178 (1956); **27**, 838, 845 (1957); **29**, 665 (1958).

bation method. With the use of high speed computers, this second method may yield a more reliable set of harmonic and anharmonic force constants, particularly when it is combined with the least squares procedure.

This line of approach was motivated from the study of the anharmonic potential function for the water molecule, which is expected to have large cubic and quartic cross terms. The direct diagonalization method is, however, first applied to and tested in diatomic molecules, the simplest molecular system with only one vibrational freedom. The vibration-rotation energy levels of a diatomic molecule are given in the form of a double power series,

$$E_{v,J} = \sum_{i,j} Y_{ij}(v+1/2)^i[J(J+1)]^j \tag{1}$$

Dunham[12)] derived the relationships between the term values Y_{ij}'s and the force constants (known as the Dunham constants a_i's). The force constants derived from Dunham's equations are compared with those obtained from the present method. Diatomic molecules are probably only molecules, for which force constants higher than quartic can be determined from the presently available data. The least-squares fit to the spectroscopic data has been made with the five parameter potential function (FPPF, quadratic through hexic) as well as the three parameter potential function (TPPF, quadratic through quartic). The truncation effect upon the values of force constants is discussed. The seven parameter potential function (SPPF, quadratic through octic) is also considered in some cases. Two diatomic molecules, CO and $H^{35}Cl$, whose vibrational levels and associated rotational constants have been known precisely up to sufficiently high levels ($v=5$ or $v=6$), are subjected to a detailed investigation. The direct diagonalization method is also attractive in handling polyatomic molecules, since no special treatment is required for the anharmonic resonances.

Hamiltonian

The vibration-rotation Hamiltonian for a diatomic molecule is given as[12)]

$$\mathbf{H} = \mathbf{H}_{\mathrm{VIB}} + \mathbf{H}_{\mathrm{ROT}}, \tag{2}$$

$$\mathbf{H}_{\mathrm{VIB}} = (1/2)\omega_e(q^2+p^2) + k_3q^3 + k_4q^4 + k_5q^5 + \cdots \tag{3}$$

$$\begin{aligned}\mathbf{H}_{\mathrm{ROT}} &= B_e(J_x{}^2+J_y{}^2)(1-2\gamma^{1/2}q+3\gamma q^2-4\gamma^{3/2}q^3+)\cdots \\ &= B_e(J_x{}^2+J_y{}^2)\sum_{k=0} R_k q^k \,. \end{aligned} \tag{4}$$

The Hamiltonians as well as all constants are expressed in cm^{-1} units and the operators are dimensionless: $p=\hbar^{-1}(\partial T/\partial q)$, $J_x=\hbar^{-1}P_x$, and $J_y=\hbar^{-1}P_y$. B_e is an equilibrium rotational constant, w_e is a harmonic frequency, and k_i's are anharmonic force constants.[13)] The quantity $\gamma=(2B_e/\omega_e)$ represents 'smallness' in perturbation treatment and $R_k=(-1)^k\gamma^{(k/2)}\times(k+1)$ reflects the effect of normal vibration upon the rotational Hamiltonian.

Pure Vibrational Problem. Non-vanishing matrix elements of $(p^2+q^2)/2$, q^3, q^4, q^5, q^6, q^7, and q^8 in the harmonic oscillator wave functions are given in Table A–1 in the Appendix. The contribution of each force constant to the vibrational Hamiltonian matrix $\mathbf{H}_{\mathrm{VIB}}$ might be represented in matrix form, $\mathbf{A}^{(i)}$. The first few nonvanishing elements in each A-matrix are also given in Table A–2 in the Appendix. The final $\mathbf{H}_{\mathrm{VIB}}$ is given as matrix sum

$$\mathbf{H}_{\mathrm{VIB}} = \sum_{i=2} k_i \mathbf{A}^{(i)}, \tag{5}$$

where $k_2=\omega_e$. When n basis functions are chosen, an n by n secular equation in the form of

$$\mathbf{H}_{\mathrm{VIB}}\mathbf{L}_i = \mathbf{L}_i \boldsymbol{\nu}_i \tag{6}$$

is solved for eigen vector L_i and eigen value ν_i. The eigen vectors are normalized to unity: $\mathbf{L}\ \tilde{\mathbf{L}}=\tilde{\mathbf{L}}\ \mathbf{L}=\mathbf{E}$, where $\mathbf{E}$ is a unit matrix.[14)]

Vibration-Rotation Energy. The rotational-energy for the vth vibrational state is expressed as

$$E_{v,J} = B_vJ(J+1) - D_vJ^2(J+1)^2, \tag{7}$$

where J is a rotational quantum number. The spacings for rotational energy levels are much narrower than those for vibrational levels, and use of the ordinary perturbation method is justified. Therefore, $\mathbf{H}_{\mathrm{ROT}}$ in Eq. (4) is treated as a perturbing term, and the first-order vibration-rotation energy $E_{v,J}{}^{(1)}$ is given as

$$\begin{aligned} E_{v,J}{}^{(1)} &= B_e\langle J|J_x{}^2+J_y{}^2|J\rangle \sum_{k=0} R_k\langle v|q^k|v\rangle \\ &= B_eJ(J+1)\sum_{k=0} R_k\langle v|q^k|v\rangle \,. \end{aligned} \tag{8}$$

The 'true' wave function for the vth vibrational level is represented as a linear combination of the harmonic oscillator basis functions φ_n's:

$$|v> = \sum_{n=0} a_{vn}|n> \tag{9}$$

Throughout this paper, the indices n and m are used to indicate the harmonic oscillator wave functions $\varphi_n{}^0(q)$ and $\varphi_m{}^0(q)$, and v and v' refer to the true (perturbed) vibrational states. The coefficients a_{vn} are the components of the vth eigen vector. Since φ^0's are normalized and orthogonal, B_v is computed as

$$B_v = B_e\sum_{k=0} R_k\langle v|q^k|v\rangle = B_e[1+\sum_{k=1} R_k \sum_{n,m} a_{vn}a_{vm}\langle n|q^k|m\rangle]. \tag{10}$$

Similarly, the centrifugal distortion constant D_v in Eq. (7) can be obtained by applying the second-order perturbation treatment: $E_{v,J}{}^{(2)}=\sum_{v\neq v'} H_{vv'}{}^{(1)}H_{v'v}{}^{(1)}/(E_v{}^{(0)}-E_{v'}{}^{(0)})$.

The alternative method for obtaining the vibration-rotation energy levels is more direct. Since the rotational Hamiltonian $\mathbf{H}_{\mathrm{ROT}}$ for a diatomic molecule is diagonal with respect to the rotational quantum number J, the entire vibration-rotation Hamiltonian matrix is factored into a number of subma-

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12) J. L. Dunham, *Phys. Rev.*, **41**, 721 (1932).

13) The force constants k_n's in Eq. (3) are related with the Dunham constants a_m's in the following equation,

$$2k_{n+2}=\omega_e\gamma^{n/2}a_n\cdot(n=1,2,3,\cdots)$$

14) A similar treatment was carried out by Heilbronner *et al.*[15)] but they used a very limited number of basis functions.

15) E. Heilbronner, Hs. H. Guntherd, and R. Gerdil, *Helv. chim. Acta*, **39**, 1171 (1956).

trices, each of which is constituted from the states with identical J values. For non-zero J-values, the terms originated from $\mathbf{H}_{\mathrm{ROT}}$ are treated as effective potential constants which modify the values of k_i in Eq. (3). The values of B_v and D_v are obtained from a direct calculation of vibration-rotation energies. $E_{v,J}$. The B_v values computed from the perturbation method, Eq. (10), are in excellent agreement with those obtained directly. The perturbation method, which is much quicker, is usually used in the present study. The direct method, however, excels the perturbation method when the vibration-rotation wave functions are to be computed. When various vibration-rotation dipole moment matrix elements $R_{v,J}{}^{v',J'}$ are evaluated for CO and HCl, the direct method is used.

Numerical Analysis

The numerical computations have been carried out on a HITAC 5020 E digital computer of the Computation Centre in the University of Tokyo. In order to preserve the desired number of significant figures, double precision arithmetic (64 bits) was used. For most practical purposes, however, the single precision is adequate. The vibrational energy levels and associated rotational constants are taken from the recent high resolution measurements on the vibration-rotation bands of CO and $H^{35}Cl$.[16,17] Their values are listed in Table 1 along with the term values Y_{ij}'s and the potential constants a_n's derived by these authors.

Preliminary Calculation. a) *Number of Basis Functions*: The vibrational energy levels ($v \leqq 6$ for CO and $v \leqq 5$ for HCl) are calculated from a trial set of the FPPF for both CO and HCl.[18] The number of basis functions is varied from 7 to 50. Convergence of eigen values is appreciably slower in HCl but is completed for the above levels when 30 basis functions are used. Similar results are obtained for the TPPF. Thus, 30 basis functions are used throughout this work, and errors resulting from the truncation of the Hamiltonian matrix are expected to be negligible. A reasonable convergence is obtained for the fundamentals and the first overtones of both CO and HCl and the second overtone of CO with ten basis functions. This implies that the present method is applicable to triatomic molecules. b) *Frequencies*: As shown in Table 1, Rank *et al.* derived the values of the first five force constants from the observed frequencies and rotational constants. The vibrational energy levels for CO and HCl are calculated from these force constants by three different methods, and they are given in Columns (i)-(iii) of Table 2. These energy levels are obtained (i) by direct diagonalization of a 30 by 30 vibrational Hamiltonian matrix, (ii) by the usual second order approximation, where x_e and α_e are given as

$$x_e = (3B_e/2)(5a_1{}^2/4-a_2) = (3/2)(5k_3{}^2/2\omega_e-k_4) \tag{11}$$

and

$$\alpha_e = -(6B_e{}^2/\omega_e)(1+a_1) = -(6B_e{}^2/\omega_e)[1+k_3(2/\omega_e B_e)], \tag{12}$$

and (iii) by using Dunham's formulae[19] (Eq. (15)

TABLE 1. OBSERVED ENERGY LEVELS AND ROTATIONAL CONSTANTS (in cm^{-1}) USED IN THE PRESENT STUDY
Derived Dunham's Constants a_k and Term Values Y_{ij} are also listed

	(a) CO		(b) HCl	
	ν	B_v	ν	B_v
$v=0$	0	1.922521	0	10.440254
$v=1$	2143.2740	1.905014	2885.9775	10.136228
$v=2$	4260.0646	1.887513	5667.9841	9.834665
$v=3$	6350.436	1.870010	8346.7816	9.534845
$v=4$	8414.458	1.852513	10922.803	9.236010
$v=5$	10452.170	1.835010	13396.217	8.93743
$v=6$	12463.70	1.817521		
	$Y_{10}=2169.8232$	$Y_{01}=1.931274$	$Y_{10}=2990.9463$	$Y_{01}=10.593416$
	$Y_{20}=-13.2932$	$Y_{11}=-0.017507$	$Y_{20}=-52.8185$	$Y_{11}=-0.307181$
	$Y_{03}=0.0114_4$	$Y_{21}=1\times10^{-6}$	$Y_{30}=0.22437$	$Y_{21}=0.0017724$
			$Y_{40}=-0.01218$	
	$k_3=-123.47086$	$a_1=-2.6974$	$k_3=-297.6209$	$a_1=-2.3645$
	$k_4=8.70732_9$	$a_2=4.5065$	$k_4=38.8222_2$	$a_2=3.6647$
	$k_5=-0.48555_1$	$a_3=-5.9589$	$k_5=-4.1711_1$	$a_3=-4.6783$
	$k_6=0.02422_2$	$a_4=7.0457$	$k_6=0.37099$	$a_4=4.9440$
	$(\omega_e \doteqdot Y_{10})$	$(B_e \doteqdot Y_{01})$	$(\omega_e=2991.0904$	$B_e=10.593553)$

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16) D. H. Rank, A. G. St. Pierre, and T. A. Wiggins, *J. Mol. Spectry.*, **18**, 418 (1965).

17) D. H. Rank, B. S. Rao, and T. A. Wiggins, *ibid*, **17**, 122 (1965).

18) The lowest eigen value is usually negative. The energy scale is readjusted so that the ground vibrational level is always at origin.

19) Since these force constants were obtained from Dunham's formulas, the calculated frequencies in (iii) are expected to agree closely with the observed frequencies. The discrepancies found in the actual calculated frequencies are due to neglect of the terms ($\approx B_e{}^3/\omega_e{}^2$) in Y_{20} when Dunham's constants were derived.

TABLE 2. COMPARISON OF CALCULATED FREQUENCIES AND ROTATIONAL CONSTANTS (in cm^{-1}) BY METHODS (i)—(iv)

(a) CO

ν_v	(i) Direct	(ii) 2nd-order	(iii) 4th-order	(iv) Direct[a]	(v) (i)—(ii)	(vi) (i)—(iii)	(vii) (i)—(iv)
$v=1$	2143.30	2143.24	2143.29	2143.23	6	1	7
$v=2$	4260.22	4259.39	4260.10	4259.81	33	12	41
$v=3$	6350.99	6349.96	6350.51	6349.49	103	48	150
$v=4$	8415.97	8413.45	8414.58	8411.88	252	139	409
$v=5$	10455.69	10450.35	10452.39	10446.33	534	330	936
$v=6$	12470.83	12460.66	12464.00	12451.96	1017	683	1887
B_v							
$v=0$	1.922520	1.922521	1.922521	1.922515	−1	−1	5
$v=1$	1.905025	1.905014	1.905022	1.904984	9	3	41
$v=2$	1.887557	1.887508	1.887524	1.887389	49	34	168
$v=3$	1.870143	1.870001	1.870030	1.869674	142	113	469
$v=4$	1.852824	1.852495	1.852536	1.851771	329	288	1053
$v=5$	1.835653	1.834988	1.835045	1.833596	665	608	2057
(b) HCl							
ν_v							
$v=1$	2887.23	2885.45	2886.44	2883.72	172	79	351
$v=2$	5676.36	5665.27	5669.67	5662.20	1110	670	2416
$v=3$	8380.41	8339.44	8351.02	8280.09	4097	2939	10032
$v=4$	11022.48	10907.98	10931.85	10645.93	11450	9063	37655
$v=5$	13634.86	13370.87	13413.51	13115.58	26399	22135	51928
B_v							
$v=0$	10.440579	10.439966	10.440887	10.439494	613	−308	1085
$v=1$	10.139657	10.132792	10.138699	10.128533	6865	958	11124
$v=2$	9.851493	9.825618	9.840339	9.797745	25875	11154	53748
$v=3$	9.590328	9.518444	9.545806	9.403426	71884	44522	186902
$v=4$	9.375818	9.211127	9.255101	8.365634	—	—	—
$v=5$	9.224414	8.904096	8.968223	8.316344	—	—	—

a) Without hexic off-diagonal matrix elements.

in Ref. 12). The differences (i)–(ii) and (i)–(iii) are given, respectively, in Columns (v) and (vi). They show that these approximation methods break down rapidly in higher vibrational levels. The discrepancies are much larger in HCl, and it is alarming that even for the first overtone of HCl, the calculated frequencies in (ii) and (iii) are off from the exact solution by about 11 and 7 cm^{-1}, respectively.

c) *Rotational Constants.* As given in Eq. (4), the rotational Hamiltonian of a diatomic molecule is expressed as a power series expansion of the dimensionless normal coordinate q, and the terms $k=0$ through $k=6$ are first retained in the present calculation. The calculated values for the rotational constants are given in Columns (i)–(iv) of Table 2. The rotational constants, B_v, may be regarded as the sum of terms $B_v(k)=B_e \cdot R_k \langle v | q^k | v \rangle$. The contribution of each $B_v(k)$ term is listed in Table 3 for the $v=0$, $v=1$, and $v=5$ levels of CO and HCl. The convergence is satisfactory for the low vibrational levels of CO and still good for the $v=5$ level.[20] For HCl, it is satisfactory only for the $v=0$ and $v=1$ levels. It becomes slower in higher vibrational levels. When the least-squares adjustment of force constants is attempted for the HCl molecule, the rotational Hamiltonian is expanded further to the $k=8$ term. Contributions from $B_v(7)$ and $B_v(8)$ are added in Table 3-b.[21]

d) Effect of Off-diagonal Matrix Elements. In the second order perturbation treatment in polyatomic molecules, where harmonic, cubic, and quartic force constants are retained, the off-diagonal contributions of the quartic force constants to the energies are neglected. Only exceptions are the cases in which second order anharmonic resonances are apparent. In the same sense, the off-diagonal contributions of the hexic force constant can be neglected in the fourth order approximation, and the diagonalized results without hexic off-diagonal terms are

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[20] To estimate the maximum error due to the neglect of higher terms, $B_5(7)+B_5(8)$ is calculated later, which gives 9×10^{-6} cm^{-1}.

[21] Even though the terms up to $k=8$ are retained, convergence is slow and unsatisfactory for the higher levels. This forces us to put lighter weights (usually 0.01) on these rotational constants, when the least-squares adjustment is made.

TABLE 3. CONVERGENCE OF ROTATIONAL CONSTANT EXPANSION: $B_v(k)$ VALUES ARE LISTED FOR THE $v=0$, $v=1$, $v=2$, AND $v=5$ LEVELS (in cm^{-1})

(a) CO

	$v=0$	$v=1$	$v=2$	$v=5$
B_v (total)	1.922520	1.905025	1.887557	1.835653
$B_v(0)=B_e$	1.931274	1.931274	1.931274	1.931274
$B_v(1)$	−0.013965	−0.042127	−0.070622	−0.157765
$B_v(2)$	0.005279	0.016361	0.028223	0.068763
$B_v(3)$	−0.000092	−0.000610	−0.001680	−0.008600
$B_v(4)$	0.000024	0.000133	0.000378	0.002264
$B_v(5)$	-0.000000_7	−0.000007	−0.000031	−0.000348
$B_v(6)$	0.000000_2	0.000001	0.000005	0.000076
(b) HCl				
B_v (total)	10.440586	10.139765	9.852153	9.238361
$B_v(0)=B_e$	10.593553	10.593553	10.593553	10.593553
$B_v(1)$	−0.268496	−0.814129	−1.365128	−2.804660
$B_v(2)$	0.120556	0.396735	0.724505	1.890411
$B_v(3)$	−0.007246	−0.049633	−0.141149	−0.696959
$B_v(4)$	0.002391	0.015124	0.048392	0.331940
$B_v(5)$	−0.000241	−0.002594	−0.011550	−0.134309
$B_v(6)$	0.000070	0.000710	0.003530	0.058385
$B_v(7)$	−0.000010	−0.000149	−0.000948	−0.024268
$B_v(8)$	0.000003	0.000041	0.000287	0.010321

$B_5(7)+B_5(8)=-0.000009$ cm^{-1} for CO.

given in Column (iv) of Table 2. Deviations (i)-(iv) in Column (vii) resemble those in column (v) in the case of CO, and are especially small for the low vibrational levels. As for HCl, the neglect of hexic off-diagonal terms drastically lowered the calculated frequencies. This can be interpreted that the terms like $k_7q^7+k_8q^8$ are necessary to account for the vibrational frequencies of HCl, and the SPPF is also tested in HCl.

Least-Squares Adjustment of Force Constants

Method of Least-Squares. The least-squares corrections to the initial values of force constants are found by solving well-known simultaneous linear equations

$$(\tilde{\mathbf{J}}\mathbf{P}\mathbf{J})\Delta\mathbf{K} = \tilde{\mathbf{J}}\mathbf{P}\Delta\boldsymbol{\nu}. \tag{13}$$

J, **P**, $\Delta\mathbf{K}$, and $\Delta\boldsymbol{\nu}$ have their usual meaning. In the anharmonic potential problem, a finite difference method has been used to evaluate the elements of Jacobian matrix **J**.[1] One advantage in the numerical diagonalization method is that we can use the techniques developed for normal coordinate analysis. From the first order perturbation method,[22] the Jacobian matrix element for the frequency ν_h with a change in the values of k_i is given by

$$\delta\nu_h/\delta k_i = (\tilde{\mathbf{L}}\mathbf{A}^{(i)}\mathbf{L})_{hh}, \tag{14}$$

where $\mathbf{A}^{(i)}$ and $\mathbf{L}$ are given in Eqs. (5) and (6). The elements for the rotational constant B_v are slightly more complex, Nakagawa and Shimanouchi[23] and Mills[24] evaluated the changes in eigen vectors due to a small change in a force constant k_i. Applying their results to the present case, we have

$$\Psi_v = \Psi_v{}^0 + \sum_{v'\neq v} P_{vv'}\Psi_{v'}{}^0, \tag{15}$$

where $P_{v,v'}=\Delta k_i(\tilde{\mathbf{L}}\mathbf{A}^{(i)}\mathbf{L})_{vv'}/(\nu_v{}^0-\nu_{v'}{}^0)$ and $\Psi_{v'}{}^0$'s are the wave functions with $\Delta k_i=0$. As given in Eq. (10), $B_v{}^0$ for $\Delta k=0$ is expressed as

$$B_v{}^0 = B_e\sum_{k=0} R_k\langle v|q^k|v\rangle$$

and

$$B_v \approx B_e\sum_{k=0} R_k\langle v|q^k|v\rangle + 2\sum_{v'\neq v} P_{vv'}\langle v|q^k|v'\rangle, \tag{16}$$

$$\delta B_v/\delta k_i \approx 2B_e\sum_{k=0}(\delta P_{vv'}/\delta k_i)\langle v|q^k|v'\rangle$$

$$= 2B_e\sum_{k=0} R_k\sum_{v'\neq v}(\tilde{L}_0A^{(i)}L_0)_{vv'}\langle v|q^k|v'\rangle/(\nu_v{}^0-\nu_v{}^0) \tag{17}$$

Application to CO and HCl. The least-squares adjustment of force constants has been made for the FPPF as well as the TPPF. The calculation has been made for the latter to see the truncation effect upon the harmonic, cubic, and quartic force constants. The vibrational frequencies and the rotational constants, are used as observational data. The results for CO and HCl are given separately in Tables 4—7. Only a minimum number of data is used to obtain Sets 1 and 2, *i.e.* ν_1, ν_2, B_0, and B_1. Six frequencies ν_1—ν_6 and five rotational constants B_0—B_4 are used in Sets 5 and 6. Sets 3 and 4 are intermediate cases. Sets 1,3, and 5 are obtained by solving a full Hamiltonian, while the quartic off-diagonal matrix elements are ignored in obtaining Sets 2,4, and 6. Similarly, in the FPPF, the hexic off-matrix ele-

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[22] T. Miyazawa, *Nippon Kagaku Zasshi*, **76**, 1132 (1955).

[23] I. Nakagawa and T. Shimanouchi, *ibid.*, **80**, 128 (1965).

TABLE 4. CONVERGED SETS OF FORCE CONSTANTS FOR CO[a] (in cm^{-1})

NO	NP	NV	NR	OD	SUMD	ω_e	k_3	k_4	k_5	k_6	B_e
1	3	2	2		0.0068	2171.3892	−122.3237	7.4843			
2	3	2	2	α	0.0092	2166.7975	−122.6360	10.1409			
3	3	4	3		0.75	2171.3381	−114.0623	5.6035			
4	3	4	3	α	4.3	2163.4794	−110.5233	7.3836			
5	3	6	5		5.0	2171.2725	−109.7213	4.7350			
6	3	6	5	α	63.0	2158.7036	−107.7104	7.2988			
7	5	6	5		0.0015	2169.8196	−123.5093	8.7279	−0.47603	0.01726	
8	5	6	5	α	0.0045	2169.9376	−122.6191	8.3809	−0.50297	0.05744	
9	6	6	5		0.00016	2169.9191	−123.5529	8.7317	−0.46782	0.01579	1.931241
7′	5	6	5		0.0050	2169.8234	−123.5757	8.7442	−0.47695	0.01722	
8′	5	6	5	α	0.011	2170.1693	−123.6326	8.5976	−0.41933	0.02281	
9′	6	6	5		0.0019[c]	2169.8160	−123.5962	8.7538	−0.47958	0.01747	1.931289
LIT.[b]						2169.8232	−123.4709	8.7073	−0.48555	0.02422	1.931274

a) NP: number of adjustable parameters, NV and NR: numbers of respective vibrational levels and rotational constants used as data, OD: α in this column indicates that the off-diagonal matrix elements of the highest order force constants are neglected, and SUMD: the sum of weighted squared deviations.

b) See Table 1.

c) The least-squares dispersions of the force constants in Set 9′ are follows; $\sigma(\omega_e)=0.0154$, $\sigma(k_3)=0.0276$, $\sigma(k_4)=0.0052$, $\sigma(k_5)=0.0050$, $\sigma(k_6)=0.00090$, and $\sigma(B_e)=0.000014\ \mathrm{cm}^{-1}$.

TABLE 5. DIFFERENCES BETWEEN OBSERVED AND CALCULATED FREQUENCIES AND ROTATIONAL CONSTANTS (Obsd-Calcd) FOR CO

Obsd	Sets	1	2	3	4	5	6	7	8	9	7′	8′	9′
ν													
$v=1$	2143.274	0	0	−324	1375	−734	4193	−11	−26	3	22	−60	−10
$v=2$	4260.065	0	0	79	17	−801	3409	−23	3	0	14	2	−22
$v=3$	6350.436	3766	−2106	466	−1296	−405	36	−17	19	−3	−7	22	9
$v=4$	8414.458	15608	−8689	−80	606	138	−3244	14	6	10	−17	22	9
$v=5$	10452.170	40525	−22383	2700	9363	350	−3416	21	−38	2	−32	−58	14
$v=6$	12463.700	84591	−45902	−8645	29381	307	3091	0	16	10	0	23	−9
$B_v\times 100$													
$v=0$	192.252	11	−22	−108	−127	−155	−158	0	−7	4	2	8	0
$v=1$	190.501	95	−79	−319	−332	−450	−429	−1	−16	3	3	9	1
$v=2$	188.751	291	−178	−530	−446	−730	−622	−2	−13	1	4	−2	1
$v=3$	187.001	381	−331	−750	−456	−1001	−726	5	3	−3	2	−12	0
$v=4$	185.251	1103	−553	−987	−345	−1267	−726	−8	35	−7	0	11	−2

Differences are given from the last significant figure.

TABLE 6. CONVERGED SETS OF FORCE CONSTANTS FOR HCl[a] (in cm^{-1})

NO	NP	NV	NR	OD	SUMD	ω_e	k_3	k_4	k_5	k_6	k_7	k_8	B_e
1	3	2	2		0.030	3013.6517	−305.0572	30.3793					
2	3	2	2	α	0.72	2963.8588	−277.7799	44.5324					
3	3	3	3		48.3	3026.2281	−302.1949	27.6823					
4	3	3	3	α	44.9	2950.8328	−269.9356	43.2287					
5	3	5	5		497	3008.0991	−258.4481	17.5360					
6	3	5	5	α	120	2944.6010	−276.0102	47.1034					
7	5	5	5		0.075	2992.0378	−299.6250	39.1738	−3.71343	0.17951			
8	5	5	5	α	0.36	2993.4178	−295.9522	36.3554	−3.45646	0.54440			
9	6	5	5		0.033	2992.2876	−300.2986	39.4324	−3.75365	0.18197			10.594752
10	7	5	5		0.030	2991.8183	−299.0935	39.0356	−3.88475	0.27635	−0.01859	0.00125	
11	8	5	5		0.019[c]	2992.2963	−300.2911	39.4315	−3.87787	0.25233	−0.01401	0.00095	10.595805
LIT.[b]						2991.0104	−297.6209	38.8222	−4.17110	0.37099			10.593553

a) See Footnote a) of Table 4.

b) See Table 1.

c) The least-squares dispersions of the force constants in Set 11 are as follows; $\sigma(\omega_e)=0.0366$, $\sigma(k_3)=0.0194$, $\sigma(k_4)=0.0078$, $\sigma(k_5)=0.0056$, $\sigma(k_6)=0.0031$, $\sigma(k_7)=0.0018$, $\sigma(k_8)=0.00026$, and $\sigma(B_e)=0.00028\ \mathrm{cm}^{-1}$.

TABLE 7. DIFFERENCES BETWEEN OBSERVED AND CALCULATED FREQUENCIES AND ROTATIONAL CONSTANTS (Obsd-Calcd) FOR HCl

Obsd	Sets	1	2	3	4	5	6	7	8	9	10	11
ν												
$v=1$	2885.978	−13	2	−5236	4581	−7980	8079	64	−240	−18	45	−32
$v=2$	5667.984	−7	−21	4026	−3761	−5872	−710	82	162	10	59	38
$v=3$	8346.728	−35794	33121	1365	978	2857	−5369	−57	122	−85	−68	−48
$v=4$	10922.803	−146606	129416	58504	40064	8751	2643	5	−102	14	26	23
$v=5$	13396.217	−366387	282606	−204103	109902	−4661	−227	−2	54	−31	−4	−3
$B_v\times 100$												
$v=0$	1044.025	156	−813	−24	−1502	−3466	−895	73	−133	9	65	−72
$v=1$	1013.623	−72	256	136	−2190	−9144	−508	55	−135	85	82	78
$v=2$	983.467	−3705	6445	−1685	1331	−13711	3612	−200	294	−98	−67	0
$v=3$	953.467	−13023	18774	−7991	9497	−18091	11010	−550	1332	−393	−278	−18
$v=4$	923.601	−28992	35970	−20550	20974	−23702	18657	−984	3090	−789	−557	−45

Differences are given from the last significant figure.

ments are ignored in Set 8, while a full Hamiltonian is solved for Sets 7 and 9. In Set 9, the equilibrium rotational constant B_e is treated as an adjustable parameter, in other sets its value is fixed (1.931274 cm^{-1} for CO and 10.593553 cm^{-1} for HCl). The relative weights of the rotational constants and vibrational frequencies might affect the outcome. In the present calculation, $B_v\times 10^2$ is usually entered as input data.[25] In Sets 7′–9′ of CO, $B_v\times 10^3$ is used to see the effect due to the change in the relative weight. From the consideration of accuracy in evaluating rotational constants, less weights have to be given to B_3 and B_4 of HCl, usually $B_v\times 10$ being used as data.

TABLE 8. THE CALCULATED AND OBSERVED FREQUENCIES AND ROTATIONAL CONSTANTS (in cm^{-1}) FOR ISOTOPIC CO AND HCl

(a) CO

		Obsd	Calcd (Set 9)
$^{13}C^{16}O$	ν_{0-1}	2096.071	2096.072
	B_0	1.8380	1.8379
	B_1	1.8216	1.8216

(b) HCl

		Obsd	Calcd (Set 7)
$H^{37}Cl$	ν_{0-1}	2883.871	2883.810
	ν_{0-2}	5663.926	5663.849
	B_0	10.4243	10.4238
	B_1	10.1209	10.1207
	B_2	9.8213	9.8224
$D^{35}Cl$	ν_{0-1}	2091.061	2091.148
	ν_{0-2}	4128.433	4128.496
	B_0	5.392261	5.392168
	B_1	5.279816	5.279477
	B_2	5.168106	5.168317
$D^{37}Cl$	ν_{0-1}	2088.073	2088.150
	ν_{0-2}	4122.594	4122.657
	B_0	5.3757	5.3764
	B_1	5.2673	5.2642
	B_2	5.1537	5.1535

Agreement between the calculated and experimental values in HCl is less satisfactory, and the seven parameter potential function (SPPF) is also tested. The results are included in Sets 10 and 11 of Tables 6 and 7. B_e is treated as a variable in Set 11.

Isotopic Species. Only a limited number of data is available for the isotopic species of CO and HCl,[26–28] and no least-squares fit of force constants has been attempted. Within the limit of Born-Oppenheimer approximation, however, the force constants $k_j^{(i)}$ for the isotopic species are related with those in the parent species k_j by means of

$$k_j^{(i)} = k_j(\mu/\mu^{(i)})^{j/4}, \quad (j=2,3,4,\cdots) \tag{18}$$

where μ and $\mu^{(i)}$ are the reduced masses of the parent and isotopic species, respectively. $B_e^{(i)}$ is given as $B_e^{(i)}=(\mu/\mu^{(i)})B_e$.[29] The results are summarized in Table 8, where no significant discrepancies are detected between the calculated and observed frequencies and rotational constants.

Discussion

Force Constants. In CO, the values of the five parameter force constants are not so sensitive to the change of the relative weights, but the effect may be seen in Table 5, where the differences between the observed and calculated frequencies and rota-

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[24] I. M. Mills, *J. Mol. Spectry.*, **5**, 334 (1960).

[25] This is equivalent to weighting the rotational constants a hundred times heavier than the frequencies The frequencies are known with the accuracy of a few thousandths of a wave number. The accuracies of the rotational constants for the low vibrational levels are estimated in the order of 10^{-5} cm^{-1}

[26] E. K. Plyler, L. R. Blaine, and E. D. Tidwell, *J. Res. Natl. Bur. Standards*, **55**, 183 (1955).

[27] D. H. Rank, D. P. Eastman, B. S. Rao, and T. A. Wiggins, *J. Opt. Soc. Amer.*, **52**, 1 (1962).

[28] D. V. Webb and K. N. Rao, *J. Mol. Spectry.*, **28**, 121 (1968).

[29] Note that $q=\gamma^{-1/2}\Delta r/r_e=(\Delta r/r_e)(\omega_e/2B_e)^{1/2}$, $B_e=\hbar/(4\pi r_e^2 c\mu)$, and $\omega_e=(1/2\pi)(K_e/\mu)^{1/2}$.

tional constants are listed. Regardless of the choice in the weighting systems, the first three force constants, *i.e.* ω_e, k_3, and k_4 of the FPPF converge to almost the same values. The values of k_5 and k_6 are more sensitive to the handling of data and to the method of calculation. The force constant k_6 converges to a larger value in Set 8. In the perturbation treatment, the off-diagonal contribution of hexic force constant is discarded, since its contribution to the vibrational energy is expected to be small and is of the same order as the diagonal contribution from the neglected higher order terms. As seen from Column (vii) of Table 2, however, the above statement is not adequate for CO and the discrepancy as large as 18 cm^{-1} is found for the $v=6$ level, while the diagonal contribution from k_8 is expected to be less than 1 cm^{-1}. A trial calculation is carried out by using the force constants in Set 9 plus $k_7=-0.001$ cm^{-1} and $k_8=0.0001$ cm^{-1}.[30] The calculated frequencies for the $v=5$ and $v=6$ levels decrease only by 2 and 4 cm^{-1}, respectively. The truncation errors for k_5 and k_6 are much smaller in Set 9, and it is regarded as the best set so far obtained.

From the calculation of the FPPF, we were able to determine the precise values of the first three parameters. ω_e, k_3, and k_4. However, in the potential functions of triatomic molecules from which the present study was initiated, we can hardly expand the potential function beyond quartic terms for parctical reasons. The least-squares adjustment of the TPPF is therefore attempted to seek the most appropriate method and the handling of data to obtain the reasonable values for these three constants. It is clearly seen from Table 4 that the force constants in Sets 1 and 2 are much closer to the values found in the FPPF. The deviations of these force constants from the 'true' values are almost the same in both sets but differing in sign. The average values of the force constants in Sets 1 and 2, $\omega_e=2169.09$, $k_3=-122.48$, and $k_4=8.8126$ cm^{-1}, are much close to the values found in Set 9. These results might be useful when the anharmonic potential functions of polyatomic molecules are dealt with.

The conclusion analogous to the case of CO may be drawn on the converged values of force constants for HCl: the first three force constants in the FPPF, especially those in Sets 7 and 9 converge to almost the same values. As for the TPPF, Sets 1 and 2, in which the minimum number of data is used, yield force constants closer to those in the FPPF. Much closer fit is also obtained when the average values of force constants in Sets 1 and 2 are taken: $\omega_e=2988.76$, $k_3=-291.42$, and $k_4=37.46$ cm^{-1}. However, the values of the first three force constants in Set 8 deviate from those in Sets 7 and 9 by 2—10%. They are much larger than the corresponding deviations found in CO. The overall fit of the calculated frequencies and rotational constants to the experimental values are poorer in HCl. The value $\gamma=(2B_e/\omega_e)$, which is a measure of smallness in perturbation treatment, is 0.007 for HCl in contrast to 0.0017 for CO. The ratio of k_{n+1}/k_n is about 0.01 for CO but close to 0.1 for HCl. This, in conjunction with the relatively large value of γ, makes the convergence much slower. Thus the SPPF where the potential function is expanded to the $k=8$ term was also tested. The results are included in Tables 6 and 7. Since the higher order force constants are considered, the converged values for k_5 and k_6 in Sets 10 and 11 are most reliable, and they are found closer to those found in Sets 7 and 9. This confirms the conclusion drawn earlier on HCl and CO. As far as the FPPF is concerned, the solution of the full vibrational Hamiltonian is preferable.

When the equilibrium rotational constant is treated as an adjustable parameter, a slight increase in the value of B_e serves for the improvement in the least-squares fit. The change in the B_e value is larger in HCl, but the corresponding decrease in the internuclear distance is in the order of 0.0001 Å. Table 9 summarizes the force constants obtained by the ordinary perturbation formulas and by the present method. As far as the general pattern of potential function in diatomic molecule is concerned, the force constants calculated from Dunham's equations, Eq. (15) in Ref. 12, or from the much simpler second-

TABLE 9. THE FIRST THREE FORCE CONSTANTS (in cm^{-1}) OF CO AND HCl DERIVED BY VARIOUS METHODS

(a) CO

	2nd-Order	4th Order	Direct (Set 7)	Direct (Set 9)
ω_e	2169.7574	2169.8232	2169.8234	2169.8160
k_3	−123.4685	−123.4709	−123.5757	−123.5962
k_4	8.7369	8.7073	8.7442	8.7538
B_e	1.931274	1.931274	1.931274	1.931289

(b) HCl

	2nd Order	4th Order	Direct (Set 7)	Direct (Set 9)	Direct (Set 11)
ω_e	2989.9489	2991.0904	2992.0378	2992.2876	2992.2963
k_3	−295.7798	−297.6209	−299.6250	−300.2986	−300.2911
k_4	38.4928	38.8222	39.1738	39.4324	39.4315
B_e	10.592267	10.593553	10.593553	10.594752	10.595815

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[30] This would be an over estimation for the force constants.

Table 10. The derived force constants from the model potential functions (cm^{-1})

	(a) CO			(b) HCl		
	Set 9	Morse	Exp. Morse	Set 10	Morse	Exp. Morse
ω_e	2169.8160	2169.8160	2169.8160	2991.8183	2991.8183	2991.8183
k_3	−123.5912	−123.5962	−123.5962	−299.0935	−299.0935	−299.0935
k_4	8.7538	8.2138	8.6402	39.4315	34.8839	36.6960
k_5	−0.47958	−0.40102	−0.46369	−3.88475	−2.98917	−3.45629
k_6	0.01747	0.01573	0.01797	0.27635	0.20586	0.27080
k_7				−0.01859	−0.01062	−0.01947
k_8				0.00125	0.00060	0.00108
		$A=83592.70$	$A_1=124873.08$		$A=37419.82$	$A_1=55898.75$
		$a=0.113923$	$a=0.093210$		$a=0.163588$	$a=0.163588$
			$A_2=-27749.57$			$A_2=-12421.90$

order equations, Eqs (16) and (17), have sufficient accuracies, and errors are probably within a few percent. More careful considerations seem to be necessary for more quantitative arguments, such as spectroscopic detection on the deviations from the Born-Oppenheimer behavior. Dunham's equations are sometimes insufficient for attaining the required accuracy, and the relationship between the spectroscopic term value Y_{ij} and the force constants must be examined carefully. Herman and Ashgarrian[31] tried to explain the discrepancy between the observed and theoretically predicted $Y_{02}(\approx D_e)$ values of HCl from the deviations of Born-Oppenheimer oscillators. Their failure obviously stems from neglect of contributions of the higher order force constants to Y_{02}. A more careful treatment such as given recently by Bunker[32] seems necessary.

As already stated, we have triatomic molecules in mind, and CO may serve as a model for CO_2, and HCl for H_2O. The parameter $\gamma=2B_e/\omega_e$ of CO_2 is less than one third of the corresponding value of CO (0.00058 as compared with 0.00178 of CO), and the least-squares determinatation based on Nielsen's second order perturbation treatment for this molecule[1,2] seems to be adequate. A preliminary calculation shows that the calculated values given in Ref. 2 do not differ significantly from those obtained from the diagonalization method. From the results of HCl, overall difficulties are anticipated for the treatment of anharmonic potential of H_2O. Inclusion of higher order force constants seems to be necessary at least for those related with the hydrogen stretching coordinates. However, some values may be estimated from the lower order force constants by assuming a suitable model potential. The Morse function[33] with two adjustable parameters A and a,

$$V(q) = A[1-\exp(-aq)]^2 \tag{19}$$

is probably the simplest potential for the bond-stretch. These constants can be determined from w_e and k_3 by $a=-2k_3/\omega_e$ and $A=\omega_e^3/8k_3^2$, and higher force constants evaluated from Eq. (19). This is done for CO and HCl, and the results, given in Table 10, show that the bond stretching potential qualitatively follows the pattern of the Morse function[1-3,6] Quantitatively, however, the prediction of the simple Morse function is not very satisfactory. In HCl the k_4 value is about 25% off from the converged one. In order to increase the freedom, the expanded Morse function[34] is also considered;

$$V(q) = \sum_{i=1}^{2} A_i[1-\exp(aq)]^{i+1} \tag{20}$$

The constants A_1, A_2, and a can be determined from ω_3, k_3, and k_4 from the relations

$$\omega_e = 2A_1a^2 \tag{21}$$

$$k_3 = (A_2-A_1)a^3 \tag{22}$$

$$k_4 = (3/2)(7A_1/18) - A_2a^4 \tag{23}$$

which leads to the quadratic equation for a

$$F(a) = a^2 + (36k_3/11\omega_e)a + (24k_4/11\omega_e) = 0. \tag{24}$$

The remaining higher order force constants can be obtained,

$$k_5 = -(1/4)[(A_1-5A_2)]a^5, \tag{25}$$

$$k_6 = (3/4)[(31A_1/270)-A_2]a^6. \tag{26}$$

In the cases for CO and HCl, rigorous solutions for Eq. (24) give imaginary roots for a. However, if we use the value of a which makes the above $F(a)$ minimum $a=-(18k_3/11w_e)$, we have much improved results which are given in the third column of Table 10.

In conclusion, the following remarks can be made. (1) The truncation effect upon the highest order force constant retained in the potential function is in the order of 10—20%, but larger deviations must be tolerated for the hydrogen containing molecules. In the latter, it is preferable to use the FPPF, since the effects of the quintic and hexic force constants to low vibrational levels are not negligible. (2) In order to calculate the rotational constants with accuracies comparable to those attained experimentally, the terms up to $k=6$ should be retained in the rotational Hamiltonian. More terms are necessary for the HCl

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31) R. M. Herman and A. Asgharrian, *J. Chem. Phys.*, **45**, 2433 (1966).

32) P. R. Bunker, *J. Mol. Spectry.*, **35**, 306 (1970).

33) P. M. Morse, *Phys. Rev.*, **34**, 37 (1929).

34) A. S. Coolidge, H. M. Jones, and E. L. Vernon, *Phys. Rev.*, **54**, 726 (1938).

molecule. (3) In the TPPF, use of the minimum number of data seems preferable. When the least-squares fit is carried out, solutions with and without the quartic off-diagonal elements must be considered. The results indicate the error limits for these force constants.

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Appendix

The non-vanishing matrix elements in the harmonic oscillator representation $\langle n|q^k|n-m\rangle$ are listed in Table A-1. The terms from $k=1$ to $k=8$ are included in the table. The matrix element $\langle n|q^k|n+m\rangle$ can be obtained from the corresponding expression for $\langle n|q^k|n-m\rangle$ by replacing n with $n+m$. Note also that $\langle n|q^2+p^2|n\rangle=2n+1$ and $\langle n|q^2+p^2|n+2\rangle=0$.

In Table A-2, non-vanishing matrix elements of $A_{nm}{}^{(i)}$ ($n\leq 10$, $m\leq 10$, and $i\leq 8$) are shown.

TABLE A-1. NON-VANISHING MATRIX ELEMENTS $(n|q^k|n')$

k	n'	$(n\|q^k\|n')$	k	n'	$(n\|q^k\|n')$
1	$n-1$	$(n/2)^{1/2}$	6	$n-4$	$(3/4)(n-3/2)[n(n-1)(n-2)(n-3)]^{1/2}$
2	n	$n+1/2$	6	$n-6$	$(1/8)[n(n-1)(n-2)(n-3)(n-4)(n-5)]^{1/2}$
2	$n-2$	$[n(n-1)]^{1/2}/2$	7	$n-1$	$(35/8)(n^3+2n)(n/2)^{1/2}$
3	$n-1$	$(3/2)n(n/2)^{1/2}$	7	$n-3$	$(21/8)(n^2-2n+2)[n(n-1)(n-2)/2]^{1/2}$
3	$n-3$	$[n(n-1)(n-2)/8]^{1/2}$	7	$n-5$	$(7/8)(n-2)[n(n-1)(n-2)(n-3)(n-4)/2]^{1/2}$
4	n	$(3/2)(n+1/2)^2+(3/8)$	7	$n-7$	$(1/8)[n(n-1)(n-2)(n-3)(n-4)(n-5)$
4	$n-2$	$(n-1/2)[n(n-1)]^{1/2}$			$\times(n-6)/2]^{1/2}$
4	$n-4$	$(1/4)[n(n-1)(n-2)(n-3)]^{1/2}$	8	n	$(35/8)[(n+1/2)^4+(7/2)(n+1/2)^2+(9/16)]$
5	$n-1$	$(5/2)(n/2)^{1/2}(n^2+1/2)$	8	$n-2$	$(7/4)(2n^3-3n^2+7n-3)[n(n-1)]^{1/2}$
5	$n-3$	$(5/4)(n-1)[n(n-1)(n-2)/2]^{1/2}$	8	$n-4$	$(7/8)(2n^2-6n+7)[n(n-1)(n-2)(n-3)]^{1/2}$
5	$n-5$	$(1/4)[n(n-1)(n-2)(n-3)(n-4)/2]^{1/2}$	8	$n-6$	$(1/4)(2n-5)[n(n-1)(n-2)(n-3)(n-4)(n-5)]^{1/2}$
6	n	$(5/2)(n+1/2)^3+(25/8)(n+1/2)$	8	$n-8$	$(1/16)[n(n-1)(n-2)(n-3)(n-4)(n-5)$
6	$n-2$	$(15/8)(n^2-n+1)[n(n-1)]^{1/2}$			$\times(n-6)(n-7)]^{1/2}$

TABLE A-2. NON-VANISHING MATRIX ELEMENTS OF $A_{nm}{}^{(i)}$ ($n\leq 10$, $m\leq 10$, and $i\leq 8$)

n	m	$A_{nm}{}^{(2)}$	$A_{nm}{}^{(4)}$	$A_{nm}{}^{(6)}$	$A_{nm}{}^{(8)}$	n	m	$A_{nm}{}^{(3)}$	$A_{nm}{}^{(5)}$	$A_n{}^{m(7)}$
0	0	0.0	0.0	0.0	0.0	0	1	1.060660	2.651650	9.280777
1	1	1.0	3.0	11.25	52.5	1	2	3.0	11.25	52.5
2	2	2.0	9.0	45.0	262.5	2	3	5.511352	29.08767	176.8225
3	8	3.0	18.0	116.25	840.0	3	4	8.485281	58.33631	445.4773
4	4	4.0	30.0	240.0	2100.0	4	5	11.85854	100.7976	933.8601
5	5	5.0	45.0	431.25	4462.5	5	6	15.58846	158.0496	1727.721
6	6	6.0	63.0	705.0	8452.5	6	7	19.64370	231.5151	2922.001
7	7	7.0	84.0	1076.25	14700.0	7	8	24.0	322.5	4620.0
8	8	8.0	108.0	1560.0	23940.0	8	9	28.63783	432.2190	6932.740
9	9	9.0	135.0	2171.25	37012.5	9	10	33.54102	561.8120	9978.453
10	10	10.0	165.0	2925.0	54862.5					

n	m	$A_{nm}{}^{(4)}$	$A_{nm}{}^{(6)}$	$A_{nm}{}^{(8)}$	n	m	$A_{nm}{}^{(3)}$	$A_{nm}{}^{(5)}$	$A_{nm}{}^{(7)}$
0	2	2.121320	7.954951	37.12311	0	3	0.866025	4.330127	22.73317
1	3	6.123724	32.14955	192.8973	1	4	1.732051	12.99038	90.93267
2	4	12.12436	84.43748	636.5287	2	5	2.738613	27.38613	244.4212
3	5	20.12461	176.0904	1620.0313	3	6	3.872983	48.41229	528.6623
4	6	30.12474	318.3637	3479.4076	4	7	5.123475	76.85213	995.2351
5	7	42.12482	522.5097	6634.6583	5	8	6.480741	113.41296	1701.194
6	8	56.12486	799.7793	11589.784	6	9	7.937254	158.7451	2708.588
7	9	74.12489	1161.4229	18932.784	7	10	9.486833	213.4537	4084.086
8	10	90.12491	1618.6909	29335.659					

n	m	$A_{nm}{}^{(4)}$	$A_{nm}{}^{(6)}$	$A_{nm}{}^{(8)}$	n	m	$A_{nm}{}^{(5)}$	$A_{nm}{}^{(7)}$
0	4	1.224745	9.185587	64.29911	0	5	1.936492	20.33316
1	5	2.738613	28.75543	258.7989	1	6	4.743416	66.40783
2	6	4.743416	64.03613	713.8842	2	7	8.874120	155.2971
3	7	7.245688	119.5538	1597.674	3	8	14.49138	304.3189
4	8	10.24695	199.8155	3120.197	4	9	21.73707	532.5581
5	9	13.74773	309.3239	5538.460	5	10	30.74085	860.7439
6	10	17.74824	452.5801	9131.469				

n	m	$A_{nm}^{(6)}$	$A_{nm}^{(8)}$	n	m	$A_{nm}^{(7)}$	n	m	$A_{nm}^{(8)}$
0	6	3.354102	46.95743	0	7	6.274950	0	8	12.54990
1	7	8.874120	159.7342	1	8	17.74824	1	9	37.64990
2	8	17.74824	390.4613	2	9	37.64970	2	10	84.18729
3	9	30.74085	799.2622	3	10	68.73864			
4	10	40.60556	1458.167						

The terms contributing to zero point energy, *i. e.* $\omega_e/2$, $(3k_4/4)$, $(15\,k_6/8)$, and $(105\,k_8/16)$, are subtracted from the corresponding diagonal matrix elements.