On the Green's Function Approach and the Parametric Study of Force Constants

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A detailed study of the Green's function analysis of the vibrations of substituted and perturbed molecules is made. The similarity in approach of this procedure with the parametric study of force constants is pointed out. The significance of the signs of the different parameters entering the "mixing parameter matrix" is discussed for any nth order case, using the definition of potential energy distribution.

Introduction

In previous papers [1, 2], a critical survey of the method of Green's function analysis for the calculation of force constants [3–6] was made and the similarity of the results obtained using this procedure and those determined by employing the L-Matrix Approximation Method [7, 8] was pointed out. In the earlier works, a correction to the equation for the eigenvector matrix $\boldsymbol{L}$ given in the original references [5, 6] was also indicated.

One of the authors has recently made extensive studies [9, 10] of various molecular constants (potential energy distributions [10a], force constants and compliances [10b–d], mean amplitudes of vibration [10c, d] and Coriolis coupling constants [10c, e]) using parametric representation for $n = 2$ cases. It is the aim of the present work to discuss some aspects of the Green's function approach and to point out the similarities with the parametric study of molecular constants.

Some Aspects of the Green's Function Approach

The Green's function approach provides direct relationship between the vibrations of the parent and the perturbed molecules through the so-called "mixing parameter matrix" (which determines the nature of mixing of different external symmetry coordinates belonging to any irreducible representation in the corresponding normal coordinates) without invoking a force field model (i. e. the equations do not involve the force constants explicitely). In arriving at the transformation from the cartesian to the familiar Wilson's force constant matrix [11], the authors [5] assumed that the mixing parameter matrix $\boldsymbol{A}$ diagonalizes the dynamical matrix $\boldsymbol{D}^{\mathrm{s}}$ (for definition of $\boldsymbol{D}^{\mathrm{s}}$, see Refs. [3] and [5]). However, it is shown below that only $\boldsymbol{A}^{+}$ diagonalizes $\boldsymbol{D}^{\mathrm{s}}$.

Considering the expressions for the potential and the kinetic energies in terms of the cartesian coordinates, one has the following equations:

$$2V = \boldsymbol{X}^{+}\boldsymbol{F}_X\boldsymbol{X}, \tag{1}$$

$$2T = \dot{\boldsymbol{X}}^{+}\boldsymbol{M}\dot{\boldsymbol{X}} \tag{2}$$

where $\boldsymbol{X}$ is a column matrix containing the cartesian coordinates of the N atoms of the molecule ($\boldsymbol{X}^{+}$ is a $1\times 3N$ matrix) $\boldsymbol{F}_X$ the force constant matrix conjugate to the X coordinates ($\boldsymbol{F}_X$ is a symmetric $3N\times 3N$ matrix) and $\boldsymbol{M}$ is a diagonal matrix whose elements are the masses of the N atoms ($\boldsymbol{M}$ is a $3N\times 3N$ matrix). $\dot{\boldsymbol{X}}$ refers to the time derivative of $\boldsymbol{X}$. Using the definition of the dynamical matrix $\boldsymbol{D}$ in the cartesian coordinate system, given by the relation

$$\boldsymbol{D} = \boldsymbol{M}^{-1/2}\boldsymbol{F}_X\boldsymbol{M}^{-1/2} \tag{3}$$

and the mass-weighted cartesian coordinates defined by

$$\boldsymbol{q} = \boldsymbol{M}^{1/2}\boldsymbol{X}. \tag{4}$$

Equation (1) can be simplified to yield:

$$2V = \boldsymbol{X}^{+}\boldsymbol{M}^{1/2}\boldsymbol{D}\boldsymbol{M}^{1/2}\boldsymbol{X} = (\boldsymbol{M}^{1/2}\boldsymbol{X})^{+}\boldsymbol{D}(\boldsymbol{M}^{1/2}\boldsymbol{X}) = \boldsymbol{q}^{+}\boldsymbol{D}\boldsymbol{q}. \tag{5}$$

The mass-weighted cartesian coordinates q_i are linear combinations of the external symmetry coordinates S_i^{E} through the relation:

$$\boldsymbol{q} = \boldsymbol{S}\boldsymbol{S}^{\mathrm{E}}. \tag{6}$$

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Hence Eq. (5) can be rewritten as:

$$2V = (\boldsymbol{S}^{\mathrm{E}})^{+}\boldsymbol{S}^{+}\boldsymbol{D}\,\boldsymbol{S}(\boldsymbol{S}^{\mathrm{E}}) = (\boldsymbol{S}^{\mathrm{E}})^{+}\boldsymbol{D}^{\mathrm{s}}(\boldsymbol{S}^{\mathrm{E}}) = \boldsymbol{Q}^{+}\boldsymbol{\Lambda}\,\boldsymbol{Q} \qquad (7)$$

where Q_i are the normal coordinates and Λ_i are the eigenvalues (proportional to the spectral frequencies and comparing the six zero values which correspond to translations and rotations of the molecule; for linear molecules the rotational degrees of freedom are limited to two). In a similar way, Eq. (2) can be rewritten in the form:

$$2T = (\dot{\boldsymbol{S}}^{\mathrm{E}})^{+}\boldsymbol{I}(\dot{\boldsymbol{S}}^{\mathrm{E}}) = (\dot{\boldsymbol{Q}})^{+}\boldsymbol{I}(\dot{\boldsymbol{Q}}) \qquad (8)$$

where $\boldsymbol{I}$ is the $(3N \times 3N)$ identity matrix. Use of the relation (see Ref. [3])

$$\boldsymbol{A}\,\boldsymbol{S}^{\mathrm{E}} = \boldsymbol{Q} \qquad (9)$$

in Eq. (7) leads to the equation

$$(\boldsymbol{S}^{\mathrm{E}})^{+}\boldsymbol{D}^{\mathrm{s}}(\boldsymbol{S}^{\mathrm{E}}) = (\boldsymbol{A}^{+}\boldsymbol{Q})^{+}\boldsymbol{D}^{\mathrm{s}}(\boldsymbol{A}^{+}\boldsymbol{Q}) = \boldsymbol{Q}^{+}\boldsymbol{\Lambda}\,\boldsymbol{Q} \qquad (10)$$

i. e. $$\boldsymbol{Q}^{+}(\boldsymbol{A}\,\boldsymbol{D}^{\mathrm{s}}\,\boldsymbol{A}^{+})\,\boldsymbol{Q} = \boldsymbol{Q}^{+}\boldsymbol{\Lambda}\,\boldsymbol{Q}\,. \qquad (11)$$

In other words, it is seen from Eq. (11) that the following relation holds:

$$\boldsymbol{A}\,\boldsymbol{D}^{\mathrm{s}}\,\boldsymbol{A}^{+} = \boldsymbol{\Lambda}\,. \qquad (12)$$

This implies that the $\boldsymbol{A}^{+}$ matrix diagonalizes $\boldsymbol{D}^{\mathrm{s}}$ to give the eigenvalues $\boldsymbol{\Lambda}$. Equation (12) contrasts with the relation given by the original authors [5], i. e.

$$\boldsymbol{A}^{+}\boldsymbol{D}^{\mathrm{s}}\,\boldsymbol{A} = \boldsymbol{\Lambda}\,. \qquad (13)$$

Except this, all other relations derived by Wolfram and coworkers are correct.

The equality

$$\boldsymbol{B}\,\boldsymbol{B}^{+} = \boldsymbol{G} \qquad (14)$$

comes directly from the definition of $\boldsymbol{B}$ [5, 1-2], i. e.

$$\boldsymbol{B} = (\boldsymbol{U}\,\boldsymbol{C}\,\boldsymbol{S})_{\text{truncated}} \qquad (15)$$

where $\boldsymbol{U}$ is the transformation matrix between the internal symmetry and the internal coordinates and $\boldsymbol{C}$ is the transformation matrix between the internal and the mass-weighted cartesian coordinates. Hence, we get

$$(\boldsymbol{U}\,\boldsymbol{C}\,\boldsymbol{S})_{\text{truncated}}(\boldsymbol{U}\,\boldsymbol{C}\,\boldsymbol{S})^{+} = \boldsymbol{U}\,\boldsymbol{C}\,\boldsymbol{C}^{+}\boldsymbol{U}^{+} = \boldsymbol{U}\,\boldsymbol{g}\,\boldsymbol{U}^{+} = \boldsymbol{G}\,. \qquad (16)$$

Due to a typographical mistake, it was given in Ref. [1] that

$$\boldsymbol{U}\,\boldsymbol{C}(\boldsymbol{U}^{+}\,\boldsymbol{C}^{+}) = \boldsymbol{G}\,. \qquad (17)$$

Some Remarks on $\boldsymbol{A}$ and $\boldsymbol{D}^{\mathrm{s}}$

Some interesting consequences follow from Equations (12). Using the definitions of $\boldsymbol{D}^{\mathrm{s}}$ and $\boldsymbol{D}$ as given in Eqs. (7) and (3) respectively, Eq. (12) can be rewritten as:

$$\boldsymbol{A}(\boldsymbol{S}^{+}\boldsymbol{D}\,\boldsymbol{S})\,\boldsymbol{A}^{+} = \boldsymbol{A}(\boldsymbol{S}^{+}\boldsymbol{M}^{-1/2}\boldsymbol{F}_{X}\boldsymbol{M}^{-1/2}\boldsymbol{S})\,\boldsymbol{A}^{+} = \boldsymbol{\Lambda}\,. \qquad (18)$$

Or, $$(\boldsymbol{S}\,\boldsymbol{A}^{+})^{+}\boldsymbol{D}(\boldsymbol{S}\,\boldsymbol{A}^{+}) = \boldsymbol{\Lambda}\,. \qquad (19)$$

In other words, $\boldsymbol{D}$ is diagonalized by the product matrix $(\boldsymbol{S}\,\boldsymbol{A}^{+})$ to yield the eigenvalues $\boldsymbol{\Lambda}$. Since $\boldsymbol{D}$ is a symmetric matrix, its eigenvector matrix must be orthogonal. A comparison of the product matrix $(\boldsymbol{S}\,\boldsymbol{A}^{+})$ with Eqs. (6) and (9) shows that the eigenvetor matrix of $\boldsymbol{D}$ is the transformation matrix between the mass-weighted cartesian and the normal coordinate. Since the trace of a matrix is unaffected by a similarity transformation, it follows that

$$\mathrm{Tr}\,\boldsymbol{D}^{\mathrm{s}} = \mathrm{Tr}\,\boldsymbol{\Lambda} = \sum_{i=1}^{3N}\Lambda_i\,. \qquad (20)$$

A similar relationship exists between (Det. $\boldsymbol{D}^{\mathrm{s}}$) and the product of the quantities related to the frequencies. Further, since $\boldsymbol{D}^{\mathrm{s}}$ and $\boldsymbol{D}$ are related to each other by a similarity transformation, Eq. (20) holds for the matrix $\boldsymbol{D}$ also.

It is possible to obtain an approximate relationship between the "mixing parameter matrix" and the isotope shift $(\Delta\lambda/\lambda)$ for heavy atom substitution using the first order perturbation theory. Equation (12) for an isotopic molecule would read:

$$\boldsymbol{A}(\boldsymbol{D}^{\mathrm{s}} + \boldsymbol{\Delta}\boldsymbol{D}^{\mathrm{s}})\,\boldsymbol{A}^{+} = \boldsymbol{\Lambda} + \boldsymbol{\Delta}\boldsymbol{\Lambda}\,. \qquad (21)$$

Expanding Eq. (21) and making use of Eq. (12), one obtains:

$$\boldsymbol{A}\,\boldsymbol{\Delta}\boldsymbol{D}^{\mathrm{s}}\,\boldsymbol{A}^{+} = \boldsymbol{\Delta}\boldsymbol{\Lambda} \qquad (22)$$

where

$$\boldsymbol{\Delta}\boldsymbol{D}^{\mathrm{s}} = \boldsymbol{K} + \boldsymbol{K}^{+} \quad \text{with} \quad \boldsymbol{K} = \boldsymbol{M}^{-1/2}\boldsymbol{F}_{X}\cdot\boldsymbol{\Delta}(\boldsymbol{M}^{-1/2}).$$

The more widely used parameter $(\Delta\lambda/\lambda)$ is thus related to the "mixing parameter matrix" $\boldsymbol{A}$ through the approximate equation:

$$\boldsymbol{A}\,\boldsymbol{\Delta}\boldsymbol{D}^{\mathrm{s}}(\boldsymbol{D}^{\mathrm{s}})^{-1}\,\boldsymbol{A}^{+} = \boldsymbol{\Delta}\boldsymbol{\Lambda}\,\boldsymbol{\Lambda}^{-1}. \qquad (23)$$

It is interesting to explore whether the Green's function approach has any decisive advantage over the conventional methods of determining the force constants and other related molecular constants. As indicated in our earlier work [2], the various molecular

constants can be determined using the Green's function procedure, when once the $\boldsymbol{A}$ matrix has been constructed. It is evident from Eq. (13) that a one to one correspondence exists between $\boldsymbol{D}^s$ and $\boldsymbol{A}$. In other words, the mixing parameter matrix can be easily generated if $\boldsymbol{D}^s$ is known. The matrix $\boldsymbol{D}^s$ can in turn be constructed, if the cartesian force constant matrix $\boldsymbol{F}_X$ is known. The elements of $\boldsymbol{F}_X$ are linear functions of the Wilson's internal force constants. Hence, it is clear that whatever ambiguities or difficulties are present in the conventional methods (in determining the internal force constants), they are encountered in the Green's function procedure also.

Comparison between the Green's Function Procedure and the Parametric Study of Force Constants

It was already pointed out in our earlier papers [1, 2] that in many quadratic cases, the $\boldsymbol{B}$ matrix is essentially identical with the $\boldsymbol{L}_a$ matrix obtained using the $\boldsymbol{L}$-matrix approximation method [7, 8]. In such cases, the following relation was shown to be valid:

$$\boldsymbol{L} = \boldsymbol{L}_a \boldsymbol{A}^+ \tag{24}$$

where $\boldsymbol{L}_a$ is defined by

$$\left.\begin{matrix}(\boldsymbol{L}_a)_{ij} = 0 \\ \lambda_j < \lambda_i\end{matrix}\right\} \text{ if } i < j\,. \tag{25}$$

In deriving this relation [Eq. (24)], the triviality in the signs of the diagonal $\boldsymbol{L}$-matrix elements was not mentioned. In a more general form, Eq. (24) would read as:

$$\boldsymbol{L} = \boldsymbol{L}_a^p \, \boldsymbol{\varepsilon} \, \boldsymbol{A}^+ \tag{26}$$

where $\boldsymbol{L}_a^p$ refers to the $\boldsymbol{L}$ matrix lower triangular in nature with positive diagonal elements and $\boldsymbol{\varepsilon}$ is any one of the 2^n diagonal matrices with elements equal to ± 1. It should be pointed out that the results obtained using $\boldsymbol{L}_a$ and $\boldsymbol{L}_a^p$ for the force constants, compliance, mean amplitudes of vibration and potential energy distribution are identical [12]. A given $\boldsymbol{\varepsilon}$ matrix fixes the sign of the elements of any one column of the $\boldsymbol{L}$ matrix and hence, the sign of the off-diagonal elements of the Coriolis coupling constant matrix is determined by the sign of the different elements in the diagonal $\boldsymbol{\varepsilon}$ matrix. Consequently, one has the relation

$$\zeta_{ij}(\boldsymbol{L}_a) = \varepsilon_i \varepsilon_j \zeta_{ij}(\boldsymbol{L}_a^p)\,. \tag{27}$$

Taking into account the fact that $\boldsymbol{L}_a^p$ is the matrix used in the parametric study of molecular constants [9, 10], the $\boldsymbol{L}$ matrix for a general quadratic ($n = 2$) case may be written as:

$$\boldsymbol{L} = \begin{bmatrix} (G_{11})^{1/2} & 0 \\ 0 & (G_{22})^{1/2} \end{bmatrix} \begin{bmatrix} 1 & 0 \\ -\sin 2\psi & \cos 2\psi \end{bmatrix} \cdot \begin{bmatrix} \varepsilon_1 & 0 \\ 0 & \varepsilon_2 \end{bmatrix} \begin{bmatrix} A_{11} & A_{21} \\ A_{12} & A_{22} \end{bmatrix} \tag{28}$$

where

$$\sin 2\psi = -G_{12}/(G_{11} G_{12})^{1/2} \tag{29}$$

is the coefficient of molecular kinematic coupling [9].

The parametrized $\boldsymbol{A}$ matrix can be written as:

$$A(\alpha) = \begin{bmatrix} \cos\alpha & -\sin\alpha \\ \sin\alpha & \cos\alpha \end{bmatrix}. \tag{30}$$

Using the definition for the potential energy distribution (PED) given by the equation [9, 10a, b 13, 14]:

$$V_i^{(k)} = \sum_j L_{ik} L_{jk} F_{ij}/\lambda_k = L_{ik}(L^{-1})_{ki} \tag{31}$$

and the $\boldsymbol{L}$ matrix defined by Eqs. (28) and (30), one has the following relations:

$$V_i^{(i)} = (1 + \varepsilon_1 \varepsilon_2 \tan\alpha \tan 2\psi)/(1 + \tan^2\alpha)\,, \tag{32}$$

$$V_k^{(i)} = (1 - \varepsilon_1 \varepsilon_2 \cot\alpha \tan 2\psi)/(1 + \cot^2\alpha)\,. \tag{33}$$

Thus, it is easily seen that the parameter (α) defining the "mixing parameter matrix" is a measure of the molecular coupling.

A convenient form of the "mixing parameter matrix" $\boldsymbol{A}$ is the one defined by Cayley's formula [15–17]:

$$\boldsymbol{A} = (\boldsymbol{I} - \boldsymbol{K})(\boldsymbol{I} + \boldsymbol{K})^{-1} = 2(\boldsymbol{I} + \boldsymbol{K})^{-1} - \boldsymbol{I} \tag{34}$$

where $\boldsymbol{K}$ is an antisymmetric matrix and $\boldsymbol{I}$ is the identity matrix. This form has the advantage that it is applicable for any n-th order problem and the normalization factor is automatically included in the different terms forming the $\boldsymbol{A}$ matrix. This parametric form is similar to the one suggested by Pulay and Török [16, 17] except that they do not use the initial solution corresponding to the $\boldsymbol{L}_a^p$ matrix given by Eq. (25) with positive diagonal elements.

Significance of the Signs of the Different Parameters Entering the Mixing Parameter Matrix $\boldsymbol{A}$

The solution obtained for the $\boldsymbol{A}$ matrix is generally not unique, even for quadratic ($n = 2$) cases. Thus, the Green's function approach yields two sets of $\boldsymbol{A}$ matrices for $n = 2$ cases, both of which are consistent with the observed isotopic shifts for symmetrical substitution, the Coriolis coupling constants

etc. In a majority of cases, it is possible to select the "true set" using intuitive reasoning. The mathematical basis for such ambiguities in the conventional approach of determining the force constants from additional data for $n=2$ cases has been discussed by Hoy et al. [18]. As a possibility of resolving this ambiguity, these authors [18] suggested the use of data on asymmetric isotopic substitution or the bonded mean amplitude of vibration. In this section, we discuss some physical significance of the signs of the different parameters entering the antisymmetric $\boldsymbol{K}$ which in turn defines the "mixing parameter matrix" $\boldsymbol{A}$ [see Equation (34)].

Using a $\boldsymbol{K}$ matrix of the form

$$\boldsymbol{K}=\begin{bmatrix} 0 & a' \\ -a' & 0 \end{bmatrix}, \tag{35}$$

the $\boldsymbol{A}$ matrix can be written as

$$\boldsymbol{A}=1/k^2\begin{bmatrix} (1-a'^2) & -2a' \\ 2a' & (1-a'^2) \end{bmatrix} \tag{36}$$

where $k^2=(1+a'^2)$.

Equation (32) corresponding to PED accordingly takes the form:

$$V_i^{(i)}=(1+\varepsilon_1\varepsilon_2 a_1\tan 2\psi)/(1+a_1^2) \tag{37}$$

where $a_1=2a'/(1-a'^2)$. The value of the parameter a' is small if proper correspondence between the external symetry coordinates and the corresponing normal coordinates is made (i. e. when the fact that the contribution of S_i^{E} to Q_i is predominant is taken into account). It becomes then evident that the constraint [9, 10a]:

$$0<V_i^{(i)}<1 \tag{38}$$

would in cases when $\tan 2\psi$ is greater than a' imply that the sign of $(\varepsilon_1\varepsilon_2 a')$ is opposite to that of $\tan 2\psi$ and in short to that of $-G_{12}$ (see Ref. [19] for some other consequences of this fact). Since the rows and columns of the PED matrix defined by Eq. (31) add up to unity, it is also clear that Eq. (38) would mean that $V_k^{(i)}$ should in this case be positive and has a value which lies between 0 and 1. In order to see how good the constraint defined by Eq. (38) holds in $n=2$ cases, we have tabulated the PED results obtained from accurate force constants in Table 1.

Considering the convenient form of the $\boldsymbol{G}$ matrix [10d, e]:

$$\boldsymbol{G}=\boldsymbol{\sigma}\,\boldsymbol{G}^{\mathrm{N}}\,\boldsymbol{\sigma} \tag{39}$$

$$\boldsymbol{G}^{\mathrm{N}}=\begin{bmatrix} 1 & -\sin 2\psi_{12} & -\sin 2\psi_{13}\ldots & -\sin 2\psi_{1n} \\ & 1 & -\sin 2\psi_{23}\ldots & -\sin 2\psi_{2n} \\ \text{Symmetric} & & & 1 \end{bmatrix} \tag{40}$$

and $\sigma_{ij}=\delta_{ij}(G_{ii})^{1/2}$, it is possible to extend the arguments presented in the previous paragraph regarding the significance of the sign of the parameters entering the antisymmetric matrix $\boldsymbol{K}$ to any n-th order problem. The fulfilment of Eq. (38) in this instance would imply the condition:

$$\varepsilon_i\varepsilon_j a_{ij}\sin 2\psi_{ij}<0 \tag{41}$$

where

$$\boldsymbol{K}=\begin{bmatrix} 0 & a_{12} & \ldots & a_{1n} \\ -a_{12} & 0 & \ldots & a_{2n} \\ -a_{1n} & & \ldots & 0 \end{bmatrix} \tag{42}$$

and $\sin 2\psi_{ij}=-G_{ij}/(G_{ii}G_{jj})^{1/2}$. The elements ε_i are defined by the relation:

$$\boldsymbol{B}=\boldsymbol{B}^{\mathrm{p}}\,\boldsymbol{\varepsilon} \tag{43}$$

where $\boldsymbol{B}^{\mathrm{p}}$ is the $\boldsymbol{B}$ matrix defined in Eq. (15) with all positive diagonal elements.

Discussion and Conclusion

An attempt has been made in this work to clarify some aspects of the Green's function approach. It is

Table 1. Potential energy distribution (PED) calculated using accurate force constants for some XY_n type molecules [a].

Molecule	Nature of Frequence Values Used	Potential Energy Distribution $V_i^{(i)}$	$V_k^{(i)}=V_i^{(k)}$
$Os^{16}O_4$	Harmonic	1.00	0.00
$Ru^{16}O_4$	Harmonic	0.99	0.01
$^{92}MoO_4^{2-}$	Anharmonic	0.99	0.01
$^{92}MoS_4^{2-}$	Anharmonic	0.96	0.04
$Si^{35}Cl_4$	Anharmonic	0.95	0.05
$GeCl_4$	Anharmonic	1.00	0.00
$^{116}SnCl_4$	Anharmonic	1.03	−0.03
$^{32}SF_6$	Anharmonic	0.92	0.08
$^{10}BF_3$	Anharmonic	0.94	0.06
$^{14}NF_3$ (A_1 Species)	Anharmonic	0.62	0.38
$^{14}NF_3$ (E Species Set I) [b]	Anharmonic	0.85	0.15
(E Species Set II) [b]	Anharmonic	0.32	0.68

[a] The references for the accurate force constants and the vibrational frequencies for all molecules except $GeCl_4$ can be found in the work: A. Müller, K. H. Schmidt, and N. Mohan, J. Chem. Phys. **57**, 1752 [19972]; while for $GeCl_4$, the corresponding quantities may be found in the work: R. Kebabcioglu, A. Müller, C. J. Peacock, and L. Lange, Z. Naturforsch. **23 a**, 703 [1968].

[b] Two sets of force constants satisfying all the input data used (i.e. isotope shift for $^{14}N-^{15}N$ substitution, Coriolis coupling constants and the rotational distortion constants) are cited in the work of: A. Allan, J. L. Duncan, J. H. Holloway, and D. C. McKean, J. Mol. Spectrosc. **31**, 368 [1969].

shown that the Green's function method has no decisive advantage over the conventional methods. A comparison of this approach with the parametric study is made. The significance of the signs of the different parameters entering the "mixing parameter matrix" is also discussed. As seen from the numerical results presented in Table 1, the constraint implied in Eq. (38) is valid in all cases except for $SnCl_4$. In recent years, the use of cartesian force constants has been recommended [20, 21], since the usual redundancy conditions encountered in the "internal coordinate" formalism can be avoided. Specific potentials models have been suggested [20] to set up the force constants in the cartesian coordinate system. The Green's function approach provides one such mathematical basis for relating certain molecular constants such as the isotopic frequency shifts, the Coriolis coupling constants and the rotational distortion constants without involving the force constants explicitly.

Finally, it should be mentioned that not in all cases, the application of the Green's function procedure leads to analytically simple isotopic rules. When one has a molecule of the type XY_nZ_m where $d_{X-Y} \neq d_{X-Z}$ (d being the bond length), the expressions for the different isotopic rules in terms of the "mixing parameters" are in general not simple. This is because, the external symmetry coordinates corresponding to rotations involve the different bond lengths and the normalization condition $(S \cdot S^+_{\text{rotation}}) = 1$ need not lead to the elimination of bond lengths in the expression.

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