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REGULAR ARTICLE

The determination of Wilson–Decius F matrix elements from Cartesian force constants

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Abstract This work presents a new and consistent derivation of a completely general algorithm for the calculation of the **F** matrix of the Wilson–Decius FG method of vibrational analysis from a Cartesian force constant matrix, $\mathbf{F_{CART}}$. The latter is routinely determined using a computer program such as Gaussian03 once a molecular geometry optimization has successfully converged. For a molecule containing NOAT atoms, the total number of degrees of freedom, NA, is equal to 3*NOAT and the number of normal modes of vibration, NVIB, is equal to (NA − 5) or (NA − 6) for, respectively, a linear or a non-linear molecule. If one utilizes NOB internal coordinates to describe the normal vibrations then NOB must be greater than or equal to NVIB. In the former case, NRED (=NOB − NVIB) redundancies, having frequency values of zero, will be included in the solution of the problem. The algorithm utilizes two newly defined matrices, **BIN** and **GIN**, which are determined by the following two relationships: $\mathbf{BIN} = \mathbf{M^{-1}B^tGIN}, \mathbf{GIN} = (\mathbf{D_{NVIB}})(\Gamma_{\mathbf{NVIB}})^{-1}(\mathbf{D_{NVIB}})^{\mathbf{t}}$ where $\mathbf{M^{-1}}$ is a (NA × NA) diagonal matrix containing the inverses of the atomic masses three times each (to account for motions in the *x*, *y* and *z* directions), **B** is the well known (NOB × NA) rectangular matrix of the Wilson–Decius method which defines the transformation from Cartesian to internal coordinates and the superscript "t" indicates that the transpose of the matrix is to be taken. The $\mathbf{D_{NVIB}}$ and $(\mathbf{\Gamma_{NVIB}})^{-1}$ matrices are determined from the diagonalization of the (NOB × NOB) Wilson–Decius **G** matrix: $\mathbf{GD_{NOB}} = \mathbf{D_{NOB}}\Gamma_{\mathbf{NOB}}$ where $\mathbf{D_{NOB}}$ and $\mathbf{\Gamma_{NOB}}$ are the (NOB × NOB) eigenvector and eigenvalue matrices, respectively, of **G** in which the eigenvalues (and their corresponding eigenvectors) have been reorganized from highest to lowest (i.e., zero) magnitude. By this process the eigenvector matrix, $\mathbf{D_{NOB}}$, is then partitioned into two sections representing the symmetry coordinates (the first NVIB columns) and the redundant coordinates (the last NRED columns). The $\mathbf{D_{NVIB}}$ matrix is then defined as the (NOB × NVIB) rectangular portion of $\mathbf{D_{NOB}}$ which corresponds to the symmetry coordinates (that is, the first NVIB columns of $\mathbf{D_{NOB}}$) and $(\mathbf{\Gamma_{NVIB}})^{-1}$ is a (NVIB × NVIB) diagonal matrix composed of the inverses of the non-zero eigenvalues of the **G** matrix arranged from lowest to highest magnitude. With these matrices at hand, it is then possible to calculate the Wilson–Decius **F** matrix with the following transformation: $\mathbf{F} = \mathbf{BIN^tF_{CART}BIN}$. With properly determined **F** and **G** matrices, it is then possible to perform a complete normal coordinate analysis of a molecule whose optimized geometry and Cartesian force constant matrix were originally determined through ab initio or density-functional calculations. The method is completely general and allows for the choice between a set of non-symmetrized internal coordinates, a set of symmetry adapted linear combinations of internal coordinates or a set of symmetry coordinates. The procedure is illustrated, via the Supplementary Material 1, with a number of practical examples. A discussion of the criteria necessary for a proper choice of a set of internal coordinates which may be used for a vibrational analysis is also included in this paper.

Dedicated to Professor Sandor Suhai on the occasion of his 65th birthday and published as part of the Suhai Festschrift Issue.

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1 Introduction

The widespread use of electronic structure computer programs, such as Gaussian03 [1], has enabled chemists and physicists to determine a vast array of molecular and electronic properties. Of particular importance to vibrational analysts has been the ability to calculate the frequencies and atomic displacements of the normal modes of vibration of a molecular species determined at its optimized geometry (sometimes referred as the "equilibrium geometry"). A large collection of papers has grown in the literature over the last decade or two which attests to the excellent agreement between experimental and theoretical results.

The determination of the normal coordinates of vibration and the optimized geometry in the various versions of the Gaussian program is usually performed within a Cartesian coordinate framework. Accordingly, the Cartesian force constant (or Hessian) matrix, $\mathbf{F_{CART}}$, contains the second partial derivatives of the potential, V, with respect to displacements of the atoms in Cartesian coordinates [2]:

$$(\mathrm{F_{CART}})_{ij} = \left(\frac{\partial^2 V}{\partial X_i \partial X_j}\right)_0 \tag{1}$$

where X_i and X_j represent any of the Cartesian displacement coordinates: Δx_1, Δy_1, Δz_1, …, Δz_{NOAT}, and NOAT is the number of atoms in the molecule (see Table 1). Both i and j run over the total number of degrees of freedom; that is:

$$i = 1, \ldots, \mathrm{NA} \tag{2}$$

$$j = 1, \ldots, \mathrm{NA} \tag{3}$$

where NA = 3*NOAT. The subscript "0" in Eq. 1 indicates that the derivatives are evaluated at the equilibrium positions of the atoms, where the first derivatives are zero.

Internal coordinates generated using the Wilson–Decius FG method [3–7] are derived so that rotational and translational modes are eliminated [8–12], leaving purely vibrational atomic motions in which a change of one in the interatomic distance (i.e., a bond stretch in a diatomic molecule) is used as the basis for normalization. Gaussian vibrational analyses, on the other hand, assume a normalization scheme in which Cartesian displacements of one are defined as the unit. In addition, a Schmidt orthogonalization is utilized to generate the NVIB (=NA − 5 for linear molecules or NA − 6 for non-linear molecules; see Table 1) linear combinations of Cartesian displacements which are orthogonal to the five or six rotational and translational vectors. The back-transformation of the Hessian matrix (for a mass-weighted Cartesian basis set) to a force constant matrix appropriate for the coordinates generated by the Schmidt orthogonalization is then a simple similarity transformation (see Eq. 6 of [2]). Unfortunately, the force constants obtained by this method are, in general, incompatible with the kinetic energy terms derived within the Wilson–Decius formulation because of this alternate method of orthonormalization.

Table 1 Definitions of dimensions

Dimension	Definition
NOAT	Number of atoms in the molecule
NA	Total number of degrees of freedom
	3*NOAT
NOB	Number of B matrix elements
	Number of internal coordinates
NVIB	Number of normal modes of vibration
	Number of normal coordinates
	NA − 6 for non-linear molecules
	NA − 5 for linear molecules
NRED	Number of redundant coordinates
	NOB − NVIB

The determination of the back-transformation of the Hessian matrix, which requires the inverse transformation to Wilson's well known **B** matrix, has been addressed by a number of authors. Crawford and Fletcher [12] derived the required $\mathbf{B^{-1}}$ matrix transforming symmetry to Cartesian coordinates by noting that **B** must contain translations and rotations in order to be non-singular and, hence, invertable. Crawford [13] later relabeled the $\mathbf{B^{-1}}$ matrix as **A**, a symbol which has become generally accepted throughout the vibrational literature. Califano [4] also suggested the inclusion of translations and rotations in order to force the **B** matrix to be square and non-singular, presumably with the careful choice of exactly NVIB internal coordinates which would adequately describe the complete set of normal coordinates. Arenas et al. [14] published a method for the transformation of $\mathbf{F_{CART}}$ to $\mathbf{F_{SYM}}$, the force constant matrix for symmetry coordinates. Unfortunately, the derivation included manipulations of the inverses of matrices which were clearly singular. Their justification of the validity of the method was the agreement between the frequencies computed with the two force constant matrices. Collier [15] adopted the previous method but noted the problems inherent in the nature of the Arenas $\mathbf{B^{-1}}$ matrix without further justification. Pulay [16, 17] derived an expression for the transformation of the harmonic components of the Cartesian to internal force constants

which incorporated any one from a set of non-singular matrices similar in form to Wilson's **G** matrix. He noted that an infinite set of such matrices existed thereby establishing the non-uniqueness of the transformation. Pulay's method was adopted by Lowe et al. [18] who incorporated it into the vibrational programs of McIntosh and Peterson [19]. A thorough treatment of the **A** matrix was derived by Winnewisser et al. [20, 21] who also showed that there were an infinite number of choices for **A** and that the inclusion of additional constraints through the use of the Eckart conditions [9] led to Crawford's expression for **A**. Murphy [22] also derived **A** for use in the determination of $\mathbf{F_{SYM}}$ in his suite of computer programs for vibrational force field calculations. Hoy et al. [23] approached the determination of anharmonic force constants through a complete redefinition of the types of internal coordinates used. In their method, curvilinear coordinates were defined and utilized in place of the rectilinear coordinates employed in the Wilson–Decius technique. Their procedure incorporated Polo's technique [24] for the determination of the $\mathbf{G^{-1}}$ and **A** matrices through the utilization of symmetrized combinations of the curvilinear coordinates.

The following account is a presentation of a new and completely consistent derivation of an algorithm for obtaining the harmonic components of the force constant (or **F**) matrix elements which are compatible with the Wilson–Decius method of vibrational analysis. Using this method, it is now possible to transform the Hessian ($\mathbf{F_{CART}}$) matrix generated by a Gaussian program into the **F** matrix appropriate for use with a variety of different sets of vibrational coordinates. One may now perform a normal coordinate analysis by choosing between a set of non-symmetrized internal coordinates, a set of symmetry adapted linear combinations of internal coordinates or a set of symmetry coordinates. This procedure has been incorporated into a new computer program, CART [25], which has been designed to be used with the McIntosh-Peterson suite of computer programs [19] for vibrational analysis.

2 Theory

All the dimensions of the matrices discussed in this paper are determined by five parameters basic to vibrational analysis; namely, NOAT, NA, NOB, NVIB and NRED. The definitions of these terms are given in Table 1. For convenience, a complete listing of every matrix and its dimensions is presented in Table 2. The definitions and derivations in subsequent sections will make frequent use of transposed matrices. This is indicated through the use of a superscript "t" on the matrix in question.

Table 2 Dimensions of matrices

Matrix	Number of rows	Number of columns
A	NA	NOB
B	NOB	NA
$\hat{\mathbf{B}}$	NVIB	NA
BIN	NOB	NA
C	NA	NVIB
D	NOB	NOB
$\mathbf{D_{NOB}}$	NOB	NOB
$\mathbf{D_{NVIB}}$	NOB	NVIB
$\mathbf{E_{NA}}$	NA	NA
$\mathbf{E_{NOB}}$	NOB	NOB
$\mathbf{E_{NVIB}}$	NVIB	NVIB
M	NA	NA
$\mathbf{M^{-1}}$	NA	NA
F	NOB	NOB
$\hat{\mathbf{F}}$	NVIB	NVIB
$\mathbf{F_{CART}}$	NA	NA
G	NOB	NOB
$\mathbf{G^{-1}}$	NOB	NOB
$\hat{\mathbf{G}}$	NVIB	NVIB
$\hat{\mathbf{G}}^{-1}$	NVIB	NVIB
GIN	NOB	NOB
Γ	NOB	NOB
$\mathbf{\Gamma_{NOB}}$	NOB	NOB
$\mathbf{\Gamma_{NVIB}}$	NVIB	NVIB
ΓIN	NOB	NOB
$\hat{\Gamma}$	NVIB	NVIB
$\hat{\Gamma}^{-1}$	NVIB	NVIB
R	NOB	1
$\hat{\mathbf{S}}$	NVIB	1
$\mathbf{U_{NOB}}$	NOB	NOB
$\mathbf{U_{NVIB}}$	NVIB	NOB
X	NA	1
Y	NA	NOB

2.1 The kinetic and potential energies in Cartesian and internal coordinates

If the matrices (or column vectors) of the Cartesian coordinates and their time derivatives are represented as **X** and $\dot{\mathbf{X}}$ respectively, then the expressions for the total kinetic (T) and potential (V) energies may be written as:

$$2T = \dot{\mathbf{X}}^{\mathbf{t}}\mathbf{M}\dot{\mathbf{X}} \tag{4}$$

$$2V = \mathbf{X}^{\mathbf{t}}\mathbf{F_{CART}}\mathbf{X} \tag{5}$$

where $\mathbf{F_{CART}}$ is a square matrix containing the Cartesian force constants and **M** is a diagonal matrix, in which each atomic mass has been included three times to account for motion in the x, y and z directions.

In the Wilson–Decius formulation, the matrices (or column vectors) of the internal coordinates and their time derivatives are written as $\mathbf{R}$ and $\dot{\mathbf{R}}$, respectively. The total kinetic (T) and potential (V) energies are then determined by the following expressions:

$$2T = \dot{\mathbf{R}}^{\mathbf{t}}\mathbf{G}^{-1}\dot{\mathbf{R}} \tag{6}$$

$$2V = \mathbf{R}^{\mathbf{t}}\mathbf{F}\mathbf{R} \tag{7}$$

where $\mathbf{F}$ and $\mathbf{G}$ are square matrices. $\mathbf{F}$ contains the force constants for the internal coordinates and $\mathbf{G}$, occasionally referred to as the "inverse kinetic energy" matrix, is defined as:

$$\mathbf{G} = \mathbf{B}\mathbf{M}^{-1}\mathbf{B}^{\mathrm{t}} \tag{8}$$

where $\mathbf{M}^{-1}$ is a diagonal matrix, in which the inverse of each atomic mass has been included three times to account, again, for motion in the x, y and z directions. The rectangular $\mathbf{B}$ matrix defines the transformation from Cartesian to internal coordinates by the following relationship:

$$\mathbf{R} = \mathbf{B}\mathbf{X} \tag{9}$$

Derivations of the $\mathbf{B}$ matrix elements are well documented [8] as are examples of the explicit determination of their numerical values [3, 6]. The $\mathbf{G}$ matrix is symmetric about its main diagonal (i.e., $G_{ij} = G_{ji}$) and contains only real elements.[1] This is of critical importance in the determination of symmetry coordinates.

2.2 The transformation of the F to the F_{CART} matrix

This transformation is well known [26] and is easily achieved through the use of Eqs. 7 and 9:

$$\begin{aligned} 2V &= \mathbf{R}^{\mathbf{t}}\mathbf{F}\mathbf{R} \\ &= (\mathbf{B}\mathbf{X})^{\mathbf{t}}\mathbf{F}(\mathbf{B}\mathbf{X}) \\ &= \mathbf{X}^{\mathbf{t}}\mathbf{B}^{\mathbf{t}}\mathbf{F}\mathbf{B}\mathbf{X} \\ &= \mathbf{X}^{\mathbf{t}}(\mathbf{B}^{\mathbf{t}}\mathbf{F}\mathbf{B})\mathbf{X} \\ &= \mathbf{X}^{\mathbf{t}}\mathbf{F}_{\mathbf{CART}}\mathbf{X} \end{aligned} \tag{10}$$

Therefore we may conclude that:

$$\mathbf{F}_{\mathbf{CART}} = \mathbf{B}^{\mathbf{t}}\mathbf{F}\mathbf{B} \tag{11}$$

An illustration of this type of transformation is presented for a diatomic molecule in Example 1 of the Supplementary Material 1.

2.3 The diagonalization of the G matrix and the identification of redundant coordinates

Diagonalization of the $\mathbf{G}$ matrix will produce a set of NOB real eigenvectors and eigenvalues which are defined, respectively, by the $\mathbf{D}$ and $\boldsymbol{\Gamma}$ matrices of the following equation:

$$\mathbf{G}\mathbf{D} = \mathbf{D}\boldsymbol{\Gamma} \tag{12}$$

Since $\mathbf{G}$ is a real, symmetric matrix, the eigenvectors generated by this process will be orthogonal.[2] Accordingly, the $\mathbf{D}$ matrix is generally normalized so that:

$$\mathbf{D}\mathbf{D}^{\mathbf{t}} = \mathbf{D}^{\mathbf{t}}\mathbf{D} = \mathbf{E}_{\mathbf{NOB}} \tag{13}$$

where $\mathbf{E}_{\mathbf{NOB}}$ is the identity matrix of dimension (NOB x NOB). The eigenvalues of $\mathbf{G}$ are contained within the diagonal $\boldsymbol{\Gamma}$ matrix.

The following derivations are greatly facilitated if the eigenvalues, and their corresponding eigenvectors, are reordered from the highest (i.e., most positive) to lowest (i.e., zero) value. The fully reordered $\mathbf{D}$ and $\boldsymbol{\Gamma}$ matrices will henceforth be referred to as $\mathbf{D}_{\mathbf{NOB}}$ and $\boldsymbol{\Gamma}_{\mathbf{NOB}}$. It is then possible to rewrite Eq. 12 as:

$$\mathbf{G}\mathbf{D}_{\mathbf{NOB}} = \mathbf{D}_{\mathbf{NOB}}\boldsymbol{\Gamma}_{\mathbf{NOB}} \tag{14}$$

Since $\mathbf{D}_{\mathbf{NOB}}$ is composed of the same eigenvectors as $\mathbf{D}$, except in a different order, it follows that:

$$(\mathbf{D}_{\mathbf{NOB}})(\mathbf{D}_{\mathbf{NOB}})^{\mathbf{t}} = (\mathbf{D}_{\mathbf{NOB}})^{\mathbf{t}}(\mathbf{D}_{\mathbf{NOB}}) = \mathbf{E}_{\mathbf{NOB}} \tag{15}$$

Moreover, it is possible to right multiply Eq. 14 by $(\mathbf{D}_{\mathbf{NOB}})^{\mathbf{t}}$ to obtain:

$$\mathbf{G} = (\mathbf{D}_{\mathbf{NOB}})\boldsymbol{\Gamma}_{\mathbf{NOB}}(\mathbf{D}_{\mathbf{NOB}})^{\mathbf{t}} \tag{16}$$

In the special case where NOB = NVIB and the set of internal coordinates used to construct the $\mathbf{B}$ matrix includes no redundancies then the $\mathbf{G}$ matrix will be non-singular and may be easily inverted, as rearrangement of Eq. 16 shows:

$$\begin{aligned} \mathbf{G}^{-1} &= \left((\mathbf{D}_{\mathbf{NOB}})\boldsymbol{\Gamma}_{\mathbf{NOB}}(\mathbf{D}_{\mathbf{NOB}})^{\mathbf{t}}\right)^{-1} \\ &= \left((\mathbf{D}_{\mathbf{NOB}})^{\mathbf{t}}\right)^{-1}(\boldsymbol{\Gamma}_{\mathbf{NOB}})^{-1}(\mathbf{D}_{\mathbf{NOB}})^{-1} \\ &= (\mathbf{D}_{\mathbf{NOB}})(\boldsymbol{\Gamma}_{\mathbf{NOB}})^{-1}(\mathbf{D}_{\mathbf{NOB}})^{\mathbf{t}} \end{aligned} \tag{17}$$

For the more common case where NOB > NVIB, the internal coordinate set used for the vibrational analysis must, of necessity, contain redundant coordinates in which case the $\mathbf{G}$ matrix will be singular and, hence, non-invertable.

The method of Gussoni and Zerbi [27] identifies any positive eigenvalue, and its corresponding eigenvector, as one characteristic of a symmetry coordinate whereas zero eigenvalues, and their corresponding eigenvectors, signify redundant coordinates. Thus, the first NVIB columns of $\mathbf{D}_{\mathbf{NOB}}$ and the first NVIB diagonal elements of $\boldsymbol{\Gamma}_{\mathbf{NOB}}$ will be associated with the symmetry coordinates whereas the last NRED (=NOB − NVIB) columns of $\mathbf{D}_{\mathbf{NOB}}$ and the last

[1] See, for example, page 62 of [3].

[2] See, for example, Appendix V of [3].

NRED diagonal elements of $\mathbf{\Gamma_{NOB}}$ will correspond to the redundant coordinates.

It is advantageous to define the (NOB × NVIB) rectangular portion of $\mathbf{D_{NOB}}$ which contains the first NVIB columns as a new matrix, $\mathbf{D_{NVIB}}$. The corresponding (NVIB × NVIB) portion of the eigenvalue matrix will then be defined henceforth as $\mathbf{\Gamma_{NVIB}}$. Both of these new matrices will be associated only with symmetry coordinates. Because of the orthonormal properties of $\mathbf{D_{NOB}}$ (Eq. 15), it is possible to write similar identities for $\mathbf{D_{NVIB}}$:

$$(\mathbf{D_{NVIB}})(\mathbf{D_{NVIB}})^{\mathbf{t}} = \mathbf{E_{NOB}} \tag{18}$$

$$(\mathbf{D_{NVIB}})^{\mathbf{t}}(\mathbf{D_{NVIB}}) = \mathbf{E_{NVIB}} \tag{19}$$

where $\mathbf{E_{NOB}}$ and $\mathbf{E_{NVIB}}$ represent the identity matrix of the dimension (NOB × NOB) and (NVIB × NVIB), respectively.

Example 2 of the Supplementary Material 1 presents an illustration of the generation and diagonalization of the **G** matrix of the diatomic molecule.

2.4 The generation of symmetry coordinates

One may eliminate redundant coordinates through the implementation of a set of NVIB symmetry coordinates, $\hat{\mathbf{S}}$, which are linear combinations of internal coordinates. The superscript "^" on a matrix signifies, henceforth, that it is associated with a set of symmetry coordinates, following the convention of Levin and Pearce [28]. It is convenient, at this point, to define two new matrices which are related to the $\mathbf{D_{NOB}}$ and $\mathbf{D_{NVIB}}$ matrices:

$$\hat{\mathbf{U}}_{\mathbf{NOB}} = (\mathbf{D_{NOB}})^{\mathbf{t}} \tag{20}$$

$$\hat{\mathbf{U}}_{\mathbf{NVIB}} = (\mathbf{D_{NVIB}})^{\mathbf{t}} \tag{21}$$

$\hat{\mathbf{U}}_{\mathbf{NOB}}$ and $\hat{\mathbf{U}}_{\mathbf{NVIB}}$ are, respectively, square and rectangular matrices of dimensions (NOB × NOB) and (NVIB × NOB).

The method of Gussoni and Zerbi [27] also establishes $\hat{\mathbf{U}}_{\mathbf{NVIB}}$ as the matrix which defines the transformation from internal, **R**, to symmetry coordinates, $\hat{\mathbf{S}}$, according to:

$$\hat{\mathbf{S}} = \hat{\mathbf{U}}_{\mathbf{NVIB}}\mathbf{R} \tag{22}$$

Substituting for **R** from Eq. 9, we may also write:

$$\begin{aligned}\hat{\mathbf{S}} &= \hat{\mathbf{U}}_{\mathbf{NVIB}}\mathbf{B}\mathbf{X} \\ &= \hat{\mathbf{B}}\mathbf{X}\end{aligned} \tag{23}$$

Therefore, we may define a new matrix, $\hat{\mathbf{B}}$, which defines the transformation from Cartesian to symmetry coordinates:

$$\hat{\mathbf{B}} = \hat{\mathbf{U}}_{\mathbf{NVIB}}\mathbf{B} \tag{24}$$

Because of the orthonormal nature of the eigenvectors defined by Eqs. 20 and 29, we may write the following useful identities:

$$(\hat{\mathbf{U}}_{\mathbf{NOB}})(\hat{\mathbf{U}}_{\mathbf{NOB}})^{\mathbf{t}} = (\hat{\mathbf{U}}_{\mathbf{NOB}})^{\mathbf{t}}(\hat{\mathbf{U}}_{\mathbf{NOB}}) = \mathbf{E_{NOB}} \tag{25}$$

$$(\hat{\mathbf{U}}_{\mathbf{NVIB}})(\hat{\mathbf{U}}_{\mathbf{NVIB}})^{\mathbf{t}} = \mathbf{E_{NVIB}} \tag{26}$$

$$(\hat{\mathbf{U}}_{\mathbf{NVIB}})^{\mathbf{t}}(\hat{\mathbf{U}}_{\mathbf{NVIB}}) = \mathbf{E_{NOB}} \tag{27}$$

Utilizing the definition of the $\hat{\mathbf{B}}$ matrix in Eq. 24, we may also determine the characteristics of the corresponding $\hat{\mathbf{G}}$ matrix as well.

$$\begin{aligned}\hat{\mathbf{G}} &= \hat{\mathbf{B}}\mathbf{M}^{-1}\hat{\mathbf{B}}^{\mathbf{t}} \\ &= \hat{\mathbf{U}}_{\mathbf{NVIB}}\mathbf{B}\mathbf{M}^{-1}\mathbf{B}^{t}(\hat{\mathbf{U}}_{\mathbf{NVIB}})^{\mathbf{t}} \\ &= (\hat{\mathbf{U}}_{\mathbf{NVIB}})\mathbf{G}(\hat{\mathbf{U}}_{\mathbf{NVIB}})^{\mathbf{t}} \\ &= (\mathbf{D_{NVIB}})^{\mathbf{t}}\mathbf{G}(\mathbf{D_{NVIB}}) \\ &= \mathbf{\Gamma_{NVIB}} \\ &= \hat{\Gamma}\end{aligned} \tag{28}$$

Thus $\hat{\mathbf{G}}$, $\mathbf{\Gamma_{NVIB}}$ and $\hat{\Gamma}$ are identical diagonal matrices containing only the non-zero eigenvalues of **G** arranged in descending order. As a result, all three of these matrices are non-singular and, thus, invertable.

2.5 The transformations from internal and symmetry coordinates to Cartesian coordinates

In order to achieve our final goal of the calculation of the **F** matrix from $\mathbf{F_{CART}}$, we require both matrices which back-transform from internal as well as symmetry coordinates to Cartesian coordinates. These two transformations may be defined by the following equations:

$$\mathbf{X} = \mathbf{A}\mathbf{R} \tag{29}$$

$$\mathbf{X} = \mathbf{C}\hat{\mathbf{S}} \tag{30}$$

The notation **A** appears to have originated with Crawford [13] whereas the use of **C** in Eq. 30 is new to this article. Steele [26] provided an elegant derivation of **A** which, by analogy, may be applied to the determination of **C**. Beginning with Eq. 30, we may write:

$$\begin{aligned}\mathbf{X} &= \mathbf{C}\hat{\mathbf{S}} \\ &= \mathbf{C}\hat{\mathbf{B}}\mathbf{X}\end{aligned} \tag{31}$$

Therefore we may conclude that:

$$\mathbf{C}\hat{\mathbf{B}} = \mathbf{E_{NA}} \tag{32}$$

where $\mathbf{E_{NA}}$ is the identity matrix of dimension (NA × NA). Since:

$$\hat{\mathbf{G}} = \hat{\mathbf{B}}\mathbf{M}^{-1}\hat{\mathbf{B}}^{\mathbf{t}} \tag{33}$$

we may left multiply by **C** to obtain:

$$\begin{aligned}\mathbf{C}\hat{\mathbf{G}} &= \mathbf{C}\hat{\mathbf{B}}\mathbf{M}^{-1}\hat{\mathbf{B}}^{\mathbf{t}} \\ &= \mathbf{M}^{-1}\hat{\mathbf{B}}^{\mathbf{t}}\end{aligned} \tag{34}$$

Upon right multiplication by $\hat{\mathbf{G}}^{-1}$, we have:

$$\begin{aligned}\mathbf{C} &= \mathbf{M}^{-1}\hat{\mathbf{B}}^{\mathbf{t}}\hat{\mathbf{G}}^{-1} \\ &= \mathbf{M}^{-1}\hat{\mathbf{B}}^{\mathbf{t}}\hat{\Gamma}^{-1} \\ &= \mathbf{M}^{-1}\mathbf{B}^{\mathbf{t}}\left(\hat{\mathbf{U}}_{\mathbf{NVIB}}\right)^{\mathbf{t}}\hat{\Gamma}^{-1} \\ &= \mathbf{M}^{-1}\mathbf{B}^{\mathbf{t}}(\mathbf{D}_{\mathbf{NVIB}})(\Gamma_{\mathbf{NVIB}})^{-1} \end{aligned} \tag{35}$$

Equation 35 is very similar to relationships (89) of Levin and Pearce [28], which were derived in a very different manner.

Commutation of the $\mathbf{C}$ and $\hat{\mathbf{B}}$ matrices in Eq. 32 also yields the identity matrix, but of a different dimension:

$$\begin{aligned}\hat{\mathbf{B}}\mathbf{C} &= \hat{\mathbf{B}}\mathbf{M}^{-1}\hat{\mathbf{B}}^{\mathbf{t}}\hat{\Gamma}^{-1} \\ &= \hat{\Gamma}\hat{\Gamma}^{-1} \\ &= \mathbf{E}_{\mathbf{NVIB}} \end{aligned} \tag{36}$$

Since:

$$\hat{\mathbf{S}} = \hat{\mathbf{U}}_{\mathbf{NVIB}}\mathbf{R} = (\mathbf{D}_{\mathbf{NVIB}})^{\mathbf{t}}\mathbf{R} \tag{37}$$

It then follows that:

$$\begin{aligned}\mathbf{X} &= \mathbf{C}\hat{\mathbf{S}} \\ &= \mathbf{M}^{-1}\mathbf{B}^{\mathbf{t}}(\mathbf{D}_{\mathbf{NVIB}})(\Gamma_{\mathbf{NVIB}})^{-1}(\mathbf{D}_{\mathbf{NVIB}})^{\mathbf{t}}\mathbf{R} \end{aligned} \tag{38}$$

In the special case where NVIB = NOB, Eq. 36, upon substitution of the identity in Eq. 17, becomes:

$$\begin{aligned}\mathbf{X} &= \mathbf{M}^{-1}\mathbf{B}^{\mathbf{t}}(\mathbf{D}_{\mathbf{NOB}})(\Gamma_{\mathbf{NOB}})^{-1}(\mathbf{D}_{\mathbf{NOB}})^{\mathbf{t}}\mathbf{R} \\ &= \mathbf{M}^{-1}\mathbf{B}^{\mathbf{t}}\mathbf{G}^{-1}\mathbf{R} \end{aligned} \tag{39}$$

which yields the traditional form of the $\mathbf{A}$ matrix [13, 26]:

$$\mathbf{A} = \mathbf{M}^{-1}\mathbf{B}^{\mathbf{t}}\mathbf{G}^{-1} \tag{40}$$

Using arguments analogous to those shown above, it may be shown that commutation of the $\mathbf{A}$ and $\mathbf{B}$ matrices obey the following two identities:

$$\mathbf{AB} = \mathbf{E}_{\mathbf{NA}} \tag{41}$$

$$\mathbf{BA} = \mathbf{E}_{\mathbf{NOB}} \tag{42}$$

2.6 The transformation of the F_{CART} to the F matrix

We may combine Eqs. 5, 30 and 35 to obtain the transformation of $\mathbf{F}_{\mathbf{CART}}$ to $\hat{\mathbf{F}}$:

$$\begin{aligned}2V &= \mathbf{X}^{\mathbf{t}}\mathbf{F}_{\mathbf{CART}}\mathbf{X} \\ &= (\mathbf{C}\hat{\mathbf{S}})^{\mathbf{t}}\mathbf{F}_{\mathbf{CART}}(\mathbf{C}\hat{\mathbf{S}}) \\ &= \hat{\mathbf{S}}^{\mathbf{t}}\mathbf{C}^{\mathbf{t}}\mathbf{F}_{\mathbf{CART}}\mathbf{C}\hat{\mathbf{S}} \\ &= \hat{\mathbf{S}}^{\mathbf{t}}\left(\mathbf{C}^{\mathbf{t}}\mathbf{F}_{\mathbf{CART}}\mathbf{C}\right)\hat{\mathbf{S}} \\ &= \hat{\mathbf{S}}^{\mathbf{t}}\hat{\mathbf{F}}\hat{\mathbf{S}} \end{aligned} \tag{43}$$

Therefore:

$$\hat{\mathbf{F}} = \mathbf{C}^{\mathbf{t}}\mathbf{F}_{\mathbf{CART}}\mathbf{C} \tag{44}$$

where

$$\mathbf{C} = \mathbf{M}^{-1}\mathbf{B}^{\mathbf{t}}(\mathbf{D}_{\mathbf{NVIB}})(\Gamma_{\mathbf{NVIB}})^{-1} \tag{45}$$

We may now obtain the final transformation by, again, recognizing that since:

$$\hat{\mathbf{S}} = \hat{\mathbf{U}}_{\mathbf{NVIB}}\mathbf{R} = (\mathbf{D}_{\mathbf{NVIB}})^{\mathbf{t}}\mathbf{R} \tag{46}$$

Equation 43 may then be transformed as:

$$\begin{aligned}2V &= \hat{\mathbf{S}}^{\mathbf{t}}\hat{\mathbf{F}}\hat{\mathbf{S}} \\ &= ((\mathbf{D}_{\mathbf{NVIB}})^{\mathbf{t}}\mathbf{R})^{\mathbf{t}}\hat{\mathbf{F}}(\mathbf{D}_{\mathbf{NVIB}})^{\mathbf{t}}\mathbf{R} \\ &= \mathbf{R}^{\mathbf{t}}(\mathbf{D}_{\mathbf{NVIB}})\hat{\mathbf{F}}(\mathbf{D}_{\mathbf{NVIB}})^{\mathbf{t}}\mathbf{R} \\ &= \mathbf{R}^{\mathbf{t}}\mathbf{F}\mathbf{R} \end{aligned} \tag{47}$$

It follows that:

$$\begin{aligned}\mathbf{F} &= (\mathbf{D}_{\mathbf{NVIB}})\hat{\mathbf{F}}(\mathbf{D}_{\mathbf{NVIB}})^{\mathbf{t}} \\ &= (\mathbf{D}_{\mathbf{NVIB}})\mathbf{C}^{\mathbf{t}}\mathbf{F}_{\mathbf{CART}}\mathbf{C}(\mathbf{D}_{\mathbf{NVIB}})^{\mathbf{t}} \\ &= \mathbf{Y}^{\mathbf{t}}\mathbf{F}_{\mathbf{CART}}\mathbf{Y} \end{aligned} \tag{48}$$

where

$$\begin{aligned}\mathbf{Y} &= \mathbf{C}(\mathbf{D}_{\mathbf{NVIB}})^{\mathbf{t}} \\ &= \mathbf{M}^{-1}\mathbf{B}^{\mathbf{t}}(\mathbf{D}_{\mathbf{NVIB}})(\Gamma_{\mathbf{NVIB}})^{-1}(\mathbf{D}_{\mathbf{NVIB}})^{\mathbf{t}} \end{aligned} \tag{49}$$

It is convenient to define two new matrices at this point:

$$\mathbf{GIN} = (\mathbf{D}_{\mathbf{NVIB}})(\Gamma_{\mathbf{NVIB}})^{-1}(\mathbf{D}_{\mathbf{NVIB}})^{\mathbf{t}} \tag{50}$$

$$\mathbf{BIN} = \mathbf{M}^{-1}\mathbf{B}^{\mathbf{t}}\mathbf{GIN} \tag{51}$$

Then the transformation of Eq. 48 may be rewritten in its final form as:

$$\mathbf{F} = \mathbf{BIN}^{\mathbf{t}}\mathbf{F}_{\mathbf{CART}}\mathbf{BIN} \tag{52}$$

Examples of this type of transformation are presented in Examples 3–6 of the Supplementary Material 1.

2.7 The properties of the BIN and GIN matrices

The **GIN** matrix has the same formal structure as the $\mathbf{G}$ matrix. This is easily seen by the expansion of Eq. 50:

$$\mathrm{GIN}_{ij} = \sum_{k=1}^{\mathrm{NVIB}} (\mathrm{D}_{\mathrm{NVIB}})_{ik}(1/\gamma_k)(\mathrm{D}_{\mathrm{NVIB}})_{jk} \quad \begin{matrix} i = 1,\ldots,\mathrm{NOB} \\ j = 1,\ldots,\mathrm{NOB} \end{matrix} \tag{53}$$

where γ_k is the kth diagonal element (or eigenvalue) of the $\mathbf{\Gamma}_{\mathbf{NVIB}}$ matrix. The **GIN** matrix is also a real, symmetric matrix, like $\mathbf{G}$. This is readily apparent by explicit determination of the GIN_{ji} element and comparison with Eq. 53:

$$\mathrm{GIN}_{ji} = \sum_{k=1}^{\mathrm{NVIB}} (\mathrm{D}_{\mathrm{NVIB}})_{jk}(1/\gamma_k)(\mathrm{D}_{\mathrm{NVIB}})_{ik} \quad \begin{matrix} i = 1,\ldots,\mathrm{NOB} \\ j = 1,\ldots,\mathrm{NOB} \end{matrix} \tag{54}$$

In the special case where NOB = NVIB and no redundancies exist within the set of internal coordinates used for the analysis, Eq. 50 is identical with (17). Thus:

$$\mathbf{GIN} = \mathbf{G}^{-1} \quad \text{for NOB} = \text{NVIB} \tag{55}$$

In addition, the **BIN** matrix is identical with the **A** matrix of Eq. 40:

$$\mathbf{BIN} = \mathbf{A} \quad \text{for NOB} = \text{NVIB} \tag{56}$$

and serves as a pseudo "inverse" matrix for **B** (see Eqs. 41 and 42. Thus, the notations used for these two new matrices may be viewed as acronyms of their function.

2.8 The computation of the GIN matrix within the CART program

An alternate, but numerically equivalent, method of calculating the elements of the **GIN** matrix is utilized within the CART computer program; specifically, through the use of the following equation:

$$\mathbf{GIN} = (\mathbf{D_{NOB}})\mathbf{\Gamma IN}(\mathbf{D_{NOB}})^{\mathbf{t}} \tag{57}$$

where **ΓIN** is a diagonal matrix with elements similar to those of $(\mathbf{\Gamma_{NVIB}})^{-1}$, as detailed by the following discussions.

If NOB = NVIB and no redundancies exist within the set of internal coordinates, then $\mathbf{\Gamma_{NOB}}$ contains no zero eigenvalues and, thus, the diagonal elements of **ΓIN** are simply given by:

$$\Gamma\mathrm{IN}_{ii} = (1/\gamma_i) \quad i = 1,\ldots,\mathrm{NOB} \tag{58}$$

In this case, **ΓIN**, $(\mathbf{\Gamma_{NVIB}})^{-1}$ and $(\mathbf{\Gamma_{NOB}})^{-1}$ are identical diagonal matrices. Moreover, Eqs. 17, 50 and 57 are also identical and, ultimately, yield identical **BIN** matrices.

If NOB > NVIB then $\mathbf{\Gamma_{NOB}}$ contains NRED zero elements. Since division by zero is undefined, the diagonal elements of **ΓIN** which would correspond to the NRED zero eigenvalues of $\mathbf{\Gamma_{NOB}}$ are then simply zeroed out themselves. That is:

$$\Gamma\mathrm{IN}_{ii} = (1/\gamma_i) \quad i = 1,\ldots,\mathrm{NVIB} \tag{59}$$

$$\Gamma\mathrm{IN}_{ii} = 0 \quad i = \mathrm{NVIB}+1,\ldots,\mathrm{NOB} \tag{60}$$

This procedure yields matrix elements identical to those derived by Eq. 53. This may be easily demonstrated by expanding Eq. 57:

$$\begin{aligned} \mathrm{GIN}_{ij} &= \sum_{k=1}^{\mathrm{NVIB}} (\mathrm{D}_{\mathrm{NOB}})_{ik}(1/\gamma_k)(\mathrm{D}_{\mathrm{NOB}})_{jk} \\ &\quad + \sum_{k=\mathrm{NVIB}+1}^{\mathrm{NOB}} (\mathrm{D}_{\mathrm{NOB}})_{ik}(0)(\mathrm{D}_{\mathrm{NOB}})_{jk} \\ &= \sum_{k=1}^{\mathrm{NVIB}} (\mathrm{D}_{\mathrm{NOB}})_{ik}(1/\gamma_k)(\mathrm{D}_{\mathrm{NOB}})_{jk} \\ &= \sum_{k=1}^{\mathrm{NVIB}} (\mathrm{D}_{\mathrm{NVIB}})_{ik}(1/\gamma_k)(\mathrm{D}_{\mathrm{NVIB}})_{jk} \quad \begin{matrix} i = 1,\ldots,\mathrm{NOB} \\ j = 1,\ldots,\mathrm{NOB} \end{matrix} \end{aligned} \tag{61}$$

Clearly, Eqs. 53 and 61 are identical.

3 Summary

The calculation of the **F** matrix through the use of Eqs. 50, 51 and 52 clearly depends on the diagonalization of the **G** matrix. Evaluation of the latter, in turn, depends on the choice of internal coordinates to be used in the vibrational analysis. Therefore the successful calculation of the elements of the **F** matrix depends critically on the proper choice of a set of coordinates. For a given molecule, the determination of the majority within this set is usually obvious. However, for very low energy skeletal motions, such as torsions, wags and bends involving heavy atoms, that choice can be problematic and usually requires careful consideration.

A correctly chosen basis set must meet the following three criteria:

(1) Diagonalization of the **G** matrix must generate NVIB non-zero eigenvalues. The number of redundant coordinates, NRED, is then properly calculated as the difference between NOB and NVIB. Failure to meet this most basic requirement demands a reexamination of the basis set elements.

(2) The magnitudes of the smallest non-zero eigenvalues of **G** must be sufficiently large to ensure that the corresponding **F** matrix elements also have the proper absolute value. The generation of unusually small eigenvalues of the **G** matrix will result in the calculation of force constants whose magnitudes are not only too large (to compensate for the abnormally small eigenvalues) but are also usually far outside their normally expected range of values (a useful compendium of bond stretching and angle bending force constants has been given by Wilson, Decius

and Cross[3]). If atomic masses and molecular bond lengths are measured in atomic mass units and Ångstroms, respectively, then eigenvalues with magnitudes smaller than 10^{-5} or 10^{-6} are usually indicative that one or more critically important coordinates have been inadvertently omitted from the analysis. An eigenvalue spectrum exhibiting a reasonable range of positive magnitudes is generally indicative of a well chosen set of internal or symmetry coordinates.

(3) The magnitudes of the primary force constants (that is, the diagonal elements of the **F** matrix) for internal coordinates which are related by symmetry must be identical. Failure to meet this basic requirement is usually an indication that one or more basis set elements have either been incorrectly defined or overlooked in the original set.

A well chosen set of internal or symmetry coordinates will satisfy all three of the requirements elaborated above. Conversely, if a set of coordinates satisfies these criteria then it may be taken as a positive indication that the chosen set is indeed appropriate for a vibrational analysis of the molecule under study.

In summary, the application of the **GIN** and **BIN** matrices to the $\mathbf{F}_{\mathbf{CART}}$ matrix, through Eqs. 50, 51 and 52, yields the **F** matrix for a set of internal coordinates which satisfy the three criteria detailed above. In conjunction with the original **G** matrix, it may be used to generate a complete normal coordinate analysis [3, 5–7] of any discrete molecule with a properly converged Cartesian force field. This is most easily accomplished through the use of the suite of computer programs written by McIntosh and Peterson [19]. Of particular interest within such an analysis, the potential energy distribution (**POT**) matrix, based on the method of Morino and Kuchitsu [29], is invaluable in the assessment of the percentage contributions of each internal coordinate to any given normal coordinate. The new CART computer program has been designed to interface between the BMAT (or UMAT) and ATOM2 programs of the suite mentioned above to facilitate such an analysis [25].

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[3] See Tables 8-1 and 8-2 of [3].

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