IMPLICATION METHODS

FOR THE DETERMINATION OF

QUADRATIC FORCE CONSTANTS

by

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ABSTRACT

Currently the formulation of a valid force constant
matrix poses the largest problem in the normal coordinate
analysis or the mechanical interpretation of vibrational
spectra. Usually a preselected set of trial force constants
is iteratively corrected by means of first order perturbation
theory and the principle of least squares. This thesis
breaks that tradition and operates the normal coordinate
analysis through an implied force constant matrix, $F = L^{-t}\Lambda L^{-1}$,
where $LL^t = G$, the familiar Wilson G-matrix. The Λ-matrix is
composed of the experimental vibrational frequencies for a
selected basis molecule and the L-matrix is parameterized in
a general way. The L-matrix parameters are varied until the
implied force constant matrix generates an optimum mechanical
picture of the basis molecule and its isotopic homologs. How-
ever this thesis emphasizes the vibrational fundamentals of
isotopic homologs in specifying the implied force field.

In application six L-matrix parameters encompass the
sixty-three planar vibrational frequencies of ethylene and its
deuterohomologs with slightly less error than traditional
calculations using as many as fifteen potential energy
parameters. As well, the implied force constants comply with
the existing picture of chemical bonding without deliberate a
priori reference to it. In particular, aspects of the
hybrid orbital force field are confirmed without prior constraints.

In more detailed computational studies the implied force field has revealed a systematic trend in anharmonic effects which can be understood in terms of different vibrational amplitudes for different isotopic homologs. The influence of vibrational amplitude has been parameterized and included within the implication method as a simple anharmonicity correction. For example, one L-matrix parameter and three vibrational amplitude parameters encompass the nine observed vibrational frequencies of water and its deuterohomologs with an average frequency error of 0.4 cm^{-1}. Without amplitude corrections the average frequency error becomes 10.7 cm^{-1} with one L-matrix parameter or 12.8 cm^{-1} with four potential energy parameters. It is particularly significant that this simple picture of anharmonicity employs the observed vibrational frequencies rather that the empirically derived harmonic frequencies. As well, the vibrational amplitude parameters comply with expected features of potential energy surfaces such as the dissociation limit.

The principle advantage of the implication method is that there a fewer L-matrix parameters than F-matrix parameters. The principal disadvantage is that approximations and intuitive notations are not easily built into the implication method. However, as experimental information becomes more complete and better understood, the need for improved analytic foundations dominates the need for handy approximations.

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DEDICATION

to

Professor K. B. Harvey

In Memoriam

CHAPTER ONE: INTRODUCTION

(1-1)   Molecular Structure

Several branches of chemistry meet in the domain of molecular structure; here, chemists see an electronic structure superimposed on a rigid nuclear frame with specified geometry. This picture furnishes a simple basis for understanding chemical activity, for example, in terms of simple molecular orbital theory. Thus, to some extent, all measures of molecular structure belong to every branch of chemistry.

From an interior position, the study of molecular structure joins rigorous physics, abstract mathematics, and experimental information into a self-contained body of knowledge. This joining process, the analysis of molecular structure, should not be viewed as a closed ring of things to do with data and theory. Rather, especially in chemistry, the analysis of molecular structure must contribute to a perview of the topic in a way that encompasses the various contributing branches.

To achieve that objective, the chemist adds an exterior concept to his scheme of analysis. In effect, the chemist expects the parameters of molecular structure to exhibit a reasonable pattern which complies with the basic notions of chemical bonding. Existing studies confirm the expectation.

The electronic structure, when organized into chemical bonds, provides binding energy which is a function of the number of electrons, nuclear charge, and nuclear configuration. Nuclear mass does not significantly influence the binding energy. For stable molecules the binding energy is such that nuclear configuration is constrained to a neighbourhood of minimal potential energy (maximal binding energy).

This picture does not imply a rigid structure. Rather, molecular structures are semirigid geometrical entities embedded within the potential energy surface imposed by the electronic superstructure. The rigidity depends upon the curvature of the surface and the inertial mass of the nuclei.

Consequently, the analysis of molecular structure will involve much more than simple geometry. Further, if chemical bonding is recognized, more than pure physics will appear. In practice, the analysis is sufficiently cumbersome that some mathematical tools which are not part of the physics will enter the picture.

(1-2) Molecular Vibrations

Within limits, molecular vibrations or the variation in configuration is governed by the vibrational secular equations. The usual classical presentation of these

equations (1,2,3) expresses potential and kinetic energy as quadratic forms with translational and rotational kinetic energy removed. A modest quantum mechanical presentation, suitable for teaching purposes can be found in appendix one of this thesis.

The dynamic variables, configuration displacement coordinates, measure the distortion of the molecule from its equilibrium configuration - the point of minimum potential energy.

If these coordinates are defined with chemical bonding in mind, the definition of potential energy becomes greatly simplified in both approximative and interpretive aspects. Clearly bond stretching (an internuclear distance) and valence angle bending will be useful choices.

In the harmonic oscillator approximation, dynamic distortions are assumed to be sufficiently small that potential and kinetic energy can be expressed as quadratic forms in configuration displacement coordinates, ρ_i , and their conjugate momenta, p_i , respectively.

$$\text{kinetic energy} = \tfrac{1}{2} \sum_i \sum_j G_{ij} p_i p_j \tag{1.2.1}$$

$$\text{potential energy} = \tfrac{1}{2} \sum_i \sum_j F_{ij} \rho_i \rho_j \tag{1.2.2}$$

It is not possible to properly justify the kinetic
energy expression in a few lines; see Wilson Decius and
Cross (1) especially their appendix VII, or appendix
one of this thesis for an account of the kinetic energy.

Present purposes require only a clear definition of
the G-matrix elements; these depend only upon the nuclear
masses and the equilibrium geometry of the molecule. All
possible G-matrix elements for bond stretching and
valance angle bending have been tabulated in appendix VI
of Wilson, Decius and Cross (1); otherwise they may be
calculated from the following expression.

$$G_{ij} = \sum_\alpha \mu_\alpha \, (\nabla_\alpha \rho_i) \cdot (\nabla_\alpha \rho_j) \qquad (1.2.3)$$

μ_α is the reciprocal mass of the αth nucleus (or atom)
and ∇_α is the cartesian gradient for the indicated atom.
After the selected configuration coordinates have been
written as functions of the cartesian coordinates of the
individual atoms, the G -matrix follows; however,
considerable labor is involved.

From the outset little is known about the potential
energy except that the concept of chemical bonding is
involved. Currently potential energy is parameterized in
various ways and experimental information is used to

specify the parameters. The principal parameters are the quadratic force constants - the F_{ij}'s (F-matrix) of expression (1.2.2) above.

Of the several types of experimental information dependent on potential energy, fundamental vibrational frequencies have provided the bulk of what is known about potential energy parameters. Quadratic force constants and fundamental vibrational frequencies are related through the vibrational secular equations.

$$L' G L^t = I \qquad \text{the identity matrix (1.2.4)}$$

$$L^t F L = \Lambda \qquad \text{a diagonal matrix (1.2.5)}$$

Here kinetic and potential energy have been simultaneously diagonalized via the transformation

$$\wp_i = \sum_R L_{iR} Q_R \qquad (1.2.6)$$

where the Q_k are normal coordinates. In classical mechanics each normal coordinate is a periodic function of time with period ν_R . (See Wilson, Decius and Cross (1) or appendix one of this thesis for a development with physical substance.)

The diagonal Λ -matrix is related to the various periods (or frequencies) of vibration;

$$\Lambda_{RR} = \left(\nu_R / 1303.1 \right)^2 \tag{1.2.7}$$

where ν_R is the kth vibrational frequency in wavenumber units, potential energy is expressed in millidyne Angstroms, mass is expressed in atomic mass units (carbon-twelve = 12.0000), and distance is measured in Angstroms.

Matrix multiplication of (1.2.4) and (1.2.5),

$$L'GFL = \Lambda$$

shows that the Λ -matrix and the L-matrix are respectively composed of the eigenvalues and eigenvectors of the matrix product GF; consequently the relation connecting potential energy parameters and vibrational frequencies is generally cumbersome.

Usually the relation is described through perturbation techniques (1, 4, 5, 6) like those developed in the following section (1-3), Perturbation Methods. However, the bulk of this thesis seeks to establish an improved understanding of the relation by more abstract methods which are none the less more directly related to the physical problems.

(1-3) <u>Perturbation Methods</u>

In broad outline the calculation of potential energy parameters by perturbation methods involves the variation of preselected parameters until calculated information agrees with experimental information. The information to be fitted includes vibrational frequencies, their symmetry type (1,6), and when known, related mechanical quantities such as mean square amplitudes (7,8), centrifugal distortion constants (8), and Coriolis coefficients (9,10).

In rigorous applications, a given set of parameters span only the experimental information belonging to a series of isotopic homologs; moreover this information should be corrected for anharmonic effects. The work of Aldous and Mills (11) on the methyl halides represents a guidepost in rigorous applications for moderately complex molecules. (In triatomic molecules, rigor may assume meaning well beyond the scope of this thesis; see Suzuki's analysis (12) of carbon dioxide).

When rigor is relaxed, a given set of parameters may span the vibrational frequencies for a series of related molecules. The analysis of the chlorinated benzenes delineated by Scherer (14) as well as the papers of Snyder and Schachtschneider (13,15,16,17) have added substantial credence to this approach - especially when valence force fields are employed. Very briefly, the valence force

field is built on patterns which describe the chemical
bonding structure of the molecule. In this case, the
potential energy function may be assembled from potential
energy parameters belonging to a few simple bonding
units.

The perturbation methods begin with the selection
of potential energy parameters, and some of these must
be assigned nonzero initial values. Neither task should
be considered as trivial (18,19), but both the set of
parameters, ϕ_m , and adequate initial values, ϕ_m^o ,
will be assumed. Aldous and Mills (11) illustrate some
of the problems.

The G-matrix is constructed from geometric information
and the F-matrix is constructed from the parameters.

$$F = F^o + \Sigma_m \left(\partial F / \partial \phi_m \right)^o \left(\phi_m - \phi_m^o \right)$$

The matrix $\left(\partial F / \partial \phi_m \right)$ is a convenient notational device
intended to cover various kinds of parameterization (or
model-building) in quadratic potential energy functions.

First order perturbation theory (1,4,5) provides a
system of linear equations valid for small perturbations.

$$\Lambda_{RR}^o + \Sigma_m \left\{ L_o^t (\partial F / \partial \phi_m)^o L_o \right\}_{RR} (\phi_m - \phi_m^o) = \Lambda_{RR} \quad (1.3.1)$$

where

$$L_o^{-1} GF^o L_o = \Lambda^o$$

F_0^e; L_0 and Λ^0 are constructed from the ϕ^0-parameters either directly or by solving the above vibrational secular equation. (This latter problem, solving the vibrational secular equation by computer methods has been described by Shimanouchi and Suzuki (5). Schachtschneider's technical report (4) provides all relevant details for the application of perturbation methods.)

The expressions (1.3.1) represent one useful linear equation for each secure assignment of an experimental fundamental frequency; clearly more than one molecule may be involved in the set of useful linear equations.

It is assumed that experimental frequencies can be unambiguously assigned to the individual linear equations. Further it is assumed that the number of useful linear equations is larger than the number of potential energy parameters to be determined.

In equation (1.3.1), a perfect fit of experimental frequencies, Λ^e_{RR}, is not expected; consequently the errors, ϵ_R, defined by the identity

$$\Lambda_{RR} = \Lambda^e_{RR} + \epsilon_R$$

are minimized as a weighted sum of squares,

$$\sum_R W_R \epsilon_R^2$$

with respect to the parameter corrections, $\left(\phi_m - \phi_m^0\right)$.

The least squares solution (4,5,6,11),

$$\phi_m = \phi_m^o + \sum_R \left\{ (J^t W J)^{-1} J^t W \right\}_{mR} \left(\Lambda_{RR}^a - \Lambda_{RR}^o \right) \qquad (1.3.2)$$

where $\qquad J_{mR} = \left(L_o^t (\partial F / \partial \phi_m)^o L_o \right)_{RR}$

and W is a diagonal matrix of positive weighting factors, provides improved estimates of the potential energy parameters; however, because higher order perturbation terms have been ignored, the above cycle of calculations requires iteration.

The perturbation method outlined above suffers one major difficulty; both initial and target parameterization must exhibit a satisfactory formulation from the outset.

Quite generally, initial parameterization is oversimplified and target parameterization involves the identification of next-most significant factors. Except (perhaps) for the hybrid orbital force field of Mills (11,20,21,22), the guidelines for ab initio target parameterization are seriously limited; see Aldous and Mills (11).

The validity of initial parameters is readily tested through the calculated vibrational frequencies and normal modes; unfortunately the value of a target parameterization is not easily tested. Schachtschneider's multiple regression analysis (4) has been applied with convincing success; see Gayles, King and Schachtschneider (19).

To understand the results of a faulty target parameterization, let us define simple circumstances for illustrative purposes. Consider three linear equations in two parameters; each linear equation provides a straight line in parameter space (with allowance for error, each line becomes a band or strip). The intersection point(s) of the lines or bands specify the parameters; however a genuinely unique specification need not appear, as is illustrated in cases B and C below.

CASE A   CASE B   CASE C
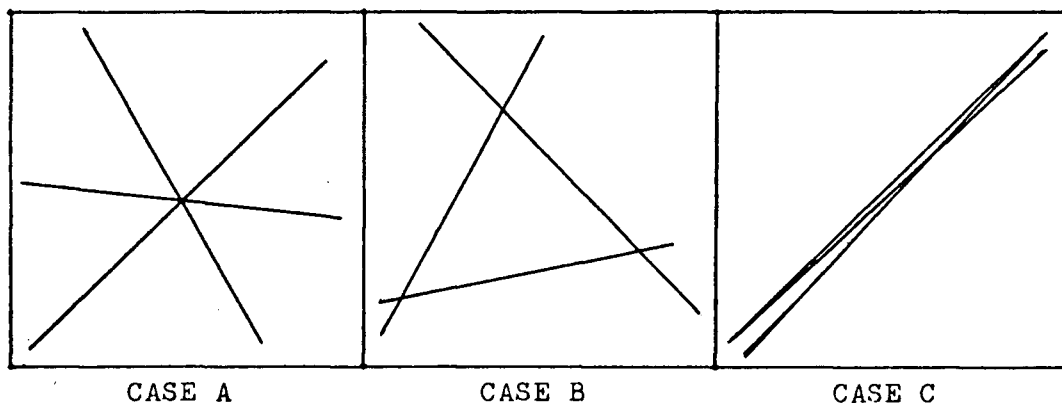
Case A, included for visual reference, indicates a physically significant specification of the parameters; the three lines intersect near a common point.

Case B fails to specify significant parameters; the failure may be due to a poor choice of parameters or it may be due to more deeply rooted effects such as failure of the harmonic oscillator approximation itself.

Here equation (1.3.2) provides a solution with little physical significance. In case B situation, the weighting factors will unduly influence the specification of parameters as has been shown by Nibler and Pimentel (23).

Case C, ill-conditioning, provides no unique solution; with error bands, the three lines become a single hand - the equivalent of one equation. More experimental information may specify a unique solution; thus the parameters need not be incorrectly chosen. However, within the limitations imposed by the given experimental information, the parameterization must be considered faulty.

Both cases B and C fail to provide a unique specification of the parameters, but only case C, ill-conditioning, has received deliberate attention in the literature (5,6,11,24) - probably due to the failure of equations (1.3.2).

In more general examples, similar uniqueness problems will appear but with complications that quickly become less and less tractable.

In short summary, perturbation methods expect more fore-knowledge than is provided by the existing guidelines to chemical bonding.

(1-4) Implication Methods

If the normal coordinates or the L-matrix of equation 1.2.6 were specified by some means, then the complete set of quadratic force constants, the F-matrix would be specified by inversion of equation 1.2.5.

$$F = L^{-t} \Lambda L^{-1} \tag{1.4.1}$$

where Λ is determined by experimental vibrational frequencies. This approach, the basis of implication methods, was noted by William J. Taylor in 1950 (25).

It is the objective of this thesis to devise both rigorous methods and intuitive grounds for specifying the L-matrix.

The implication methods, developed in subsequent chapters, have revealed aspects of potential energy, experimental information, and even geometric details (25) which have not or could not be determined by perturbation methods. These

methods appear to furnish a more definitive tool for the analysis of small molecule information; moreover, implication methods have indicated a fresh approach, partitioning and participation, to the analysis of larger molecules.

Implication methods are not entirely new; Pulay and Torok (27), Freeman (28) and others (29,30,31) have discussed specific forms of the L-matrix which may serve useful purposes. In particular Strey's minimized bending force constants (32) indicate useful initial parameterization, but his technique is limited to simple molecules where initial parameterization is not needed.

Though still in the formative stages, the implied force field obtained by implication methods offers several significant advantages over the parameterized force field obtained by perturbation methods.

(1) Implication methods are constrained to positive definite force constant matrices as required by a minimum in the potential energy surface (3); perturbation methods need not obey this constraint.

(2) The positive definite constraint improves uniqueness in a specification of the force constants.

(3) An improved description of nonuniqueness can be obtained in that the range of possible solutions can be examined.

(4)   Initial parameterization of the potential energy can be helpful, but it is not essential.

(5)   Implication methods help to identify essential force constants when target parameterization is involved.

(6)   The 'mixing parameters' of implication methods are fewer in number than the potential energy parameters of equivalent form.

When applied to the molecules selected in this thesis implication methods have;

(7)   presented a simple account of major anharmonic effects;

(8)   confirmed some aspects of the hybrid orbital force field of Mills (21) without assuming it;

(9)   shown the harmonic bending fundamental of HOD (33) to be inconsistant with respect to the other harmonic fundamentals of water;

(10)   shown geometric distortions to be an important factor in the analysis of solid state spectra (see McQuaker (26) for a description of this application).

However implication methods suffer one serious disadvantage. It is difficult, but not entirely impossible to invoke approximate descriptions involving the principles of chemical bonding. This is a natural feature of the perturbation methods.

CHAPTER TWO: SIMPLE MIXING IMPLICATION METHODS

If point group theory predicts n_k vibrations in the kth symmetry species, then the N_V distinct vibrational frequencies, the N_F distinct quadratic force constants, and the N_L distinct L-matrix elements are numbered as follows (1) :

$$N_V \equiv \sum_k n_k$$

$$N_F \equiv \tfrac{1}{2}\sum_k n_k(n_k+1)$$

$$N_L \equiv \sum_k n_k^2$$

The distinct L-matrix elements are constrained by N_F equations of the form,

$$LL^t = G$$

thus the L-matrix exhibits N_V fewer degrees of freedom than the F-matrix.

$$N_K \equiv N_L - N_F = \tfrac{1}{2}\sum_k n_k(n_k-1) = N_F - N_V$$

The basic hypothesis overlaying this entire thesis is that molecular mechanics can be securely analyzed in terms of the L-matrix belonging to a preselected basis molecule. The

main support for this hypothesis stems from the reduced
number of parameters involved in the mechanical picture.

The quadratic force constants are formed by
implication through the observed vibrational frequencies
and L-matrix belonging to the basis molecule.

$$ F = L^{-t} \Lambda L^{-1} $$

Any mechanical quantity that is a function of the
quadratic force constants is also a function of the L-
matrix belonging to the basis molecule. These related
mechanical quantities include the vibrational frequencies
of isotopic homologs of the basis molecule (1),
centrifugal distortion constants (8), Coriolis coupling
constants (9, 10), and mean square amplitudes of
vibration (7, 8).

In effect the N_V vibrational frequencies of the basis
molecule eliminate N_V parameters from the mechanical picture.
However, the L-matrix, for the basis molecule only, needs
to be expressed in terms of the N_K independent parameters it
contains as will be done in the following section.

The case where $N_K = 1$ has been designated as simple
mixing; here the implication method is somewhat less abstract
than the more general case dealt with in chapter three.

As yet the mechanical picture has been limited to isotopic homologs; here only deuterium substitution provides sufficient information to specify the L-matrix. Other isotopic substitutions appear to have too small an effect on vibrational frequencies to allow a proper interpretation of the mechanical picture by either implication or perturbation methods (34) without the aid of constraints (35) or mechanical information other than vibrational frequencies. However, the isotopic homologs of atoms heavier than deuterium have not been as thoroughly studied by implication methods as the hydrogenic homologs.

The failure of the harmonic oscillator approximation is already known through application of the product rules (1) and many previous force constant calculations. In section two of this chapter, we suggest a novel anharmonicity correction with an apparent physical basis which allows us to use the observed vibrational frequencies with almost as much success as derived harmonic frequencies (2).

The final section of this chapter is given over to calculations involving the simple mixing implication method.

(2-1) The Implied Force Field

When the L-matrix is expressed in the form,

$$L = U \Gamma^{1/2} P \qquad (2.1.1)$$

U and P are orthogonal matrices if Γ is diagonal such that

$$U^t G U = \Gamma \qquad (2.1.2)$$

The P-matrix encompasses exactly the N_K parameters needed to span the family.

Equation (1.2.4) is obeyed for all orthogonal P-matrices.

$$L^{-1} G L^{-t} = P^t \Gamma^{-1/2} U^t G U \Gamma^{-1/2} P = P^t P = I \qquad (2.1.3)$$

But the implied force constant matrix,

$$F = L^{-t} \Lambda L^{-1} = U \Gamma^{-1/2} P \Lambda P^t \Gamma^{-1/2} U^t \qquad (2.1.4)$$

will not exhibit its proper point group symmetry (1) unless the P-matrix exhibits the property:

$P_{ij} = 0$ unless Λ_{ii} and Λ_{jj} designate vibrations belonging to the same symmetry species. (2.1.5)

The proof of this fact depends upon the application of point group theory in molecular vibrations (1). If a molecule exhibits symmetry, there exists a simple orthogonal transformation matrix, S , such that

$$S^t G S = G'$$

and $\quad S^t F S = F'$

where G' and F' are in a block diagonal form consistant with the symmetry of the molecule. Each distinct block belongs to a different symmetry species.

Clearly there exists an orthogonal matrix μ also in block form, such that

$$\mu^t G' \mu = \Gamma$$

Both G and G' have the same eigenvalues (1), and, because both μ and S are orthogonal,

$$U = S\mu$$

Consequently the equal matrices,

$$U^t F U = \mu^t F' \mu = \Gamma^{-\frac{1}{2}} P \Lambda P^t \Gamma^{-\frac{1}{2}}$$

are also in block form consistant with the symmetry of the molecule. Notice the essential block form of the P-matrix.

In combination (2.1.4) and (2.1.5) provide an N_K parameter family of implied force constant matrices if P is not specified. The role of the P-matrix is to mix the Λ_{ii} belonging to the same symmetry species. Here the P-matrix contains N_L elements constrained by N_F conditions of orthogonality. N_K degrees of freedom remain.

In general applications, the family is generated by the orthogonal matrix $\mathcal{C}^K$ where K is a skew symmetric matrix. This will be developed in later chapters.

However when exactly two fundamentals, ν_i and ν_j belong to the same symmetry species, the mixing is simple. In simple mixing the family is generated by a single mixing parameter; here an alegraic form is preferred by the author.

$$P_{ii} = P_{jj} = (1 + x^2)^{-1/2}$$
$$- P_{ji} = P_{ij} = x(1 + x^2)^{-1/2}$$
$$P = I \qquad \text{elsewhere} \qquad (2.1.6)$$

Substitution of (2.1.6) into (2.1.4) gives a one parameter family of force constant matrices generated by the mixing parameter x .

$$F = F^\circ + A \, X(1+X^2)^{-1} + B \, X^2(1+X^2)^{-1}$$

$$F^\circ \equiv U \Gamma^{-1} \Lambda U^t$$

$$A \equiv U \Gamma^{-\frac{1}{2}} a \, \Gamma^{-\frac{1}{2}} U^t$$

$$B \equiv U \Gamma^{-\frac{1}{2}} b \, \Gamma^{-\frac{1}{2}} U^t$$

$$a_{ij} = a_{ji} = \Lambda_{jj} - \Lambda_{ii} \qquad a = 0 \text{ elsewhere}$$

$$-b_{jj} = b_{ii} = \Lambda_{jj} - \Lambda_{ii} \qquad b = 0 \text{ elsewhere} \qquad (2.1.7)$$

If the mathematical formalism of equations (2.1.6) and (2.1.7) were reduced to the form of 2 x 2 matrices, then isotopic homologs of lesser point group symmetry could not be treated by convenient means.

When the mixing fundamentals are degenerate, the P, a and b matrix elements are repeated so as to comply with the degeneracy. As well, the corresponding columns of the U-matrix must be formed into properly oriented linear combinations so that the optimum symmetry factorization is obtained (1).

It has been assumed that each normal coordinate defined by the L-matrix can be assigned an experimental vibrational frequency.

With the implied force constant matrix now expressed in terms of an unspecified mixing parameter, it is possible to calculate the vibrational frequencies of any isotopic homolog of the basis molecule as a function of the mixing parameter.

The corresponding experimental frequencies then specify the mixing parameter and by implication, the force constants. However, various isotopic vibrational frequencies specify various mixing parameters and implied force constants. The range of specified values indicates the error or dispersion to be associated with the implied force constants. These errors are to be associated with the harmonic oscillator approximation rather than the implication method.

(2-2) A Simple Anharmonicity Correction

According to the Born-Oppenheimer approximation potential energy is independent of nuclear mass (2); consequently quadratic (and higher) force constants are considered to be isotopic invariants.

But the harmonic oscillator approximation includes only quadratic force constants and at least one very important feature of the potential energy surface is ignored. All stretching **coordinates** are expected to exhibit a dissociation limit. In this case the potential energy <u>surface</u> is expected to exhibit less-than-quadratic curvature.

Consequently, for isotopic homolog studies within the harmonic oscillator approximation it is natural to associate smaller effective force constants with larger amplitudes of vibration.

The same argument applies to valence angle bending

coordinates as well. One needs to consider the limiting
values of potential energy for large distortions of the
molecule.

We have incorporated these qualitative features of
potential energy into the harmonic oscillator approximation
as follows. The effective quadratic force constants for
different isotopic homologs are related through amplitude
factors, the β's below.

$$\tilde{F}_{ij} \text{ (isotopic homolog)} = \beta_i \beta_j F_{ij} \text{ (basis molecule) (2.2.1)}$$

The β's can be treated as a diagonal matrix.

To a first approximation, a distinct β is needed for
each distinct isotopically substituted coordinate. For water
and its deuterohomologs, only three amplitude factors are
needed:

$$\beta \text{(OD)}, \qquad \beta \text{(HOD) and} \qquad \beta \text{(DOD)}.$$

Here (OD) designates the OD stretching coordinate; (HOD) and
(DOD) designate valence angle bending coordinates.

The amplitude factors are easily calculated via the
determinants of the vibrational secular equations for the isotopic
homologs. The homolog is noted with a tilde.

$$|GF| = |\Lambda| \qquad \text{and} \qquad |\tilde{G}\tilde{F}| = |\tilde{\Lambda}|$$

Here both Λ and $\tilde{\Lambda}$ are composed of experimental vibrational
frequencies. Substitution of (2.2.1) for $\tilde{F}$ gives the simple

equation:

$$|\beta|^2 = \frac{|\tilde{\Lambda}||G|}{|\Lambda||\tilde{G}|}$$

(2.2.2)

Each symmetry species of each isotopic homolog furnishes an equation of the type (2.2.2); it is usually possible to obtain the individual amplitude factors by considering all equations of the type (2.2.2) in combination.

Calculations presented in the following section show that:

(1) Expected trends for less-than-quadratic curvature are confirmed.

(2) A few amplitude factors enable the use of observed frequencies with nearly as much success as the harmonic frequencies (2) which are not generally available.

(3) The bending coordinates contribute almost as much to the anharmonicity as do the stretching coordinates.

(2-3) Applications of Simple Mixing Methods

In our initial work, simple mixing was to be no more than a prologue to general studies; however, simple mixing itself began to grow into a powerful analytic method. The advantage of simple mixing appeared from the outset.

Using perturbation methods Shimanouchi and Suzuki (5) report force constants for the harmonic frequencies of H_2O, HDO, and D_2O determined by Benedict, Gailer and Plyer (33). Unfortunately the symmetric stretching fundamental for D_2O was misprinted. In their calculation Shimanouchi and Suzuki could not detect the rather large misprint error; they use the correct value in a later note (36). This simple oversight is very important; it unambiguously demonstrates the inadequacy of perturbation methods in the analysis of quantitative experimental information.

By contrast, the simple mixing method showed a gross error which proved to be no more than the misprint already noted. Moreover simple mixing methods show that the harmonic bending fundamental of HOD is uniquely inconsistent (see table one). This fact has not been previously noted elsewhere; a minor revision of the anharmonicity constants associated with this vibration is suggested.

Harmonic frequencies are rarely available. A comparison of implied force fields for different basis molecules using the observed frequencies or zero-one transitions, H_2O and D_2O for example, revealed the anharmonicity picture described in the previous section. Calculations will show that zero-one transitions can be used with nearly as much confidence as the harmonic frequencies.

Finally, within our research group, simple mixing methods became sufficiently well understood that molecular distortions in the solid state were explored (26). Usually geometric para-

meters are not investigated by means of vibration spectros-
copy.

Though a substantial number of simple mixing molecules
have been studied with various objectives in mind, the pres-
entation here shall be limited to genuinely new information.
In particular, the anharmonicity picture of the previous section
will be established.

A few preliminary notes and notational devices will
simplify the presentation of the computations.

(1) All frequencies are expressed in cm^{-1}.

(2) A stretching coordinate is designated as (XY) and
the associated bond length as r(XY). Both are in A.

(3) A valence angle bending coordinate is noted as
(XYZ) and is expressed in radian measure. The equilibrium bond
angle, Θ(XYZ), will be expressed in degrees as is usual. Y
designates the central atom.

(4) Force constant units are as follows:

Stretch-stretch	millidynes/ A
Stretch-bend	millidynes/radian
bend-bend	millidyne- A/(radian)^2

(5) Force constants are noted with the appropriate co-
ordinate pair in parentheses and separated by a colon. Common
atoms within the coordinate pair are underlined. Sometimes this
provides a unique notation for all quadratic force constants.

For example, in methane, the stretch-stretch force constants are F(CH:CH) and F(CH:CH), the stretch-bend constants are F(CH:HCH) and F(CH:HCH), and the bend-bend constants are F(HCH:HCH), F(HCH:HCH) and F(HCH:HCH). For diagonal or principal force constants, all atoms are underlined. If some atoms are underlined, the force constant will be said to be connected. If no atoms are underlined, the force constant is unconnected.

This notation devised here saves constant reference to related figures and diagrams; however, it is not yet sufficiently well defined for general usage.

(2-3a) H_2O, HDO and D_2O: Harmonic Fundamentals

Benedict, Gailer, and Plyer (33) have analyzed the vibration-rotation bands for water and its deuterohomologs; the harmonic frequencies were established by empirical methods (2) which involve only experimental data.

For H_2O, the basis molecule, the two symmetric frequencies are

$$\omega_1 = 3832.2$$

$$\omega_2 = 1648.5$$

and the antisymmetric frequency is

$$\omega_3 = 3942.5$$

Analyses of the rotational bands furnish the geometric parameters

$$r(OH) = 0.9572 \text{ Å}$$

$$Cos \; \Theta(HOH) = -0.25210$$

$$\text{or} \quad \Theta(HOH) = 104.6°$$

This information enables us to calculate the quadratic force constants and the harmonic frequencies of the isotopic homologs as a function of the mixing parameter. These quantities were calculated over a large range, but only the interesting portions shall be reported here.

TABLE 1:   Calculated Harmonic Fundamentals: HDO and D_2O.

X	HDO			D_2O*	
0.000	1445.9	2822.7	3888.4	1208.8	2757.3
-0.050	1444.7	2824.1	3889.9	1205.8	2764.3
-0.100	1442.9	2827.2	3890.3	1202.6	2771.5
-0.150	1440.7	2832.0	3889.7	1199.5	2778.7
-0.200	1438.0	2838.4	3888.2	1196.4	2785.8
EXPTL.	1440.2	2824.3	3889.8	1206.4	2763.8**
X=-0.045	1444.8	2824.0	3889.8	1206.1	2763.6
ERROR	-4.6	0.3	0.0	0.3	0.2

* ω_3 for D_2O is not a function of the mixing parameter. The calculated and experimental values agree exactly 2888.8.

**   Misprinted as 2783.8 in (33). See (36).

Of the five fundamentals tabulated in table one, four of the experimental values appear in the domain predicted by a mixing parameter in the following interval.

$$- 0.051 \leq X \leq - 0.037$$

The bending fundamental for HOD sits by itself at $X = -0.156$. It is clearly inconsistent with respect to the remaining fundamentals including those of the basis molecule. Excluding the outlier and including the three basis frequencies, the mean error in fitting the experimental data is 0.1 cm^{-1}. Shimanouchi and Suzuki, who did not detect an outlier, report a mean error 1.3 cm^{-1} (36).

The above interval for the mixing parameter places the implied force constants in the domain specified by table 2.

TABLE 2: Harmonic Force Constants H_2O, HDO, D_2O

force constants	THIS WORK	SHIMANOUCHI and SUZUKI
F(OH:OH)	8.4534 ± 0.0002	8.4522 ± 0.0079
F(OH:OH)	-0.0999 ± 0.0002	-0.1053 ± 0.0079
F(OH:HOH)	0.2276 ± 0.0160	0.1608 ± 0.0606
F(HOH:HOH)	0.6977 ± 0.0016	0.6929 ± 0.0019
Mean frequency error	0.1 cm^{-1}	1.3 cm^{-1}

Though the force constants of Shimanouchi and Suzuki (36) do not substantially differ from the implied force constants of this work, their dispersions do. The larger force constant

dispersions and larger mean frequency error are due to the fact that perturbation methods fail to detect inconsistent data.

The implication method clearly identifies the inconsistent frequency in this case.

(2-3b) $\underline{H_2O, \; HDO, \; D_2O: \quad Observed \; Fundamentals}$

Benedict, Gailer and Plyer (33) have reported the observed fundamentals, zero-one transitions, for H_2O, HDO and D_2O. For H_2O, the basis molecule, the two symmetric frequencies are

$$\nu_1 = 3656.7$$

$$\nu_2 = 1594.6$$

and the antisymmetric fundamental is

$$\nu_3 = 3755.8$$

The bond length and valence angle are as before. Again the fundamental frequencies of HDO and D_2O are calculated as a function of the mixing parameter; however, the corresponding experimental values do not place the mixing parameter in a small interval.

TABLE 3: Calculated Fundamentals: HDO and D_2O

X	HDO			D_2O*	
0.30	1395.1	2718.2	3679.1	1183.7	2599.0
0.20	1398.2	2703.2	3691.9	1179.8	2607.6
0.10	1399.5	2694.0	3101.2	1174.9	2618.5
0.00	1398.6	2691.5	3707.0	1169.3	2631.0
-0.10	1395.7	2695.8	3708.8	1163.3	2644.6
-0.20	1391.0	2706.5	3706.8	1157.3	2658.3
-0.30	1384.9	2722.4	3701.2	1151.6	2671.4
-0.40	1378.1	2742.3	3692.3	1146.5	2683.2
EXPTL.	1402.2	2726.7	3707.5	1178.3	2671.5
X=-0.25	1388.0	2713.9	3704.4	1154.4	2664.9
error (cm^{-1})	14.2	12.8	3.0	23.9	6.6

* ν_3(calculated) = 2752.1 ν_3(exptl.) = 2788.1

Beyond the fact that Table 3 fails to indicate a clearly significant mixing parameter, little can be said except that the errors appear to be systematic in that the bending frequencies fall together at one end of the range and the OD stretching fundamentals fall at the other end. The least squares fit, X= -0.25, gives errors of the same sign.

The implied force constants specified by the interval

$$-0.30 \leq \chi \leq 0.10$$

are poorly defined but comparable to those reported by Shimanouchi and Suzuki (5).

TABLE 4:   Force Constants: H_2O, HDO, D_2O

	Implied (H_2O basis)	Shimanouchi and Suzuki
F(OH:OH)	7.59 ± 0.10	7.67 ± 0.11
F(OH OH)	-0.10 ± 0.10	-0.15 ± 0.11
F(OH:HOH)	0.13 ± 0.66	-0.17 ± 0.42
F(HOH:HOH)	0.70 ± 0.06	0.67 ± 0.04
mean frequency error	10.7 cm^{-1}	12.8 cm^{-1}

The anharmonicity correction described in section two of this chapter improves the calculation by more than one order of magnitude. β(OD) can be calculated from the antisymmetric fundamentals of H_2O and D_2O through equation (2.2.2). Next β(DOD) is calculated from the symmetric frequencies of H_2O and D_2O and β(OD) calculated previously. Finally β(HOD) is calculated from all of the vibrational frequencies of H_2O and HDO. These amplitude factors

$$\beta(OD) = 1.013133$$
$$\beta(DOD) = 1.009937$$
$$\beta(HOD) = 1.002664$$

furnish the force constant trends

$$F\ (\underline{OH}:\underline{OH})\ <\ F(\underline{OD}:\underline{OD})$$

$$F(\underline{HOH}:\underline{HOH})<\ F(\underline{HOD}:\underline{HOD})<\ F(\underline{DOD}:\underline{DOD})$$

which are consistent with less than quadratic curvature for both bending and stretching distortions of water.

When vibrational frequencies are calculated via equation (2.21) as a function of the mixing parameter, the observed frequencies furnish a clear and distinct specification of the mixing parameter and subsequently implied force constants.

TABLE 5:   Calculated Fundamentals with Amplitude Factors HDO and $D_2\underline{O}$.

X	HDO			D_2O*	
0.05	1403.2	2726.8	3704.8	1183.8	2659.0
0.00	1402.4	2726.6	3707.1	1180.9	2665.6
-0.05	1401.1	2728.1	3708.5	1177.9	2672.4
-0.10	1399.4	2731.1	3709.9	1174.9	2679.3
EXPTL.	1402.2	2726.7	3707.5	1178.3	2671.5
X=-0.04	1401.4	2727.8	3708.2	1178.5	2671.0
error	0.8	-1.1	-0.7	-0.2	-0.5

*   The experimental and calculated values for ν_3 agree exactly. These are used to calculate β(OD).

Table Five shows that the mixing parameter falls in the interval

$$-0.05 < X < 0.00$$

which in turn provides implied force constants

$$F(\underline{OH}:\underline{OH}) = 7.681 \pm 0.003$$

$$F(\underline{OH}:\underline{OH}) = -0.080 \pm 0.003$$

$$F(\underline{OH}:H\underline{OH}) = 0.274 \pm 0.063$$

$$F(H\underline{OH}:H\underline{OH}) = 0.663 \pm 0.009$$

$$\text{mean frequency error} = 0.4 \text{ cm}^{-1}$$

In this calculation $F(\underline{OH}:H\underline{OH})$ is clearly positive as predicted by Mills' (21) hybrid orbital force field. Without anharmonicity corrections, the sign of this constant is not clearly defined (see table Four).

(2-3c) HCCH, HCCD, AND DCCD : Observed Fundamentals

According to the symmetry of linear molecules, the longitudinal and transverse modes do not mix in the harmonic oscillator approximation, Here only the longitudinal modes will be considered.

For the basis molecule, HCCH, the two symmetric longitudinal fundamentals have been placed at

$$\nu_1 = 3372.9$$

$$\nu_2 = 1974.0$$

and the antisymmetric fundamental has been placed at

$$\nu_3 = 3285.8$$

These values, and those of the isotopic homologs, were selected
out of the literature by Pimentel and Nibler (23); the combin-
ation, $\nu_2 + \nu_4 + \nu_5$, is very close to ν_3 and reported values for
ν_3 vary to some extent.

Without amplitude factors, the observed fundament-
als of HCCD and DCCD place the mixing parameter in the interval,

$$0.09 < X < 0.16$$

In the interval the minimum errors attainable cover-
age as 10.5 cm^{-1}. This compared with the average error obtained
by Nibler and Pimentel (23) which ranges from 8.2 to 10.1 cm^{-1}
depending on their choice of weighting factors. As well, the
implied force constants agree with their force constants.

The introduction of amplitude factors reduces freq-
uency errors and force constant dispersions by nearly an order of
magnitude; however, amplitude corrections for the nonisotopically
substituted coordinate (CC) are required.

$$\beta (CD) = 1.011654$$

for HCCD $\qquad \beta(CC) = 1.001905$

for DCCD $\qquad \beta(CC) = 1.004785$

Again the trend expected for a potential with a dissociation limit
is obeyed. The effective quadratic force constant decreases with
increasing amplitude.

With these amplitude factors the observed fundamentals

of HCCD and DCCD place the mixing parameter in the interval:

$$0.112 < X < 0.118.$$

The minimum mean frequency error attainable is reduced to 0.9 cm^{-1}.

TABLE 6:   Vibrational Fundamentals: deutero-acetylenes

observed	calculated with	
	No amplitude factors	Amplitude factors
ν_1(HCCD) = 3335.6	3333.1	3333.4
ν_2(HCCD) = 1853.8	1845.5	1855.1
ν_3(HCCD) = 2583.6	2562.4	2583.6
ν_1(DCCD) = 2705.3	2687.4	2708.0
ν_2(DCCD) = 1769.6	1752.6	1768.0
ν_3(DCCD) = 2439.2	2411.1	2439.2
mean frequency error	10.5 cm^{-1}	0.9 cm^{-1}

The implied force constants and their dispersions are given in table Seven along with the force constants calculated via perturbation methods (without anharmonicity corrections) by Nibler and Pimentel (23). Notice that the implied interaction constants are not clearly different from zero but the constants obtained by usual methods indicate, with limited confidence, otherwise for F(CH:CC).

TABLE 7:   Force Constants: Acetylene

	Implied*: HCCH BASIS	NIBLER & PIMENTEL.
F($\underline{CH}$:$\underline{CH}$)	5.920 ± 0.005	5.906 ± 0.043
F(CH:CH)	0.014 ± 0.005	-0.033 ± 0.043
F($\underline{CC}$:$\underline{CC}$)	15.677 ± 0.026	16.066 ± 0.222
F($\underline{CH}$:$\underline{CC}$)	-0.005 ± 0.020	-0.109 ± 0.069
mean frequency error	0.9 cm^{-1}	8.2 cm^{-1}

* The amplitude factors employed here will be found in the pre-
ceding text.

        This calculation shows that anharmonic effects of
the type under consideration need not be confined to nonisotopically
substituted coordinates.   Implication methods confirm this with a
certainty equal to the certainty in the assigned fundamentals.

        To be physically significant, amplitude factors should
be subject to unambiguous interpretation.   The amplitude factors
associated with the (CC) – stretching force constants should not
be interpreted via the amplitude of the (CC) – stretching coordin-
ate.   In acetylene, the amplitude factors which modify F($\underline{CC}$:$\underline{CC}$)
belong more properly to the transverse modes of vibration.

        The appropriate limit to be considered is designated
by large transverse displacements of acetylene.   In this case it
is reasonable to associate a (CC) – double bond with large trans-
verse displacements.   For smaller displacements something less

than triple bond strength can be assumed.
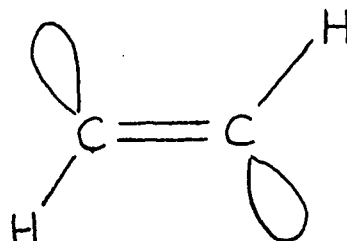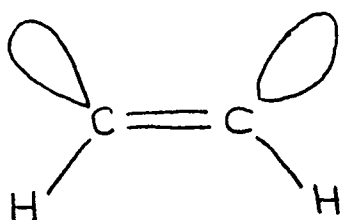
and

Consequently it is plausible to expect $F(\underline{CC}:\underline{CC})$ to decrease as the average transverse displacements increase. The expected trend $F(CC:CC)_{HCCH} < F(\underline{CC}:\underline{CC})_{HCCD} < F(\underline{CC}:\underline{CC})_{DCCD}$ is confirmed by the calculated amplitude factors.

Multiple bond anharmonicity of the kind described here may be expected for the multiple bonds contained in planar molecules. In the planar molecule, the amplitude of the out-of-plane modes will determine the multiple bond amplitude factors.

(2-3d)   Methane and Deuterohomologs: Observed Fundamentals

If the 29 distinct fundamentals of methane and its deuterohomologs can be encompassed by a single mixing parameter and three amplitude factors, $\beta(CD)$, $\beta(HCD)$, and $\beta(DCD)$, then the power of implication methods and the simple picture of anharmonic effects will have withstood a very severe test.

Jones and McDowell (37) have reviewed, measured and assigned the fundamentals of methane and its deuterohomologs. The four fundamentals of CH_4, the basis molecule, are

$$\nu_1(A_1) = 2916.5$$
$$\nu_2(E) = 1534.0$$
$$\nu_3(F_2) = 3018.7$$
$$\nu_4(F_2) = 1306.0$$

Rotational analysis provides the bond length.

$$r\ (CH) = 1.0936\ \overset{o}{A}$$

The tetrahedral symmetry defines the bond angles.

Without amplitude corrections, the 25 observed fundamentals of the four deuterohomologs fail to imply a well defined solution. A least squares solution is included in table eight as a reference for the frequency errors.

β (DCD) was calculated from ν_2 for CH_4 and CD_4. β (CD) was calculated from ν_3 and ν_4 for CH_4 and CD_4. β (HCD) was calualated as an average from the observed fundamentals of the three mixed deuterohomologs (and methane).

$$\beta\,(CD) = 1.01417$$
$$\beta\,(DCD) = 1.00635$$
$$\beta\,(HCD) = 1.00421$$

These amplitude factors resemble those determined for water and they comply with the expected trend.

TABLE 8:   Vibrational Fundamentals: Deuteromethanes

Observed		Calculated	Calculated
CDH_3	1155 (E)	1155	1159
	1300 (A_1)	1303	1306
	1471 (E)	1472	1473
	2200 (A_1)	2185 +	2215 +
	2945 (A_1)	2946	2946
	3021 (E)	<u>3017</u>	<u>3017</u>
mean frequency error		4.0	4.7
CD_2H_2	1033 (A_1)	1026	1032
	1090 (B_1)	1084	1089
	1234 (B_2)	1232	1237
	1329 (A_2)	1329	1334
	1436 (A_1)	1434	1436
	2202 (A_1)	2142 +	2172 +
	2234 (B_2)	2229	2260
	2976 (A_1)	2971	2972
	3013 (B_1)	<u>3016</u>	<u>3016</u>
mean frequency error		10.0	8.1
CD_3H	1003 (A_1)	997	1002
	1036 (E)	1029	1036
	1291 (E)	1289	1295
	2142 (A_1)	2101 +	2131 +
	2263 (E)	2229 +	2259
	2993 (A_1)	<u>2994</u>	<u>2994</u>
mean frequency error		15.2	3.5
CD_4	997 (F_2)	991	997
	1092 (E)	1085	1092
	2108 (A_1)	2063 +	2092 +
	2259 (F_2)	<u>2226</u> +	<u>2258</u>
mean frequency error		22.9	4.3
overall mean frequency error		10.4	4.1

* with amplitude corrections given in the text.

✝ error larger than 10 cm^{-1}.

Comparison of calculated frequencies given in table Eight indicates a substantial reduction in the error following the inclusion of amplitude corrections but not as much as was obtained in the previous examples. Most of the persisting error is contained in the (CD) - stretching frequencies; apparently each homolog needs its own amplitude factor for this coordinate.

A fact more significant than the error reduction is that most of the observed frequencies imply a mixing parameter in a small interval,

$$- 0.18 < X < - 0.24,$$

when the amplitude factors are employed. In turn this mixing parameter interval implies force constants as follows:

$$F(\underline{CH}:\underline{CH}) = 4.966 \pm 0.009$$

$$F(\underline{CH}:\underline{CH}) = 0.028 \pm 0.009$$

$$F(\underline{HCH}:\underline{HCH}) = 0.443 \pm 0.003$$

$$F(\underline{CH}:\underline{HCH}) = 0.104 \pm 0.020$$

$$F(\underline{CH}:\underline{HCH}) = -0.104 \pm 0.020$$

$$F(\underline{HCH}:\underline{HCH}) = -0.093$$

$$F(\underline{HCH}:\underline{HCH}) = -0.072 \pm 0.003$$

The redundant coordinate system employed to describe methane, briefly described as 4(CH) + 6 (HCH), exhibits the symmetry coordinates, $2A_1 + E + 2F_2$ (1). The genuine vibrations are $A_1 + E + 2F_2$; thus two of the A_1 force constants,

$$F(CH:HCH,A_1) = F(\underline{C}H:\underline{H}CH) + F(\underline{C}H:H\underline{C}H)$$

$$F(HCH:HCH,A_1) = F(\underline{H}CH:\underline{H}CH) + 4(H\underline{C}H:H\underline{C}H) + F(H\underline{C}H:HC\underline{H}),$$

are often said to be indeterminate (1, 38, 39). We have reviewed the redundant coordinate system and have added new arguments in favour of the deterministic school of thought (40,41). These arguments (and counter arguments) are collected in appendix two of this thesis where it is shown that both of the force constants in question here are zero. In the present case

$$F(\underline{C}H:\underline{H}CH) = - F(\underline{C}H:H\underline{C}H)$$

which agrees with the hybrid orbital force field proposed by Mills (21).

In simple mixing situations it is possible to express the vibrational frequencies belonging to isotopic homologs of a basis molecule as a function of a single mixing parameter. The corresponding observed frequencies locate the mixing parameter in a specified interval which in turn places the implied force constants in specified intervals.

As shown through the preceding examples, implication methods prove to be a powerful technique for the analysis of experimental information.

CHAPTER THREE: GENERAL MIXING IMPLICATION METHODS

Generalization of the simple mixing method depends on the completion of several tasks.

(1)   The orthogonal P-matrix of equation (2.1.4) must be generalized and parameterized.

(2)   The N_K parameters need to be expressed in terms of related mechanical information such as the vibrational frequencies of isotopic homologs.

(3)   An estimate of error or dispersion within the implied force constants needs to be formulated.

These aspects of the general problem are developed in the following three sections of this chapter; the fourth section is given over to applications.

(3-1) K- Space

The desired parameterization of a generalized orthogonal matrix is achieved by the orthogonal form

$$P = P_o \, e^{K} \qquad\qquad (3.1.1)$$

where P_o is orthogonal and denotes a convenient expansion point. The exponential matrix defined and reviewed in appendix three, is orthogonal when the K-matrix is skew symmetric, $K_{ij} = -K_{ji}$.

The task of determining a useful P_o depends upon useful approximations. This topic is explored in chapter four of this thesis; however, the identity matrix, $P_o = I$ is sometimes

adequate. On substitution of (3.1.1) into (2.1.1), (2.1.4) and (2.1.5), the generalized implication equations are obtained.

$$L = U\Gamma^{-1/2}P_0\mathcal{C}^K \qquad (3.1.2)$$

$$F = U\Gamma^{-1/2}P_0\mathcal{C}^K\Lambda\bar{\mathcal{C}}^K P_0^t\Gamma^{-1/2}U^t \qquad (3.1.3)$$

$$(P_0)_{ij} = K_{ij} = 0 \qquad \text{unless } \Lambda_{ii} \text{ and } \Lambda_{jj} \text{ designate genuine vibrations belonging to the same symmetry species} \qquad (3.1.4)$$

As in the simple mixing case, these equations refer only to a/specified basis molecule with well known vibrational fundamentals. Again, parameters belonging to the basis molecule are developed from related mechanical information, most conveniently the vibrational frequencies of its isotopic homologs.

For present purposes, assume that the matrix,

$$L_0 = U\Gamma^{-1/2}P_0 \qquad (3.1.5),$$

dictates a specified ordering of the Λ - matrix. If symmetry species are identified by experimental means, then the problem is reduced. If qualitative normal coordinates are known then the

problem of ordering the Λ - matrix is solved; however, such knowledge can be aafely assumed only in the case of small or very symmetrical molecules. This problem is studied in greater depth in chapter four.

As noted in chapter two, a K-space expansion contains fewer parameters than the F-space expansion; thus the magnitude of a general force field specification is reduced from the outset.

(3-2) Isotopic Homologs in K-space

The vibrational secular equation for an isotopic homolog can be arranged in a form most suitable for the problem in mind,

$$\tilde{P}^t \Lambda^{1/2} P^t \Gamma^{-1/2} U^t \tilde{G} U \Gamma^{-1/2} P \Lambda^{1/2} \tilde{P} = \tilde{\Lambda} \qquad (3.2.1)$$

where U, Γ, Λ and P belong to the basis molecule and $\tilde{P}, \tilde{G}$ and $\tilde{\Lambda}$ belong to the isotopic homolog. However, $\tilde{P}$ is not related to the isotopic homolog in the same way that $\dot{P}$ is related to the basis molecule. Rather it expresses the isotopic $\tilde{L}$-matrix in terms of the basis L-matrix.

$$\tilde{L} = L \Lambda^{-1/2} \tilde{P} \tilde{\Lambda}^{1/2} \qquad (3.2.1)$$

Equation (3.2.1) can be formulated from the vibrational secular equation in determinant form,

$$\left| \tilde{G} F - \tilde{\lambda} I \right| = 0$$

by substituting (2.1.4) and rearranging to yield

$$\left| \Lambda^{1/2} P^t \Gamma^{-1/2} U^t \widetilde{G} U \Gamma^{-1/2} P \Lambda^{1/2} - \tilde{\lambda} I \right| = 0$$

a contained matrix which is symmetric and diagonalized by an orthogonal $\widetilde{P}$.

A small perturbation in K-space is predicted by the partial derivative

$$\left(\frac{\partial \widetilde{\Lambda}_{RR}}{\partial K_{mn}} \right)_o = 2 \left(\tilde{\Lambda}_o \right)_{RR} \widetilde{P}^o_{nR} \widetilde{P}^o_{mR} \frac{\Lambda_{nn} - \Lambda_{mm}}{\sqrt{\Lambda_{nn} \Lambda_{mm}}} \qquad (3.2.3)$$

where $P = P_o e^K$ furnishes the K-space perturbation and

$$\widetilde{P}^t_o \Lambda^{1/2} P^t_o \Gamma^{-1/2} U^t \widetilde{G} U \Gamma^{-1/2} P_o \Lambda^{1/2} \widetilde{P}_o = \tilde{\Lambda}_o \qquad (3.2.4)$$

represents the expansion point.

Equation (3.2.3) depends on properties of the exponential matrix designated in appendix three.

In application, equations (3.2.3) and (3..2.4) provide the nucleus of an extremely efficient computational scheme. The U-matrix provides automatic symmetry factorization of the G-matrix (see section 1 of chapter two). An equivalent formulation in F-space requires $2N_M$ matrix diagonalizations per isotopic homolog (N_M homologs) or large storage capabilities; the K-space formulation required $N_M - 1$ matrix diagonalizations with partial pre-diagonalization provided by the U-matrix.

What remains is the solution of linear equations of the form

$$\tilde{\Lambda}_{RR} = (\tilde{\Lambda}_0)_{RR} + \sum_{\Lambda_{mm} > \Lambda_{nn}} (\partial \tilde{\Lambda}_{RR} / \partial K_{mn})_0 \, K_{mn} \qquad (3.2.5)$$

which has already been discussed in equations (1.3.1) and (1.3.2). Equation (3.2.5) is a Taylor series expansion of $\tilde{\Lambda}_{RR}$.

Given a sufficient body of experimental information, the K-matrix elements are calculated and the exponential matrix e^K is formed. But higher terms in the expansion of (3.2.1) are ignored; thus the P -matrix is replaced by $P_0 e^K$ and the calculation is iterated until convergence is attained.

(3-3)   Implied Dispersion

In simple mixing, the implication methods provide an easily understood projection scheme for determining the error associated with implied force constants. In general mixing situations, error or dispersion can be established by more general methods.

Consider a force constant matrix, F_0 , such that for a series of isotopic homologs:

$$L_0^t \, F_0 \, L_0 = \Lambda_0 \qquad (3.3.1)$$

the corresponding implied force field

$$F = L_0^{-t} \Lambda L_0^{-1}$$

is composed from the experimental frequencies. The scatter in the

implied force constants for a series of isotopic homologs
defines our measure of implied dispersion.

The dispersion can be concisely expressed in terms
of the maximum frequency error.

$$\Delta = max \, | \nu_R - \nu_R^0 | \tag{3.3.2}$$

$$|F_{ij} - F_{ij}^0| \leq \frac{\Delta}{751} \left(\bar{G}_{ii}^{-1} \right)^{1/2} \left(\bar{F}_{jj}^{0} \right)^{1/2} \tag{3.3.3}$$

and

$$|F_{ij} - F_{ij}^0| \leq \frac{\Delta}{751} \left(\bar{G}_{jj}^{-1} \right)^{1/2} \left(F_{ii}^0 \right)^{1/2} \tag{3.3.4}$$

The proof follows:

$$\left| F_{ij} - F_{ij}^0 \right| = \left| \sum_R \left(\bar{L_0}^{-1} \right)_{Ri} \left(\bar{L_0}^{-1} \right)_{Rj} \left(\Lambda_{RR} - \Lambda_{RR}^0 \right) \right|$$

set: $\Delta_R \equiv \nu_R - \nu_R^0$

where ν_R^0 is calculated and ν_R is experimental.

$$\left| F_{ij} - F_{ij}^0 \right| \cong 2(1303.1)^2 \left| \sum_R \left(\bar{L_0}^{-1} \right)_{Ri} \left(\bar{L_0}^{-1} \right)_{Rj} \Delta_R \nu_R^0 \right|$$

Terms of the order Δ_R^2 are ignored. The Cauchy inequality
(42) provides

$$\left| F_{ij} - F_{ij}^0 \right| \leq \frac{2}{(1303.1)^2} \left(\sum_R \left(\bar{L_0}^{-1} \right)_{Ri}^2 \Delta_R^2 \right)^{1/2} \left(\sum_R \left(\bar{L_0}^{-1} \right)_{Rj}^2 \left(\nu_R^0 \right)^2 \right)^{1/2}$$

All $\Delta_R^2 \lessgtr \Delta^2$ consequently equation (3.3.3) is obtained. Recall

$$\sum_R \left(\bar{L_0}^{-1} \right)_{Ri}^2 = \left(\bar{G}^{-1} \right)_{ii}$$

Polo (43) has written explicit expressions for $\bar{G}^{-1}$ - matrix elements; however exact expressions are not needed to estimate force constant dispersions. Study of Polo's work will justify the following approximate expressions.

For a stretching coordinate:

$$\bar{G}^{-1}_{ss} \leq \frac{M_A M_B}{M_A + M_B}$$

$$M_\delta = \sum_{\alpha \in \delta} m_\alpha$$

where $\delta = A$ or B
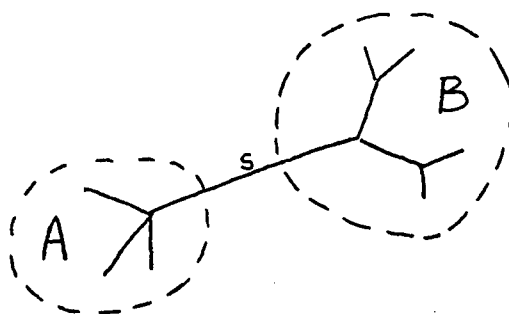
The sets of atoms A and B are disjoint and cover all atoms in the molecule.

For a valence angle bending coordinate:

$$\bar{G}^{-1}_{\theta\theta} \leq \frac{I_A I_B}{I_A + I_B}$$

$$I_\delta = \sum_{\alpha \in \delta} m_\alpha r_\alpha^2$$
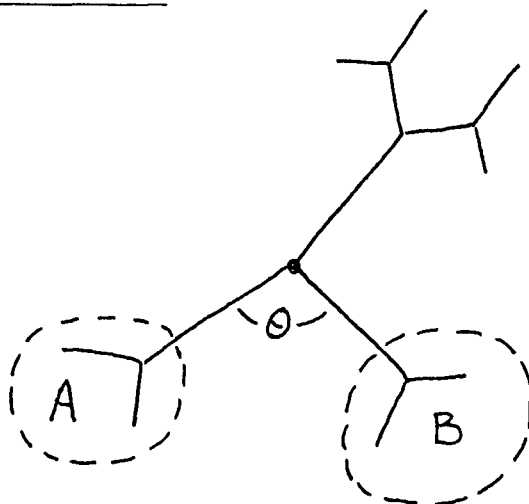
where r_α is the distance from the central atom in the bending coordinate to the $\alpha^{\underline{th}}$ atom. The set A designates all atoms connected to one branch of the angle and B designates all of the atoms connected to the second branch of the angle. Neither set includes the apex atom or atoms belonging to the other branches.

In combination with implied force constants and a frequency error, the approximate inverse G-matrix elements give an estimate of the error or dispersion to be associated with the implied force constants when isotopic frequency information is the determining factor.

The implied dispersions of equations (3.3.2), (3.3.3) and (3.3.4) will not always agree with statistical dispersions calculated by means of the formulation of Overend and Scherer (46). Qualitative agreement between the two sets of dispersions can be expected for the principal force constants, but for some of the off diagonal force constants dispersions will be very significantly different.

Most of the differences are due to the different meaning that the two expressions of dispersion carry. The implied dispersions tell how much the implied force constants must be changed to cover all vibrational frequencies; by contrast, the dispersions of Overend and Scherer tell how much the force constants can be varied without exceeding a specified frequency error.

However the statistical dispersions of Overend and Scherer may in some cases seriously overestimate the dispersion as will be shown by the following argument. Since the potential

energy surface exhibits a minimum the force constant matrix is positive definite (3, 44). In turn, this requires the force constants to obey inequalities of the kind (45).

$$F_{ii} > 0$$

$$F_{ij}^2 < F_{ii} F_{jj} \qquad\qquad (3.3.5)$$

For dichloromethane Shimanouchi and Suzuki (5) report force constants and dispersions calculated by the Overend-Scherer method as follows: (only the magnitude of the numbers is important here.)

$$F_{22} = 3.8 \pm 10.0$$

$$F_{24} = 0.2 \pm 32.1$$

$$F_{44} = 1.3 \pm 23.3$$

Clearly the positive definite rules, equations (3.3.5), cannot be obeyed over the full range of the reported dispersions.

Briefly perturbation methods assume force constants to be independent variables not constrained by the positive definite rules; consequently dispersion can be inflated. By contrast, implied force constants are always positive definite if the Λ-matrix is positive definite (3). In the current context, positive definite means that every distortion from equilibrium configuration generates an increase in potential energy; otherwise equilibrium

configuration would not correspond to a minimum in potential energy.

In summary neither measure of dispersion provides exactly what is wanted. Implied dispersion may be too small but the Overend-Scherer dispersions may be too large. Neither tells how unique the specified force constants are. Continued work in this area will reveal more appropriate measures of significance; the implied force field seems to be more subject to development along the lines of uniqueness.

(3-4)   Selected Applications in K-Space

The interplay of calculation of experimental inform-ation and of the connecting mathematical structure generally influences the development of the mathematical structure in a favorable manner. From the beginning of this project, calculat-ions and mathematical structure were built in parallel. In this way several uninteresting notions were eliminated, and several interesting notions were uncovered.

In the present situation the need for parallel calcul-ations resulted in two limitations. Configuration coordinates were limited to bond stretching and valence angle bending. When isotopic substitution lowers the point group symmetry within a series of isotopic homologs special control mechanisms for degener-ate fundamentals are required for the application of implication methods; these have not yet been included in the general mixing program. In effect, symmetric tops are excluded until a modified edition of the program is written.

A program designed for general application has not yet been written; it awaits the completion of several added tasks. The K-space pictures of centrifugal distortion constants (8), Coriolis coupling coefficients (9, 10), and the mean square amplitudes of electron diffraction experiments (7, 8) need to be developed and cast into the language of automatic computing. Further, the K-space picture awaits the development of various approximation techniques. To some extent, the groundwork for these tasks is established in the following chapter.

Thus **far** only the vibrational fundamentals of isotopic homologs - as a means to specify the implied force field - have been discussed. Of three isotopic series studied,

a) formaldehyde and its deuterohomologs

b) ethylene and its deuterohomologs

c) dichloromethane and its deuterohomologs,

only formaldehyde and ethylene specify well defined implied force fields of the most general quadratic form. As could be expected in dichloromethane, the mixing of ν (CCl, A_1) and ν(ClCCl, A_1) is not specified by the vibrations of the deuterohomologs. Perturbation methods also fail to specify a general force field for dichloromethane as has been shown by Shimanouchi and Suzuki (5)

Though a complete mechanical picture of implication methods is not yet available, the present calculations demonstrate the effectiveness of more general implication methods. The calculations for formaldehyde and ethylene illustrate the positive cases.

In the case of dichloromethane, calculations will not be presented; here it is important that implication methods do not indicate uniqueness when the experimental information employed does not provide it. Several distinctly different force fields which provided very small frequency errors were determined for dichloromethane; additional experimental information must be included to specify a single force field.

(3-4a) Formaldehyde and its Deuterohomologs

Shimanouchi and Suzuki (5) have reviewed the fundamentals of formaldehyde and its Deuterohomologs and calculated the general quadratic force constants. Their carefully executed perturbation study forms a reference for comparison with the implication method.

The in-plane normal coordinates of the C_{2V} molecules, briefly represented in the form $3A_1 + 2B_1$ (see footnote), indicate nine quadratic force constants but only four mixing parameters. Consequently, the implication method is easier to apply, faster to converge and initial estimates of the force constants are not needed. The calculated force constants and frequency errors differ somewhat from those of Shimanouchi and Suzuki (5).

The symmetry species notation used here for formaldehyde and later for ethylene is used consistently throughout the literature even after the Joint Commission on Spectroscopy published its recommendations (47) for the selection of molecular axes. For small molecules the earlier rule (2), $I_{xx} \leq I_{yy} \leq I_{zz}$, seems useful and clear enough.

TABLE 9: Vibrational Frequencies: H_2CO, HDCO, D_2CO.

Observed		CALCULATED	
		Shimanouchi & Suzuki (10)	This Work
H_2CO	2780 (A_1)	2796.3 (-16.3)*	2780.0 (0.0)
	1743.6 (A_1)	1752.7 (-9.1)	1743.6 (0.0)
	1503 (A_1)	1510.6 (-7.6)	1503.0 (0.0)
	2874 (B_1)	2871.9 (2.1)	2874.0 (0.0)
	1280 (B_1)	1273.2 (6.8)	1280.0 (0.0)
D_2CO	2055.8 (A_1)	2049.0 (6.8)	2045.7 (10.1)
	1700 (A_1)	1694.3 (5.6)	1679.7 (20.3)
	1105.7 (A_1)	1102.0 (3.6)	1095.8 (9.9)
	2159.7 (B_1)	2167.6 (-7.9)	2178.0 (18.3)
	990 (B_1)	994.4 (-4.4)	995.9 (-5.9)
HDCO	2844.1 (A')	2833.7 (10.3)	2831.8 (12.3)
	2120.7 (A')	2116.6 (4.1)	2105.0 (15.7)
	1723.4 (A')	1720.0 (3.4)	1717.0 (6.4)
	1400 (A')	1397.1 (2.9)	1399.1 (0.9)
	1041 (A')	1042.1 (-1.1)	1038.6 (2.4)
mean error			
	H_2CO	8.4	0.0
	HDCO ±	5.8	7.5
	D_2CO	4.4	12.9
	Overall mean error	6.2	6.8 cm^{-1}

* (observed - calculated)

The implied force constants belong to the basis molecule, H_2CO, and the corresponding vibrational frequencies are calculated without error. In terms of the mean error in the frequencies, the four parameter K-space fit is very nearly as good as the nine parameter F-space fit.

The five configuration coordinates required to span the in-plane modes of formaldehyde can be represented in the form: 2(CH) + (CO) + (HCH) + (OCHH)

Though appendix three shows that a redundant coordinate system can be used, non-redundant coordinate systems are used whenever possible. Consequently an in-plane-wag has been defined as follows: (OCXY) = (OCX) - (OCY).

The geometric parameters selected by Shimanouchi and Suzuki (5) have been employed so that the calculations will be comparable in every way.

$$r(CH) = 1.1139 \overset{\text{o}}{A}$$
$$r(CO) = 1.2078 \overset{\text{o}}{A}$$
$$\Theta(HCH) = 116.56^{\text{o}}$$

The implied dispersions for the implied force constants are based on the maximum frequency error, 20 cm^{-1}. By contrast, the dispersions reported by Shimanouchi and Suzuki are, in several cases, much larger. The larger intervals specify the range of variation that an individual force constant can display without exceeding a specified frequency error. The smaller intervals specify the range of variation necessary to match exactly all of the frequencies employed.

(OCHH) contributes only to the B_1 modes while (HCH) and (CO) contribute only to the A_1 modes; consequently point group theory (1) requires that both F(O̲C̲HH:C̲O̲) and F(O̲C̲HH:H̲C̲H̲) be identically zero. As well, symmetry properties require F(OC̲HH:C̲H) = - F(OC̲HH:C̲H).

TABLE 10: The force Constants of Formaldehyde.

Force Constant	Implication	Perturbation
F(C̲H:C̲H)	4.320 ± 0.063	4.361 ± 0.084
F(C̲H:C̲H)	0.089 ± 0.063	0.092 ± 0.084
F(C̲O:C̲O)	13.415 ± 0.309	12.577 ± 0.271
F(C̲O:C̲H)	0.295 ± 0.140	0.704 ± 0.409
F(H̲C̲H:H̲C̲H)	0.819 ± 0.022	0.840 ± 0.034
F(H̲C̲H:C̲H)	0.156 ± 0.037	-0.115 ± 0.255
F(H̲C̲H:C̲O)	-0.920 ± 0.082	-0.448 ± 0.146
F(OC̲HH:OC̲HH)	0.445 ± 0.032	0.432 ± 0.014
F(OC̲HH:C̲H)	-0.115 ± 0.046	-0.071 ± 0.126

Neither the implied force constants nor the frequency errors calculated by implication methods differ greatly from those obtained by Shimanouchi and Suzuki (5). Consequently the four parameter implication method appears to be equivalent to the more cumbersome perturbation method.

The implied force constants are heavily biased to the basis molecule; whether or not this bias can be used to advantage awaits further analysis.

Toward the end of this chapter it will be shown that implied force constants display a pattern of consistency which agrees with some of the principles of the hybrid orbital force field of Mills (21). The implication method generalizes without loss of significance - in terms of frequency errors or molecular structure.

(3-4b) Ethylene and its Deuterohomologs.

In conjunction with experimental work Crawford, Lancaster, and Inskeep have calculated the quadratic force constants of ethylene (48) from the vibrational frequencies of the two homologs, C_2H_4 and C_2D_4. They imposed one constraint, F(HCH:CH) = 0, and did not attempt to adjust their force constants to minimize frequency errors.

Later Brodersen (49) repeated the determination with a deliberate attempt to minimize frequency errors and without constraints. Again the full symmetry homologs dominated the calculation; intermediate homologs were used to define one of the force constants. Though Brodersen's choice of fundamentals differed little from those of Crawford, Lancaster and Inskeep, the reported force constants differ significantly (see table eleven); however, the Brodersen force constants can be viewed as a refinement of the earlier work.

Since automatic computing became available, a general valence force field for ethylene has not been reported. Scherer and Overend have reported a six parameter Urey Bradley force field (UBFF) (50). More recently Fletcher and Thompson have reported a ten parameter Hybrid Orbital force field (HOFF) (22).

Automatic computing would enable the use of data from all the deuterohomologs and provide minimum frequency errors in the least squares sense. In effect the implied force field reported here completes the refinement of the quadratic force constants for ethylene.

The fifty-four fundamentals of the six deutero-ethylenes (51) are used to fix the six mixing parameters for the basis molecule $H_2C_2H_2$. Though significant differences appear, the implied force constants appear to be a refinement of the earlier work reported by Brodersen.

It is possible to classify the vibrations of the deuteroethylenes under the point group of the potential energy, D_{2h}. When isotopic substitution reduces the point group symmetry, D_{2h} - species are scrambled but in accord with the lower point group. Consequently all vibrations can be classified by enclosing the scrambled D_{2h} - species in parentheses.

$$H_2C_2H_2 + D_2C_2D_2 \quad : \quad 3A_g + 2B_{1g} + 2B_{2u} + 2B_{3u}$$
$$HDC_2H_2 + HDC_2D_2 \quad : \quad (3A_g + 2B_{1g} + 2B_{2u} + 2B_{3u})$$
$$trans - HDC_2HD \quad : \quad (3A_g + 2B_{1g}) + (2B_{2u} + 2B_{3u})$$
$$cis \quad -HDC_2HD \quad : \quad (3A_g + 2B_{2u}) + (2B_{1g} + 2B_{3u})$$
$$1,1\text{-dideuteroethylene} : (3A_g + B_{3u}) + (2B_{1g} + 2B_{2u})$$
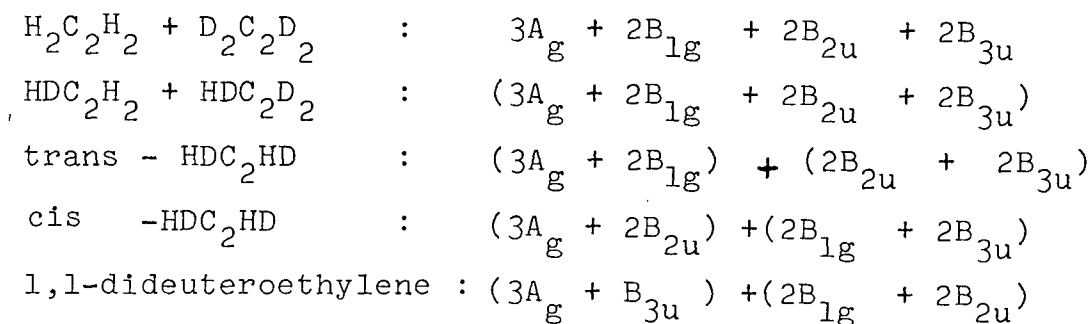
This notation immediately reveals the information needed to formulate the product rules. Further it shows at a glance the dependence of vibrational frequencies on symmetry factored force constants.

For example, in trans dideuteroethylene, the five symmetric vibrations, $(3A_g + 2 B_{1g})$, depend on the six A_g-force constants and the three B_{1g}-force constants. In K-space these five vibrations depend on the three A_g and the one B_{1g} mixing parameters. This structure carries over to the K-space perturbation equations, (3.2.5), and is of great help in assigning experimental frequencies to the individual linear equations. It should be realized that the classification under D_{2h}, $(3A_g + 2B_{1g}) + (2B_{2u} + 2B_{3u})$, means exactly the same thing as the classification, $5A_g + 4B_u$, obtained under C_{2h}; however, the D_{2n} notation emphasizes the underlying structure.

The vibrations of the basis molecule, $H_2C_2H_2$, indicate fifteen independent quadratic force constants but only six mixing parameters.

The planar configuration coordinates adopted for this study,

$$4(CH) + (CC) + 2(HCH) + 2(CCHH),$$

contribute to the vibrations as follows:

$$4(CH) \qquad A_g + B_{1g} + B_{2u} + B_{3u} \quad.$$

$$(CC) \qquad A_g$$

$$2(HCH) \qquad A_g + B_{3u}$$

$$2(CCHH) \qquad B_{2u} + B_{1g}$$

Fortunately the CH-stretching vibrations and the (CC)-stretching vibration are known to be characteristic; thus no problems are expected in structuring the implied force field.

For clarity let us note that

$$2(CCHH) = \begin{cases} (CCHH)_1 = \beta_1 - \beta_2 \\ \\ (CCHH)_2 = \beta_3 - \beta_4 \end{cases}$$
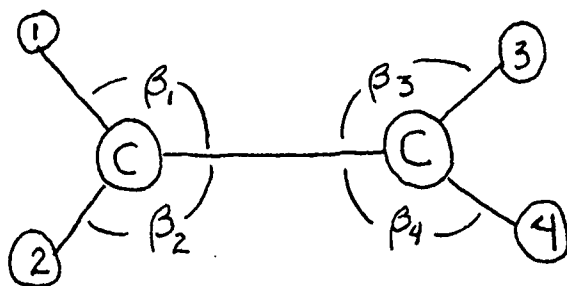
The symmetry properties of the configuration coordinate impose five symmetry restrictions on the force constants,

$$F(\underline{CC}HH:\underline{CC}) = 0$$

$$F(C\underline{CHH}:\underline{HCH}) = 0$$

$$F(\underline{CC}HH:H\underline{C}H) = 0$$

$$F(C\underline{CHH}:\underline{CH}) + F(\underline{CC}HH:\underline{CH}) = 0$$

$$F(\underline{CC}HH:\underline{CH}, \text{ cis}) + F(\underline{CC}HH:CH, \text{ trans}) = 0$$

In this calculation the geometric parameters selected by Herzberg (2) have been employed.

$$r(CH) = 1.086 \text{ Å}$$

$$r(CC) = 1.339 \text{ Å}$$

$$\Theta(HCH) = 117.6^\circ$$

Beginning with $P_0 = I$ in equation (3.2.4), mean

error in the frequencies of 20.6 cm^{-1}, the K-space iteration
sequence described in section (3-2) proceeds smoothly to the
implied force constants given in table eleven and calculated
frequencies given in table twelve.

The largest frequency error appears in the (CC)-
stretching frequency for 1,1-dideuteroethylene (the calculated
frequency falls 33 cm^{-1} below the observed frequency). In
fact all of the implied (CC) stretching fundamentals fall below
the observed fundamental. The same discrepancy appears in
formaldehyde for the (CO)-stretching fundamentals. In these
cases; multiple bond anharmonicity like that described for
acetylene is suspected.

The remaining large frequency errors in the deutero-
ethylenes appear, as expected, in the (CD)-stretching frequencies.

The force constant dispersions, calculated by the
implication technique of section (3-3), have not been included
in table eleven. Dispersions based on twice the mean frequency
error are reported separately below. All but eleven of the calcul-
ated frequencies fall within this range. For the principal
force constants the implied dispersions are comparable to those

	implied	Fletcher & Thompson (22)
F(CC:CC)	±0.18	±0.15
F(CH:CH)	±0.044	±0.036
F(HCH:HCH)	±0.013	±0.008
F(CCHH:CCHH)	±0.018	±0.009

determined by Fletcher and Thompson. The remaining implied dis-
persions are geometric means of the above values, see equation (3.3.3).

TABLE 11:   The Force Constants of Ethylene

	Crawford Lancaster & Inskeep (48)	Brodersen (49)	Scherer & Overend (50)	Fletcher & Thompson (22)	This work
F(CC:CC)	10.896	11.08	9.038	9.305	11.184
F(CH:CH)	6.126	4.77	5.149	5.168	5.004
F(HCH:HCH)	0.731	0.708	0.661	0.683	0.725
F(CCHH:CCHH)	0.373	0.334	0.248	0.269	0.332
F(HCH:CC)	-0.920	-0.826	-0.264	-0.273	-0.943
F(HCH:CH)	0.369	0.130	-0.123	0.087	0.182
F(HCH:CH)	0.000	0.141	0.000	0.000	0.241
F(HCH:HCH)	0.035	-0.012	0.000	0.022	0.066
F(CCHH:CH)	0.511	-0.163	0.123	0.098	-0.199
F(CCHH:CH, cis)	0.234	-0.332	0.000	0.000	-0.313
F(CCHH:CCHH)	0.035	0.006	-0.048	-0.048	0.014
F(CH:CC)	0.000	0.00	0.367	0.000	-0.154
F(CH:CH)	0.043	0.02	0.000	-0.012	0.031
F(CH:CH, Cis)	-0.020	-0.06	0.000	-0.018	-0.104
F(CH:CH, trans)	0.050	0.14	0.000	-0.018	0.089
Constraints	F(CH:HCH) = O	NONE	UBFF*	HOFF	NONE
Parameters	14	15	6	10	6
mean error (cm^{-1})	13.4	8.1	12.0	8.8	6.5

*   This is the valence bonding   image of the Urey Bradley force field (14).

TABLE 12: Vibrational Fundamentals: ethylene and deuterohomologs

SYMMETRY	OBSERVED	IMPLIED	BRODERSEN	MOLECULE
	3026	3026	3026	
	1623	1623	1630	
$3A_g$	1342	1342	1350	
	3103	3103	3110	
$2B_{1g}$	1236	1236	1238	
	3106	3106	3110	
$2B_{2u}$	810	810	815	
	2990	2990	3001	
$2B_{3u}$	1444	1444	1455	
mean frequency error		0.0	6.0	$H_2C_2H_2$
	2660	2238	2253	
	1518	1508	1511	
$3A_g$	985	977	978	
	2310	2312	2308	
$2B_{1g}$	1011	1007	1009	
	2345	2336	2340	
$2B_{2u}$	584	576	580	
	2200	2169	2189	
$2B_{3u}$	1078	1065	1067	
mean frequency error		11.8	6.2	$D_2C_2D_2$
	3017	2998	3009	
	2230	2231	2236	
	1585	1552	1561	
	1384	1387	1402	
$(3A_g + 2B_{3u})$	1031	1024	1022	
	3093	3096	3100	
	2334	2334	2336	
	1150	1153	1155	
$(2B_{1g} + 2B_{2u})$	660	664	668	
mean frequency error		8.1	9.7	$ASYM-H_2C_2D_2$

SYMMETRY	OBSERVED	IMPLIED	BRODERSEN	MOLECULE
	3059	3069	3066	
	2299	2283	2300	
	1571	1562	1574	
	1218	1213	1209	
$(3A_g + 2B_{2u}$	646	647	652	
	3054	3051	3057	
	2254	2238	2253	
	1342	1336	1335	
$(2B_{1g} + 2B_{3u})$	1039	1043	1048	
mean frequency error		7.8	5.8	$CIS-HDC_2HD$
	3045	3043	3069	
	2285	2285	2279	
	1571	1562	1572	
	1286	1281	1284	
$(3A_g + 2 B_{1g})$	1004	1000	1007	
	3065	3059	3040	
	2273	2268	2298	
	1299	1288	1280	
$(2B_{2u} + 2B_{3u})$	678	659	664	
mean frequency error		6.9	13.2	$TRANS-HDC_2HD$

H_2C_2HD		$(3A_g + 2B_{1g} + 2B_{2u} + 2B_{3u})$	D_2C_2HD
OBSERVED	IMPLIED	IMPLIED	OBSERVED
3096	3101	3051	3049
3061	3062	2331	2332
3002	3000	2269	2281
2276	2278	2205	2222
1606	1589	1532	1547
1401	1401	1280	1289
1290	1288	1043	1045
1129	1128	994	999
713	716	612	610
mean frequency error	3.7	7.2	

Neither Crawford, Lancaster and Inskeep nor Brodersen present calculated frequencies for the low symmetry homologs. Fletcher and Thompson calculate frequencies for H_2C_2HD and report a mean frequency error 9.1 cm^{-1} for this molecule. The six parameter Urey Bradley force field is too highly constrained to compare calculated frequencies.

If the five calculations are intercompared by multiplying the mean frequency error and the number of adjustable parameters, then the implied force field takes first rank. Moreover by this measure of merit, the hybrid orbital force field follows the Urey Bradley force field.

(3-4c) Chemical Significance

On one hand quadratic force constants are mechanical
parameters consistant with mechanical information of exper-
imental origin. On the other hand, as measures of bonding
forces and interactions, quadratic force constants should
comply with chemical bonding structure. Consequently the
quadratic force constant serves both physical and chemical
purposes. Physical significance, though subject to well
defined measurement, is limited to pure mechanics. Chemical
significance establishes itself through chemical bonding
and is subject to a wider interpretation, but chemical sig-
nificance is not subject to well defined measurement.

Because implied force constants are formulated with
minimal reference to chemical bonding structures, their
chemical significance needs deliberate emphasis. In some
respects, it is remarkable that implied force constants
exhibit any degree of chemical significance at all.

Ethylene and formaldehyde are in fact closely related
molecules; if one CH_2-group of ethylene is regarded as a
single atom, the resultant molecule would be an isotopic
homolog of formaldehyde. Table thirteen shows that force
constants for the two related molecules exhibit unexpected
sign and size agreement. However the bonding unit, $H_2C=$,
does not possess a set of force constants which are largely
independent of the substituent as has been shown (17,20)
for the bonding unit H_3C- .

TABLE 13:   Similar Implied Force Constants

	Formaldehyde (X= oxygen)	Ethylene (X= Carbon)
F(CH:CH)	4.320	5.004
F(CX:CX)	13.415	11.184
F(CH:CH)	0.089	0.031
F(CH:CK)	0.295	-0.154
F(HCH:HCH)	0.819	0.725
F(CH:HCH)	0.156	0.182
F(CX:HCH)	-0.920	-0.943
F(XCHH:XCHH)	0.445	0.332
F(XCHH:CH)	-0.115	-0.199

The similarities confirm some of the principles used by Mills in the hybrid orbital force field (21). He suggests that

$$F(HCH:CH) = k\ F(CH:CH)$$

$$F(HCH:CX) = k^1 F(CX:CX)$$

where the constants k and k^1 depend mostly upon hybridization and to some extent on the nature of the substituent. If sp^2 hybridization dominates other effects, then $k^1 = -2k$.

In both formaldehyde and ethylene the central atom is hybridized and the hybridization constants should be nearly the same.

HYBRIDIZATION CONSTANTS

	formaldehyde	ethylene
k	0.0361	0.0364
k^1	-0.0686	-0.0841
k^1/k	-1.90	-2.31

The hybridization constants, k, are nearly equal for the two molecules. Those involving the double bonds, k^1, are comparable and related to the single bond hybridization constant, k, the expected way. It is gratifying to confirm these aspects of the hybrid orbital force field (21) without assuming it. However, the hybrid orbital force field predicts $F(\text{CCHH:CH}) = F(\text{HCH:CH})$, but the implied force constants agree more closely with a Urey Bradley force field here (14),

$$F(\text{CCHH:CH}) = - F(\text{HCH:CH}).$$

As well, neither of the model force fields includes stretching interactions but the implied force field indicates definite stretching interactions.

As shown by Heath and Linnett (52), interaction force constants can be interpreted on strictly geometrical grounds. Let all coordinates except $\mathcal{R}_i$ and $\mathcal{R}_j$ be fixed at their equilibrium values. Let $\mathcal{R}_j$ be assigned a definite displacement, Δ_j. These constrained conditions imply a pseudo-equilibrium value, $\mathcal{R}_i^o$, for the internal coordinate associated with $\mathcal{R}_i$ in that the potential energy is minimized.

$$\mathcal{R}_i^o - \mathcal{R}_i^e = -\frac{F_{ij}}{F_{jj}} \Delta_j$$

In formaldehyde, if the (CO) bond is stretched, the (CH) bond is shortened. In ethylene, if the (CC) bond is shortened the (CH) bond is lengthened. Consequently the psuedo-equilibrium geometry of formaldehyde tends toward the equilibrium geometry of ethylene and conversely. In this sense the only signature disparity in table thirteen is quite creditable.

The very few implied force constants now in hand do not provide a sufficient foundation for a general discussion of their special chemical significance; however, these examples indicate the definite value of continued studies with implication methods.

CHAPTER FOUR: APPROXIMATION TECHNIQUES

Thus far the implication method has been limited to the case where there exists sufficient experimental information to specify all quadratic force constants. Clearly larger molecules with low symmetry, methylamine for example, need not submit to such a general approach. Consequently, further progress with implication methods will depend upon approximation techniques which either operate entirely within the implication scheme or cooperate with the more traditional methods of parameterized potential energy.

The weighted trace equations delineated in section one of this chapter provide some information about the latter objective: cooperation of implication methods and traditional parameterization of molecular potential energy.

Fortunately the implication scheme lends itself to a unique approximative technique whenever some vibrations of a molecule can be said to be characteristic vibrations. The second section of this chapter describes the role of characteristic vibrations in the analysis of the vibrational secular equations entirely within the implication scheme.

(4-1)   The Weighted Trace Equations

Consider the function

$$Trace \ WF = \sum_i \sum_j W_{ij} F_{ij} \qquad (4.1.1)$$

where

$$F = U \Gamma^{-1/2} P_0 \, e^{Ks} \Lambda \, e^{-Ks} P_0^t \Gamma^{-1/2} U^t \qquad (4.1.2)$$

as defined in equations (3.1.3) and s is an ordering parameter - see appendix three. The weighting matrix W is some specified matrix with the same symmetry as the F-matrix. In essence, it/forms various linear combinations of force constants; explicit choices for the W-matrix will follow from the general development.

Notice that

$$Trace \; WF = Trace \left(P_0^t \Gamma^{-1/2} U^t W U \Gamma^{-1/2} P_0 \right) \left(e^{Ks} \Lambda \, e^{-Ks} \right)$$

Thus P_0 is defined such that

$$P_0^t \Gamma^{-1/2} U^t W U \Gamma^{-1/2} P_0 = \mathcal{W} \qquad (4.1.3)$$

where $\mathcal{W}$ is a diagonal matrix.

The diagonal $\mathcal{W}$-matrix entries are the eigenvalues of the matrix product, $\bar{G}' W$.

The techniques described in appendix three give the general weighted trace equation:

$$\lambda_R \equiv \Lambda_{RR} \qquad w_R \equiv \mathcal{W}_{RR}$$

$$Trace \; WF = \sum_R \mathcal{W}_R \lambda_R + s^2 \sum_{\lambda_i > \lambda_j} (\lambda_i - \lambda_j)(w_i - w_j) K_{ij}^2$$

+ higher terms $\qquad (4.1.4)$

Consequently

Trace WF is maximum if $\omega_i < \omega_j$

Trace WF is minimum if $\omega_i > \omega_j$

Trace WF is saddle point if $\omega_i = \omega_j$

with respect to the mixing parameter K_{ij} .

Suppose that the three force constants F_{mm}, F_{mn} and F_{nn} dominate the two vibrational frequencies λ_n and λ_m (or the mixing parameter K_{mn} is most important). Then equations (4.1.3) and (4.1.4) provide bounds for the force constants. ($\lambda_n > \lambda_m$)

$$G_{mm}^{-1} \lambda_m \leq F_{mm} \leq G_{mm}^{-1} \lambda_n$$

$$G_{nn}^{-1} \lambda_m \leq F_{nn} \leq G_{nn}^{-1} \lambda_n$$

$$2F_{mn} \leq G_{mn}^{-1}(\lambda_n + \lambda_m) + (\lambda_n - \lambda_m)\sqrt{G_{mm}^{-1} G_{nn}^{-1}} \tag{4.1.5}$$

$$2F_{mn} \geq G_{mn}^{-1}(\lambda_n + \lambda_m) - (\lambda_n - \lambda_m)\sqrt{G_{mm}^{-1} G_{nn}^{-1}} .$$

Equations (4.1.5) are formed from three different W-matrices - one to select each different force constant.

The inequalities (4.1.5) are exact for the vibrational secular equation of order two. Otherwise they are not exact but they may indicate important interaction force constants.

For example, the two B_{2u} modes of benzene and the inverse G-matrix elements (symmetry factored) (1) give the following bounds for the symmetry factored force constants.

$$3.353 \leq F(CC:CC,B_{2u}) \leq 4.375$$

$$0.916 \leq F(HCCC:HCCC,B_{2u}) \leq 1.195$$

$$-1.658 \leq F(HCCC:CC,B_{2u}) \leq -0.593$$

Here the application of (4.1.5) is exact and limits for an essential interaction constant have been set by simple means. Thus, $F(HCCC:CC,B_{2u})$ has not been specified but it cannot be zero. The importance of this interaction constant has already been established (53).

Equations (4.1.5) may prove most useful in selecting important interaction constants. Another way of identifying important interaction force constants by implication methods follows.

Assume an approximate force constant matrix F_o and solve the secular equations

$$L_o^t \, F_o \, L_o = \Lambda_o$$

where Λ_o represents calculated frequencies.

The associated implied force field

$$F = L_o^{-t} \, \Lambda \, L_o^{-1}$$

may well indicate important corrections to the approximate force constants used to assemble F_o. The Λ-matrix is composed of experimental frequencies. In this application the dispersion equations, (3.3.3) and (3.3.4), show that if the calculated and observed frequencies are close, so are the trial and implied force constants close. Consequently like

the perturbation method itself, this approach may assume
more fore-knowledge than is provided by the existing
guidelines to chemical bonding.

Yet it is believed that the implied force constant
matrix associated with approximate force constants will
provide a less cumbersome approach than perturbation methods
when the problem is too complex to solve entirely within
the perturbation scheme.

(4-2) Participation and Molecular Partitioning

It is often possible to associate selected
vibrational frequencies with selected parts of the whole
molecule - usually chemical groups such as $-NH_2$ or $-CH_3$.
If a vibrational frequency belongs to a chemical group, then
the remaining atoms participate to a much lesser extent in
that vibration. This section considers the partitioning of
a molecule into two sets of atoms and describes the
participation of the individual sets in the various
vibrations.

Characteristic frequencies are closely related to
mass dependence within the vibrational secular equations.
Characteristic frequencies will depend mostly on selected
atoms and consequently their masses.

Differentiation of the matrix equations

$$G = L L^t \qquad \text{and} \qquad L^t F L = \Lambda$$

with respect to the reciprocal mass of the $\beta^{\underline{th}}$ atom

leads to the equations:

$$L^{-1}\left(\frac{\partial G}{\partial \mu_\beta}\right)L^{-t} = L^{-1}\frac{\partial L}{\partial \mu_\beta} + \left(L^{-1}\frac{\partial L}{\partial \mu_\beta}\right)^t \tag{4.2.1}$$

$$\frac{\partial \Lambda}{\partial \mu_\beta} = \Lambda L^{-1}\frac{\partial L}{\partial \mu_\beta} + \left(\Lambda L^{-1}\frac{\partial L}{\partial \mu_\beta}\right)^t \tag{4.2.2}$$

Both Λ and $\partial \Lambda/\partial \mu_\beta$ are diagonal. Consequently

$$\Lambda L^{-1}\frac{\partial L}{\partial \mu_\beta} = \frac{1}{2}\left(\frac{\partial \Lambda}{\partial \mu_\beta}\right) + K_\beta \tag{4.2.3}$$

Where K_β is a skew symmetric matrix.

In combination (4.2.1) and (4.2.3) provide the

fundamental mass equation.

$$L^{-1}\frac{\partial G}{\partial \mu_\beta}L^{-t} = \Lambda^{-1}\frac{\partial \Lambda}{\partial \mu_\beta} + [\Lambda^{-1}, K_\beta]$$

Because $\quad [\Lambda^{-1}, K_\beta]_{jj} = 0$

$$\left(L^{-1}\frac{\partial G}{\partial \mu_\beta}L^{-t}\right)_{jj} = \Lambda_{jj}^{-1}\frac{\partial \Lambda_{jj}}{\partial \mu_\beta} = \frac{\partial \ln \Lambda_{jj}}{\partial \mu_\beta} \tag{4.2.4}$$

The G-matrix is of the form

$$G_{ij} = \sum_\alpha \mu_\alpha (\nabla_\alpha \rho_i)\cdot(\nabla_\alpha \rho_j)$$

therefore (see appendix one)

$$\left(\frac{\partial G}{\partial \mu_\beta}\right)_{ij} = \left(\nabla_\beta \rho_i\right) \cdot \left(\nabla_\beta \rho_j\right)$$

which is positive semi definite (44),

$$\frac{\partial \ln \Lambda_{jj}}{\partial \mu_\beta} \geqslant 0$$

and moreover $\qquad G = \sum_\alpha \mu_\alpha \left(\partial G / \partial \mu_\alpha\right)$ (4.2.5)

Thus the equation $\qquad L^{-1} G L^{-t} = I$

gives $\qquad \sum_\alpha \mu_\alpha \dfrac{\partial \ln \Lambda_{jj}}{\partial \mu_\alpha} = 1$ (4.2.6)

Consequently the quantity

$$\rho_{\alpha j} \equiv \mu_\alpha \left(L^{-1} \frac{\partial G}{\partial \mu_\alpha} L^{-t}\right)_{jj} = \mu_\alpha \frac{\partial \ln \Lambda_{jj}}{\partial \mu_\alpha}$$ (4.2.7)

can be viewed as the participation of the αth atom in the jth vibrational frequency.

As well, it can be established that

$$\sum_j P_{\alpha j} = \mu_\alpha \, \text{Trace} \; G^{-1} \frac{\partial G}{\partial \mu_\alpha}$$

$$= \mu_\alpha \frac{\partial \ln |G|}{\partial \mu_\alpha} \tag{4.2.8}$$

The latter equation follows from the identity (54).

$$\frac{1}{|G|} \frac{\partial |G|}{\partial G_{ij}} = \left(G^{-1} \right)_{ij}$$

Partitioning.

Let a molecule be partitioned such that each of its atoms belongs to either the set A or the set B. Define the participation matrices:

$$\Pi(A) = \sum_{\alpha \in A} \mu_\alpha \left(L^{-1} \frac{\partial G}{\partial \mu_\alpha} L^{-t} \right)$$

$$\Pi(B) = \sum_{\alpha \in B} \mu_\alpha \left(L^{-1} \frac{\partial G}{\partial \mu_\alpha} L^{-t} \right) \tag{4.2.9}$$

Both $\Pi(A)$ and $\Pi(B)$ are square positive semidefinite matrices and their diagonal elements are sums of atom-participations. Through (4.2.5) they sum to the identity matrix

$$\Pi(A) + \Pi(B) = I \tag{4.2.10}$$

and they obey positive semidefinite inequalities (45).

$$\Pi(A)_{ii} \geqslant 0 \qquad \Pi(A)_{ij}^2 \leq \Pi(A)_{ii} \, \Pi(A)_{jj}$$

For a nonplanar molecule

$$\text{rank } \Pi(A) \leq 3N_A$$

where N_A is the number of atoms in A (44,45).

The quantity $\Pi(A)_{jj}$ defines the participation of the $A \underline{\text{th}}$ set of atoms in the $j \underline{\text{th}}$ vibration. If the $A \underline{\text{th}}$ set of atoms does not participate in the $n \underline{\text{th}}$ vibration, then

$$\Pi(A)_{nn} = 0 \qquad \Pi(B)_{nn} = 1$$

and the positive semidefinite inequality

$$\Pi(A)_{nj}^2 \leq \Pi(A)_{nn} \, \Pi(A)_{jj}$$

gives $\quad \Pi(A)_{nj} = 0 \qquad$ for all j

again $\quad \Pi(B)_{nj} = 0 \qquad$ for all j except j=n

recall $\quad \Pi(A) + \Pi(B) = I$

moreover note the strong implication of null participation

$$\Pi(A)_{nn} = 0 \quad \text{implies} \quad \mu_\alpha \frac{\partial \ln \Lambda_{nn}}{\partial \mu_\alpha} = 0$$

for all α contained in the A-set.

Consequently isotopic substitution within the A -set leaves the characteristic vibrations of the B - set invariant. This fact provides a test for the validity of null participation !

As an example of partitioning and participation let us consider methylamine. Let there be six modes characteristic of the methyl-set, three modes characteristic of the amine-set, and six mixed modes.
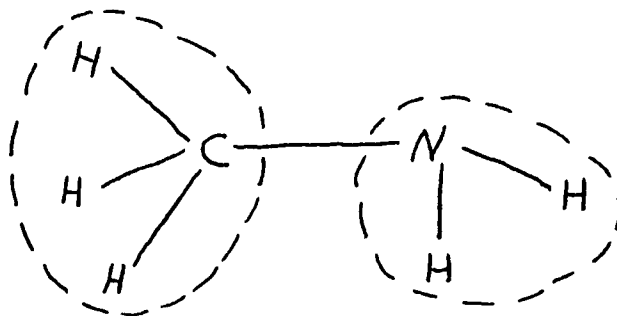
The principles just described require $\pi(CH_3)$ and $\pi(NH_2)$ to be of the form given by table fourteen. Unity designates the identity matrix and the arrows show the inter-relationships used to formulate $\pi(CH_3)$ and $\pi(NH_2)$.

TABLE 14:   Participation Matrices for Methylamine

The distribution of unit, nonzero, and zero blocks in the participation matrices for $(CH_3) - (NH_2)$; the arrows summarize the derivation of the zero-blocks for limited participation.

$$\pi(CH_3)$$

(CH_3)-MODES UNITY $4A' + 2A''$	ZERO	ZERO ↑
ZERO	MIXED MODES NONZERO $3A' + 3A''$	ZERO ↑
ZERO ◄	ZERO ◄	ZERO (NH_2)-MODES

◄——— 6 ———►◄——— 6 ———►◄——— 3 ———►

ZERO ———► (CH_3)-MODES ↓	ZERO ———►	ZERO ———►
ZERO ↓	MIXED MODES NONZERO $3A' + 3A''$	ZERO
ZERO	ZERO	(NH_2)-MODES UNITY $2A' + A''$

$$\pi(NH_2)$$
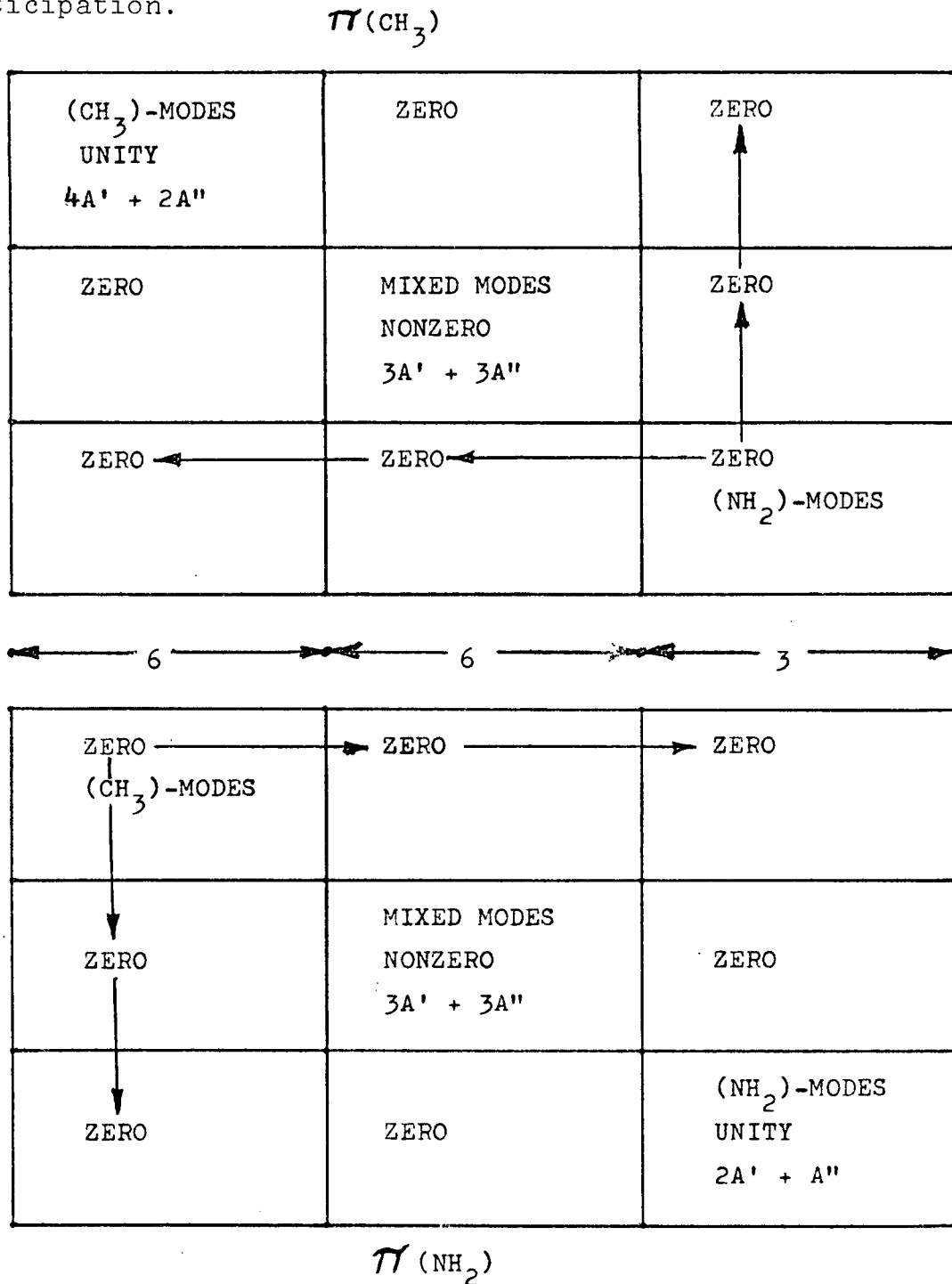
The symmetry species show the further factorization obtained when methylamine is given a plane of symmetry.

The fundamentals assigned by Dellepiane and Zerbi (55) support the hypothesis of complete separation. The three modes characteristic of amine are easily identified.

CH_3NH_2		CD_3NH_2
3361	A'	3361
1623	A'	1624
3427 cm^{-1}	A"	3427 cm^{-1}

It is important to note that these invariant fundamentals support the hypothesis of null participation over the methyl group. Similarly for the six methyl modes:

CH_3NH_2		CH_3ND_2
2961	A'	2961
2820	A'	2817
1473	A'	1468
1430	A'	1430
2985	A"	2985
1476 cm^{-1}	A"	1485 cm^{-1}

And these fundamentals support the hypothesis of null participation over the amine group. Note the violation of the rule of monotony (1) which states that all vibrational frequencies must decrease upon heavier isotopic substitution (see equation 4.2.7).

The question as to how limited participation information can be used in connection with implication methods now arises.

$\Pi(A)$ and $\Pi(B)$ can be written in the form:

$$\Pi(A) = P^t \Gamma^{-1/2} U^t \left\{ \sum_{\alpha \in A} \mu_\alpha \frac{\partial G}{\partial \mu_\alpha} \right\} U \Gamma^{-1/2} P$$

$$P = P_0 \mathcal{C}^K \tag{4.2.11}$$

$$\Pi(A) = \mathcal{C}^{-K} \phi_A \mathcal{C}^K$$

where

$$P_0^t \Gamma^{-1/2} U^t \left\{ \sum_{\alpha \in A} \mu_\alpha \frac{\partial G}{\partial \mu_\alpha} \right\} U \Gamma^{-1/2} P_0 = \phi_A$$

and ϕ_A is a diagonal matrix

The matrices

$$\Gamma^{-1/2} U^t \left\{ \sum_{\alpha \in A} \mu_\alpha \frac{\partial G}{\partial \mu_\alpha} \right\} U \Gamma^{-1/2} \qquad \Gamma^{-1/2} U^t \left\{ \sum_{\alpha \in B} \mu_\alpha \frac{\partial G}{\partial \mu_\alpha} \right\} U \Gamma^{-1/2}$$

and

sum to the identity matrix, therefore they commute and are simultaneously diagonalized by a single orthogonal P_0 .

According to the principles set down in appendix three for the exponential matrix and the principles of limited participation, the skew-symmetric K-matrix of equation (4.2.11) exhibits the mixing property:

$$K_{ij} = 0$$ unless Λ_{ii} and Λ_{jj} represent genuine vibrations of the same symmetry species and cover the same set of atoms.

In the present example, the selected forms of the Π — matrices cause the methyl-modes to mix only with themselves, the amine-modes to mix only with themselves and the mixed-modes to mix only with themselves. The mixed modes are not coupled to any of the characteristic modes; this is a remarkable and unexpected property !

With a plane of symmetry methylamine exhibits 66 independent possible quadratic force constants or 51 possible general mixing parameters. But if limited participation is assumed - and experimental evidence validates the assumption - the number of mixing parameters is reduced to 14.

Through molecular partitioning it seems quite likely that reasonable implied force constants could be obtained for a class of more complex molecules. As well partitioning applies in other senses. The G-matrix can be partitioned into two parts, $G(A)$ and $G(B)$ such that $$G(A) + G(B) = G$$ with much the same results.

The atom-participation densities, $\rho_{\alpha j}$, provide an interesting description of vibrational modes. The equation

$$\rho_{\alpha j} \equiv \left(\partial \ln \Lambda_{jj} / \partial \ln \mu_{\alpha} \right)$$

provides meaning in that $\rho_{\alpha j}$ is directly related to small isotopic shifts.

EPILOGUE

Unfortunately the exploration of implication methods in the description of molecular mechanics and chemical bonding structure is not yet complete but this thesis has established the basic approach to a cumbersome problem by new methods. The ingredients of the implication method include two important factors.

An experimentally well known basis molecule is adopted and its vibrational frequencies remove a corresponding number of parameters from the pure mechanical description. The reduced parameterization has been cast into a mathematical form that is handy in computations as well as analysis, as delineated in chapter four.

Application of the implication technique has led to a simple account of some dominating anharmonic effects. If continued application of the method is as rewarding, then further studies are definitely warranted. To this end, the concepts of participation and molecular partitioning appear to offer the optimum prospects.

If molecules not rich in hydrogen are to be considered in more rigorous terms, the role of mechanical information other than vibrational frequencies must be included in the implication scheme. Jones, Asprey and Ryan (34) have shown that a complete picture of mechanical information is essential in the perturbation method.

Therefore, the limitation to hydrogen rich molecules is not specific for the implication method. The limitation is merely one of development within the implication method.

When the molecular system precludes a more rigorous approach, it is plausible that implication techniques may contribute substantially to a simple but proper parameterization of the potential energy function.

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APPENDIX ONE: THE VIBRATIONAL SECULAR EQUATIONS

- A Simplified Quantum Mechanical Description -

The concepts of classical mechanics, mainly well defined trajectories, fail to provide a genuine description of microsystems (56, 57).   In some examples such as the hydrogen atom, the failure of classical concepts is substantial; in other cases such as the harmonic oscillator, classical concepts remain adequate within limits, especially for polyatomic molecules.   Consequently, a classical picture of molecular vibrations has persisted while the necessary concepts of quantum mechanics grew to dominate the description of microsystems, especially molecular structure.

Though chemists are not quantum mechanicians, they are becoming more and more quantum oriented; classical mechanics has in fact almost entirely disappeared from the latticework of chemical logic.   Thus, to the student of physical chemistry, a classical picture of molecular vibrations is built upon unfamiliar, almost irrelevant, foundations.

A quantum mechanical description of molecular vibrations falls within the quantum picture usually presented to chemists; moreover both molecular vibrations and the existing quantum picture would benefit from a connected development.

Quantum descriptions including molecular vibrations already exist but these (1, 56, 57) are written for the experienced spectroscopic specialists or the pure mechanicians. In short, a handy reference for molecular vibrations, written in quantum mechanical language suitable for introductory purposes, is not known (to the author).

The following description is intended to serve the above-stated purposes; it includes all classical information, captures the flavor of rigor in quantum mechanics and provides a firm foundation for further rigor and detail.

(I-1) Transformation of the Schrodinger Equation

The Cartesian coordinate Schrodinger equation for N particles of reciprocal mass μ_α interacting under a potential energy function V, governs the total energy of

$$\left\{ \sum_\alpha \mu_\alpha \nabla_\alpha^2 + 2\hbar^{-2}(E-V) \right\} \Psi = 0 \tag{I.1.1}$$

the system, E, and the probability, $\Psi^*\Psi$, of a configuration specified by the Cartesian coordinates $(X_\alpha, Y_\alpha, Z_\alpha)$ where α counts particles.

In the Cartesian Schrodinger equation (I.1.1)

$$\nabla_\alpha \equiv \left(\frac{\partial}{\partial X_\alpha}, \frac{\partial}{\partial Y_\alpha}, \frac{\partial}{\partial Z_\alpha} \right)$$

$$\nabla_\alpha^2 \equiv \left(\frac{\partial^2}{\partial X_\alpha^2} + \frac{\partial^2}{\partial Y_\alpha^2} + \frac{\partial^2}{\partial Z_\alpha^2} \right)$$

$\hbar$ is Planck's constant;

Ψ the Cartesian wave function, is a function of
    Cartesian coordinates.

V the potential energy, is a function of the configuration of the molecule (in the absence of significant external influences). It is invariant with respect to rotations and translations. For present purposes electronic motion is considered to be embedded within the potential energy function; see the Born-Oppenheimer separation of electronic and nuclear motion (2).

μ_α Whether or not the electronic masses should be included in the masses of the individual particles under consideration is not completely clear. The Born-Oppenheimer separation calls for nuclear masses but detailed studies usually employ atomic masses with satisfactory agreement (2).

The invariance of the potential energy with respect to rotation and translation, as well as the principles of chemical bonding, suggests a transformation of coordinates. New coordinates would include three translation coordinates, three rotation coordinates and (3N-6) coordinates of configuration - bond lengths, valence angles, and related geometric measures. The transformation is curvilinear.

To this end let the transformation properties of (I.1.1) be established; let the new coordinates be designated as t_i.

The rules of partial differentiation (42) establish the identity:

$$\frac{\partial \Psi}{\partial X_\alpha} = \sum_i \left(\frac{\partial t_i}{\partial X_\alpha}\right)\left(\frac{\partial \Psi}{\partial t_i}\right)$$

(I.1.2)

Differentiation of (I.1.2) with respect to X_α provides a second identity:

$$\frac{\partial^2 \Psi}{\partial X_\alpha^2} = \sum_i \sum_j \left(\frac{\partial t_i}{\partial X_\alpha}\right)\left(\frac{\partial t_j}{\partial X_\alpha}\right)\frac{\partial^2 \Psi}{\partial t_i \partial t_j} +$$

$$+ \sum_j \frac{\partial^2 t_j}{\partial X_\alpha^2} \frac{\partial \Psi}{\partial t_j}$$

(I.1.3)

When cast into generalized coordinates, the kinetic part of the Cartesian coordinate Schrodinger equation becomes

$$\sum_\alpha \mu_\alpha \nabla_\alpha^2 \Psi = \sum_i \sum_j G_{ij} \frac{\partial^2 \Psi}{\partial t_i \partial t_j} + \sum_j g_j \frac{\partial \Psi}{\partial t_j}$$

(I.1.4)

where the following quantities have been defined for brevity.

$$G_{ij} \equiv \sum_\alpha \mu_\alpha (\nabla_\alpha t_i)\cdot(\nabla_\alpha t_j)$$

(I.1.5)

$$g_j \equiv \sum_\alpha \mu_\alpha \nabla_\alpha^2 t_j$$

(I.1.6)

With reflection, paper, and pencil, the first of these quantities (I.1.5) will be recognised as the familiar G-matrix of Wilson, Decius and Cross (1); this form, but not the derivation, of the G-matrix has been previously written by Malhiot and Ferigle (58). However, in the present context, the G-matrix elements may be dynamic variables.

From the outset, quantum mechanics furnishes a natural and efficient origin for the G-matrix; in classical mechanics the origin of the G-matrix can be cumbersome.

As could be expected, quantum mechanics leads to new terms without simple classical analogs; the g's of (I.1.6) - local angular momentum? - contribute to the zero point energy and generate distortions in the average geometry of the molecule depending on the vibrational state of the molecule (within the harmonic oscillator approximation.) (We are not prepared to endow these higher order kinetic energy terms with physical significance.)

Equation (I.1.4) is nothing more than a generalized Laplacian operator; the simple derivation and form of (I.1.4) gives it some advantage, depending on objective, over the equivalent expression found in Margenau and Murphy (54) and the usual quantum mechanical textbooks (1, 57). In our notation, the usual generalized Laplacian reads:

$$\nabla^2 \equiv \sum_i \sum_j |G|^{1/2} \frac{\partial}{\partial t_i} |G|^{-1/2} G_{ij} \frac{\partial}{\partial t_j} \qquad (\text{I.1.7})$$

where $|G|$ is the determinant of the G-matrix (including rotation and translation).

The equivalence of (I.1.4) and (I.1.7) can be seen through the action of the operator (I.1.7) on the generalized coordinates themselves.

$$\nabla^2 t_n = \sum_i |G|^{1/2} \frac{\partial}{\partial t_i} |G|^{-1/2} G_{in} \qquad \text{(I.1.8)}$$

recall: $\nabla^2 t_n = g_n \qquad \frac{\partial t_n}{\partial t_j} = \delta_{ij}$ (the identity matrix)

With reflection, (I.1.8) brings (I.1.7) into the form (I.1.4); the converse, (I.1.4) to (I.1.7) is much more difficult.

The transformation is not yet complete. The transformed wavefunction carries a density factor if it is to preserve its meaning as a probability distribution when squared (57).

$$\Psi \text{(Cartesian)} = |G|^{1/4} \psi \text{(generalized)}$$

Consequently the generalized Schrodinger equation is frequently expressed in the form (1, 36).

$$\left\{ |G|^{-1/4} \nabla^2 |G|^{1/4} + 2\hbar^{-2}(E-V) \right\} \psi = 0$$

But the Cartesian wave function can be retained if its meaning and the role of the density factor is recalled.

(I-2) <u>Separation of Rotation, Translation and Configuration</u>

The three following translational coordinates define

the centre of mass of the molecule; these are dynamic

variables.

$$X_0 = \bar{M}^1 \sum_\alpha m_\alpha X_\alpha$$

$$Y_0 = \bar{M}^1 \sum_\alpha m_\alpha Y_\alpha$$

$$Z_0 = \bar{M}^1 \sum_\alpha m_\alpha Z_\alpha$$

(I.2.1)

where $$M = \sum_\alpha m_\alpha$$

and m_α is the mass of the αth particle.

The three rotational coordinates for a semirigid body

appear to be difficult to define (56); however the 3N

Cartesian vector quantities below will be shown to exhibit

desired mechanical properties.

$$\nabla_\alpha R_x = m_\alpha \{ \quad 0 \quad , (Z_\alpha - Z_0), -(Y_\alpha - Y_0)\}$$

$$\nabla_\alpha R_Y = m_\alpha \{-(Z_\alpha - Z_0), \quad 0 \quad , (X_\alpha - X_0)\}$$

$$\nabla_\alpha R_z = m_\alpha \{(Y_\alpha - Y_0), -(X_\alpha - X_0), \quad 0 \quad \}$$

(I.2.2)

Here, R_x, R_y, and R_z are presumed to be rotational

coordinates.

With these rotational and translational coordinates, the G-matrix takes the form:

$$G = \begin{pmatrix} G(\text{translation}) & 0 & 0 \\ 0 & G(\text{rotation}) & 0 \\ 0 & 0 & G(\text{configuration}) \end{pmatrix}$$

(I.2.3)

When the potential energy is a function of configuration only, the Schrodinger equation, according to the above representation, separates into translational, rotational and vibrational parts. The separation of translation is rigorous but the separation of rotation depends upon the rigidity of the molecule.

For rotation and translation the higher order kinetic terms, (I.1.6), are all identically zero; thus the decoupling is complete.

The matrix form (I.2.3) is most easily derived by considering the translational (and rotational) G-matrix elements in a Cartesian vector form. Let t denote a generalized coordinate.

$$\left\{ G(X_o, t), G(Y_o, t), G(Z_o, t) \right\} = \bar{M}' \sum_\alpha \nabla_\alpha t$$

$$\left\{ G(R_x, t), G(R_y, t), G(R_z, t) \right\} = \sum_\alpha (\nabla_\alpha t) \times (\vec{\pi}_\alpha)$$

where $\vec{\pi}_\alpha \equiv \left(X_\alpha - X_o, Y_\alpha - Y_o, Z_\alpha - Z_o \right)$

Rotational and all configurational coordinates exhibit the property:

$$\sum_{\alpha} \mathbf{V}_{\alpha} t = (0,0,0)$$

And all configuration coordinates exhibit the property:

$$\sum_{\alpha} (\mathbf{V}_{\alpha} t) \times (\mathbf{r}_{\alpha}) = (0,0,0)$$

These properties can be verified by carrying out the indicated operations for the various coordinates.

With very little labor it can be shown that

$$G(\text{translation}) = M^{-1} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$G(\text{rotation}) = \begin{pmatrix} I_{xx} & -I_{xy} & -I_{xz} \\ -I_{yx} & I_{yy} & -I_{yz} \\ -I_{zx} & -I_{zy} & I_{zz} \end{pmatrix}$$

and the most common configuration G-matrix elements have been tabulated elsewhere; otherwise these can be written via (I.1.5).

The moment of inertia tensor, G(rotation), depends upon the orientation of the molecule and its instantaneous configuration; thus the separation of rotation and configuration (or vibration) is not complete. Vibration-rotation

interactions are discussed by Wilson, Decius and Cross
(1, see Chapter 11) and in greater detail by Bodi (56);
however, both references employ the Eckart conditions
and differ from this development in that respect.

Because the Eckart conditions have not been invoked
here, linear molecules are not exceptional cases (from
the outset); moreover the equations derived thus far need
not be constrained to rigid systems. However, the physical
substance of this development, which depends on equations
(I.2.2), the rotational coordinates, remains largely
unexplored.

Equations (I.2.2) have not been previously written but
here they indicate a useful role in the analysis of molecular
mechanics. The author suggests that these equations be
named "the Harvey conditions" in memory of K.B. Harvey,
director of this research.

(1-3) The Vibrational Schrodinger Equation

After the separation of rotation and translation the
vibrational Schrodinger equation remains to be solved. An
approximate solution adequate for many purposes can be
obtained by replacing kinetic energy coefficients by either
their average or equilibrium values and expressing the
potential energy as a quadratic form in configuration-
displacement coordinates, Q_i . Here it is assumed that

the molecule remains near its equilibrium configuration while it vibrates.

To solve the vibrational Schrodinger equation,

$$\sum_i \sum_j G_{ij} \frac{\partial^2 \Psi}{\partial \rho_i \partial \rho_j} + \sum_i g_i \frac{\partial \Psi}{\partial \rho_i} + 2\hbar^{-2}\left(E - \tfrac{1}{2}\sum_i \sum_j F_{ij} \rho_i \rho_j\right)\Psi = 0 \tag{I.3.1}$$

when G_{ij}, g_i and F_{ij} are all constant coefficients, a linear transformation of the form,

$$\rho_k = \sum_j L_{kj} Q_j \tag{I.3.2}$$

$$Q_j = \sum_k (L^{-1})_{jk} \rho_k \tag{I.3.3}$$

such that

$$L^{-1} G L^{-t} = I \quad \text{(the identity matrix)} \tag{I.3.4}$$

$$L^t F L = \Lambda \quad \text{(a diagonal matrix)} \tag{I.3.5}$$

reduces (I.3.I) to a sum of independent quantum oscillators in the normal coordinates, Q_j .

$$\sum_j \left(\frac{\partial^2}{\partial Q_j^2} + \ell_j \frac{\partial}{\partial Q_j} - \hbar^{-2} \Lambda_{jj} Q_j^2 \right)\Psi = -2\hbar^{-2} E \Psi \tag{I.3.6}$$

Except for the terms

$$\ell_j \equiv \sum_n g_n \bar{L}'_{jn} \qquad \text{(I.3.7)}$$

the solution of (I.3.6) is a product of harmonic oscillator wavefunctions and the energy is a sum of harmonic oscillator energies (1). With nonzero ℓ_n's , standard methods for solving differential equations (42) indicate a solution as follows:

$$E = \left\{ \sum_n \frac{1}{2}\left(\frac{\hbar \ell_n}{2}\right)^2 + \left(V_n + \frac{1}{2}\right) \hbar \sqrt{\Lambda_{nn}} \right\} \qquad \text{(I.3.8)}$$

$$V_n = 0, 1, 2 \cdots$$

$$\Psi = \prod_n \phi_n(Q_n) \qquad \text{(I.3.9)}$$

$$\phi_n = N_{V_n} e^{-\frac{1}{2}\chi_n^2} H_{V_n}(\xi_n) \qquad \text{(I.3.10)}$$

$$\chi_n \equiv \xi_n + \frac{\ell_n}{2}\left(\frac{\hbar^2}{\Lambda_{nn}}\right)^{1/4} \qquad \text{(I.3.11)}$$

$$\xi_n \equiv \Lambda_{nn}^{1/4} Q_n / (\hbar)^{1/2} \qquad \text{(I.3.12)}$$

H_{V_n} is the $V_n \underline{}^{th}$ hermite polynomial

N_{V_n} is the normalizing factor

For the wavefunctions (I.3.10) the expected value of the normal coordinates is not zero. For example,

$$\langle 0| Q_n |0\rangle = - \frac{\hbar \ell_n}{2\sqrt{\Lambda_{nn}}}$$

and the magnitude of the shift depends on the quantum numbers.

The added zero-point energy is simply the potential energy of the molecule when it assumes its expected ground state configuration.

$$\frac{1}{2} \sum_n \Lambda_{nn} \langle 0| Q_n |0\rangle^2 = \frac{1}{2} \sum_n \left(\frac{\hbar \ell_n}{2} \right)^2$$

However the physical significance of these higher order kinetic terms, given the approximations invoked, is not yet certain.

APPENDIX TWO: REDUNDANT COORDINATE SYSTEMS

Redundant coordinate systems are sometimes needed for
the analysis of molecular structure in familiar geometrical
terms. This appendix deals with the question as to whether
or not redundant coordinates imply related interdependencies
for mechanical quantities such as force constants as has
been suggested by Hubbard (40) and Gold, Dowling and Meister
(41). Crawford and Overend (39) have attempted to show
that such relations for force constants are in fact
arbitrary.

All of these authors have treated the redundant
coordinate system as though the coordinates were independent
variables subject to constraints or redundancy conditions.
Potential energy is expressed as a Taylor series in redundant
coordinates.

In their approach it is not clear that the Taylor series
coefficients, formed by partial differentiation, can be
called upon without substantial justification when the
coordinates cannot be independent. Unfortunately the
previously cited authors have not considered the propriety
of the Taylor series coefficients when redundant coordinate
systems are employed.

Further, there is something intrinsically unsatisfying
with an ab-initio expression of potential energy in terms
of redundant coordinates. If necessary, one can accept the

notion of potential energy in terms of redundant coordinates but only as a derived or auxiliary quantity - not as an initial assumption or intrinsic property.

In this appendix, the redundant coordinate system and all related quantities shall be strictly referred to a non redundant coordinate system. The significant step here is that the transformation matrix is not square and therefore not invertible in the usual simple way.

Our approach provides the supplementary information needed to resolve the indeterminacy noted by Crawford and Overend (39). The two approaches are infact complementary rather than contradictory.

(II-1) Transformations involving redundant coordinates

As geometrical quantities defined on a set of points or atoms, the redundant coordinates (ρ) can be defined without question in terms of nonredundant coordinates (t).

$$\rho_n = \sum_k \left(\frac{\partial \rho_n}{\partial t_k}\right)_0 t_k + \quad \text{higher terms} \quad \text{(II.1.1)}$$

Clearly every configuration of the molecule specifies exactly all of the non redundant coordinates and all of the redundant coordinates. Consequently the relation between redundant coordinates and nonredundant coordinates is one-to-one, in terms of the molecular configuration. This means

that the inverse transformation exists even though the
matrix $\left(\partial \rho_n / \partial t_k\right)_0$ is not square!

For infinitesmal distortions, equations (II.1.1)
define an overdetermined system of linear equations; thus
the nonredundant coordinates can be expressed in terms of
the redundant coordinates.

$$\text{Let} \qquad S_{nk} = \left(\partial \rho_n / \partial t_k\right)_0 \qquad\qquad \text{(II.1.2)}$$

The matrix $\left(S^t S\right)^{-1} S^t$ is the left hand inverse of
the matrix S ,

$$\left\{\left(S^t S\right)^{-1} S^t\right\} S = \left(S^t S\right)^{-1}\left(S^t S\right) = I$$

$\left(S^t S\right)$ is a square matrix of full rank and (3N-6) x (3N-6),
where N is the number of atoms.

$$\text{Therefore:} \quad t_k = \sum_n \left\{\left(S^t S\right)^{-1} S^t\right\}_{kn} \rho_n \qquad\qquad \text{(II.1.3)}$$

If the potential energy is properly defined in terms of
nonredundant coordinates,

$$2V = \sum_i \sum_j F_{ij} t_i t_j$$

substitution of (II.1.3) provides an equivalent expression
in terms of redundant coordinates.

$$2V = \sum_m \sum_n (F_R)_{mn} \rho_m \rho_n$$

where the F_R-matrix,

$$F_R \equiv S(S^tS)^{-1}F(S^tS)^{-1}S^t \tag{II.1.4}$$

represents the force constant matrix for redundant coordinates. As well

$$G_R = SGS^t \tag{II.1.5}$$

$$L_R = SL \tag{II.1.6}$$

where L_R and G_R are redundant coordinate representations of L and G for nonredundant coordinates.

Pseudo inverses of F_R, G_R and L_R, noted as $\overline{F}_R$, $\overline{G}_R$ and $\overline{L}_R$ respectively, can be written in the form

$$\overline{F}_R = SF^{-1}S^t \tag{II.1.7}$$

$$\overline{G}_R = S(S^tS)^{-1}G^{-1}(S^tS)^{-1}S^t \tag{II.1.8}$$

$$\overline{L}_R = L^{-1}(S^tS)^{-1}S^t \tag{II.1.9}$$

Decius (8) has shown that F^{-1} gives the potential energy in terms of generalized forces - a fact later iterated by Cyvin (7).

Decius and Oden (59), because the inverse transformation is not needed to formulate $\bar{F}_R$, have used the above relation to specify all of the constants involved in $\bar{F}_R$.

The eigenvectors of G_R which correspond to zero eigenvalues span the null space of the S-transformation (impossible configurations of the molecule). Let

N_V = 3N-6 the number of genuine vibrations

N_R be the number of redundant coordinates

U_R be the orthogonal matrix with diagonalizes G_R

$$U_R^t G_R U_R = \Gamma_R$$

where Γ_R is diagonal but $N_R - N_V$ of the diagonal entries are zero.

Let U_R be partitioned as a matrix

$$U_R = (U | U_R) \qquad \text{such that}$$

$$G_R U = U \Gamma \qquad \text{and} \qquad G_R U_R = 0$$

where U_R are eigenvectors with zero eigenvalues and U are eigenvectors with nonzero eigenvalues noted by the diagonal $N_V \times N_V$ matrix Γ.

$$S^t U_R = 0 \quad \text{(see reference 42)} \qquad \text{(II.1.10)}$$

therefore $\qquad F_R U_R = S(S^t S)^{-1} F (S^t S)^{-1} S^t U_R = 0 \qquad$ (II.1.11)

and $\qquad U_R^t F_R U_R = 0 \qquad\qquad\qquad\qquad$ (II.1.12)

Equations (II.1.11) and (II.1.12) which follow from (11.1.4) and (II.1.10) provide the relations needed to define the so called indeterminate force constants arising from the redundant coordinate system.

It will be observed that the equations of this thesis are correct as written if the U-matrix is understood to be composed of the eigenvectors of the G_R matrix with nonzero eigenvalues. Here the U-matrix need not be square but its columns remain orthogonal.

In summary once it is realized that all coordinate transformations covering the possible configurations of a molecule are one-to-one whether the transformation generates redundant coordinates or not, then the redundancy conditions on force constants follow via the inverse transformation.

APPENDIX THREE: THE EXPONENTIAL MATRIX

The exponential matrix is defined like the exponential function,

$$e^{Ks} \equiv \sum_{n=0}^{n \to \infty} K^n s^n / n!$$

where K is a square matrix and s is an ordering parameter. The ordering parameter enables us to establish the essential properties of the exponential matrix with little algebraic labor. For example, the formula

$$\frac{\partial e^{Ks}}{\partial s} = K e^{Ks} = e^{Ks} K$$

is easily derived.

More general properties can be established by considering the matrix function

$$H \equiv e^{Ks} \Omega e^{-Ks}$$

where Ω is, for the present purpose, a square matrix; K and s are as defined above.

Matrix differentiation gives

$$\frac{\partial H}{\partial s} = [K, H] = e^{Ks} [K, \Omega] e^{-Ks}$$

The $(n+1)^{th}$ derivative can be expressed in terms of the nth derivative,

$$\left(\frac{\partial}{\partial s}\right)^{n+1} H = \left(\frac{\partial}{\partial s}\right)^n \frac{\partial H}{\partial s} = \left(\frac{\partial}{\partial s}\right)^n [K, H]$$

$$= \left[K, \left(\frac{\partial}{\partial s}\right)^n H\right]$$

Consequently
$$\frac{\partial H}{\partial s} = [K, H]$$

$$\frac{\partial^2 H}{\partial s^2} = [K, [K, H]]$$

$$\frac{\partial^3 H}{\partial s^3} = [K, [K, [K, H]]]$$

In our applications we are interested in the H-matrix as a perturbed form of the Ω -matrix and conversely. The H and Ω matrices are related through the K-matrix and ordering parameter by the expansion about $S = 0$.

$$H = \Omega + [K, \Omega] s + [K, [K, \Omega]] s^2/2! +$$

+ higher terms

recall that:
$$\underset{S \to 0}{\text{Limit}} H = \Omega$$

When Ω is the identity matrix, the above equations show that
$$e^{Ks} e^{-Ks} = I \qquad \text{(the identity matrix)}$$

or
$$\left(e^{Ks}\right)^{-1} = e^{-Ks}$$

As well, when the K-matrix is skew symmetric (skew hermitian),

$$K^\dagger = -K$$

the exponential form is orthogonal (unitary).

$$\left(e^{Ks}\right)^\dagger = e^{-Ks}$$

Consequently the Ω-matrix can be viewed as a diagonal matrix composed of the eigenvalues of H; in this case the orthogonal matrix e^{Ks} represents the eigenvectors of H.

The exponential matrix may appear in the literature of mathematics (60) usually in connection with the theory of lie groups. Applications of the exponential matrix have not been extensive in chemistry nor in any area where mathematics is more a tool than a logical art. Yet its properties indicate that it can be a useful tool.