PART III

A new technique for force field refinement
CHAPTER 5

A NEW ITERATIVE TECHNIQUE FOR INVERSE VIBRATIONAL ANALYSIS

A B S T R A C T

A new iterative technique, which uses experimental data to refine the force field obtained initially employing any usual approximate method, is reported. The computational procedure along with the parametric representation of isotopic frequencies, Coriolis coupling constants, rotational distortion constants and mean amplitudes of vibration is given. In the parametric representation of rotational distortion parameters \( \tau_{\alpha\beta\gamma\delta} \), compact quadratic equations connecting the \( \tau \) parameters and the angle parameters are derived. The derivation of the formula that combines all the angle parameters yielded by the number of input data used for the refinement is given and its meaning as a semiempirical formula that is useful in refining the force field to become consistent with the input data is discussed.
5.1 Introduction

Methods employed in the inverse vibrational analysis are numerous [1.16 - 1.42]. The methods, which use empirical constraints [1.16 - 1.28], are approximate and those, which use additional experimental data [1.27 - 1.42], are comparatively more accurate. The method of Redington and Alijibury [1.26] falls under the first category. Nevertheless, the method is important because of the following.

Redington's concepts of restoring force constants [Section 1.5.2] and the $F_{\text{stp}}$ function [Section 1.5.4] are quite useful. While the maximal property of the former eliminates multiplicity of solutions [Chapter 2] in the inverse vibrational problem, that of the latter evolves a general criterion for checking the vibrational assignment [Chapter 3] whenever ambiguity arises. More important than these two uses is the fact that Redington's force field is of high structure correlation efficiency as is evident from Chapter 4.

Therefore, there is reason to believe that Redington's procedure, though yields only approximate force field, keeps intact all the information regarding the properties of the molecule within the force field. With the intention of tapping this potential source of information and at the same time
obtaining an accurate force field, a new iterative technique is proposed in this chapter. This technique uses experimentally observed data to refine the force field obtained initially employing Redington's method. The refined force field retains its structure correlation efficiency and becomes accurate in reproducing other molecular constants.

5.2 The new iterative technique

5.2.1 The procedure

The new procedure consists in refining Redington's force field using the available experimental data through a further set of \( n(n-1)/2 \) angle parameters \( \theta_{ij} \) with \( i, j = 1, 2, 3, \ldots, n \) and \( i < j \). \( n \) is the order of the problem. The method permits the use of all the observed molecular constants of different types; isotopic frequencies, Coriolis coupling constants, rotational distortion constants, mean amplitudes of vibration etc.

Parametric form of \( F \) matrix is given by

\[
F = \tilde{L}^{-1} A \Lambda \tilde{A} L^{-1}
\]

where \( L \) is the initial normal coordinate transformation matrix which, indeed, is the final \( L \) matrix of Redington's method. That is the reason why \( L_0 \) remains replaced by \( L \) in eqn.5.1 which, otherwise, is the same as eqn.1.28. \( A \) is the parameter matrix given by

\[
A = \prod A_{ij}, \quad i, j = 1, 2, 3, \ldots, n \text{ and } i < j.
\]
$A$ is an unit matrix except for the elements

\[ a_{ii} = a_{jj} = \Theta_{ij} \]

and \[ a_{ij} = -a_{ji} = \Theta_{ij}. \]

Thus, the semi normal coordinate transformation matrix $L$ is first parametrically treated with $n(n-1)/2 \phi_{ij}$ parameters obtained through $F$ critical point solution [Section 1.5.4] and further treated with another set of $\Theta_{ij}$ parameters in the refinement part.

$\Theta_{ij}$ takes care of the mixing between the $i$th and the $j$th modes. Each of the experimental data provides for a quadratic equation in $\Theta_{ij}$ in terms of the elements of the $L^{-1}$ matrix [given in Sections 5.2.2 to 5.2.5]. As the $L$ matrix has already been brought close to the true one by the $\phi_{ij}$ parameters, only finer adjustments among the different modes need to be taken care of in the refinement part. Therefore, of the two solutions of the quadratic equation, that of smaller numerical value is chosen. If the total number of observed constants used is $N$, an equal number of $\Theta_{ij}$'s are obtained. $N$ here is equal to the sum of the numbers of constants of the different types used. If $N_1$ isotopic frequencies, $N_2$ Coriolis coupling constants, $N_3$ rotational distortion constants etc., are used, $N = N_1 + N_2 + N_3 + \ldots$. The true $\Theta_{ij}$ is obtained from

\[ 2\Theta_{ij} = \frac{1}{N} \sum_{l=1}^{N} \Theta_{ijl} \Theta_{ijl}. \]
When any one $\theta_{ij}$ is used to form the matrix $A_{ij}$, the force field becomes consistent with the $l$th input constant, whereas the true $\theta_{ij}$ obtained using eqn.5.4 tends to make the force field become consistent with all the $N$ constants.

At this stage it is necessary to digress to consider the parametric representation of the molecular constants and the derivation and meaning of eqn.5.4 [Section 5.2.6].

5.2.2 Parametric representation of isotopic frequencies

Eqn. 2.5

$$K \Lambda^{-1} = \tilde{\Lambda} B \Lambda,$$

relates the isotopic shifts $\Delta \lambda$'s to the angle parameters and the $L^{-1}$ elements. The diagonal elements of $K \Lambda^{-1}$ are $\frac{\Delta \lambda}{\Lambda}$ and $B$ is given by

$$B = L^{-1} \Delta G L^{-1},$$

where $\Delta G = G - G^*$, $G^*$ being the inverse kinetic energy matrix of the isotopic species.

In the refinement technique, only one pair of modes is considered at a time (ith and jth; $i, j = 1,2, ..., n$ with $i < j$), i.e., the mixing between the ith and the jth modes through the parameter $\theta_{ij}$ only is considered at a time. Therefore, with $A = A_{ij}$, eqn.5.5 yields

$$\frac{\Delta \lambda_i}{\Lambda_i} = B_{ii} C_{ij}^2 \theta_{ij} - 2B_{ij} S_{ij} \theta_{ij} + B_{jj} S_{ij}^2 \theta_{ij}$$

5.7
and
\[ \frac{\Delta \Lambda_j}{\Lambda_j} = B_{ii} S^2 \theta_{ij} + 2B_{ij} S \theta_{ij} C \theta_{ij} + B_{jj} C^2 \theta_{ij}. \]  
5.8

Multiplying the LHS of equations 5.7 and 5.8 by \((S^2 \theta_{ij} + C^2 \theta_{ij})\);
dividing throughout by \(C^2 \theta_{ij}\) and rearranging the terms one gets

\[ ( B_{jj} - \frac{\Delta \Lambda_i}{\Lambda_i} ) T^2 \theta_{ij} - 2B_{ij} T \theta_{ij} + ( B_{ii} - \frac{\Delta \Lambda_i}{\Lambda_i} ) = 0 \]
5.9

and

\[ ( B_{ii} - \frac{\Delta \Lambda_j}{\Lambda_j} ) T^2 \theta_{ij} + 2B_{ij} T \theta_{ij} + ( B_{jj} - \frac{\Delta \Lambda_j}{\Lambda_j} ) = 0 \]
5.10

where \(T\) stands for the tangent of the angle \(\theta_{ij}\).

If \(\Delta \Lambda_i\) is the \(i\)th constant in the list of input data,
eqn.5.9 gives \(\theta_{ij}'\). Similarly, eqn. 5.10 gives \(\theta_{ijm}\) if \(\Delta \Lambda_j\) is the
\(m\)th constant.

5.2.3 Parametric representation of Coriolis coupling constants

Eqn.1.42
\[ \zeta^\alpha = L^{-1} C^\alpha L^{-1} \]  
5.11
gives the Coriolis coupling constants of the degenerate modes of
vibration of a molecule about the axis \(\alpha\) (\(\alpha = x, y, z\)).
With
the final normal coordinate transformation matrix of Redington’s
method as the \(L\) matrix, further refinement of \(L\) is possible
through the angle parameter matrix \(A\). In that case eqn.5.11
becomes

\[ \zeta^{\alpha} = A L^{-1} C^{\alpha} L^{-1} A = A J A \]  \hspace{1cm} 5.12

where

\[ J = L^{-1} C^{\alpha} L^{-1}. \]  \hspace{1cm} 5.13

Since the eqn. 5.12 is similar to eqn. 5.5 the equations analogous to equations 5.9 and 5.10 respectively are

\[ (J_{ij} - \zeta_{ii}) T_{ij}^{2} \theta_{ij} - 2 J_{ij} \theta_{ij} + (J_{ii} - \zeta_{ii}) = 0 \]  \hspace{1cm} 5.14

and

\[ (J_{ii} - \zeta_{ii}) T_{ij}^{2} \theta_{ij} + 2 J_{ij} \theta_{ij} + (J_{jj} - \zeta_{jj}) = 0. \]  \hspace{1cm} 5.15

5.2.4 Parametric representation of rotational distortion constants

The relations connecting the rotational distortion constants and the rotational distortion parameters \( \tau_{\alpha\beta\gamma\delta} \) are given in Section 1.8. The \( \tau \) parameters can directly and easily be parametrically represented. In the parametric form, equations 1.47 and 1.48 respectively are

\[ a^{(\alpha\omega)} = 2 A L^{-1} H^{(\alpha\omega)} = A b^{(\alpha\omega)} \]  \hspace{1cm} 5.16

and

\[ a^{(\alpha\beta)} = -2 A L^{-1} H^{(\alpha\beta)} = A b^{(\alpha\beta)} \]  \hspace{1cm} 5.17

where

\[ b^{(\alpha\omega)} = 2 L^{-1} H^{(\alpha\omega)} \] and \[ b^{(\alpha\beta)} = -2 L^{-1} H^{(\alpha\beta)}. \]
For $\alpha = \beta = \gamma = \delta = x, y$ or $z$, substitution of eqn. 5.16 into eqn. 1.45 gives

\[
\left( \frac{b_1}{\omega_1} \right)^2 + \left( \frac{b_2}{\omega_2} \right)^2 + \ldots + \left( \frac{b_i C \Theta_{i,j} - b_j S \Theta_{i,j}}{\omega_i} \right)^2
\]

\[
+ \left( \frac{b_{i+1}}{\omega_{i+1}} \right)^2 + \ldots + \left( \frac{b_i S \Theta_{i,j} + b_j C \Theta_{i,j}}{\omega_j} \right)^2
\]

\[
+ \left( \frac{b_{j+1}}{\omega_{j+1}} \right)^2 + \ldots + \left( \frac{b_n}{\omega_n} \right)^2 = - \frac{(\hbar I_o^{0})^4}{K} \tau_{\alpha\alpha\alpha\alpha} \tag{5.18}
\]

Multiplying the terms not involving $\Theta_{i,j}$ by $(C^2 \Theta_{i,j} + S^2 \Theta_{i,j})$ and then all the terms by

\[
\frac{1}{C^2 \Theta_{i,j}} \prod_{p=1}^{n} \omega_p^2
\]

one gets

\[
\left\{ (b_i^2 \omega_i^2 + b_j^2 \omega_j^2) \prod_{p=1}^{n} \omega_p^2 + \sum_{q=1}^{n} \left[ b_i^2 \prod_{p=1}^{n} \omega_p^2 \right] \right\}_{\text{Ex } i \& j}
\]

\[
+ \sum_{q=1}^{n} \left[ b_i^2 \prod_{p=1}^{n} \omega_p^2 \right]_{\text{Ex } q}
\]

\[
+ 2 \frac{b_i b_j (\omega_i^2 - \omega_j^2)}{\prod_{p=1}^{n} \omega_p^2} T \Theta_{i,j}
\]

\[
+ \left\{ (b_i^2 \omega_i^2 + b_j^2 \omega_j^2) \prod_{p=1}^{n} \omega_p^2 + \sum_{q=1}^{n} \left[ b_i^2 \prod_{p=1}^{n} \omega_p^2 \right] \right\}_{\text{Ex } i \& j}
\]

\[
+ \left\{ (b_i^2 \omega_i^2 + b_j^2 \omega_j^2) \prod_{p=1}^{n} \omega_p^2 + \sum_{q=1}^{n} \left[ b_i^2 \prod_{p=1}^{n} \omega_p^2 \right] \right\}_{\text{Ex } q}
\]

\[
+ P \tau_{\alpha\alpha\alpha\alpha} \right\} = 0 \tag{5.19}
\]
where \( P = \frac{(n \mathbf{I}^\alpha \mathbf{I}^\beta)^4}{K} \prod_{p=1}^{n} \omega_p^2 \) and \( b \)'s are the elements of the column matrix \( \mathbf{b}^{(\alpha \beta)} \).

For \( \alpha = \gamma = x, y \) or \( z \) and correspondingly \( \beta = \delta = y, z \) or \( x \), substitution of eqn. 5.17 into eqn. 1.45 gives an equation of the same form as eqn. 5.19, but with

\[
P = \frac{n^4 (I^\alpha I^\beta)^2}{K} \prod_{p=1}^{n} \omega_p^2 \quad \text{and} \quad \tau = \tau^{\alpha \beta \gamma},
\]

\( b \)'s being the elements of the matrix \( \mathbf{b}^{(\alpha \beta \gamma)} \).

And finally for \( \alpha = \beta = x, y, \) or \( z \) and correspondingly \( \gamma = \delta = y, z \) or \( x \), substitution of eqn. 5.16 and eqn. 5.16 with \( \alpha \alpha \) replaced by \( \gamma \gamma \) into eqn. 1.45 yields

\[
\begin{align*}
\left[ \begin{array}{c}
\left( \frac{b_{i}^{\alpha \alpha} \gamma_{i}^{\gamma \gamma} \omega_{i}^{2} + b_{j}^{\alpha \alpha} \gamma_{j}^{\gamma \gamma} \omega_{j}^{2}}{p} \right)^{n} \prod_{p=1}^{n} \omega_{p}^{2} + \sum_{q=1}^{n} \left[ \begin{array}{c}
\frac{b_{q}^{\alpha \alpha} \gamma_{q}^{\gamma \gamma} \prod_{p=1}^{n} \omega_{p}^{2} }{p} \\
\prod_{q=1}^{n} \omega_{q}^{2} \\
\end{array} \right]_{Ex i \& j} \\
\end{array} \right]
\end{align*}
\]

\[
+ P \tau^{\alpha \alpha \gamma \gamma} \left( I_{ij} \right)_{ij} + \left[ \begin{array}{c}
\left( \frac{b_{i}^{\alpha \alpha} \gamma_{i}^{\gamma \gamma} \omega_{i}^{2} + b_{j}^{\alpha \alpha} \gamma_{j}^{\gamma \gamma} \omega_{j}^{2}}{p} \right)^{n} \prod_{p=1}^{n} \omega_{p}^{2} + \sum_{q=1}^{n} \left[ \begin{array}{c}
\frac{b_{q}^{\alpha \alpha} \gamma_{q}^{\gamma \gamma} \prod_{p=1}^{n} \omega_{p}^{2} }{p} \\
\prod_{q=1}^{n} \omega_{q}^{2} \\
\end{array} \right]_{Ex i \& j} \\
\end{array} \right]
\]

\[
+ P \tau^{\alpha \alpha \gamma \gamma} = 0
\]

5.20
\[ P = \frac{h^4(I_\alpha I_\gamma)}{K} \prod_{p=1}^{n} \omega_p. \]

In all the above expressions, 'Ex i' means excluding i.

Equations 5.19 and 5.20 permit the use of experimental values of \( \tau_{xxxx}, \tau_{yyyy}, \tau_{zzzz}, \tau_{xxyy}, \tau_{yyzz}, \tau_{zxxz}, \tau_{xyxy}, \tau_{yzyz} \) and \( \tau_{zxzx}. \)

5.2.5 Parametric representation of vibrational mean amplitudes

The parametric form of eqn.1.40, in the usual notations, is

\[ \Sigma = L\Lambda\Delta \Lambda L. \]

Expansion of the above equation yields relations connecting each of the n diagonal elements of the symmetrised mean square amplitude matrix \( \Sigma \) of the block of vibrations considered, the vibrational frequencies, the L matrix elements and each of the \( n(n-1)/2 \) angle parameters \( \Theta_{ij} \). On rearrangement of the terms, \( n^2(n-1)/2 \) quadratic equations are obtained. These equations are

\[
\begin{align*}
\left[ \sum_{s=1}^{n} \sum_{t=1}^{n} L_{ks}^2 \Delta_{lt} - \Sigma_{kk} \right] T_{ij}^2 + 2 \sum_{k=1}^{n} L_{ki} L_{kj} (\Delta_{ij} - \Delta_{ji}) T_{ij} \\
+ \sum_{s=1}^{n} \sum_{t=1}^{n} L_{ks}^2 \Delta_{lt} - \Sigma_{kk} \right] = 0
\end{align*}
\]

for \( k = 1, 2, \ldots, n \) and \( i, j = 1, 2, 3, \ldots, n \) with \( i < j \).

The \( \Sigma_{kk} \) values can be calculated from the experimentally observed mean amplitudes of vibration of the bonded atom pairs using the
relations such as 3.11 and in turn equations 5.22 are solved for $\Theta_{ij}$.

Similar equations can be formed for the off-diagonal elements of the $\Sigma$ matrix also. The values of these elements are calculated from the mean vibrational amplitudes of the bonded and nonbonded atom pairs using the relations such as 3.11 and hence the solutions of the equations for $\Theta_{ij}$.

5.2.6 The derivation and meaning of eqn.5.4

Eqn.5.4 is semiempirical. It was aimed at a $\Theta_{ij}$ that produces an $F$ matrix, each of the elements of which is the mean of the corresponding elements of the $F$ matrices obtained using the individual parameters $\Theta_{ij1}$, $\Theta_{ij2}$, ..., $\Theta_{ijN}$. It will be evident from the following that such an angle parameter does not exist.

With a single parameter $\Theta_{ij}$, eqn. 5.1 gives the expression for the force constant $F_{kk}$, in terms of the $L^{-1}$ elements, as

$$F_{kkl} = \sum_{i=1}^{N} \sum_{j=1}^{N} \left[ L_{ik} \Theta_{ijl} - L_{jk} \Theta_{ijl} \right]^{2} A_{i}$$

$$+ \sum_{i=1}^{N} \sum_{j=1}^{N} \left[ L_{ik} \Theta_{ijl} + L_{jk} \Theta_{ijl} \right]^{2} A_{j}$$

$$+ \sum_{i=1}^{N} \sum_{j=1}^{N} \left[ L_{ik} \Theta_{ijl} + L_{jk} \Theta_{ijl} \right]^{2} A_{n}$$

On rearranging the terms it becomes

$$F_{kkl} = \sum_{i=1}^{N} \sum_{j=1}^{N} \left[ L_{ik}^{2} A_{i} + L_{jk}^{2} A_{j} \right] C^{2} \Theta_{ijl}$$
The mean of all the N number of $F_{kkl}$'s is obtained as

$$F_{kk} \text{(average)} = L^2_{ik} \Lambda_i + \ldots + \left( L^2_{ik} \Lambda_i + L^2_{jk} \Lambda_j \right) \frac{1}{N} \sum_{l=1}^{N} C^2_{ijl}$$

$$+ \left( L^2_{jk} \Lambda_j + L^2_{ik} \Lambda_i \right) \frac{1}{N} \sum_{l=1}^{N} S^2_{ijl}$$

$$+ 2 L_{ik} L_{jk} (\Lambda_i - \Lambda_j) \frac{1}{N} \sum_{l=1}^{N} S_{ijl} C_{ijl} + \ldots + L^2_{nk} \Lambda_n. \quad 5.25$$

If there exists a single angle parameter $\theta_{ij}$ that can give $F_{kk}$ the same value as the above $F_{kk} \text{(average)},$

$$F_{kk} \text{(average)} = L^2_{ik} \Lambda_i + \ldots + \left( L^2_{ik} \Lambda_i + L^2_{jk} \Lambda_j \right) C^2_{ij}$$

$$+ \left( L^2_{jk} \Lambda_j + L^2_{ik} \Lambda_i \right) S^2_{ij}$$

$$+ 2 L_{ik} L_{jk} (\Lambda_i - \Lambda_j) S_{ijl} C_{ijl} + \ldots + L^2_{nk} \Lambda_n. \quad 5.26$$

From equations 5.25 and 5.26 one gets

$$C^2_{ij} = \frac{1}{N} \sum_{l=1}^{N} C^2_{ijl} \quad 5.27$$

$$S^2_{ij} = \frac{1}{N} \sum_{l=1}^{N} S^2_{ijl} \quad 5.28$$
and 
\[ S_{2\theta} = \frac{2}{N} \sum_{l=1}^{N} S_{\theta l} C_{\theta l} \]

Substitution from equations 5.27 and 5.28 into the LHS of eqn. 5.29 does not yield the RHS of eqn. 5.29. This shows that \( \theta_{ij} \) does not exist. However, for a given set of \( \theta_{ij} \)'s, while the \( \theta_{ij} \)'s of 5.27 and 5.28 coincide, 5.29 gives a value which is only slightly different. But, only 5.29, which is nothing but eqn. 5.4, decides the sign of the \( \theta_{ij} \) parameter and hence it has been chosen to obtain the true \( \theta_{ij} \) from.

5.2.7 The iteration

This is in continuation of 'the procedure ' [Section 5.2.4]. \( \theta_{12} \) is the free parameter, i.e., \( \theta_{12} \) is the first parameter to be fixed using \( N \) experimental data, Redington's \( L \) matrix and eqn. 5.4. The other parameters are fixed in succession in the order \( \theta_{19}, \theta_{14}, \ldots, \theta_{1n}, \theta_{29}, \ldots, \theta_{2n}, \theta_{34}, \ldots, \theta_{(n-2)n} \) and \( \theta_{(n-1)n} \), but from the \( L \) matrices constrained by the already fixed parameters. This statement is made clear in the following paragraph.

\( \theta_{19} \) is obtained following the same procedure but using \( L_{A_{12}} \) in the place of \( L \). For \( \theta_{14} \), the corresponding 'initial normal coordinate transformation matrix' is \( L_{A_{12} A_{19}} \) and for \( \theta_{2n} \), it is \( L_{A_{12} A_{19} A_{14}} \ldots A_{1n} A_{29} \ldots A_{2(n-1)} \). Thus, for \( \theta_{(n-1)n} \), it is \( L_{A_{12} A_{1n} A_{23} \ldots A_{2(n-1)} A_{2n} A_{34} \ldots A_{3(n-1)} A_{3n} \ldots A_{(n-2)(n-1)} A_{(n-2)n}} \).

After \( \theta_{(n-1)n} \) is determined, the calculations are repeated starting from \( \theta_{12} \). When this process is repeated the
numerical value of a given $\theta_{ij}$ is found to decrease. The iteration is continued until anyone $\theta_{ij}$ parameter becomes zero or insignificantly small. This ensures that the final $L$ matrix, i.e.,

$$L A_{12} A_{13} \ldots A_{1n} A_{23} \ldots A_{2(n-1)} A_{2n} A_{34} \ldots A_{3(n-1)} A_{3n} A_{45} \ldots A_{(n-2)n} A_{(n-1)n},$$

has attained optimum balancing among all the input data, i.e., the force field has attained the optimum consistency with all the observed constants used as input data. In certain cases, it may become oscillatory after a few steps and the iteration is continued up to that stage beyond which $\theta_{ij}$ becomes oscillatory.

5.3 Distinctive features of the technique

The new technique can be used to refine not only Redington's force field but any reasonable force field obtained using any method. The final normal coordinate transformation matrix of that method is used as $L$ in the refinement process.

It is comprehensive in the sense that all the available observed constants can be used as input data so that the force field becomes consistent with all of these constants. Parametric representation of electrooptic parameter and vibrational band intensity is not given here because these are not used in the present study.

When applied to the force field obtained using FCPF critical point procedure of Redington, it is expected to yield a refined force field of high structure correlation efficiency and of greater accuracy in reproducing the other molecular constants.
Since the modes are considered in pairs (i.e., only any two modes at a time) the refinement procedure is applicable to problems of any order.

The ease and elegance of the method makes it applicable to systems of any type and it is not tailored to suit any particular type or a few types of molecules.

It has been successfully applied to a number of molecules of different types. The results and findings in the case of five different types of molecules are presented in the following five chapters [Chapters 6 to 10].