

CHAPTER II

THEORETICAL CONSIDERATIONS AND CALCULATIONS

2.1 Principle of the Wilson GF Matrix Method²

The method is used to analyze problems in molecular vibrations. The first step is to derive expressions for the kinetic and potential energies in terms of some convenient set of co-ordinates, usually internal co-ordinates, R.

A general quadratic field has the form

$$2V = \sum_i \sum_j f_{ij} R_i R_j \quad \dots\dots(1)$$

where R_i and R_j are internal co-ordinates and $f_{ij} = \partial^2 V / \partial R_i \partial R_j$.

The above equation can be written in a matrix form

$$2V = \text{---} \square \parallel \quad (2)$$

For small displacements of the atoms the kinetic energy T is given by a similar expression, involving the time derivatives of the co-ordinate

$$R_i = (\partial R_i / \partial T):$$

$$2T = \overset{\cdot}{R} M R \text{ or } 2T = \text{---} \square \parallel \quad (3)$$

The M matrix is a function of the atomic masses and geometry of the molecule; when these parameters are known, their determination is straight forward but tedious. Partly for this reason, the kinetic

energy is often characterized by an alternate equation involving the momenta P , conjugate to the co-ordinates R :

$$2T = \dot{P}G\dot{P} \text{ or } 2T = \begin{matrix} \text{---} & \square & \text{---} \\ & & \end{matrix} \quad (4)$$

The G matrix is evidently related to M matrix; by making use of the definition of the momenta

$$P = M\dot{R} \text{ or } \begin{matrix} \text{---} \\ \end{matrix} = \begin{matrix} \square & \text{---} \\ & \end{matrix} \quad (5)$$

to substitute for P in (4), it is easy to show that

$$GM = I \text{ or } M = G^{-1} \quad (6)$$

where I is identity matrix, and equation (6) shows that M and G are inverse matrices.

Since, in general, there will be non-zero cross terms in the expression for both V and T , the co-ordinates, R , must be transformed into a new set of n displacement normal co-ordinates Q through the relation

$$R = L Q, \quad (7)$$

Q being a column vector. By appropriate choice of L , both the potential and the kinetic energy can be written as

$$2V = \dot{Q}' \Lambda Q \quad (8)$$

$$2T = \dot{Q}' \dot{Q} \quad (9)$$

where Λ is a diagonal matrix of the frequency parameter λ_k . Using (7) to substitute for R in equations (2) and (4), and comparing the result with (8) and (9), we find:

$$L' F L = \Lambda$$

and

$$L' M L = T$$

combining these two equations gives:

$$F L = M L \Lambda \quad (10)$$

On multiplying (10) by $G = M^{-1}$, we obtain:

$$G F L = L \Lambda \quad (11)$$

The secular equations which specify the acceptable values of the diagonal element λ_k of Λ may be written as:

$$|F - \lambda M| = 0 \quad (12)$$

and

$$|G F - \lambda I| = 0 \quad (13)$$

The force constants, F and the frequencies, λ can thus be solved by using (12) and (13).

The computation can be simplified further by introducing symmetry co-ordinates S. Let the internal co-ordinates R be transformed by:

$$S = U R \quad (14)$$

where U is an orthogonal matrix ($U'U = I$) whose elements must satisfy the following,

$$\sum_k (U_{jk})^2 = 1 \quad (\text{normalization})$$

$$\sum_k U_{jk} U_{lk} = 0 \quad (\text{orthogonality})$$

Furthermore, the symmetry of the molecule must be taken into consideration in constructing the U matrix. The new sets of co-ordinates, S_1, S_2, \dots, S_j thus obtained are linear combinations of internal co-ordinates and are called (internal) symmetry co-ordinates.

In order to set up the secular equation in terms of symmetry co-ordinates, it is necessary to convert the kinetic and potential energies in terms of these co-ordinates, and these may be written as,

$$2V = R'FR = S'FS \quad (15)$$

$$2T = \dot{R}'G^{-1}\dot{R} = \dot{S}'G^{-1}\dot{S} \quad (16)$$

where F and G characterize V and T in terms of the symmetry co-ordinates, then the necessary relations are easily obtained by substituting from (14) in (15) and (16). They are

$$F = U'^{-1}FU^{-1} = UFU' \quad (17)$$

$$G = UGU' \quad (18)$$

Solution of the secular equation

$$\mathfrak{S} \mathfrak{L} = \mathfrak{L} \Lambda \quad \text{cf. (11)} \quad (19)$$

will now give the transformation matrix \mathfrak{L} that defines the normal co-ordinates in terms of the symmetry co-ordinates:

$$S = \mathfrak{L} Q \quad (20)$$

To obtain the normal co-ordinates in terms of the original internal co-ordinates, we must combine (14) and (20) to obtain:

$$R = LQ = U^{-1} \mathfrak{L} Q = U' \mathfrak{L} Q$$

Equation (19) can be rewritten as before

$$|\mathfrak{S} \mathfrak{L} - \lambda I| = 0 \quad \text{cf. (13)} \quad (21)$$

2.2 The Urey-Bradley Force Field (UBFF)

This assumption was made by Urey and Bradley³ who propose the use of a mixed potential function, that is, a function which is basically of the valence force type, but which includes, in addition, some central force terms between nonbonded atoms. This potential has been best used by Simanouti⁴ in the case of tetrahedral molecules in the evaluation of potential constants.

The Urey-Bradley potential Function is expressed as,

$$\begin{aligned} V = & \sum_{i=1}^4 \left[K'_i r_i \Delta r_i + \frac{1}{2} K_i (\Delta r_i)^2 \right] \\ & + \sum_{i < j} \left[H'_{ij} r_{ij}^2 \Delta \alpha_{ij} + \frac{1}{2} H_{ij} (r_{ij} \Delta \alpha_{ij})^2 \right] \\ & + \sum_{i < j} \left[F'_{ij} q_{ij} \Delta q_{ij} + \frac{1}{2} F_{ij} (\Delta q_{ij})^2 \right], \end{aligned}$$

where r 's are the bond lengths, α 's the bond angles, q 's the distances between atoms not bonded directly, and r_{ij} represents $(r_i r_j)^{1/2}$. K , K' , H , H' , F and F' are the force constants, the last two of which are the repulsion constants between nonbonded atoms. The constants with primes are linear terms and those without are quadratic terms.

Using the relation

$$q_{ij}^2 = r_i^2 + r_j^2 - 2 r_i r_j \cos \alpha_{ij}$$

q_{ij} can be expressed in terms of Δr_i , Δr_j and $\Delta \alpha_{ij}$. Finally, by assuming that all the bond angles are tetrahedral in the equilibrium position and substituting the value of r_i and q_i the potential energy can be expressed as follows:

$$\begin{aligned} V = & \frac{1}{2} \sum_{i=1}^4 \left[K_i + F'_{ij} + 2F_{ij} \right] \Delta r_i^2 \\ & + \frac{1}{2} \sum_{i < j} \left[H_{ij} - \frac{2}{3} F'_{ij} - \frac{1}{3} F_{ij} \right] (r_{ij} \Delta \alpha_{ij}) \\ & + \sum_{i < j} \left[-\frac{1}{3} F'_{ij} + \frac{2}{3} F_{ij} \right] (\Delta r_i \Delta r_j) \\ & + \sum_{i \neq j} \left[\frac{\sqrt{2}}{3} F_{ij} + \frac{\sqrt{2}}{3} F_{ij} \right] (\Delta r_i) (r_{ij} \Delta \alpha_{ij}) \\ & + \sum_{i \neq j \neq k} \left[\left(-\frac{2}{3} F'_{ij} \right) (r_{ij} \Delta \alpha_{ij}) (r_{ik}) (\Delta \alpha_{ik}) \right] \end{aligned} \quad (1)$$

To express the vibrational kinetic energy with the valence force co-ordinates, Shimanouchi⁴ uses the method developed by Wilson⁵ and for the four frequencies, A, E, and two F's, of MX_4 molecules, the following \mathcal{F} and \mathcal{G} matrices are obtained:

$$G_A = \mu_X, \quad (\text{II})$$

$$F_A = K + 4F, \quad (\text{III})$$

$$G_E = 3\mu_X, \quad (\text{IV})$$

$$F_E = H - \frac{1}{3}F' + \frac{1}{3}F, \quad (\text{V})$$

$$G_{F_2} = \begin{vmatrix} 2\mu_X + \frac{16}{3}\mu_M & -\frac{8}{3}\mu_M \\ -\frac{8}{3}\mu_M & \mu_X + \frac{4}{3}\mu_M \end{vmatrix} \quad (\text{VI})$$

$$F_{F_2} = \begin{vmatrix} H - \frac{5}{3}F' + \frac{1}{3}F & \frac{2}{3}(F' + F) \\ \frac{2}{3}(F' + F) & K + \frac{4}{3}(F' + F) \end{vmatrix} \quad (\text{VII})$$

where μ_X and μ_M are the reciprocals of the masses of the X atom and M atom, respectively.

From above, the secular equations for the three types of vibration are:

for A_1 type:

$$\lambda_1 = G_A F_A \quad (\text{VIII})$$

for E type:

$$\lambda_2 = G_E F_E \quad (\text{IX})$$

and for F_2 vibrations they are:

$$\lambda_3 + \lambda_4 = \text{Trace } G_{F_2} F_{F_2}, \quad (\text{X})$$

$$\text{and } \lambda_3 \lambda_4 = |G_{F_2}| |F_{F_2}| \quad (\text{XI})$$

2.3 The Teller - Redlich⁶ Product Rule

This rule relates the product of the frequencies of a given symmetry of a molecule to the product of the corresponding frequencies of same isotopically related molecule. The ratio is a function of the molecular geometry and the nuclear masses. It depends on the numbers of rotations and translations belonging to the symmetry species. It also depends on whether or not the coordinates of the isotopic nuclei generate a representation of the symmetry species. Moreover, it is assumed that the change in mass will not alter the numerical values of the force constants. On this assumption, the product rule should hold rigorously for the zero-order frequencies ω_i and at least to a good approximation for the observed fundamental ν_i (or, in other words, the first vibrational quanta) for any mass differences.

In case of the tetrahedral MX_4 molecule, the product rule formulae quoted by Herzberg⁷ are: for the totally symmetric and for the doubly degenerate vibrations,

$$\frac{\omega_1^{(i)}}{\omega_1} = \frac{\omega_2^{(i)}}{\omega_2} = \sqrt{\frac{m_y}{m_y^{(i)}}} \quad (\text{XII})$$

and for the two triply degenerate vibrations,

$$\frac{\omega_3^{(i)} \omega_4^{(i)}}{\omega_3 \omega_4} = \frac{m_y}{m_y^{(i)}} \sqrt{\frac{m_x^{(i)} + 4 m_y^{(i)}}{m_x + 4 m_y} \cdot \frac{m_x}{m_x^{(i)}}} \quad (\text{XIII})$$

where the superscript (i) refers to the isotopic molecules, ω is the frequency, and m the mass.

It is noteworthy that according to equation (I) no isotope shift occurs in ω_1 and ω_2 if only the central atom is replaced by an isotope since in these vibrations the M atom does not move.