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To the Graduate Council:

I am submitting herewith a dissertation written by Suc Kyuen Suh entitled "The Theoretical Analysis of Vibrations of Chain Molecules." I have examined the final electronic copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Physics.

W. E. Deeds, Major Professor

We have read this dissertation and recommend its acceptance:

C. J. Craven, R. J. Lovell, K. L. Hertsel, D. D. Wilson, O. G. Harrold

Accepted for the Council:

Carolyn R. Hodges

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)

June 15, 1961

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Major Professor

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Accepted for the Council:

J. E. Spivey

Dean of the Graduate School

THE THEORETICAL ANALYSIS OF VIBRATIONS OF CHAIN MOLECULES

A Dissertation
Submitted to
the Graduate Council of
The University of Tennessee

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy

by
Suc Kyuen Suh
August 1961

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CHAPTER I

INTRODUCTION

In this dissertation we shall be concerned with the vibrational spectra of large chain molecules.

It is well known that, if a molecule is perturbed by a collision or electromagnetic radiation, it may undergo a transition from one stationary state of energy E'' to another of energy E' . During this transition, a photon of frequency $\nu = \frac{|E' - E''|}{h}$ may be absorbed if E' is greater than E'' , or emitted if E' is less than E'' . The frequency ν of this absorption or emission line can be considered as one of the "characteristic" frequencies of the molecule. The characteristic frequencies which appear in the infrared and Raman spectra of a molecule are essentially the frequencies of its vibration and rotation. For a complete utilization of spectral data, it is necessary to make a mathematical study of the vibrations of the atoms, and often also of the rotations of the molecules. For large molecules, such as are considered in this dissertation, the rotation-vibration spectra are not readily resolved and only a vibrational analysis can be made. Actually, the rotations turn out to be special forms of normal modes of vibration in this method of treatment. A vibrational analysis correlated with spectral data may be made to yield values of interatomic distances, force constants, symmetry of configuration, and structural properties of the molecule. Our main aim in the vibrational analysis of molecules is to make an accurate determination of the field of force, that is, of the force constants, from the observed fundamental frequencies. A comparison of the

different force constants in a given molecule and of the force constants of different molecules with similar chemical structure gives valuable information on the nature of the forces holding the atoms together, or, in other words, on the electronic structure of the molecule.

On the basis of an elementary theory of valence, we would expect the C-H bond, as an example, to have essentially the same electronic structure and therefore the same force constant in different molecules. However, on closer examination it is found that this invariance of the force constants holds exactly only if the bond is in similar surroundings. Crawford and Brinkley^{1*} and others have shown for a number of molecules that by taking over not only the stretching or bending force constants but also the interaction force constants from other molecules with the same groups, some or all of the normal frequencies may be predicted to within 1 or 2 per cent of the observed values.

It is clear that such a procedure is of great importance since in this way it is possible to find the correct assignment of the observed frequencies in more complicated molecules or even to obtain approximate values for these frequencies without actual observation. It must be realized, however, that with increasing accuracy of observations and calculations slight differences in the force constants are to be expected since there will always be some difference in the surroundings of a given group in different molecules.

*All references are listed numerically in Bibliography.

Both the infrared and Raman spectra of a molecule provide us with information on the frequencies of vibration, but not all transitions which occur in the Raman spectrum may occur in the infrared, and vice versa. This is due to the fact that the infrared and Raman activity of a molecule depend on different properties of the molecule. That is, the infrared activity depends on the nature of the dipole moment and the Raman activity depends on the nature of the polarizability of the molecule.

The vibrational analysis of large molecules quickly becomes very difficult as the number of atoms is increased, even with the simplifications which may be possible because of symmetry. In order to prevent the vibrational analysis from becoming prohibitively complex, we must content ourselves with an approximate treatment that is workable in preference to a more exact treatment which is not. The first assumption that we shall make is that the restoring forces binding the atoms of the molecule to their equilibrium positions are linear in the displacements since the anharmonic contribution to the restoring forces is an infinitesimal of higher order with respect to the atomic displacements.

The idea of reduction-type analysis^{2,3,4} in which a complicated molecule is regarded as being made of coupled simpler groups of atoms called "characteristic groups," provided a starting point for the analysis of many complicated molecules. However, the characteristic groups were considered to be point masses. This restriction was removed by the multiple-origin method,⁵ in which the characteristic groups are allowed to rotate, translate and have internal motions. In fact, no approximation at all are required in this method of formulating the vibrational problem, other than the usual assumption of small oscillations.

The number of subdivisions into which one mentally divides a large molecule is arbitrary, but, on a chemical and physical basis, it is most reasonable to divide large molecules into smaller sections which appear to have a very strong chemical affinity, such as methyl groups and methylene groups. One could also mentally split large molecules into sections which appear appropriate because of the symmetry involved. Fortunately, these two considerations, chemical affinity and symmetry, usually lead to the same scheme for subdividing a molecule, and then we can take as the "characteristic groups," those which, because of their strong chemical affinity, often appear in numerous, symmetrical positions throughout a molecule.

Most large molecules are made possible by the chemical activity of certain polyvalent atoms which can combine with other atoms to form elongated, chain-like structures. Such varied and important substances as oils, gasolines, silicones, cellulose, natural and synthetic rubbers, proteins, and plastics are formed of such chains. With the aid of the methods given in this dissertation, one can systematically treat the vibration problem of any large molecule which consists of such a chain.

CHAPTER II

GENERAL THEORY OF MOLECULAR VIBRATIONS

A. Quantum Mechanical Treatment

The energies which a molecule can have are given simply as eigenvalues of the Schrödinger equation,

$$H^{OP} \Psi = E \Psi. \quad (2-1)$$

As a first approximation to the correct solution, we can put

$$\Psi = \Psi_{trans.} \Psi_{rot.} \Psi_{vib.} \Psi_{spin} \Psi_{elec.} \quad (2-2)$$

$$E = E_{trans.} + E_{rot.} + E_{vib.} + E_{spin} + E_{elec.} \quad (2-3)$$

where $\Psi_{trans.}$, $\Psi_{rot.}$, $\Psi_{vib.}$, Ψ_{spin} , $\Psi_{elec.}$ and $E_{trans.}$, $E_{rot.}$, $E_{vib.}$, E_{spin} , $E_{elec.}$ are wave functions and energy eigenvalues corresponding to translational, rotational, vibrational, spin and electronic motions, respectively. In this case, the Schrödinger equation is separable. In this dissertation we shall be concerned mainly with the vibrational part of the Schrödinger equation,

$$H_{vib.}^{OP} \Psi_{vib.} = E_{vib.} \Psi_{vib.} \quad (2-4)$$

Without subscript, we write this equation as

$$H^{OP} \Psi = E \Psi. \quad (2-5)$$

When we substitute the expression for the Hamiltonian into the equation (2-5), we have

$$\left(-\hbar^2 \sum_i \frac{1}{2m_i} \nabla_i^2 + V \right) \Psi = E \Psi \quad (2-6)$$

as the vibrational part of the time-independent Schrödinger equation for a polyatomic molecule with N atoms and $(3N-6)$ vibrational degrees of freedom

where the range of i is from 1 to $(3N-6)$. In general the matrix elements of H^{OP} in the Ψ basis, which we designate by

$$H_{nm} = (\Psi_n, H \Psi_m),$$

are not diagonal. By choosing a different basis, i.e., transforming from Ψ to ϕ , we can diagonalize the Hamiltonian.

Regarding the sets $\{\Psi_i\}$ and $\{\phi_i\}$ as alternative sets of unit vectors in the infinite dimensioned Hilbert space, the unitary transformation corresponds to a rotation in this space. The unitary matrix \underline{S} gives the coordinates of Ψ_n in the ϕ basis as follows:

$$\Psi_n = \sum_k S_{kn} \phi_k \quad (2-7)$$

$$\Psi_m = \sum_l S_{lm} \phi_l \quad (2-8)$$

The matrix elements of H^{OP} transform as

$$\begin{aligned} H_{nm} &= (\Psi_n, H \Psi_m) = \sum_k \sum_l S_{kn}^* S_{lm} (\phi_k, H \phi_l) \\ &= \sum_{k,l} S_{kn}^* S_{lm} H'_{kl} = \sum_l S_{nk}^+ H'_{kl} S_{lm} = (S^{-1} H' S)_{nm}. \end{aligned}$$

Therefore, we have the matrix equation

$$\underline{H} = \underline{S}^{-1} \underline{H}' \underline{S}$$

or

$$\underline{S} \underline{H} = \underline{H}' \underline{S} \quad (2-9)$$

From this we can see that

$$\sum_k S_{nk} H_{km} = \sum_l H'_{nk} S_{lm} = \sum_k E_n \delta_{nk} S_{km} = E_n \sum_k S_{nk} \delta_{km}$$

since H is diagonal in ϕ basis. Therefore

$$\sum_k S_{nk} (H_{km} - E_n \delta_{km}) = 0$$

is a set of linear homogeneous equations in S_{nk} with n fixed. Dropping the subscript n , we have

$$\left| H_{km} - E \delta_{km} \right| = 0 . \quad (2-10)$$

This determinant is called a secular determinant, and its roots give the eigenvalues of the energy. For each eigenvalue the S_{nk} can be found to within an arbitrary normalizing factor from the above linear equations.

If we assume that the intermolecular forces are linear and express all quantities in terms of the normal coordinates Q_i , on which the wave function ϕ is based, the vibrational Schrodinger equation becomes

$$\sum_i \frac{d^2 \phi}{dQ_i^2} + \frac{2}{\hbar^2} (E - \frac{1}{2} \sum_i K_i Q_i^2) \phi = 0 \quad (2-11)$$

where K_i is the force constant associated with Q_i . If we assume that

$$\phi = \prod_i \phi_i(Q_i) \text{ and } E = \sum_i E_i ,$$

we get $(3N-6)$ simple harmonic oscillator wave equations

$$\frac{d^2 \phi_i}{dQ_i^2} + \frac{2}{\hbar^2} (E_i - \frac{1}{2} K_i Q_i^2) \phi_i = 0 . \quad (2-12)$$

The allowed energies for the i^{th} normal mode are, if it is non-degenerate

$$E_i = h \nu_i (n_j + \frac{1}{2}) , \quad (2-13)$$

where $\nu_i = \frac{\sqrt{K_i}}{2\pi}$ and the j^{th} quantum number n_j is some non-negative integer.

Since the normal modes are simple harmonic oscillations, the selection rules are $\Delta n_j = \pm 1$, in which case a photon of frequency ν_i is absorbed or emitted. Thus, there are at most $(3N-6)$ allowed frequencies, corresponding to the $(3N-6)$ possible values of i , if the force field is truly linear.

B. Classical Theory of Molecular Vibrations

It is a well-known fact that, for particles as massive as protons and neutrons, the laws of classical mechanics can be applied with sufficient accuracy for most purposes.

The electronic energy levels are so widely spaced that transitions between them produce lines in the visible or ultra-violet region of the spectrum.

Under the conditions to be considered in this dissertation, the energies involved are so low that the molecules will usually remain in the electronic ground state. In this case, to a very good approximation, we can neglect the contribution of the electrons to the rotational and vibrational energies of a molecule. Therefore, as a first approximation, we can consider a molecule to be a collection of N rotators, elastically bound to certain equilibrium positions, the whole collection being free to translate, rotate, and vibrate. If N is the number of groups, K is the number of atoms per group, there are NK atoms in the molecule (neglecting end effects) and $3(NK)-6$ degrees of vibrational freedom. But we set it up with $3NK$ coordinates, of which six turn out to have zero frequencies and are the translations and the rotations.

We shall use the generalized coordinates q_1, q_2, \dots, q_n , where $n = 3NK$, to specify the configuration of the system of coupled rigid rotators. Furthermore, we shall limit ourselves for the present time to consideration of conservative systems in which the forces acting on the individual rotators are derivable from a potential function V of the form $V = V(q_1, q_2, \dots, q_n)$.

The deviations of the generalized coordinates from equilibrium configuration will be denoted by η_i . Then we have $q_i = q_{0,i} + \eta_i$, and these η_i may be taken as the new generalized coordinates of the motion.

The potential function V can be expanded in a Maclaurin's series in the neighborhood of the equilibrium configuration with the form,

$$V = V(q_1, q_2, \dots, q_n) = V(0) + \sum_i \left(\frac{\partial V}{\partial q_i} \right)_0 \eta_i + \frac{1}{2} \sum_{i,j} \left(\frac{\partial^2 V}{\partial q_i \partial q_j} \right)_0 \eta_i \eta_j + \dots, \quad (2-14)$$

where the subscript zero indicates that the derivatives are evaluated at equilibrium.

In order that the equilibrium configuration of the rotator shall be stable, V must be a positive definite function of the η_i , so that any displacement of a rotator from its equilibrium position will increase the potential energy, and V must contain no terms linear in the coordinates, so that the generalized force $f_i = \frac{\partial V}{\partial q_i}$ vanishes in the equilibrium position.

For the sake of definiteness, we shall set $V(0) = 0$, so that the potential energy is zero at equilibrium. Then we can write

$$V = \frac{1}{2} \sum_{i,j} K_{ij} \eta_i \eta_j + \frac{1}{6} \sum_{i,j,k} K_{ijk} \eta_i \eta_j \eta_k + \dots \quad (2-15)$$

where $K_{ij} = \left(\frac{\partial^2 V}{\partial q_i \partial q_j} \right)_0$, $K_{ijk} = \left(\frac{\partial^3 V}{\partial q_i \partial q_j \partial q_k} \right)_0$, \dots .

If we assume that the generalized restoring forces, F_i , acting when the rotator is slightly displaced from its equilibrium configuration, are linear in the coordinates η_i , then the terms higher than the second in the potential function must vanish.

Now we can write

$$V = \frac{1}{2} \sum_{i,j} K_{ij} \eta_i \eta_j \quad (2-16)$$

where $K_{ij} = K_{ji}$.

The kinetic energy of the system is a positive definite quadratic function of the velocities \dot{q}_i and is given in general by

$$T = \frac{1}{2} \sum_{i,j} m_{ij} \dot{q}_i \dot{q}_j \quad (2-17)$$

where the m_{ij} are functions of the masses of the atoms and the coordinates q_i .

The coefficients m_{ij} can, on the assumption of small displacements of the q_i , be expanded about the equilibrium configuration in a Maclaurin series of the coordinates q_i :

$$m_{ij}(q_1, q_2, \dots, q_n) = m_{ij}(q_{10}, q_{20}, \dots, q_{n0}) +$$

$$\sum_k \left(\frac{\partial m_{ij}}{\partial q_k} \right)_0 \eta_k + \frac{1}{2} \sum_{k,l} \left(\frac{\partial^2 m_{ij}}{\partial q_k \partial q_l} \right)_0 \eta_k \eta_l.$$

As equation (2-17) is already quadratic in the \dot{q}_i 's, the lowest non-vanishing approximation to the kinetic energy expression is obtained by dropping all but the first term in the expansion of m_{ij} . Then we can write

$$T = \frac{1}{2} \sum_{i,j} m_{ij} \dot{q}_i \dot{q}_j = \frac{1}{2} \sum_{i,j} m_{ij} \dot{\eta}_i \dot{\eta}_j, \dots \quad (2-18)$$

where $m_{ij} = m_{ji}$ and m_{ij} are constants now.

The Lagrangian is given by

$$L = \frac{1}{2} \sum_{i,j} (m_{ij} \dot{\eta}_i \dot{\eta}_j - K_{ij} \eta_i \eta_j)$$

Taking the η_i 's as new generalized coordinates, the Lagrange equations,

$$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{\eta}_i} \right) - \frac{\partial L}{\partial \eta_i} = 0,$$

give the following 3NK equations of motion:

$$\sum_j m_{ij} \ddot{\eta}_j + \sum_j K_{ij} \eta_j = 0 \quad (2-19)$$

where the range of j is from 1 to 3NK.

Since the equations of motion (2-19) are linear differential equations with constant coefficients, we are led to try an oscillatory solution of the form

$$\eta_j = \eta_{j0} e^{-i\omega t} \quad (2-20)$$

It is understood that it is the real part of equation (2-20) that is to correspond to the actual motion. Substituting equations (2-20) into the equations of motion, we obtain the following equation for the amplitude factors:

$$\sum_j (K_{ij} \eta_{0j} - \omega^2 m_{ij} \eta_{0j}) = 0 \quad (2-21)$$

Equations (2-21) constitute 3NK linear homogeneous equations for the η_{0j} 's and consequently can have a non-trivial solution only if the determinant of the coefficients vanishes:

$$\left| K_{ij} - \omega^2 m_{ij} \right| = 0. \quad (2-22)$$

This determinantal condition is, in effect, an algebraic equation of the (3NK)th degree for ω^2 . The roots $\lambda_r = \omega_r^2$ of the secular determinant (2-22) provide the frequencies for which equation (2-20) represents a correct solution to the equations of motion. Since the potential energy V is a positive definite form, the roots λ_r of this secular determinant will all be positive and real and can be represented by ω_r^2 , where ω_r can also be taken to be real and positive.

Mathematically it is always possible to obtain a non-singular real transformation,

$$\eta_j = \sum_k c_{jk} q_k \quad (2-23)$$

which will simultaneously diagonalize T and V in such a way that

$$T = \frac{1}{2} \sum_i \dot{q}_i^2 \quad \text{and} \quad V = \frac{1}{2} \sum_i \lambda_i q_i^2. \quad (2-24)$$

Furthermore, the coefficients λ_i in V are exactly the roots of the determinantal equation

$$|K_{ij} - \omega^2 m_{ij}| = 0. \quad (2-25)$$

Equation (2-25) is the so-called secular equation, and the transformation (2-23) is the one which will transform the quantum mechanical Schrödinger equation (2-6) into the normal form (2-11).

When we rewrite the transformation equation (2-23),

$$\eta_i = \sum_k a_{ik} q_k \quad (2-23)'$$

then we have

$$q_i = \sum_k b_{ik} \eta_k \quad (2-26)$$

where $\underline{b} = \underline{\tilde{a}} = \underline{a}^{-1}$, and we can obtain

$$\underline{\tilde{a}} \underline{m} \underline{a} = \underline{1} \quad (2-27)$$

$$\underline{\tilde{a}} \underline{K} \underline{a} = \underline{\lambda} \quad (2-28)$$

where $\underline{a} = (a_{ij})$, $\underline{m} = (m_{ij})$, $\underline{K} = (K_{ij})$, and $\underline{\lambda} = (\lambda_{ii})$.

From equations (2-27) and (2-28), we can obtain

$$(\underline{K} - \underline{\lambda} \underline{m}) \underline{\tilde{a}} = \underline{0}. \quad (2-29)$$

After we solve the secular equation (2-25) and obtain the roots λ_i , we

can substitute the values of λ_r into equation (2-29) and solve for the a_{ij} . Thus, we can get the desired transformation matrix (a_{ij}) .

It is a usual procedure to use the established methods of classical mechanics to find the desired transformation to normal coordinates, after which the more precise quantum mechanical expressions for the energy can be used to replace the less accurate classical ones.

C. Multiple Origin Method for Large Molecules

Deeds⁵ introduced the so-called "Multiple Origin Method" for the analysis of vibrational modes of large molecules. This Multiple Origin Method, or M. O. M., has the following advantages in the analysis of large molecules:

a) Immediate diagonalization of the kinetic energy function T if rectangular coordinates are used to describe the position of the center of mass of each characteristic group, principal axes of rotary inertia for the equilibrium configuration are used as the moving coordinate system, and the ordinary normal coordinates are used for the internal motions of each characteristic group.

b) This method yields a symmetrical secular determinant.

When we write $T_{tr,i}$ for the kinetic energy of translation of the center of mass of the i^{th} characteristic group, $T_{rot.,i}$ for its kinetic energy of rotation as an instantaneously rigid body, and $T_{int.,i}$ for the

kinetic energy of its internal vibrations, then we may write the kinetic energy of the whole molecule as

$$T = \sum_i T_{tr.,i} + \sum_i T_{rot.,i} + \sum_i T_{int.,i} \quad (2-30)$$

In order that we may have the kinetic energy of the whole molecule as in equation (2-30), we have to impose the so-called Eckart conditions⁶ on the internal coordinates of "characteristic groups."

Consider an inertial coordinate system XYZ and a moving coordinate system which has its origin given by the position vector \vec{R} in the inertial system and which is rotating with angular velocity $\vec{\omega}$. If a mass point has a position vector \vec{r} and velocity \vec{v} in the moving reference frame, then the absolute velocity \vec{V} of the mass point, with respect to the inertial frame is given by

$$\vec{V} = \dot{\vec{R}} + \vec{v} + \vec{\omega} \times \vec{r} \quad (2-31)$$

The kinetic energy of the mass point with respect to the inertial frame is given by

$$\frac{1}{2} m \vec{V} \cdot \vec{V} = \frac{1}{2} m [\dot{\vec{R}}^2 + v^2 + (\vec{\omega} \times \vec{r})^2 + 2 \dot{\vec{R}} \cdot \vec{v} + 2 \dot{\vec{R}} \cdot (\vec{\omega} \times \vec{r}) + 2 \vec{v} \cdot (\vec{\omega} \times \vec{r})] \quad (2-32)$$

If there are K particles, with masses m_i and velocities \vec{V}_i , we can simply add their kinetic energies, which are scalar quantities,

$$T = \sum_i T_i = \sum_i \frac{1}{2} m_i \vec{V}_i \cdot \vec{V}_i = \frac{1}{2} \sum_i m_i [\dot{\vec{R}}^2 + v_i^2 + (\vec{\omega} \times \vec{r}_i)^2 + 2 \dot{\vec{R}} \cdot \vec{v}_i + 2 \dot{\vec{R}} \cdot (\vec{\omega} \times \vec{r}_i) + 2 \vec{\omega} \cdot (\vec{r}_i \times \vec{v}_i)] \quad (2-33)$$

where the range of i is from 1 to K where K is the number of particles in the system under discussion.

If the origin of the moving coordinate system is taken at the center of mass of the system, then we have

$$\sum_i m_i \vec{r}_i = 0 \quad (2-34)$$

$$\frac{d}{dt} \sum_i m_i \vec{r}_i = 0 = \sum_i m_i \vec{v}_i + \vec{\omega} \times \sum_i m_i \vec{r}_i = \sum_i m_i \vec{v}_i \quad (2-35)$$

In this case, equation (2-33) becomes

$$T = \frac{1}{2} M \dot{\vec{R}}^2 + \sum_i \left(\frac{1}{2} m_i v_i^2 \right) + \frac{1}{2} \sum_i m_i (\vec{\omega} \times \vec{r}_i)^2 + \vec{\omega} \cdot \sum_i m_i (\vec{r}_i \times \vec{v}_i) \quad (2-36)$$

where $\sum_i m_i = M$.

If we also require that the moving coordinate system rotates with atoms in the system when they tend to rotate as a rigid body, then we have

$$\sum_i m_i (\vec{r}_i^0 \times \vec{v}_i) = 0 \quad (2-37)$$

where \vec{r}_i^0 is the equilibrium position vector of the i^{th} atom, \vec{v}_i its instantaneous velocity vector in the moving system. Now we have

$$\vec{r}_i = \vec{r}_i^0 + \delta \vec{r}_i$$

and

$$\begin{aligned} \sum_i m_i (\vec{r}_i \times \vec{v}_i) &= \sum_i m_i (\vec{r}_i^0 \times \vec{v}_i) + \sum_i m_i (\delta \vec{r}_i \times \vec{v}_i) = \\ &= \sum_i m_i (\delta \vec{r}_i \times \vec{v}_i) \end{aligned} \quad (2-38)$$

by virtue of equation (2-37). $\sum_i m_i (\delta \vec{r}_i \times \vec{v}_i)$ is the internal angular momentum resulting from degenerate normal modes or certain superpositions of normal modes.

Thus we have

$$T = \frac{1}{2} M \dot{\vec{r}}^2 + \frac{1}{2} \sum_i m_i (\vec{\omega} \times \vec{r}_i)^2 + \sum_i (\frac{1}{2} m_i v_i^2) + \vec{\omega} \cdot \sum_i m_i (\vec{r}_i \times \vec{v}_i), \quad (2-39)$$

where $\frac{1}{2} M \dot{\vec{r}}^2$ is the kinetic energy of translation of the center of mass of the whole system relative to the inertial system, $\frac{1}{2} \sum_i m_i (\vec{\omega} \times \vec{r}_i)^2$ is the kinetic energy of rotation of the system of K atoms as a quasi-rigid body about its center of mass, $\sum_i (\frac{1}{2} m_i v_i^2)$ is the kinetic energy of translation of the atoms inside the moving coordinate systems, and $\vec{\omega} \cdot \sum_i m_i (\vec{r}_i \times \vec{v}_i)$ is the Coriolis interaction energy, which will be assumed to be negligible. Therefore, we have for the kinetic energy,

$$T \text{ (for one group)} = \frac{1}{2} M \dot{\vec{r}}^2 + \frac{1}{2} \sum_i m_i (\vec{\omega} \times \vec{r}_i)^2 + \frac{1}{2} \sum_i (\frac{1}{2} m_i v_i^2) \quad (2-40)$$

The conditions that $\sum_i m_i \vec{r}_i = 0$ and $\sum_i (\vec{r}_i^0 \times m_i \vec{v}_i) = 0$ are known as the Eckart Conditions.⁶

We notice from equations (2-37) that under the conditions

$\sum_i m_i (\vec{r}_i^0 \times m_i \vec{v}_i) = 0$ each atom does not necessarily have zero angular momentum. But we have to orient the moving coordinate axes in a particular way with respect to the moving atoms to satisfy the Eckart Conditions. One of these moving coordinate systems is taken for each of the characteristic groups in the molecule, hence the name "multiple origin method."

D. Group Theory

Methods of group theory are very helpful in the solution of physical problems involving symmetrical systems. The group theory method offers a convenient and systematic method of classifying various types of molecules and their properties, and gives insight into methods of breaking up complicated problems into smaller pieces. In this section we limit our discussion to those topics which we shall use in this dissertation.

Any set of "operators" A, B, C, \dots , for which a law of combination is defined and which has the four properties stated below constitutes a "group."

(1) The set is closed in the sense that the combination of any two elements gives an element already in the set.

(2) The set contains the identity element E .

(3) Every element of the set has an inverse.

(4) The associative law holds for all elements.

Let us consider two groups, G and G' containing elements A, B, C, \dots and A', B', C', \dots respectively. If there is a one-to-one correspondence between products in the two groups, such that $AB = C$ when $A'B' = C'$, then a simple isomorphism is said to exist between the two groups. The simple isomorphism of groups is an important property because all of the groups simply isomorphic to each other will have a one-to-one correspondence between their multiplication tables and in other properties.

We shall set up groups of matrix operators which are simply isomorphic to groups of geometrical operators, and we shall use the properties of the matrix operator groups in solving problems involving the corresponding

geometrical operator groups.

A "covering operation" can be defined as a geometrical operation which takes a symmetrical figure into a new configuration indistinguishable from the original one. The group of transformation matrices corresponding to the group of covering operations can be taken as a "representation" of that group of geometrical operations. It should be noted that each of the representation matrices is a "unitary matrix" and all the general properties of unitary matrices apply to them.

A matrix A is reducible when it is possible to perform a unitary transformation of the form $\underline{X} A \underline{X}^{-1}$ which changes the matrix into one having more steps than it originally contained. A matrix representation of a group is said to be reducible when all the matrices in the representation can be broken up in exactly corresponding ways into smaller steps by a unitary transformation. A representation is said to be irreducible when it is not possible to break up all the matrices in the representation into smaller steps by a unitary transformation. There are always as many linearly independent irreducible representations of a group as there are classes of elements. A reducible representation of a group can be expressed as a linear combination of the irreducible representations of that group. The complete set of elements conjugate to each other in a given group is said to form a "class" of that group. The "character" of an operator of a given class is the sum of the diagonal elements of any representing matrix. If a covering operation of the molecular symmetry group transforms the i^{th} characteristic chemical group into the j^{th} , then the secular determinants going with the chemical groups are identical. This is a basic idea of the "reduction-type" analysis of vibrations of molecules.

Consider a group G of order h , and let R denote an arbitrary operation of the group. If we have a set of ℓ coordinates S_β ($\beta = 1, \dots, \ell$), and if, for every operation R of the group G , the coordinates S_β undergo a linear transformation

$$RS = \Gamma(R) S \quad (2-41)$$

where the matrices $\Gamma(R)$ form an irreducible representation of the group G , then the coordinates S_β are called symmetry coordinates.

The potential energy must belong to the totally symmetrical species under all covering operations because it is a scalar function.

If it is written in terms of symmetry coordinates, then there may be no cross-products in the potential energy expression between symmetry coordinates of different species, or between symmetry coordinates belonging to different rows of the same species. The same is true of the kinetic energy expression, but there is ordinarily no doubt about the terms which occur in it.

The expressions for the kinetic and potential energy are, therefore, considerably simplified when symmetry coordinates are used (assuming that the molecule has some sort of symmetry), and it follows that the form of the secular determinant will also be simplified. To be specific, the secular determinant will break up into blocks along the principal diagonal, each block corresponding to each of those symmetry coordinates which transform according to the same row of a given irreducible representation. Those blocks corresponding to different rows of the same irreducible representation are identical.

E. Valence Displacement Coordinates

Valence displacement coordinates are measures of the stretching, bending, or twisting of a molecular chemical valence bond. The importance of such valence displacement coordinates is due to the fact that the force constants associated with such coordinates have been calculated for simple molecules, and the values found may be used in more complicated molecules to a fairly good degree of approximation. For example, the force constant associated with $\text{H}-\text{C}-$ stretching is approximately 4.8×10^5 dynes/cm., regardless of the particular molecule in which the H-C configuration appears. We shall assume that the matrices of the irreducible representations of this symmetry group of the molecule under study are explicitly known and that we have chosen a set of valence displacement coordinates whose transformation properties under the symmetry operation are also known.

Then, we can find a complete set of symmetry coordinates \underline{S} in terms of the set of valence displacement coordinates \underline{R} with a relation

$$\underline{S} = \underline{U}\underline{R} \quad (2-42)$$

where \underline{U} is a unitary matrix.

Symmetry coordinates \underline{S} , which are related to valence displacement coordinates according to (2-32) will be called valence symmetry coordinates.

F. Repeating Unit and "Unit Cell"

The formation of long chain molecules depends upon the presence of chemically active, multivalent atoms, such as carbon and silicon, which can join with at least two other atoms to form the so-called "repeating units" in the chain.

Nitrogen, phosphorus, oxygen, and sulfur atoms also play important parts in many chain molecules.

The repeating unit in a chain molecule is defined as a set of atoms which, when translated along the axis of the chain by integral multiples of its own length and rotated by the same integral multiples of a certain angle, will generate the chain molecule. Molecules containing many repeating units will form helices, in general.

The assumption of repeating units does not really restrict the generality of the analysis since a repeating unit can be as long as desired, up to the length of the entire molecule. These repeating units may have one or more characteristic groups of atoms which appear to act as chemical units.

The structures for some important types of chain molecules are shown in Figure 1.

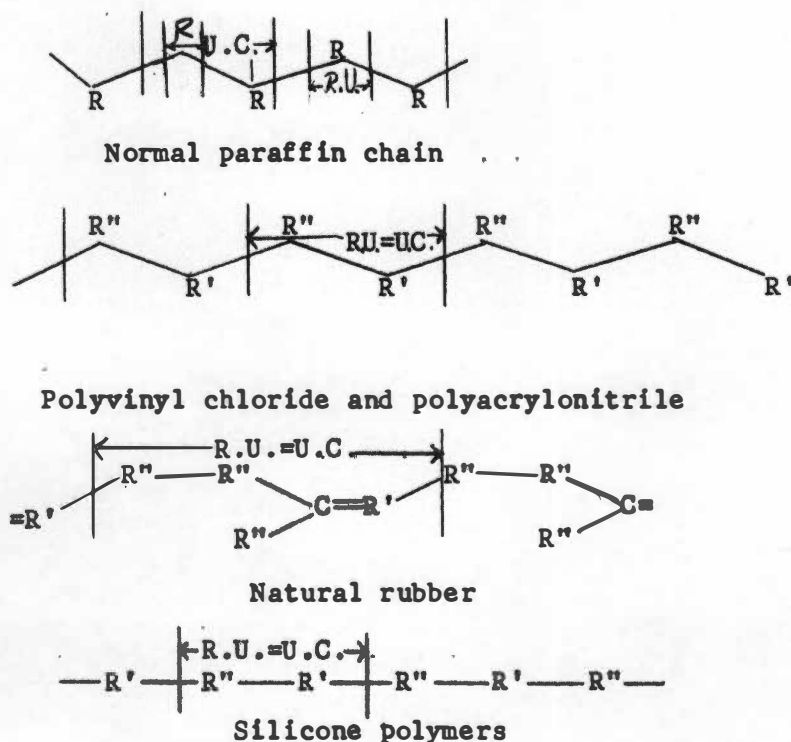


Figure 1. Characteristic Groups (R's), Repeating Units (R.U.) and Unit Cell (U.C.) for Some Well-Known Type of Chain Molecules.

If the angle of rotation from one repeating unit to the next is zero, then the repeating units become identical with the so-called "unit cell" in crystallography.

G. Amplitude Phase Difference

We first assume that all particles in the infinite chain molecule are simultaneously executing simple harmonic motion with the same frequency. We know that this assumption is permissible if the molecule is a stable one. Suppose that there is a phase difference ϕ between corresponding particles in two adjacent repeating units. From the symmetry of the repeating units, there must be the same phase difference between the corresponding parts of any two adjacent repeating units in the chain. Furthermore, this rule will hold for any pair of corresponding particles in adjacent repeating units. This symmetry rule may be stated as follows:

If a stable molecule is being traversed by a travelling wave, the phase differences between the various parts of the molecule must satisfy the same covering operations as the molecule itself.

The simplest way to prove this useful rule is to observe that the wave should be propagated through the molecule in exactly the same way, regardless of whether or not the molecule has been subjected to a covering operation, and of course the wave would be affected if the phase differences were changed. We have already used the symmetry rule in the argument that there must be the same phase difference ϕ between all pairs of corresponding parts of all adjacent repeating units because of the translational symmetry (with rotation included) of the repeating units.

The most general solution to the vibration problem consists of a superposition of waves travelling in both directions along the chain. It is well-known that the superposition of two sinusoidal waves of equal amplitudes and wavelengths will give rise to a system of standing waves, and it is these standing waves, of different frequencies and wavelengths, which are the normal modes of chain molecules. The framework modes are roughly analogous to the familiar transverse, longitudinal, and torsional standing waves observed in vibrating strings, and there are much more general types of standing waves corresponding to the various internal motions of the characteristic groups. The phase differences actually apply to waves travelling along the chains. In a standing wave, all particles have the same phase, or differ in phase by integral multiples of π . All atoms in a given repeating unit are regarded as having the same phase, and the phase differences between adjacent repeating units are all equal.

If the ends of the chain are perfectly free, the travelling waves will be reflected at the ends without loss of amplitude, since there is no means for the energy to escape, but there may be a change of phase, $2\pi\epsilon$, where $0 \leq \epsilon \leq 1$.

The sum of the incident and reflected waves is

$$q_n = q_{ni} + q_{nr} = q_{no} \left[e^{i(\omega t + n\delta)} + e^{i(\omega t - n\delta - 2\pi\epsilon)} \right] = 2 q_{no} e^{i(\omega t - \epsilon\pi)} \cos(n\delta + \epsilon\pi), \quad (2-43)$$

which represents standing waves.

These standing waves are the normal modes of chain molecules - the different modes being given by different wavelengths of the standing waves and by different types of waves: transverse, longitudinal, torsional and

so on. The factors ϕ and ϵ in equation (2-41) are determined by the boundary conditions on the wave.

If the ends of the chain are free, the shearing stresses and bending moments must vanish there. For a chain composed of discrete mass elements, such as we are considering, the shearing stresses and bending moments are given by finite difference equations and are proportional, respectively, to the third and second differences of the q_n .

Setting the third differences equal to zero, for coordinates which have the same directions in adjacent groups, gives us the condition that

$$\Delta_n^3 q_n = q_{n+1} - 3q_n + 3q_{n-1} - q_{n-2} = 0 = 16 q_{no} e^{i(\omega)t - \epsilon\pi}.$$

$$\sin^3 \frac{1}{2} \phi \sin \left[(n-1)\phi + \epsilon\pi \right] \quad (2-44)$$

where $n = 1, N$.

The only term in the above equation which depends upon n is the last factor. Hence we must have

$$\frac{1}{2} \phi + \epsilon\pi = m'\pi,$$

and

$$(N - \frac{1}{2}) \phi + \epsilon\pi = m''\pi$$

where m' and m'' are integers. Subtracting the first of these equations from the second gives

$$(N - 1)\phi = (m'' - m')\pi = m\pi$$

where m is an integer, or

$$\phi = m\pi / N - 1. \quad (2-45)$$

For infinite chains the values of ϕ are continuous, but for finite chains they have N possible values separated by integral multiples of $\frac{\pi}{(N-1)}$.

H. Selection Rules

If anharmonicity is neglected, only the "fundamental" frequencies of simple harmonic oscillations are infrared or Raman active.

In unsymmetrical molecules, every normal vibration is connected with a change of dipole moment. That is, all normal vibrations are infrared active, although they may be great differences in the magnitudes of the changing dipole moment and therefore in the intensity of infrared absorption.

Only in symmetrical molecules may there be vibrations during which the change of dipole moment is exactly zero and which are, therefore, infrared inactive.

According to classical electrodynamics, any motion of an atomic system that is connected with a change of its dipole moment leads to the emission or absorption of radiation. A change of the quadrupole moment or of the magnetic dipole moment may also lead to emission or absorption of radiation.

But in the infrared, the intensity of this emission or absorption is entirely negligible.

In order that a fundamental frequency shall appear in the Raman spectrum, the polarizability of the molecule must change during the vibration considered.

The magnitude of the induced dipole moment \vec{P} is given by

$$|\vec{P}| = \alpha |\vec{E}| \quad (2-46)$$

where \vec{E} is the electric vector of the incident radiation of frequency ν and α is the polarizability. If α changes during the vibration i with

frequency ν_i , \vec{P} will change with the frequencies $\nu + \nu_i$ and $\nu - \nu_i$ as well as with the frequency ν ; that is the scattered radiation will contain the frequencies $\nu \pm \nu_i$ in addition to ν . In an unsymmetrical molecule, during all normal vibrations, a periodic change of the polarizability takes place and, therefore, all normal frequencies are Raman active. In symmetrical molecules there may be vibrations during which the polarizability does not change, and which are, therefore, Raman inactive.

Quantum-mechanically the dipole moment of the molecule is represented by the matrix

$$M_{mn} = \int \psi_n^* \vec{M} \psi_n d\tau \quad (2-47)$$

where \vec{M} is a vector with components $M_x = \sum q_i x_i$, $M_y = \sum q_i y_i$, $M_z = \sum q_i z_i$, and ψ_m and ψ_n are the time-independent eigenfunctions of the system in the two energy states m and n . The transition probability W is proportional to the square of M_{mn} .

As stated in section A, we are concerned only with the vibrational part of the wave function, that is ψ_v . ψ_m and ψ_n in equation (2-47) shall be understood as the vibrational eigenfunctions in m^{th} and n^{th} vibrational energy states. Vibrational selection rules are important only when the molecule under consideration has elements of symmetry. In order that any transition may be observed, M_{mn} must be different from zero. This implies that a transition is observed only when M_{mn} remains unchanged for any of the symmetry operations permitted by the symmetry of the molecule in its equilibrium position, or in other words when M_{mn} is totally symmetrical.

Since M_x , M_y , M_z have the same behavior with respect to symmetry operations as the translations T_x , T_y , T_z in the direction of the coordinate axes, a vibrational transition $m \leftrightarrow n$ is allowed only when the product $\Psi_m^* \Psi_n$ belongs to the same species as one of the translations, T_x , T_y , T_z . In order to ascertain whether a certain transition $m \leftrightarrow n$ is allowed in the infrared, therefore, it is only necessary to see whether the species of $\Psi_m^* \Psi_n$ is the same as that of M_x , M_y or M_z . The species of the components of the dipole moment are listed in Table I.

TABLE I

SYMMETRY TYPES OF THE COMPONENTS OF THE DIPOLE MOMENT AND THE POLARIZABILITY

	C_s	C_i	C_{2h}	C_{2v}
M_x	A'	A_u	B_u	B_1
M_y	A'	A_u	B_u	B_2
M_z	A''	A_u	A_u	A_1
α_{xx}	A'	A_g	A_g	A_1
α_{yy}	A'	A_g	A_g	A_1
α_{zz}	A'	A_g	A_g	A_1
α_{xy}	A'	A_g	A_g	A_2
α_{xz}	A''	A_g	B_g	B_1
α_{yz}	A''	A_g	B_g	B_2

The intensity of scattered light depends on the induced dipole moment \vec{P} which is represented by the matrix formed from the integrals,

$$\int \Psi_m^* \vec{P} \Psi_n d\tau, \quad (2-48)$$

where \vec{P} is a vector whose components are given by

$$\begin{aligned} P_x &= a_{xx} E_x + a_{xy} E_y + a_{xz} E_z \\ P_y &= a_{yx} E_x + a_{yy} E_y + a_{yz} E_z \\ P_z &= a_{zx} E_x + a_{zy} E_y + a_{zz} E_z. \end{aligned} \quad (2-49)$$

Therefore the matrix elements are written as

$$\begin{aligned} [P_x]_{nm} &= E_x \int \Psi_m^* a_{xx} \Psi_n d\tau + E_y \int \Psi_m^* a_{xy} \Psi_n d\tau + E_z \int \Psi_m^* a_{xz} \Psi_n d\tau \\ [P_y]_{nm} &= E_x \int \Psi_m^* a_{yx} \Psi_n d\tau + E_y \int \Psi_m^* a_{yy} \Psi_n d\tau + E_z \int \Psi_m^* a_{yz} \Psi_n d\tau \\ [P_z]_{nm} &= E_x \int \Psi_m^* a_{zx} \Psi_n d\tau + E_y \int \Psi_m^* a_{zy} \Psi_n d\tau + E_z \int \Psi_m^* a_{zz} \Psi_n d\tau \end{aligned} \quad (2-50)$$

where E_x , E_y , and E_z are the components of the amplitude of the incident light wave. A Raman transition between two vibrational levels m and n is allowed if at least one of the six products, $\Psi_m^* a_{xx} \Psi_n$, $\Psi_m^* a_{xy} \Psi_n$, - - -, is totally symmetrical, that is, remains unchanged for all symmetry operations permitted by the symmetry of the molecule.

Similarly to the previous infrared selection rule, the general Raman selection rule may be stated as follows:

A Raman transition between two vibrational levels m and n is allowed if the product $\Psi_m^* \Psi_n$ has the same species as at least one of the six components a_{xx} , a_{xy} , a_{yy} , a_{yz} , a_{xz} , a_{zz} of the polarizability tensor.

In order to be able to apply this rule, we have to know the species of a_{xx} , a_{xy} , - - - for the various point groups. It is easy to find the behavior of the a_{xx} , a_{xy} , - - - with respect to symmetry operations. In Table I the species of the six components of the polarizability tensor are given for some of the important point groups.

I. Calculation of the Force Constants

The roots ω_n^2 of the vibrational secular determinant are functions of the coefficients m_{ij} and K_{ij} in T and V as we have seen in section B.

The m_{ij} are usually known from other measurements such as electron diffraction work and rotational spectra. From the observed vibrational frequencies ω_i in the infrared and Raman spectra, we can, in principle, calculate the unknown force constants K_{ij} . However, it frequently happens that there are more unknown force constants than there are observed fundamental frequencies to put into the equations.

$$\omega_{i, \text{obs.}} = \omega_{i, \text{calc.}}(m_{ij}, K_{ij}) \quad (r = 1, 2, \dots, 3N-6)$$

(2-51)

from which the force constants can be calculated. This can happen when some of the vibrational modes are inactive in both the Raman and infrared spectra or when the molecule is so complex that there are more significant interatomic bonds than there are fundamental vibrational frequencies.

CHAPTER III

GENERAL THEORY OF THE VIBRATIONS OF UNBRANCHED, ACYCLIC CHAIN MOLECULES

A. General Considerations

For a molecule or atom in a gas, the translational and rotational degrees of freedom are usually unhindered, so that they yield zero roots of the secular determinant. In a liquid the collisions between molecules or atoms occur with much greater frequency than in a gas, so that the roots corresponding to the translational and rotational degrees of freedom are no longer zero ones, but give, in general, aperiodic oscillations. Molecules, such as the long chain polymers which we shall consider, often have a regular arrangement in a crystalline lattice. In this case we can solve the vibrational problem for a relatively small section of the crystal, which is typical of the rest of the crystal. The effect of other parts of the crystal can be included by assuming that they vibrate in exactly the same way, except for possible differences of amplitude and phase. This assumption is justified by the so-called "Symmetry Rule" which we discussed in Section G of Chapter II. As soon as the polymer contains at least ten repeating units, any differences in the spectra of longer polymers are due to effects of the end groups which gradually become less important as the chain length increases. Deeds⁵ discussed

in detail these effects, including the effects of adjacent chains, mixtures of chains of different lengths, and branching on the spectra. Although it is in general very unusual to be able to obtain a high polymer in the form of a single crystal of suitable size for spectroscopic work, it is often possible to vary the degree of crystallinity in a polymer sample. Intermolecular forces are generally at least an order of magnitude smaller than the intramolecular forces which determine the values of the fundamental frequencies. This allows us to make one further assumption that the interaction forces between polymer chains are so small that the magnitudes of the fundamentals are not greatly changed by the intermolecular forces. Since the site symmetry of a molecule in a crystal is usually equal to or lower than the symmetry of the isolated molecule, the only change which can result on considering the complete crystalline arrangement is a relaxation of the selection rules predicted on the basis of the isolated molecule. Therefore, it will never happen that a mode predicted to be active in an isolated molecule is forbidden in the crystal.

When the repeating unit of the polymer contains more than one chemical unit, the normal modes of the polymer are built up essentially of the characteristic modes of each group and the framework modes which depend on the various possible amplitude phase differences between motions in neighboring groups. The frequencies of the resulting fundamentals depend upon these differences in amplitude. This dependence on amplitude was discussed in Section G of Chapter II. It is, therefore, possible

only by the detailed analysis of all of the frequencies, to obtain structural information about the molecule.

The spectrum of the amorphous form is generally much more diffuse than that of the crystalline form but bears a rather close resemblance to it. When new absorption bands are found in the amorphous form, these may be due either to breakdown of selection rules operative in the crystal or to the existence of different rotational isomers which are absent from the crystalline phase. The diffuseness associated with the spectrum in the amorphous state is probably due mainly to the random nature of the interactions which can occur between individual polymer molecules. In the crystalline state the interactions are precise and the same for each repeating unit, so that the splitting of a fundamental frequency of the repeating unit of a single polymer is correspondingly well defined. In the amorphous state, the great variety of possible intermolecular configurations will lead to an ill-defined broadening of the absorption "line."

Although the prediction and interpretation of the fundamental frequencies of the characteristic groups are usually straightforward, the determination of the fundamental frequencies of the framework vibrations may be quite complicated.

In the next section we shall consider molecular vibrations of unsymmetrical three particle systems. These normal modes of vibration of unsymmetrical three particle systems will be used as fundamental modes of the characteristic group in the complete analysis of the chain molecules. In

section C, we shall consider in detail the framework vibrations of the chain molecule.

B. Molecular Vibrations of Unsymmetrical Three Particle Systems

Most of the previous work on the small vibrations of triatomic molecules has dealt with symmetrical systems; that is, systems of the type XY_2 .^{7,8} Shaffer⁹ has, however, developed a general method applicable to unsymmetrical three particle systems.

We shall attempt a somewhat different approach to this problem. We shall adopt valence displacement coordinates as defined in Chapter II. We choose a rectangular coordinate system to specify the configuration of the group, with the origin at its center of mass. The equilibrium configuration of the group is shown in Figure 2, where r_1^0 is the equilibrium

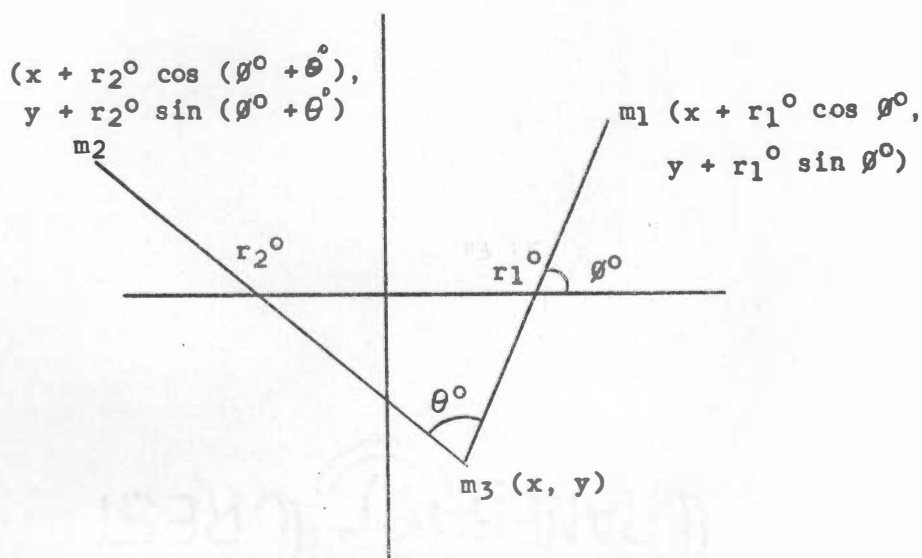


Figure 2. The Equilibrium Configuration of an Unsymmetrical Three-Particle System.

value of the distance r_1 between the particles 1 and 3, r_2^0 is the equilibrium value of the distance r_2 between the particles 2 and 3, θ^0 is the equilibrium value of the angle θ between r_1 and r_2 and ϕ^0 is the equilibrium value of the angle between r_1 and the X-axis.

The most general quadratic potential function in terms of these valence displacement coordinates is:

$$V = \frac{1}{2} [K_{r_1 r_1} (\delta r_1)^2 + K_{r_2 r_2} (\delta r_2)^2 + K_{\theta\theta} (\delta\theta)^2 + 2 K_{r_1 r_2} \delta r_1 \delta r_2 + 2 K_{r_1 \theta} \delta r_1 \delta\theta + 2 K_{r_2 \theta} \delta r_2 \delta\theta]. \quad (3-1)$$

The kinetic energy function of the system can be written as

$$T = \frac{1}{2} m_1 [(\dot{x} + \dot{r}_1 \cos \theta - r_1 \dot{\theta} \sin \theta)^2 + (\dot{y} + \dot{r}_1 \sin \theta + r_1 \dot{\theta} \cos \theta)^2] + \frac{1}{2} m_2 [\{\dot{x} + \dot{r}_2 \cos (\theta + \theta) - r_2 (\dot{\theta} + \dot{\theta}) \sin (\theta + \theta)\}^2 + \{\dot{y} + r_2 \sin (\theta + \theta) + r_2 (\dot{\theta} + \dot{\theta}) \cos (\theta + \theta)\}^2] + \frac{1}{2} m_3 (\dot{x}^2 + \dot{y}^2). \quad (3-2)$$

Since we have taken the origin of coordinates at the center of mass of the system, we can eliminate x and y through the relations

$$\sum_i m_i x_i = 0, \quad \sum_i m_i y_i = 0. \quad (3-3)$$

Without serious error, we can replace r_1 , r_2 , and θ by their equilibrium values r_1^0 , r_2^0 , θ^0 , respectively, in the coefficients of the velocity terms.

The Lagrangian function for the system will then be given as

$$L = T - V = \frac{1}{2} \mu_1 [\dot{r}_1^2 + r_1^{02} \dot{\theta}^2] + \frac{1}{2} \mu_2 [\dot{r}_2^2 + r_2^{02} \dot{\theta}^2 + 2 r_2^{02} \dot{\theta} \dot{\theta} + r_2^{02} \dot{\theta}'^2] - \mu_3 [\dot{r}_1 \dot{r}_2 \cos \theta^0 + r_1^0 \dot{r}_2 \dot{\theta} \sin \theta^0 - r_2^0 \dot{r}_1 (\dot{\theta} + \dot{\theta}) \sin \theta^0 + r_1^0 r_2^0 (\dot{\theta}^2 + \dot{\theta} \dot{\theta}) \cos \theta^0] - \frac{1}{2} [K_{r_1 r_1} (\delta r_1)^2 + K_{r_2 r_2} (\delta r_2)^2 + K_{\theta\theta} (\delta\theta)^2 + 2 K_{r_1 r_2} \delta r_1 \delta r_2 + 2 K_{r_1 \theta} \delta r_1 \delta\theta + 2 K_{r_2 \theta} \delta r_2 \delta\theta]. \quad (3-4)$$

We notice that θ is an ignorable coordinate for an isolated three particle system, and that $\dot{\theta}$ is eliminated by solving $\frac{\partial L}{\partial \dot{\theta}} = C$ for $\dot{\theta}$ and substituting this value of $\dot{\theta}$ in the $L' = L - \dot{\theta} \left(\frac{\partial L}{\partial \dot{\theta}} \right)$. C is taken as zero in order to satisfy one of Eckart Conditions.⁶

The reduced Lagrangian L' may be written as

$$\begin{aligned}
 L' = & \frac{1}{2} [\mu_1 - \rho \mu_3^2 r_2^0 \sin^2 \theta^0] \dot{r}_1^2 + \frac{1}{2} [\mu_2 - \rho \mu_3^2 r_1^0 \sin^2 \theta^0] \dot{r}_2^2 + \\
 & \frac{1}{2} \rho r_1^{02} r_2^{02} (\mu_1 \mu_2 - \mu_3^2 \cos^2 \theta^0) \dot{\theta}^2 + [-\mu_3 \cos \theta^0 + \rho \mu_3^2 r_1^0 r_2^0 \sin^2 \theta^0] \\
 & \dot{r}_1 \dot{r}_2 + \rho \mu_3 r_1^0 r_2^0 \sin \theta^0 [\mu_1 r_1^0 - \mu_3 r_2^0 \cos \theta^0] \dot{r}_1 \dot{\theta} + \rho \mu_3 r_1^0 r_2^0 \sin \theta^0 \\
 & [\mu_2 r_2^0 - \mu_3 r_1^0 \cos \theta^0] \dot{r}_2 \dot{\theta} - \frac{1}{2} [K_{r_1 r_1} (\sigma r_1)^2 + K_{r_2 r_2} (\sigma r_2)^2 + \\
 & K_{\theta \theta} (\sigma \theta)^2 + 2 K_{r_1 r_2} \sigma r_1 \sigma r_2 + 2 K_{r_1 \theta} \sigma \theta r_1 + 2 K_{r_2 \theta} \sigma \theta r_2] \quad (3-5)
 \end{aligned}$$

where

$$\begin{aligned}
 \mu_1 &= \frac{m_1 m_2 + m_1 m_3}{m_1 + m_2 + m_3}, & \mu_2 &= \frac{m_1 m_2 + m_2 m_3}{m_1 + m_2 + m_3}, \\
 \mu_3 &= \frac{m_1 m_2}{m_1 + m_2 + m_3}.
 \end{aligned}$$

and

$$\frac{1}{\rho} = \mu_1 r_1^{02} + \mu_2 r_2^{02} - 2 \mu_3 r_1^0 r_2^0 \cos \theta^0.$$

If we make the following substitutions,

$$\begin{aligned}
 \sigma r_1 &= q_1 & \text{and} & & K_{\theta \theta} &= (r_1^{02} + r_2^{02}) k_{\theta \theta} = s^2 k_{\theta \theta} \\
 \sigma r_2 &= q_2 & & & K_{r_1 \theta} &= r_1^0 k_{r_1 \theta} \\
 \sigma \theta &= q_3 & & & K_{r_2 \theta} &= r_2^0 k_{r_2 \theta}, \quad (3-6)
 \end{aligned}$$

then the reduced Lagrangian can be expressed as

$$\begin{aligned}
 L' = & \frac{1}{2} (\mu_1 - \rho \mu_3^2 r_2^0 \sin^2 \theta^0) \dot{q}_1^2 + \frac{1}{2} (\mu_2 - \rho \mu_3^2 r_1^0 \sin^2 \theta^0) \dot{q}_2^2 + \\
 & \frac{1}{2} \rho r_1^{02} r_2^{02} (\mu_1 \mu_2 - \mu_3^2 \cos^2 \theta^0) \dot{q}_3^2 + (-\mu_3 \cos \theta^0 + \rho \mu_3^2 r_1^0 r_2^0 \sin^2 \theta^0) \\
 & \dot{q}_1 \dot{q}_2 + \rho \mu_3 r_1^0 r_2^0 \sin \theta^0 (\mu_1 r_1^0 - \mu_3 r_2^0 \cos \theta^0) \dot{q}_1 \dot{q}_3 + \\
 & \rho \mu_3 r_1^0 r_2^0 \sin \theta^0 (\mu_2 r_2^0 - \mu_3 r_1^0 \cos \theta^0) \dot{q}_2 \dot{q}_3 - \frac{1}{2} [K_{r_1 r_1} (\sigma r_1)^2 + \\
 & K_{r_2 r_2} (\sigma r_2)^2 + 2 K_{r_1 r_2} \sigma r_1 \sigma r_2 + k_{\theta \theta} s^2 (\sigma \theta)^2 + 2 k_{r_1 \theta} r_1^0 \sigma \theta \sigma r_1 + \\
 & 2 k_{r_2 \theta} r_2^0 \sigma \theta \sigma r_2]. \quad (3-7)
 \end{aligned}$$

From Lagrange's equations of motion,

$$\frac{d}{dt} \left(\frac{\partial L'}{\partial \dot{q}_1} \right) - \frac{\partial L'}{\partial q_1} = 0, \quad (3-8)$$

we obtain the following equations of motion:

$$\begin{aligned} & [\mu_1 - \rho \mu_3^2 r_0^2 \sin^2 \theta^0] \ddot{q}_1 + [-\mu_3 \cos \theta^0 + \rho \mu_3^2 r_1^0 r_2^0 \sin \theta^0] \ddot{q}_2 + \\ & \rho \mu_3 r_1^0 r_2^0 \sin \theta^0 (\mu_1 r_1^0 - \mu_3 r_2^0 \cos \theta^0) \ddot{q}_3 + K_{r_1 r_1} q_1 + K_{r_1 r_2} q_2 + \\ & k_{r_1 \theta} r_1^0 q_3 = 0 \end{aligned} \quad (3-9a)$$

$$\begin{aligned} & [\mu_2 - \rho \mu_3^2 r_1^0 r_2^0 \sin^2 \theta^0] \ddot{q}_2 + [-\mu_3 \cos \theta^0 + \rho \mu_3^2 r_1^0 r_2^0 \sin^2 \theta^0] \ddot{q}_1 + \\ & \rho \mu_3 r_1^0 r_2^0 \sin \theta^0 (\mu_2 r_2^0 - \mu_3 r_1^0 \cos \theta^0) \ddot{q}_3 + K_{r_2 r_2} q_2 + K_{r_1 r_1} q_1 + \\ & k_{r_2 \theta} r_2^0 q_3 = 0. \end{aligned} \quad (3-9b)$$

$$\begin{aligned} & [\rho r_1^0 r_2^0 (\mu_1 \mu_2 - \mu_3^2 \cos^2 \theta^0)] \ddot{q}_3 + \rho \mu_3 r_1^0 r_2^0 \sin \theta^0 (\mu_1 r_1^0 - \\ & \mu_3 r_2^0 \cos \theta^0) \ddot{q}_1 + \rho \mu_3 r_1^0 r_2^0 \sin \theta^0 (\mu_2 r_2^0 - \mu_3 r_1^0 \cos \theta^0) \ddot{q}_2 + \\ & k_{\theta \theta} s^2 q_3 + k_{r_1 \theta} r_1^0 q_1 + k_{r_2 \theta} r_2^0 q_2 = 0. \end{aligned} \quad (3-9c)$$

From Chapter II, we know that all displacement coordinates must oscillate with the same frequency (which is a normal frequency), so that we can write:

$$\begin{aligned} q_1 &= q_1^0 e^{i\omega t} \\ q_2 &= q_2^0 e^{i\omega t} \\ q_3 &= q_3^0 e^{i\omega t} \end{aligned} \quad (3-10)$$

where $i = (-1)^{\frac{1}{2}}$. Substituting equations (3-10) into equations (3-9) and eliminating the common factor $e^{i\omega t}$, which is not identically zero, we obtain three homogeneous, linear equations for the amplitudes q_1^0 , q_2^0 and q_3^0 .

In order for this system of linear equations to have a non-trivial solution, the determinant of the coefficients of the amplitudes must vanish.

The secular determinant which is thus obtained is:

$$\begin{vmatrix} -\omega^2 A_{11} + K_{r_1 r_1} & -\omega^2 A_{12} + K_{r_1 r_2} & -\omega^2 A_{13} + k_{r_1 \theta} r_1^0 \\ -\omega^2 A_{12} + K_{r_1 r_2} & -\omega^2 A_{22} + K_{r_2 r_2} & -\omega^2 A_{23} + k_{r_2 \theta} r_2^0 \\ -\omega^2 A_{13} + k_{r_1 \theta} r_1^0 & -\omega^2 A_{23} + k_{r_2 \theta} r_2^0 & -\omega^2 A_{33} + k_{\theta \theta} S^2 \end{vmatrix} = 0 \quad (3-11)$$

where

$$\begin{aligned} A_{11} &= \mu_1 - \rho \mu_3^2 r_2^{02} \sin^2 \theta^0 \\ A_{22} &= \mu_2 - \rho \mu_3^2 r_1^{02} \sin^2 \theta^0 \\ A_{33} &= \rho r_1^{02} r_2^{02} (\mu_2 \mu_2 - \mu_3^2 \cos^2 \theta^0) \\ A_{12} &= -\mu_3 \cos \theta^0 + \rho \mu_3^2 r_1^0 r_2^0 \sin \theta^0 \\ A_{13} &= \rho \mu_3 r_1^0 r_2^0 \sin \theta^0 (\mu_1 r_1^0 - \mu_3 r_2^0 \cos \theta^0) \\ A_{23} &= \rho \mu_3 r_1^0 r_2^0 \sin \theta^0 (\mu_2 r_2^0 - \mu_3 r_1^0 \cos \theta^0). \end{aligned}$$

When we solve this determinant, we obtain the following algebraic secular equation;

$$\omega^6 + p\omega^4 + q\omega^2 + r = 0, \quad (3-12)$$

where

$$\begin{aligned} p &= A_{11} A_{33} K_{r_2 r_2} + A_{22} A_{11} k_{\theta \theta} S^2 - 2 A_{11} A_{23} k_{r_2 \theta} r_2^0 + A_{22} A_{33} K_{r_1 r_1} - \\ &A_{23}^2 K_{r_1 r_2} - A_{12} A_{33} K_{r_1 r_2} - A_{12}^2 k_{\theta \theta} S^2 + A_{12} A_{13} k_{r_2 \theta} r_2^0 + 2 k_{r_1 \theta} r_1^0 \\ &A_{12} A_{23} - A_{12} A_{33} K_{r_1 r_2} / - A_{11} A_{22} A_{33} + A_{12}^2 A_{33} - 2 A_{12} A_{13} A_{23} + A_{22} A_{13}^2 \\ q &= - A_{11} K_{r_2 r_2} k_{\theta \theta} S^2 + A_{11} k_{r_2 \theta}^2 r_2^{02} - A_{22} k_{\theta \theta} S^2 K_{r_1 r_1} - K_{r_1 r_1} K_{r_2 r_2} A_{33} \\ &+ 2 K_{r_1 r_1} k_{r_2 \theta} r_2^0 A_{23} + A_{12} K_{r_1 r_2} k_{\theta \theta} S^2 - A_{12} k_{r_2 \theta} k_{r_1 \theta} r_1^0 r_2^0 + \\ &A_{12} k_{\theta \theta} S^2 K_{r_1 r_2} - K_{r_1 r_2} A_{23} k_{r_1 \theta} r_1^0 + K_{r_1 r_2} A_{13} k_{r_2 \theta} r_2^0 - A_{13} K_{r_1 r_2} \\ &k_{r_2 \theta} r_2^0 + A_{13} K_{r_2 r_2} k_{r_1 \theta} r_1^0 - A_{12} k_{r_2 \theta} r_2^0 k_{r_1 \theta} r_1^0 - A_{23} K_{r_1 r_2} k_{r_1 \theta} r_1^0 \\ &+ k_{r_1 \theta}^2 r_1^{02} A_{22} + A_{13} k_{r_1 \theta} r_1^0 K_{r_2 r_2} / - A_{11} A_{22} A_{33} + A_{12}^2 A_{33} - \\ &2 A_{12} A_{13} A_{23} + A_{22} A_{13}^2 \end{aligned}$$

$$r = Kr_1r_1 Kr_2r_2 k_{\theta\theta} S^2 - Kr_1r_1 (kr_2\theta r_2^0)^2 - Kr_1r_2^2 k_{\theta\theta} S^2 + 2 Kr_1r_2 k_{r_2\theta} k_{r_1\theta} r_1^0 r_2^0 - Kr_2r_2 (kr_1\theta r_1^0)^2 - A_{11} A_{22} A_{33} + A_{12}^2 A_{33} - 2 A_{12} A_{13} A_{23} + A_{22} A_{13}^2.$$

Three roots of this algebraic equation are obtained as

$$\begin{aligned}\omega_1 &= \left(2 \sqrt{\frac{-a}{3}} \cos \frac{\theta}{3} - \frac{P}{3} \right)^{\frac{1}{2}} \\ \omega_2 &= \left\{ 2 \sqrt{\frac{-a}{3}} \cos \left(\frac{\theta}{3} + 120^\circ \right) - \frac{P}{3} \right\}^{\frac{1}{2}} \\ \omega_3 &= \left\{ 2 \sqrt{\frac{-a}{3}} \cos \left(\frac{\theta}{3} + 240^\circ \right) - \frac{P}{3} \right\}^{\frac{1}{2}}\end{aligned}\quad (3-13)$$

where

$$a = \frac{1}{3} (3q - p^2)$$

$$b = \frac{1}{27} (2p^3 - 9Pq + 27r)$$

and

$$\theta = \cos^{-1} \left(\frac{-\frac{6}{2}}{\sqrt{\frac{-a^3}{27}}} \right).$$

C. Framework Vibrations of an Infinitely Long, Zigzag Chain Molecule

Framework vibrations of an infinitely long, zigzag chain molecule which has two identical characteristic groups in one repeating unit, such as normal paraffin, was discussed in detail using the multiple origin method by Deeds.⁵

In this section we shall consider the framework vibrations of an infinitely long zigzag chain molecule which has two different characteristic groups in one repeating unit. We shall assume that the chain is not branched and that the groups are arranged in some sort of order such that the inter-

actions between adjacent groups are generally larger than those between second nearest neighbors, and so on.

The secular determinant of an infinitely long unbranched molecule with repeating units of finite length is shown in Figure 3.

$$\begin{vmatrix}
 \text{R.U.} & \text{X} & \text{Y} & \text{Z} & & & \\
 \text{X} & \text{R.U.} & \text{X} & \boxed{\text{Y}} & \text{Z} & & \\
 \text{Y} & \text{X} & \text{R.U.} & \text{X} & \text{Y} & \text{Z} & \\
 \text{Z} & \boxed{\text{Y}} & \text{X} & \text{R.U.} & \text{X} & \boxed{\text{Y}} & \text{Z} \\
 & \text{Z} & \text{Y} & \text{X} & \text{R.U.} & \text{X} & \text{Y} \\
 & & \text{Z} & \boxed{\text{Y}} & \text{X} & \text{R.U.} & \text{X} \\
 & & & \text{Z} & \text{Y} & \text{X} & \text{R.U.}
 \end{vmatrix} = 0$$

Figure 3. The Secular Determinant of an Infinitely Long Unbranched Molecule.

The blocks marked "R.U." represent the secular determinants for isolated repeating units, and the blocks marked "X, Y, Z, . . ." are interaction blocks of progressively smaller importance.

In this form the secular determinant has considerable symmetry. The blocks along the principal diagonal are all identical, and the interaction blocks at a given distance from the principal diagonal are all identical, since we can neglect end effects for this infinite chain.

Since the interaction blocks are less significant as they occur farther from the principal diagonal, we may neglect interaction terms between

the groups belonging to repeating units separated by more than two intervening units. Furthermore, if we can solve the vibrational problem for this typical section outlined by the dashed line in Figure 3, we can say that all of the other sections should vibrate in the same way with only different amplitudes.

In the treatment of the framework vibration problem of long chain molecules, we consider a "characteristic group" as a hindered, rigid rotator. The treatment given here is applicable to the framework vibration problems of many chain molecules, and in particular, those of polyvinyl chloride, polyacrylonitrile, and possibly polystyrene.

The type of zigzag chain which we are considering is a type of helical chain in which the repeating unit contains two characteristic groups. Let us assume that the rotators are numbered as shown in Figure 4 where n is any integer.

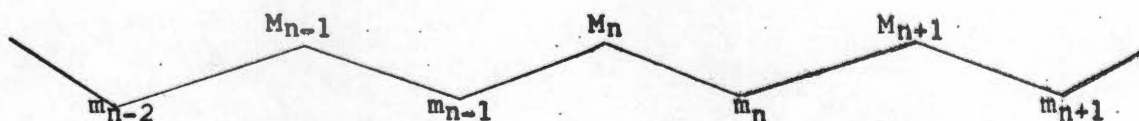


Figure 4. Configuration of a Chain Molecule with Alternating Groups.

We shall also assume that the equilibrium configuration is specified as in Figure 5.

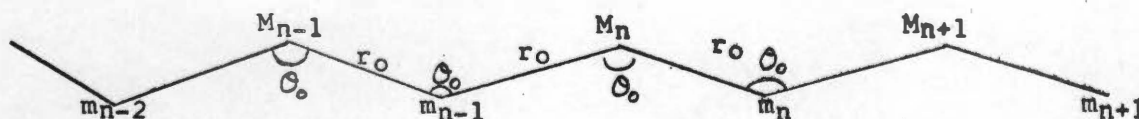


Figure 5. Equilibrium Configuration of a Zigzag Chain Molecule with Alternating Groups.

In applying the M. O. M. to this problem, we shall set up a rectangular coordinate system for each characteristic group of atoms, the x-axis parallel to the long axis of the chain in the direction of increasing n , the y-axis perpendicular to the long axis, and the z-axis perpendicular to the x and y axes in the usual right-handed sense, as shown in Figure 6.

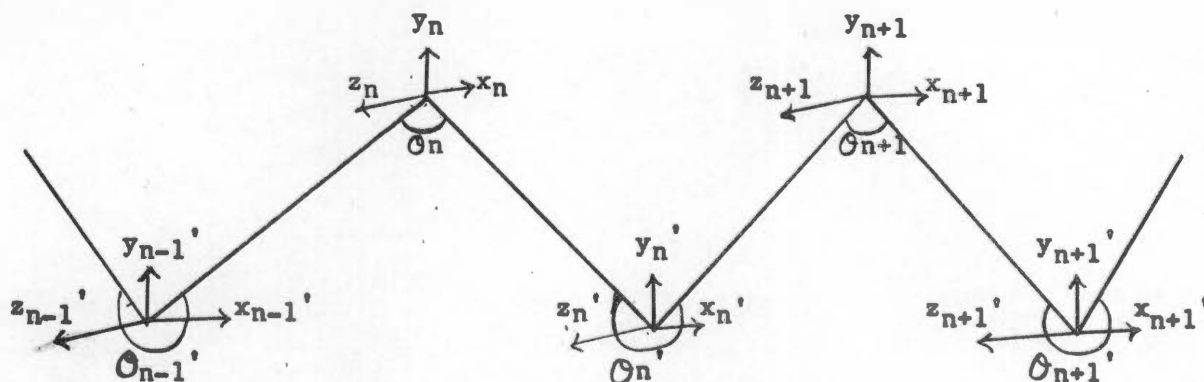


Figure 6. Rectangular Coordinates.

Let us call one of the two characteristic groups in each repeating unit an M-rotator and the other one an m-rotator. Let ξ_n , η_n , and ζ_n be the infinitesimal rectangular displacements of the center of mass of the n^{th} M-rotator from its equilibrium position in the x_n , y_n and z_n directions respectively. Let ξ_n' , η_n' , and ζ_n' be the infinitesimal rectangular displacements of the center of mass of the n^{th} m-rotator from its equilibrium position in the x_n' , y_n' , and z_n' directions respectively. Let α_n , β_n and γ_n be the infinitesimal hindered angular displacements of the n^{th} M-rotator, with their positive senses in the direction of rotation of a right-handed screw traveling in the positive x_n , y_n , and z_n directions, respectively. Let α_n' , β_n' , and γ_n' be the infinitesimal hindered angular

displacements of the n^{th} m-rotator, with their positive senses in the direction of rotation of a right-handed screw traveling in the positive x_n' , y_n' , and z_n' directions, respectively. To reduce the algebraic complexity we shall assume that x-, y-, z-, x'-, y'-, and z'- coincide with the principal axes of rotary inertia of the rigid rotators and that corresponding axes are parallel.

Under these assumptions, we can write the kinetic energy function of the chain of rigid rotators as

$$2T = \sum_n \left[M(\dot{\xi}_n^2 + \dot{\eta}_n^2 + \dot{\zeta}_n^2) + I_x \dot{\alpha}_n^2 + I_y \dot{\beta}_n^2 + I_z \dot{\gamma}_n^2 + \sum_n m(\dot{\xi}_n'^2 + \dot{\eta}_n'^2 + \dot{\zeta}_n'^2) + I_x' \dot{\alpha}_n'^2 + I_y' \dot{\beta}_n'^2 + I_z' \dot{\gamma}_n'^2 \right], \quad (3-14)$$

where the range of n, here and in the rest of this section, is from $-\infty$ to $+\infty$, M is the mass of M-rotators, m is the mass of m-rotators, and I_x , I_y , I_z , I_x' , I_y' , and I_z' are the principal moments of inertia of the M-rotators and the m-rotators about the x-, y-, z-, x'-, y'-, and z'- axes, respectively.

If the principal radii of gyration of the M-rotators and the m-rotators are a, b, c, a', b', and c' respectively, about the corresponding axes, then the kinetic energy function can be written in the form:

$$2T = M \sum_n (\dot{\xi}_n^2 + \dot{\eta}_n^2 + \dot{\zeta}_n^2 + a^2 \dot{\alpha}_n^2 + b^2 \dot{\beta}_n^2 + c^2 \dot{\gamma}_n^2) + m \sum_n (\dot{\xi}_n'^2 + \dot{\eta}_n'^2 + \dot{\zeta}_n'^2 + a'^2 \dot{\alpha}_n'^2 + b'^2 \dot{\beta}_n'^2 + c'^2 \dot{\gamma}_n'^2) \quad (3-15)$$

For physical reasons it is desirable to express the potential energy function in terms of valence displacement coordinates. Let us suppose that δr_n is the increment in the length of the bond r_n between the center of

mass of the n^{th} M-rotator and the center of mass of the n^{th} m-rotator, $\delta r_n'$ is the increment in the length of the bond r_n' between the center of mass of the n^{th} m-rotator and the center of mass of $(n+1)^{\text{th}}$ M-rotator. $\delta \theta_n$ is the increment in the bond angle θ_n between the adjacent bonds r_{n-1}' and r_n , $\delta \theta_n'$ is the increment in the bond angle θ_n' between the adjacent bonds r_n and r_n' , ϑ_n is the torsion in the bond r_n and ϑ_n' is the torsion in the bond r_n' with their positive sense such that it tries to make the chain look like a right-handed screw.

Then simple geometrical considerations show that for infinitesimal displacements, we can write the valence displacement coordinates as follows, letting $r_n \approx r_n' \approx r_0$ and $\theta_n \approx (2\pi - \theta_n') \approx \theta_0$ where r_0 is the equilibrium bond distance between adjacent rotators, and θ_0 is the equilibrium bond angle between adjacent bonds:

$$\delta r_n = (\xi_n' - \xi_n) \sin \frac{1}{2} \theta_0 + (\eta_n' - \eta_n) \cos \frac{1}{2} \theta_0$$

$$\delta r_n' = (\xi_{n+1} - \xi_n') \sin \frac{1}{2} \theta_0 + (\eta_{n+1} - \eta_n') \cos \frac{1}{2} \theta_0$$

$$\delta \theta_n = \frac{1}{r_0} (\xi_n' - \xi_{n-1}') \cos \frac{1}{2} \theta_0 - (2\eta_n - \eta_n' - \eta_{n-1}') \sin \frac{1}{2} \theta_0$$

$$\delta \theta_n' = \frac{1}{r_0} (\xi_{n+1} - \xi_n) \cos \frac{1}{2} \theta_0 - (2\eta_n' - \eta_{n+1} - \eta_n) \sin \frac{1}{2} \theta_0$$

$$\vartheta_n = \frac{1}{r_0 \sin \theta_0} (\zeta_{n+1} + \zeta_n' - \zeta_n - \zeta_{n-1}') \quad (3-16)$$

$$\vartheta_n' = \frac{1}{r_0 \sin \theta_0} (\zeta_{n+1} + \zeta_{n+1}' - \zeta_n' - \zeta_n). \quad (3-16)$$

If the principal axes of the rotators coincide with the x-, y-, and z- axes, as assumed previously, then the symmetry of this infinite chain can be considered to be that of the line group C_s , since the only covering operations, in addition to the identity and translation operations are reflections in planes perpendicular to the chain axis.

From section E of Chapter II we know that certain combinations of these valence displacement coordinates will be symmetry coordinates.

We define the covering operations which we need in this discussion as follows:

T: translation by m_1 links

where m_1 takes all integral values (positive, negative, or zero), and a "link" is the length of a repeating unit parallel to the long axis of the chain.

σ_x : reflection in plane perpendicular to the x-axes and located $2m_2$ links to the right of the n^{th} rotator.

Now we can investigate the resulting combinations and their behavior under the covering operations, as shown in Table II. Since the potential energy is a scalar function, all terms in it must be totally symmetric under all covering operations. Therefore, in the most general quadratic potential energy function there can only occur products of coordinates belonging to the same symmetry species, since such products are the only quadratic ones which will be totally symmetric under all covering operations.

The most general quadratic potential in terms of these valence coordinates is:

$$\begin{aligned}
 V = \frac{1}{2} \sum_n \bigg[& K_{rr_0} (\delta r_n)^2 + K_{r'r_0'} (\delta r_n')^2 + K_{rr'} (\delta r_n) (\delta r_n') + K_{rr_1} \\
 & (\delta r_n) (\delta r_{n+1}) + 2 K_{r'r_1'} (\delta r_n') (\delta r_{n+1}') + K_{\theta\theta_0} (\delta\theta_n)^2 + K_{\theta'\theta_0'} \\
 & (\delta\theta_n')^2 + 2 K_{\theta\theta'} (\delta\theta_n) (\delta\theta_n') + 2 K_{\theta\theta_1} (\delta\theta_n) (\delta\theta_{n+1}) + 2 K_{\theta'\theta_1'} \\
 & (\delta\theta_n') (\delta\theta_{n+1}') + K_{\theta\theta_0} \vartheta_n^2 + K_{\theta'\theta_0'} \vartheta_n'^2 + 2 K_{\theta\theta_1} \vartheta_n \vartheta_n' + 2 K_{\theta\theta_1} \vartheta_n \\
 & \vartheta_{n+1} + K_{\alpha\alpha_0} \alpha_n^2 + K_{\alpha'\alpha_0'} \alpha_n'^2 + 2 K_{\alpha\alpha'} \alpha_n \alpha_n' + 2 K_{\alpha\alpha_1} \alpha_n \alpha_{n+1} + 2 K_{\alpha'\alpha_1'} \\
 & \alpha_n' \alpha_{n+1}' + K_{\beta\beta_0} \beta_n^2 + K_{\beta'\beta_0'} \beta_n'^2 + 2 K_{\beta\beta'} \beta_n \beta_n' + 2 K_{\beta\beta_1} \beta_n \beta_{n+1} +
 \end{aligned}$$

TABLE II
TRANSFORMATION PROPERTIES OF SYMMETRY COORDINATES

Symmetry Coordinates	Covering Operations		Species
	T	σ_x	
$\delta r_n + \delta r_{n+m}$	+	+	A'
$\delta r_n' + \delta r_{n+m}'$	+	+	A'
$\delta \theta_n + \delta \theta_{n+m}$	+	+	A'
$\delta \theta_n' + \delta \theta_{n+m}'$	+	+	A'
$\gamma_n + \gamma_{n+m}$	+	+	A'
$\delta r_n - \delta r_{n+m}$	+	-	A''
$\delta r_n' - \delta r_{n+m}'$	+	-	A''
$\delta \theta_n - \delta \theta_{n+m}$	+	-	A''
$\delta \theta_n' - \delta \theta_{n+m}'$	+	-	A''
$\gamma_n - \gamma_{n+m}$	+	-	A''
$\gamma_n' - \gamma_{n+m}'$	+	-	A''
$a_n + a_{n+m}$	+	+	A'
$a_n' + a_{n+m}'$	+	+	A'
$\beta_n + \beta_{n+m}$	+	+	A'
$\beta_n' + \beta_{n+m}'$	+	+	A'
$\varrho_n + \varrho_{n+m}$	+	+	A'
$\varrho_n' + \varrho_{n+m}'$	+	+	A'
$a_n - a_{n+m}$	+	-	A''
$a_n' - a_{n+m}'$	+	-	A''
$\beta_n - \beta_{n+m}$	+	-	A''
$\beta_n' - \beta_{n+m}'$	+	-	A''
$\varrho_n - \varrho_{n+m}$	+	-	A''
$\varrho_n' - \varrho_{n+m}'$	+	-	A''

$$\begin{aligned}
& 2 K_{\beta' \beta_1'} \beta_n' \beta_{n+1}' + K_{\gamma \gamma_0} \gamma_n^2 + K_{\gamma' \gamma_0'} \gamma_n'^2 + 2 K_{\gamma \gamma_1} \gamma_n \gamma_n' + \\
& 2 K_{\gamma \gamma_1'} \gamma_n \gamma_{n+1}' + 2 K_{\gamma' \gamma_1'} \gamma_n' \gamma_{n+1}' + 2 K_{r \theta} (\delta \theta_n) (\delta r_n + \delta r_{n-1}') + \\
& 2 K_{r \theta'} (\delta \theta_n') (\delta r_n + \delta r_{n-1}') + 2 K_{a \beta} a_n (\beta_n' - \beta_{n-1}') + 2 K_{a' \beta'} a_n' \\
& (\beta_{n+1} - \beta_n) + 2 K_{a \beta_1} a_n (\beta_{n+1} - \beta_{n-1}) + 2 K_{a' \beta_1'} a_n' (\beta_{n+1}' - \beta_{n-1}') + \\
& 2 K_{a \theta} \theta_n (a_n' - a_n) + 2 K_{a \theta'} \theta_n' (a_{n+1} - a_n') + 2 K_{a \theta_1} \theta_n (a_{n+1} - a_{n-1}) + \\
& 2 K_{a \theta_1'} \theta_n' (a_{n+1}' - a_{n-1}') + 2 K_{\beta \theta} \theta_n (\beta_n' - \beta_n) + 2 K_{\beta \theta_1} \theta_n' (\beta_{n+1} - \beta_n') \\
& + 2 K_{\beta \theta_1} \theta_n (\beta_{n+1} - \beta_{n-1}) + 2 K_{\beta \theta_1'} \theta_n' (\beta_{n+1}' - \beta_{n-1}') \Big]. \quad (3-17)
\end{aligned}$$

We must now express this potential energy function in terms of the rectangular displacement coordinates $\xi, \eta, \zeta, \xi', \eta',$ and ζ' , using the definitions in (3-16).

If we also make the following substitutions:

$$\begin{aligned}
D &= \sin \frac{1}{2} \theta_0 & E &= \cos \frac{1}{2} \theta_0 \\
F &= \sin \theta_0 & G &= \cos \theta_0
\end{aligned} \quad (3-18)$$

and

$$\begin{aligned}
K_{\theta \theta_1} &= k_{\theta \theta_1} r_0^2, K_{\theta' \theta_1'} = k_{\theta' \theta_1'} r_0^2 \\
K_{\theta \theta_1} &= k_{\theta \theta_1} r_0^2 \sin^2 \theta_0, K_{r \theta_1} = k_{r \theta_1} r_0, K_{r \theta_1'} = k_{r \theta_1'} r_0 \\
K_{\theta' \theta_1'} &= k_{\theta' \theta_1'} r_0^2 \sin^2 \theta_0 \\
K_{a a_1} &= k_{a a_1} a^2, K_{a' a_1'} = k_{a' a_1'} a'^2 \\
K_{\beta \beta_1} &= k_{\beta \beta_1} b^2, K_{\beta' \beta_1'} = k_{\beta' \beta_1'} b'^2 \\
K_{\gamma \gamma_1} &= k_{\gamma \gamma_1} c^2, K_{\gamma' \gamma_1'} = k_{\gamma' \gamma_1'} c'^2 \\
K_{r \theta_1} &= k_{r \theta_1} r_0, K_{r \theta_1'} = k_{r \theta_1'} r_0,
\end{aligned}$$

where $i = 0, 1$, then the potential energy function has the following form:

$$\begin{aligned}
V &= \frac{1}{2} \sum_n \left[K_{rr_0} D^2 (\xi_n'^2 - 2 \xi_n' \xi_n + \xi_n^2) + K_{rr_0} E^2 (\eta_n'^2 + \eta_n^2 - \right. \\
& 2 \eta_n' \eta_n) + 2 K_{rr_0} DE (\xi_n' \eta_n' - \xi_n' \eta_n - \xi_n \eta_n' + \xi_n \eta_n) + K_{r' r_0'} D^2 \\
& \left. (\xi_{n+1}'^2 + \xi_n'^2 - 2 \xi_{n+1}' \xi_n') + K_{r' r_0'} E^2 (\eta_n'^2 + \eta_{n+1}'^2 - 2 \eta_n' \eta_{n+1}') \right] +
\end{aligned}$$

$$\begin{aligned}
& 2 K_r r_0 DE (-\xi_{n+1} \eta_n + \xi_{n+1} \eta_{n+1} + \xi_n \eta_n - \xi_n \eta_{n+1}) + k \theta \theta_0 E^2 \\
& (\xi_n'^2 + \xi_{n-1}'^2 - 2 \xi_n' \xi_{n-1}') + k \theta \theta_0 D^2 (4 \eta_n^2 + \eta_n'^2 + \eta_{n-1}'^2 - \\
& 4 \eta_n \eta_n' - 4 \eta_n \eta_{n-1}' + 2 \eta_n' \eta_{n-1}') - 2 k \theta \theta_0 DE (2 \xi_n' \eta_n - \xi_n' \eta_n' - \\
& \xi_n' \eta_{n-1}' - 2 \xi_{n-1}' \eta_n + \xi_{n-1}' \eta_n' + \xi_{n-1}' \eta_{n-1}') + k \theta' \theta_0' E^2 (\xi_{n+1}^2 + \\
& \xi_n^2 - 2 \xi_{n+1} \xi_n) + k \theta' \theta_0' D^2 (4 \eta_n'^2 + \eta_{n+1}'^2 + \eta_n^2 - 4 \eta_n' \eta_{n+1} - \\
& 4 \eta_n' \eta_n + 2 \eta_{n+1} \eta_n) + 2 k \theta' \theta_0' DE (2 \xi_{n+1} \eta_n' - \xi_{n+1} \eta_{n+1} - \xi_{n+1} \eta_n - \\
& 2 \eta_n' \xi_n + \xi_n \eta_{n+1} + \xi_n \eta_n) + k \theta \theta_0 (\zeta_{n+1}^2 + \zeta_n'^2 + 2 \zeta_{n+1} \zeta_n' + \\
& \zeta_n^2 + \zeta_{n-1}'^2 + 2 \zeta_n \zeta_{n-1}' - 2 \zeta_{n+1} \zeta_n - 2 \zeta_{n+1} \zeta_{n-1}' - 2 \zeta_n' \zeta_n - \\
& 2 \zeta_n' \zeta_{n-1}') + k \theta' \theta_0' (\zeta_{n+1}^2 + \zeta_{n+1}'^2 + \zeta_n'^2 + \zeta_n^2 + 2 \zeta_{n+1} \zeta_{n+1}' - \\
& 2 \zeta_{n+1} \zeta_n' - 2 \zeta_{n+1} \zeta_n - 2 \zeta_{n+1}' \zeta_n' - 2 \zeta_{n+1}' \zeta_n + 2 \zeta_n' \zeta_n) + \\
& 2 K_{rr} \{ D^2 (\xi_n' \xi_{n+1} - \xi_n'^2 - \xi_n \xi_{n+1} + \xi_n \xi_n') + DE (\xi_{n+1} \eta_n' - \\
& \xi_{n+1} \eta_n + \xi_n' \eta_n + \xi_n' \eta_{n+1} + \xi_n \eta_n' - \xi_n \eta_{n+1} - 2 \xi_n' \eta_n) + \\
& E^2 (-\eta_n'^2 + \eta_n' \eta_{n+1} + \eta_n \eta_n' - \eta_n \eta_{n+1}) \} + 2 K_{rr1} \{ D^2 (\xi_n' \xi_{n+1}' - \\
& \xi_n' \xi_{n+1} - \xi_n \xi_{n+1}' + \xi_n \xi_{n+1}) + DE (\xi_n' \eta_{n+1}' - \xi_n' \eta_{n+1} - \\
& \xi_n \eta_{n+1}' + \xi_n \eta_{n+1} + \xi_{n+1}' \eta_n' - \xi_{n+1} \eta_n' - \eta_n \xi_{n+1}' + \eta_n \xi_{n+1}) + \\
& E^2 (\eta_n' \eta_{n+1}' - \eta_n' \eta_{n+1} - \eta_n \eta_{n+1}' + \eta_n \eta_{n+1}) \} + 2 k \theta \theta' \{ E^2 \\
& (\xi_{n+1} \xi_n' - \xi_{n+1} \xi_{n-1}' - \xi_n \xi_n' + \xi_n \xi_{n-1}') - DE \\
& (2 \eta_n \xi_{n+1} - \xi_{n+1} \eta_n' - \xi_{n+1} \eta_{n-1}' - 2 \xi_n \eta_n + \xi_n \eta_n' + \xi_n \eta_{n-1}' - \\
& 2 \xi_n' \eta_n' + 2 \eta_n' \xi_{n-1}' + \eta_{n+1} \xi_n' - \xi_{n-1}' \eta_{n+1} - \xi_n' \eta_n - \eta_n \xi_{n-1}') \\
& - D^2 (5 \eta_n' \eta_n - 2 \eta_n'^2 - 2 \eta_n' \eta_{n-1}' - 2 \eta_{n+1} \eta_n + \eta_{n+1} \eta_n' + \eta_{n+1} \eta_{n-1}' - \\
& 2 \eta_n^2 + \eta_n \eta_{n-1}') \} + 2 k \theta \theta' (\zeta_{n+1}^2 + \zeta_{n+1} \zeta_n' - 2 \zeta_{n+1} \zeta_n - \\
& \zeta_{n+1} \zeta_{n-1}' + \zeta_{n+1}' \zeta_{n+1} + \zeta_{n+1}' \zeta_n' - \zeta_{n+1}' \zeta_n - \zeta_{n+1}' \zeta_{n-1}' - \\
& \zeta_n' \zeta_{n+1} - \zeta_n'^2 + \zeta_n' \zeta_{n-1}' + \zeta_n^2 + \zeta_n \zeta_{n-1}') \\
& + 2 K_r r_1 \{ D^2 (\xi_{n+1} \xi_{n+2} - \xi_{n+1} \xi_{n+1}' - \xi_n' \xi_{n+2} + \xi_n' \xi_{n+1}') \\
& + DE (-\xi_{n+1} \eta_{n+1}' + \xi_{n+1} \eta_{n+2} + \xi_n' \eta_{n+1}' - \xi_n' \eta_{n+2} - \eta_n' \xi_{n+2} +
\end{aligned}$$

$$\begin{aligned}
& \eta_n' \xi_{n+1}' + \eta_{n+1} \xi_{n+2} - \xi_{n+1}' \eta_{n+1}') + E^2 (\eta_{n+1}' \eta_n' - \eta_{n+2} \eta_n' - \\
& \eta_{n+1} \eta_{n+1}' + \eta_{n+1} \eta_{n+2}') \} + 2k_{\theta\theta_1} \{ E^2 (\xi_{n+1}' \xi_n' - \xi_n'^2 - \\
& \xi_{n+1}' \xi_{n-1}' + \xi_n' \xi_{n-1}') + DE (2 \xi_n' \eta_{n+1} - \xi_n' \eta_{n+1}' - 2 \xi_{n-1}' \\
& \eta_{n+1} + \xi_{n-1}' \eta_{n+1}' + \xi_{n-1}' \eta_n' + 2 \xi_{n+1}' \eta_n - 2 \xi_n' \eta_n - \xi_{n+1}' \eta_n' \\
& - \xi_{n+1}' \eta_{n-1}' + \xi_n' \eta_{n-1}') + D^2 (4 \eta_{n+1} \eta_n - 2 \eta_n \eta_{n+1}' - 2 \eta_n \eta_n' - \\
& 2 \eta_{n+1} \eta_n' + \eta_{n+1}' \eta_n' + \eta_n'^2 - 2 \eta_{n+1} \eta_{n-1}' + \eta_{n+1}' \eta_{n-1}' + \eta_{n-1}' \eta_n') \} \\
& + 2k_{\theta'\theta'_1} \{ E^2 (\xi_{n+2} \xi_{n+1} - \xi_{n+1}' - \xi_{n+2} \xi_n + \xi_{n+1} \xi_n) \\
& + DE (2 \xi_{n+1} \eta_{n+1}' - \xi_{n+1} \eta_{n+2} - 2 \xi_n \eta_{n+1}' + \xi_n \eta_{n+2} + \xi_n \eta_{n+1} + \\
& 2 \eta_n' \xi_{n+2} - 2 \eta_n' \xi_{n+1} - \eta_{n+1} \xi_{n+2} - \eta_n \xi_{n+2} + \xi_{n+1} \eta_n) + D^2 \\
& (4 \eta_{n+1}' \eta_n' - 2 \eta_n' \eta_{n+2} - 2 \eta_n' \eta_{n+1} - 2 \eta_{n+1} \eta_{n+1}' + \eta_{n+2} \eta_{n+1} + \\
& \eta_{n+1}^2 - 2 \eta_{n+1}' \eta_n + \eta_{n+2} \eta_n + \eta_{n+1} \eta_n) \} \\
& + 2k_{\theta\theta'_1} (\xi_{n+2} \xi_{n+1} + \xi_{n+2} \xi_{n+1}' - \xi_{n+2} \xi_n' - \xi_{n+2} \xi_n + \\
& \xi_{n+2}' \xi_{n+1} + \xi_{n+2}' \xi_{n+1}' - \xi_{n+2}' \xi_n' - \xi_{n+2}' \xi_n - \xi_{n+1}' \xi_{n+1} - \\
& \xi_{n+1}'^2 + \xi_{n+1}' \xi_n' + \xi_{n+1}' \xi_n - \xi_{n+1}^2 - \xi_{n+1} \xi_{n+1}' + \\
& \xi_{n+1} \xi_n' + \xi_{n+1} \xi_n) \\
& + k_{\alpha\alpha_0} a^2 \alpha_n^2 + k_{\alpha'\alpha'_0} a'^2 \alpha_n'^2 + 2k_{\alpha\alpha_1} a^2 \alpha_n \alpha_{n+1} + 2k_{\alpha'\alpha'_1} a'^2 \alpha_n \alpha_{n+1}' \\
& + k_{\beta\beta_0} b^2 \beta_n^2 + k_{\beta'\beta'_0} b'^2 \beta_n'^2 + 2k_{\beta\beta'} b b' \beta_n \beta_n' + 2k_{\beta\beta_1} b^2 \beta_n \beta_{n+1} + \\
& 2k_{\beta'\beta'_1} b'^2 \beta_n' \beta_{n+1}' + k_{\gamma\gamma_0} c^2 \gamma_n^2 + k_{\gamma'\gamma'_0} c'^2 \gamma_n'^2 + 2k_{\gamma\gamma'} c c' \\
& \gamma_n \gamma_n' + 2k_{\gamma\gamma_1} c^2 \gamma_n \gamma_{n+1} + 2k_{\gamma'\gamma'_1} c'^2 \gamma_n' \gamma_{n+1}' \\
& + 2k_{\tau\theta} \{ DE (\xi_n'^2 + \xi_{n-1}'^2 - 2 \xi_n' \xi_{n-1}' - 4 \eta_n^2 - \eta_n'^2 - \eta_{n-1}'^2 + \\
& 4 \eta_n \eta_n' + 4 \eta_n \eta_{n-1}' - 2 \eta_n' \eta_{n-1}') + (E^2 - D^2) (2 \xi_n' \eta_n - \xi_n' \eta_n' - \\
& \xi_n' \eta_{n-1}' - 2 \xi_{n-1}' \eta_n + \xi_{n-1}' \eta_n' + \xi_{n-1}' \eta_{n-1}') \} \\
& + 2k_{\tau\theta'} \{ DE (\xi_{n+1}^2 + \xi_n^2 - 2 \xi_n \xi_{n+1} + 4 \eta_n'^2 + \eta_n^2 + \eta_{n+1}^2 - \\
& 4 \eta_n' \eta_n - 4 \eta_n' \eta_{n+1} + 2 \eta_n \eta_{n+1}) + (E^2 + D^2) (2 \xi_{n+1}' \eta_n' - \xi_{n+1}' \eta_n - \\
& \xi_{n+1} \eta_{n+1} - 2 \xi_n \eta_n' + \xi_n \eta_n + \xi_n \eta_{n+1}') \}
\end{aligned}$$

$$\begin{aligned}
& + 2 k_r \theta_0 \left\{ DE \left(\xi_n' \xi_{n+1} + 2 \xi_n' \xi_{n-1}' - \xi_n'^2 - \xi_n' \xi_{n-1} - \right. \right. \\
& \quad \xi_{n-1}' \xi_{n+1} - \xi_{n-1}'^2 + \xi_{n-1}' \xi_{n-1} + 2 \eta_n \eta_n' - 2 \eta_n \eta_{n+1} - 2 \eta_n \eta_{n-1}' \\
& + 2 \eta_n \eta_{n-1} - \eta_n'^2 + \eta_n' \eta_{n+1} - \eta_n' \eta_{n-1} + \eta_{n-1} \eta_{n+1} + \eta_{n-1}'^2 - \\
& \quad \eta_{n-1}' \eta_{n-1} \left. \right) + E^2 \left(\xi_n' \eta_n' - \xi_n' \eta_{n+1} + \xi_n' \eta_{n-1}' - \xi_n' \eta_{n-1} - \right. \\
& \quad \xi_{n-1}' \eta_n' + \xi_{n-1}' \eta_{n+1} - \xi_{n-1}' \eta_{n-1}' + \xi_{n-1}' \eta_{n-1} \left. \right) - D^2 \left(2 \eta_n \xi_{n+1} + \right. \\
& \quad 2 \eta_n \xi_{n-1}' - 2 \eta_n \xi_n' - 2 \eta_n \xi_{n-1} - \eta_n' \xi_{n+1} - \xi_{n-1}' \eta_n' + \xi_n' \eta_n' + \\
& \quad \xi_{n-1} \eta_n' - \xi_{n+1} \eta_{n-1}' - \xi_{n-1}' \eta_{n-1}' + \xi_n' \eta_{n-1}' + \xi_{n-1} \eta_{n-1}' \left. \right) \left. \right\} \\
& + 2 k_r \theta_1' \left\{ DE \left(\xi_{n+1} \xi_{n+1}' + 2 \xi_{n+1} \xi_n - \xi_{n+1}^2 - \xi_{n+1} \xi_{n-1}' - \right. \right. \\
& \quad \xi_n \xi_{n+1}' - \xi_n^2 + \xi_n \xi_{n-1}' + 2 \eta_{n+1}' \eta_n' - 2 \eta_{n+1} \eta_n' - 2 \eta_n' \eta_{n-1}' + \\
& \quad 2 \eta_n' \eta_n - \eta_{n+1} \eta_{n+1}' + \eta_{n+1}^2 + \eta_{n+1} \eta_{n-1}' - \eta_{n+1}' \eta_n + \eta_n \eta_{n-1}' - \\
& \quad \eta_n^2 \left. \right) + E^2 \left(\xi_{n+1} \eta_{n+1}' - \xi_{n+1} \eta_{n+1} - \xi_{n+1} \eta_{n-1}' + \xi_{n+1} \eta_n - \xi_n \eta_{n+1}' + \right. \\
& \quad \xi_n \eta_{n+1} + \xi_n \eta_{n-1}' - \xi_n \eta_n \left. \right) + D^2 \left(2 \xi_{n+1}' \eta_n' + 2 \xi_n \eta_n' - 2 \xi_{n+1} \eta_n' \right. \\
& \quad - 2 \xi_{n-1}' \eta_n' - \xi_{n+1}' \eta_{n+1} - \xi_n \eta_{n+1} + \xi_{n+1} \eta_{n+1} + \xi_{n-1}' \eta_{n+1} - \\
& \quad \xi_{n+1}' \eta_n - \xi_n \eta_n + \xi_{n+1} \eta_n + \xi_{n-1}' \eta_n \left. \right) \left. \right\}. \quad (3-19)
\end{aligned}$$

Putting the expressions for T and V from equations (3-15) and (3-19) into Lagrange's equations of motion,

$$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{q}} \right) - \frac{\partial L}{\partial q} = 0 \quad \text{where } L = T - V, \quad (3-20)$$

we obtain the following equations of motion:

$$\begin{aligned}
M \ddot{\xi}_k - K_{rr0} D^2 (\xi_k' - \xi_k) + K_{rr0} DE (\eta_k - \eta_k') + K_{r'r_0} D^2 (\xi_k - \xi_{k-1}) \\
+ K_{r'r_0} DE (\eta_k - \eta_{k-1}') + k_{\theta_0} \theta_0' E^2 (2 \xi_k - \xi_{k-1} - \xi_{k+1}) - \\
k_{\theta_0} \theta_0' DE (2 \eta_{k-1}' - \eta_{k-1} - 2 \eta_k' + \eta_{k+1}) + K_{rr'} D^2 (\xi_{k-1}' - \xi_{k+1} - \xi_{k-1} - \xi_k') \\
+ K_{rr'} DE (\eta_{k-1}' - \eta_{k-1} + \eta_k' - \eta_{k+1}) + K_{rr1} DE (\eta_{k+1} - \eta_{k+1}' + \eta_{k-1} - \eta_{k-1}') \\
+ k_{\theta\theta'} E^2 (2 \xi_{k-1}' - \xi_{k-2}' - \xi_k') - k_{\theta\theta'} DE (2 \eta_{k-1} - 2 \eta_k - \eta_{k-2}' + \eta_k') \\
+ K_{r'r_1} D^2 (\xi_{k+1} + \xi_{k-1} - \xi_k' - \xi_{k-2}') + K_{r'r_1} DE (-\eta_k' - \eta_{k-2}' + \eta_{k+1} + \eta_{k-1}) \\
+ k_{\theta\theta_1} E^2 (2 \xi_{k-1}
\end{aligned}$$

$$\begin{aligned}
& + 2 \xi_{k+1} - 2 \xi_k - \xi_{k-2} - \xi_{k+2}) - k \theta' \theta_1' DE (2 \eta_{k'} - 2 \eta_{k+1}' \\
& + \eta_{k+2} + 2 \eta_{k-2}' - 2 \eta_{k-1}' - \eta_{k-2}) + k_r \theta' DE (4 \xi_k - 2 \xi_{k+1} - \\
& 2 \xi_{k-1}) + k_r \theta' (E^2 - D^2) (2 \eta_{k-1}' - \eta_{k-1} - 2 \eta_{k'} - \eta_{k+1}) + k_r \theta_1' \\
& DE (\xi_{k'} + 2 \xi_{k-1} + 2 \xi_{k+1} - 4 \xi_k - \xi_{k-2}' - \xi_{k+1}' + \xi_{k-1}') + \\
& k_r \theta_1' E^2 (\eta_{k'} - \eta_{k-2}' + \eta_{k-1} - \eta_{k+1}' + \eta_{k+1} + \eta_{k-1}') - k_r \theta_1' D^2 \\
& (-2 \eta_{k-1}' - 2 \eta_{k'} - \eta_{k+1} + \eta_{k-1}) + k_r \theta_1' DE (\xi_{k-1}' - \xi_{k+1}' - \\
& \xi_{k-2}' + \xi_{k'}) - k_r \theta_1' D^2 (2 \eta_{k-1} - 2 \eta_{k+1} - \eta_{k-1}' + \eta_{k+1}' - \eta_{k-2}' \\
& + \eta_{k'}) = 0 \quad (3-21a)
\end{aligned}$$

$$\begin{aligned}
m \ddot{\xi}_{k'} + K_{rr_0} D^2 (\xi_{k'} - \xi_k) + K_{rr_0} DE (\eta_{k'} - \eta_k) + K_{r'r_0} D^2 \\
(\xi_{k'} - \xi_{k+1}) + K_{r'r_0} DE (\eta_{k'} - \eta_{k+1}) + k \theta \theta_0 E^2 (2 \xi_{k'} - \xi_{k-1}' - \\
\xi_{k+1}') - k \theta \theta_0 DE (2 \eta_k - \eta_{k-1}' - 2 \eta_{k+1} + \eta_{k+1}') + K_{rr'} D^2 (\xi_{k+1} - \\
2 \xi_{k'} + \xi_k) + K_{rr'} DE (\eta_k + \eta_{k+1} - 2 \eta_{k'}) + k_{rr_1} D^2 (\xi_{k+1}' + \xi_{k-1}' - \\
\xi_{k+1} - \xi_{k-1}) + K_{r_1 r_1} DE (\eta_{k+1}' - \eta_{k+1} + \eta_{k-1}' - \eta_{k-1}) + k \theta \theta' E^2 \\
(2 \xi_{k+1} - \xi_{k+2} - \xi_k) - k \theta \theta' DE (2 \eta_{k'} - 2 \eta_{k+1}' + \eta_{k+2} - \eta_k) + \\
K_{r'r_1} D^2 (-\xi_k - \xi_{k+2} + \xi_{k+1}' + \xi_{k-1}') + K_{r'r_1} DE (\eta_{k+1}' - \eta_{k+2} + \\
\eta_{k-1}' - \eta_k) + k \theta \theta_1 E^2 (2 \xi_{k+1}' + 2 \xi_{k-1}' - 2 \xi_{k'} - \xi_{k+2}' - \xi_{k-2}') \\
+ k \theta \theta_1 DE (2 \eta_{k+1} - 2 \eta_{k+2} + \eta_{k+2}' + 2 \eta_{k-1} - 2 \eta_k - \eta_{k-2}') + k_r \theta DE \\
(4 \xi_{k'} - 2 \xi_{k-1}' - 2 \xi_{k+1}') + k_r \theta (E^2 - D^2) (2 \eta_k - \eta_{k-1}' - 2 \eta_{k+1} + \\
\eta_{k+1}') + k_r \theta_1' DE (\xi_k - \xi_{k+2} - \xi_{k-1} + \xi_{k+1}) - k_r \theta_1' D^2 (2 \eta_{k+1} - \\
2 \eta_k - \eta_{k+1}' + \eta_{k-1}') + k_r \theta_1 DE (\xi_{k+1} + 2 \xi_{k+1}' + 2 \xi_{k-1}' - 4 \xi_{k'} - \\
\xi_{k-1} - \xi_{k+2} + \xi_k) + k_r \theta_1 E^2 (-\eta_{k+1} + \eta_{k-1}' - \eta_{k-1} - \eta_{k+1}' + \eta_{k+2} \\
+ \eta_k) - k_r \theta_1 D^2 (2 \eta_{k+1} - 2 \eta_k - \eta_{k+1}' + \eta_{k-1}') = 0 \quad (3-21b)
\end{aligned}$$

$$\begin{aligned}
M \ddot{\eta}_k + K_{rr_0} E^2 (\eta_k - \eta_{k'}) + K_{rr_0} DE (\xi_k - \xi_{k'}) + K_{r'r_0} E^2 (\eta_k \\
- \eta_{k-1}') + K_{r'r_0} DE (\xi_k - \xi_{k-1}') + k \theta' \theta_0' D^2 (2 \eta_k - 2 \eta_{k-1}' - 2 \eta_{k'})
\end{aligned}$$

$$\begin{aligned}
& + \eta_{k+1} + \eta_{k-1}) - k_{\theta'} \theta_0' DE (-\xi_{k+1} + \xi_{k-1}) + k_{\theta\theta_0} D^2 (4\eta_k - 2\eta_{k'} \\
& - 2\eta_{k-1}') - k_{\theta\theta_0} DE (2\xi_{k'} - 2\xi_{k-1}') + K_{rr'} DE (\xi_{k'} - \xi_{k+1} + \\
& \xi_{k-1}' - \xi_{k-1}) + K_{rr'} E^2 (\eta_{k-1}' + \eta_{k'} - \eta_{k+1} - \eta_{k-1}) + K_{rr_1} DE \\
& (\xi_{k-1} - \xi_{k-1}' - \xi_{k+1}' + \xi_{k+1}) + K_{rr_1} E^2 (-\eta_{k-1}' - \eta_{k+1}' + \eta_{k+1} + \\
& \eta_{k-1}) - k_{\theta\theta'} DE (2\xi_{k+1} - 2\xi_k + \xi_{k-2}' - \xi_{k'}) + k_{\theta\theta'} D^2 (5\eta_{k'} - \\
& 2\eta_{k+1} - 2\eta_k + 2\eta_{k-1}' + \eta_{k-2}' - 4\eta_k) + k_{r'r_1} DE (\xi_{k-1} - \xi_{k-2}' + \\
& \xi_{k+1} - \xi_{k'}) + k_{r'r_1} E^2 (-\eta_{k-2}' - \eta_{k'} + \eta_{k+1} + \eta_{k-1}) - k_{\theta'\theta_1'} DE \\
& (\xi_{k-2} - \xi_{k+2}) + k_{\theta'\theta_1'} D^2 (-2\eta_{k-2}' - 2\eta_{k-1}' - 2\eta_{k'} + 2\eta_{k+1} + \\
& 2\eta_{k-1} + 2\eta_k - 2\eta_{k+1}' + \eta_{k+2} + \eta_{k-2}) + k_{\theta\theta_1} DE (2\xi_{k-1}' - 2\xi_{k-2}' + \\
& 2\xi_{k+1}' - 2\xi_{k'}) + k_{\theta\theta_1} D^2 (4\eta_{k+1} + 4\eta_{k-1} - 2\eta_{k+1}' - 2\eta_{k'} - 2\eta_{k-1}' \\
& - 2\eta_{k-2}') - k_r \theta' DE (-4\eta_k + 4\eta_{k'} + 4\eta_{k-1}' - 2\eta_{k+1} - 2\eta_{k-1}) \\
& + k_r \theta' (E^2 - D^2) (\xi_{k-1} - \xi_{k+1}) + k_r \theta_1 DE (2\eta_{k'} - \eta_{k-1}' - 2\eta_{k+1}' + \\
& \eta_{k-2}') + k_{r_1} E^2 (-\xi_{k-1}' - \xi_{k+1}' + \xi_{k-2}' + \xi_{k'}) - k_r \theta_1 D^2 (2\xi_{k+1} + \\
& 2\xi_{k-1}' - 2\xi_{k'} - 2\xi_{k-1}) + k_r \theta_1' DE (\eta_{k-1}' - \eta_{k'} - \eta_{k-2}' + \eta_{k+1}') \\
& + k_r \theta_1' E^2 (\xi_{k+1} + \xi_{k-1}) - k_r \theta_1' D^2 (-\xi_{k'} - \xi_{k-1} + \xi_{k-2}' - \\
& \xi_{k+1}' + \xi_{k+1} + \xi_{k-1}') = 0 \quad (3-21c)
\end{aligned}$$

$$\begin{aligned}
& m\dot{\eta}_{k'} + K_{rr_0} E^2 (\eta_{k'} - \eta_k) + K_{rr_0} DE (\xi_{k'} - \xi_k) + K_{r'r_0} E^2 (\eta_{k'} - \\
& \eta_{k+1}) + K_{r'r_0} DE (\xi_{k'} - \xi_{k+1}) + k_{\theta'\theta_0} D^2 (4\eta_{k'} - 2\eta_{k+1} - 2\eta_k) - \\
& k_{\theta'\theta_0} DE (2\xi_{k+1} - 2\xi_k) + k_{\theta\theta_0} D^2 (2\eta_{k'} - 2\eta_k - 2\eta_{k+1} + \eta_{k+1}' + \\
& \eta_{k-1}') - k_{\theta\theta_0} DE (\xi_{k-1}' - \xi_{k+1}') + K_{rr'} DE (\xi_{k+1} + \xi_k) + K_{rr'} E^2 \\
& (-2\eta_{k'} + \eta_{k+1} + \eta_k) + K_{rr_1} DE (\xi_{k-1}' - \xi_{k-1} + \xi_{k+1}' - \xi_{k+1}) \\
& + K_{rr_1} E^2 (\eta_{k+1}' + \eta_{k-1}' - \eta_{k+1} - \eta_{k-1}) + k_{\theta'\theta_1} DE (-\xi_{k+1} + \xi_{k+2} + \\
& \xi_k + \xi_{k+1} - 2\xi_{k'} - 2\xi_{k-1}') + k_{\theta\theta'} D^2 (5\eta_k + 4\eta_{k'} - 2\eta_{k-1}' - \\
& 2\eta_{k+1}' + 2\eta_k + \eta_{k+2})
\end{aligned}$$

$$\begin{aligned}
& + K_r r_1 DE (-\xi_k + \xi_{k-1}' - \xi_{k+2} + \xi_{k+1}') + K_r r_1 E^2 (\eta_{k+1}' + \\
& \eta_{k-1}' - \eta_{k+2} - \eta_k) - k \theta_1 DE (2\xi_k - 2\xi_{k-1} + 2\xi_{k+2} - 2\xi_{k+1}') \\
& + k \theta_1 D^2 (4\eta_{k+1}' + 4\eta_{k-1}' - 2\eta_{k+2} - 2\eta_{k+1} - 2\eta_k - 2\eta_{k-1}') + \\
& k \theta_1 DE (\xi_{k-2}' - \xi_{k+2}') + k \theta_1 D^2 (-2\eta_{k-1} - 2\eta_k - 2\eta_{k+1} + \\
& 2\eta_{k+1}' + 2\eta_{k-1}' + 2\eta_k - 2\eta_{k+2} + \eta_{k-2}' + \eta_{k+2}') + k_r \theta DE \\
& (-8\eta_k' + 4\eta_k + 4\eta_{k+1}') + k_r \theta (E^2 - D^2) (2\xi_{k+1} - 2\xi_k) + k_r \theta DE \\
& (-4\eta_k' + 4\eta_k + 4\eta_{k+1} - 2\eta_{k-1}' - 2\eta_{k+1}') + k_r \theta (E^2 - D^2) (-\xi_{k+1}' \\
& + \xi_{k-1}') + k_r \theta_1 E^2 (\xi_k - \xi_{k+2} - \xi_{k-1} + \xi_{k+1}') - k_r \theta_1 D^2 (2\xi_{k+1}' \\
& + 2\xi_k - 2\xi_{k+1} - 2\xi_{k-1}') - k_r \theta_1 DE (\eta_{k+1} - \eta_k - \eta_{k+2} + \eta_{k-1}) \\
& + k_r \theta_1 DE (2\eta_k - 2\eta_{k+1} - 2\eta_k' + \eta_{k+1} - 2\eta_{k-1} + \eta_{k+2}') + k_r \theta_1 E^2 \\
& (\xi_{k+1}' - \xi_{k-1}') - k_r \theta_1 D^2 (-\xi_{k+1} - \xi_{k-1}' + \xi_{k-1} - \xi_{k+2} + \\
& \xi_{k+1}' - \xi_k) = 0
\end{aligned} \tag{3-21d}$$

$$\begin{aligned}
& M \ddot{\zeta}_k + k \theta \theta_0 (2\zeta_k - \zeta_{k+1} - \zeta_{k-1}) + k \theta' \theta_0' (2\zeta_k - \zeta_{k+1} - \zeta_{k-1}) \\
& + k \theta \theta' (4\zeta_k - 2\zeta_{k+1} - 2\zeta_{k-1}) + k \theta \theta_1 (2\zeta_{k+1} - 2\zeta_k + 2\zeta_{k-1} \\
& - \zeta_{k+2} - \zeta_{k-2}) + k \theta' \theta_1' (2\zeta_{k+1} + 2\zeta_{k-1} - 2\zeta_k - \zeta_{k+2} - \zeta_{k-2}) \\
& + k \theta \theta_0 (2\zeta_{k-1}' - \zeta_{k-2}' - \zeta_k') + k \theta' \theta_0' (2\zeta_k' - \zeta_{k-1}' - \zeta_{k+1}') + \\
& k \theta \theta' (\zeta_{k-1}' - \zeta_{k-2}' + \zeta_k' - \zeta_{k+1}') + k \theta \theta_1 (2\zeta_k' - 2\zeta_{k-1}' + \\
& 2\zeta_{k-2}' - \zeta_{k+1}' - \zeta_{k-3}') + k \theta' \theta_1' (2\zeta_{k-1}' - 2\zeta_{k-2}' + 2\zeta_{k+1}' - \\
& 2\zeta_k') = 0
\end{aligned} \tag{3-21e}$$

$$\begin{aligned}
& m \ddot{\zeta}_k' + k \theta \theta_0 (2\zeta_k' - \zeta_{k-1}' - \zeta_{k+1}') + k \theta' \theta_0' (2\zeta_k' - \zeta_{k+1}' - \\
& \zeta_{k-1}') + k \theta \theta' (2\zeta_{k+1}' + 2\zeta_{k-1}' - \zeta_{k+2}' - \zeta_{k-2}' - 2\zeta_k') + \\
& k \theta \theta_1 (2\zeta_{k+1}' + 2\zeta_{k-1}' - 2\zeta_k' - \zeta_{k-2}' - \zeta_{k+2}') + k \theta' \theta_1' (2\zeta_{k+1}' + \\
& 2\zeta_{k-1}' - \zeta_{k+2}' - \zeta_{k-2}' - 2\zeta_k') + k \theta \theta_0 (2\zeta_{k+1} - \zeta_{k+2} - \zeta_k) + \\
& k \theta' \theta_0' (2\zeta_k - \zeta_{k+1} - \zeta_{k-1}) + k \theta \theta' (\zeta_{k+1} - \zeta_{k+2} + \zeta_k - \zeta_{k-1}) +
\end{aligned}$$

$$k_{\theta\theta_1} (2 \zeta_k - 2 \zeta_{k+1} + 2 \zeta_{k+2} - \zeta_{k-1} - \zeta_{k+3}) + k_{\theta'\theta'_1} (2 \zeta_{k+1} - 2 \zeta_{k+2}) + 2 \zeta_{k-1} - 2 \zeta_k = 0 \quad (3-21f)$$

$$M a^2 \ddot{a}_k + k_{aa_0} a^2 a_k + k_{aa'} aa' a_k' + k_{aa_1} a^2 (a_{k+1} + a_{k-1}) = 0 \quad (3-21g)$$

$$m a'^2 \ddot{a}_k' + k_{a'a_0'} a'^2 a_k' + k_{aa'} aa' a_k + k_{a'a_1'} a'^2 (a_{k+1} + a_{k-1}') = 0 \quad (3-21h)$$

$$M b^2 \ddot{\beta}_k + k_{\beta\beta_0} b^2 \beta_k + k_{\beta\beta'} \beta\beta' \beta_k' + k_{\beta\beta_1} (\beta_{k+1} + \beta_{k-1}) = 0 \quad (3-21i)$$

$$m b'^2 \ddot{\beta}_k' + k_{\beta'\beta_0'} b'^2 \beta_k' + k_{\beta\beta'} \beta\beta' \beta_k + k_{\beta'\beta_1'} (\beta_{k+1}' + \beta_{k-1}') = 0 \quad (3-21j)$$

$$M c^2 \ddot{\gamma}_k + k_{\gamma\gamma_0} c^2 \gamma_k + k_{\gamma\gamma'} cc' \gamma_k' + k_{\gamma\gamma_1} (\gamma_{k+1} + \gamma_{k-1}) = 0 \quad (3-21k)$$

$$m c'^2 \ddot{\gamma}_k' + k_{\gamma'\gamma_0'} c'^2 \gamma_k' + k_{\gamma\gamma'} cc' \gamma_k + k_{\gamma'\gamma_1'} (\gamma_{k+1}' + \gamma_{k-1}') = 0, \quad (3-21l)$$

Applying the symmetry rule, we see that the coordinates of rotators in a given repeating unit must oscillate with amplitude phase differing by integral multiples of δ . Hence we can write:

$$\begin{aligned} \xi_k &= \xi_0 e^{i(\omega t + n\delta)} & \xi_k' &= \xi_0' e^{i(\omega t + n\delta)} \\ \eta_k &= \eta_0 e^{i(\omega t + n\delta)} & \eta_k' &= \eta_0' e^{i(\omega t + n\delta)} \\ \zeta_k &= \zeta_0 e^{i(\omega t + n\delta)} & \zeta_k' &= \zeta_0' e^{i(\omega t + n\delta)} \\ a_k &= a_0 e^{i(\omega t + n\delta)} & a_k' &= a_0' e^{i(\omega t + n\delta)} \\ \beta_k &= \beta_0 e^{i(\omega t + n\delta)} & \beta_k' &= \beta_0' e^{i(\omega t + n\delta)} \\ \gamma_k &= \gamma_0 e^{i(\omega t + n\delta)} & \gamma_k' &= \gamma_0' e^{i(\omega t + n\delta)}. \end{aligned}$$

Substituting equations (3-22) into equations (3-21) and eliminating the common factor $e^{i(\omega t + n\delta)}$, which is not identically zero, we obtain an infinite number of identical sets of twelve homogeneous linear equations for the amplitudes $\xi_0, \eta_0, \zeta_0, \xi_0', \eta_0', \zeta_0', \alpha_0, \beta_0, \gamma_0, \alpha_0', \beta_0'$ and γ_0' .

In order for this system of linear equations to have a non-trivial solution, the determinant of the coefficients of the amplitudes must vanish. This determinant is the desired secular determinant which has the following form:

$$\begin{vmatrix}
 A_{11} & A_{12} & A_{13} & A_{14} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
 * & & & & & & & & & & & \\
 A_{12} & A_{22} & A_{23} & A_{24} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
 * & & & & & & & & & & & \\
 A_{13} & A_{23}^* & A_{33} & A_{34} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
 * & & & & & & & & & & & \\
 A_{14} & A_{24}^* & A_{34}^* & A_{44} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
 0 & 0 & 0 & 0 & A_{55} & A_{56} & 0 & 0 & 0 & 0 & 0 & 0 \\
 0 & 0 & 0 & 0 & A_{56}^* & A_{66} & 0 & 0 & 0 & 0 & 0 & 0 \\
 0 & 0 & 0 & 0 & 0 & 0 & A_{77} & A_{78} & 0 & 0 & 0 & 0 \\
 0 & 0 & 0 & 0 & 0 & 0 & A_{78} & A_{88} & 0 & 0 & 0 & 0 \\
 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & A_{99} & A_{9,10} & 0 & 0 \\
 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & A_{9,10} & A_{10,10} & 0 & 0 \\
 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & A_{11,11} & A_{11,12} \\
 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & A_{11,12} & A_{12,12}
 \end{vmatrix} = 0$$

(3-23)

where

$$\begin{aligned}
 A_{11} = & -M\omega^2 + K_{rr_0} D^2 + K_{r'r_0'} D^2 + k_{\theta'} \theta_0' E^2 (2 - e^{-i\delta} - e^{i\delta}) - K_{rr'} D^2 \\
 & (e^{i\delta} + e^{-i\delta}) + K_{r'r_1'} D^2 (e^{i\delta} + e^{-i\delta}) + k_{\theta'} \theta_1' E^2 (2e^{-i\delta} + 2e^{i\delta} - \\
 & 2 - e^{-2i\delta} - e^{2i\delta}) + k_r \theta_1' DE (4 - 2e^{i\delta} - 2e^{-i\delta}) + k_r \theta_1' DE (2e^{-i\delta} +
 \end{aligned}$$

$$2e^{i\delta} - 4)$$

$$A_{12} = -K_{rr_0} D^2 - K_r' r_0' D^2 e^{-i\delta} + k_{rr'} D^2 (e^{-i\delta} + 1) + k_{\theta\theta'} E^2 (2e^{-i\delta} - e^{-i\delta} - e^{-2i\delta} - 1) - K_r' r_1' D^2 (1 + e^{-2i\delta}) + k_r \theta_1' DE (1 - e^{-2i\delta} - e^{i\delta} + e^{-i\delta}) + k_r \theta_1' DE (e^{-i\delta} - e^{i\delta} - e^{-2i\delta} + 1)$$

$$A_{13} = K_{rr_0} DE + K_r' r_0' DE + k_{\theta\theta'} \theta_0' DE (e^{-i\delta} - e^{i\delta}) - K_{rr'} DE (e^{-i\delta} + e^{i\delta}) + K_{rr_1} DE (e^{i\delta} + e^{-i\delta}) - k_{\theta\theta'} DE (2e^{-i\delta} - 2) + K_r' r_1' DE (e^{i\delta} + e^{-i\delta}) - k_{\theta\theta'} \theta_1' DE (e^{2i\delta} - e^{-2i\delta}) + k_r \theta' (E^2 - D^2) (e^{i\delta} - e^{-i\delta}) + k_r \theta_1' E^2 (e^{-i\delta} + e^{i\delta}) - k_r \theta_1' D^2 (-e^{i\delta} + e^{-i\delta}) - k_r \theta_1' D^2 (2e^{-i\delta} - 2e^{i\delta})$$

$$A_{14} = -K_{rr_0} DE - K_r' r_0' DE e^{-i\delta} - k_{\theta\theta'} \theta_0' DE (2e^{-i\delta} - 2) + K_{rr'} DE (e^{-i\delta} + 1) - K_{rr_1} DE (e^{i\delta} + e^{-i\delta}) - k_{\theta\theta'} DE (1 - e^{-2i\delta}) - K_r' r_1' DE (1 + e^{-2i\delta}) - k_{\theta\theta'} \theta_1' DE (2 - 2e^{i\delta} + 2e^{-2i\delta} - 2e^{-i\delta}) + k_r \theta' (E^2 - D^2) (2e^{-i\delta} - 2) + k_r \theta_1' E^2 (1 + e^{-i\delta} - e^{-2i\delta} - e^{i\delta}) - k_r \theta_1' D^2 (-2e^{-i\delta} + 2) - k_r \theta_1' D^2 (e^{i\delta} - e^{-i\delta} + 1 - e^{-2i\delta})$$

$$A_{21} = -K_{rr_0} D^2 - K_r' r_0' D^2 e^{i\delta} + K_{rr'} D^2 (e^{i\delta} + 1) - K_{rr_1} D^2 (e^{i\delta} + e^{-i\delta}) + k_{\theta\theta'} E^2 (2e^{i\delta} - e^{2i\delta} - 1) + K_r' r_1' D^2 (-1 - e^{2i\delta}) + k_r \theta_1' DE (1 - e^{2i\delta} - e^{-i\delta} + e^{i\delta}) + k_r \theta_1' DE (e^{i\delta} - e^{-i\delta} - e^{2i\delta} + 1)$$

$$A_{22} = -m\omega^2 + K_{rr_0} D^2 + K_r' r_0' D^2 + k_{\theta\theta_0} E^2 (2 - e^{-i\delta} - e^{i\delta}) - 2K_{rr'} D^2 + K_{rr_1} D^2 (e^{i\delta} + e^{-i\delta}) + K_r' r_1' D^2 (e^{i\delta} + e^{-i\delta}) + k_{\theta\theta_1} E^2 (2e^{i\delta} + 2e^{-i\delta} - 2 - e^{2i\delta} - e^{-2i\delta}) + k_r \theta DE (4 - 2e^{-i\delta} - 2e^{i\delta}) + k_r \theta_1 DE (2e^{i\delta} + 2e^{-i\delta} - 4)$$

$$A_{23} = -K_{rr_0} DE - K_r' r_0' DE e^{i\delta} - k_{\theta\theta_0} DE (2 - 2e^{i\delta}) + K_{rr'} DE (1 + e^{i\delta}) - K_{rr_1} DE (e^{i\delta} + e^{-i\delta}) - k_{\theta\theta_1} DE (e^{2i\delta} - 1) - K_r' r_1' DE (1 + e^{2i\delta}) + k_{\theta\theta_1} DE (2e^{i\delta} - 2e^{2i\delta} + 2e^{-i\delta} - 2) + k_r \theta (E^2 - D^2) (2 - 2e^{i\delta}) - k_r \theta_1' D^2 (2e^{i\delta} - 2) + k_r \theta_1 E^2 (-e^{i\delta} - e^{-i\delta} + e^{2i\delta} + 1) - k_r \theta_1 D^2 (2e^{i\delta} - 2)$$

$$\begin{aligned}
A_{24} = & K_{rr_0} DE + K_{r,r_0}' DE - k_{\theta\theta_0} DE (-e^{-i\delta} + e^{i\delta}) - 2K_{rr}' DE + \\
& K_{rr_1} DE (e^{i\delta} + e^{-i\delta}) - k_{\theta\theta}' DE (2 - 2e^{i\delta}) + K_{r,r_1}' DE (e^{i\delta} + \\
& e^{-i\delta}) + k_{\theta\theta_1} DE (e^{2i\delta} - e^{-2i\delta}) + k_r \theta (E^2 - D^2)(-e^{i\delta} + e^{-i\delta}) \\
& - k_r \theta_1' D^2 (-e^{i\delta} + e^{-i\delta}) + k_r \theta_1 E^2 (e^{-i\delta} - e^{i\delta}) - k_r \theta_1 D^2 \\
& (-e^{i\delta} + e^{-i\delta})
\end{aligned}$$

$$\begin{aligned}
A_{31} = & K_{rr_0} DE + K_{r,r_0}' DE - k_{\theta,\theta_0}' DE (e^{-i\delta} - e^{i\delta}) - K_{rr}' DE (+e^{i\delta} + \\
& e^{-i\delta}) + K_{rr_1} DE (e^{-i\delta} + e^{i\delta}) - k_{\theta\theta}' DE (2e^{i\delta} - 2) - k_{r,r_1}' DE \\
& (e^{-i\delta} + e^{i\delta}) - k_{\theta,\theta_1}' DE (e^{-2i\delta} - e^{2i\delta}) + k_r \theta' (E^2 - D^2) \\
& (e^{-i\delta} - e^{i\delta}) - k_r \theta_1 D^2 (2e^{i\delta} - 2e^{-i\delta}) + k_r \theta_1' E^2 (e^{i\delta} + e^{-i\delta}) \\
& - k_r \theta_1' D^2 (-e^{-i\delta} + e^{i\delta})
\end{aligned}$$

$$\begin{aligned}
A_{32} = & -K_{rr_0} DE - K_{r,r_0}' DE e^{-i\delta} - k_{\theta\theta_0} DE (2 - 2e^{-i\delta}) + K_{rr}' DE (1 + \\
& e^{-i\delta}) - K_{rr_1} DE (e^{i\delta} + e^{-i\delta}) - k_{\theta\theta}' DE (e^{-2i\delta} - 1) - K_{r,r_1}' DE \\
& (1 + e^{-2i\delta}) + 2k_{\theta\theta_1} DE (e^{-i\delta} - e^{-2i\delta} + e^{i\delta} - 1) + 2k_r \theta (E^2 - \\
& D^2) (1 - e^{-i\delta}) - 2k_r \theta_1' D^2 (e^{-i\delta} - 1) + k_r \theta_1 E^2 (-e^{-i\delta} - e^{i\delta} + \\
& e^{-2i\delta} + 1) - 2k_r \theta_1 D^2 (e^{-i\delta} - 1)
\end{aligned}$$

$$\begin{aligned}
A_{33} = & -M\omega^2 + K_{rr_0} E^2 + K_{r,r_0}' E^2 + k_{\theta,\theta_0}' D^2 (2 + e^{i\delta} + e^{-i\delta}) + \\
& k_{\theta\theta_0} D^2 (4) - K_{rr}' E^2 (e^{i\delta} + e^{-i\delta}) + K_{rr_1} E^2 (e^{i\delta} + e^{-i\delta}) + k_{\theta\theta}' \\
& D^2 (-2e^{i\delta} - 6) + K_{r,r_1}' E^2 (e^{i\delta} + e^{-i\delta}) + k_{\theta,\theta_1}' D^2 (2e^{i\delta} + 2e^{-i\delta} \\
& + e^{2i\delta} + e^{-2i\delta}) + k_{\theta\theta_1} D^2 (4e^{i\delta} + 4e^{-i\delta}) + k_r \theta' DE (-4 - 2e^{i\delta} \\
& - 2e^{-i\delta})
\end{aligned}$$

$$\begin{aligned}
A_{34} = & -K_{rr_0} E^2 - K_{r,r_0}' E^2 e^{-i\delta} + k_{\theta,\theta_0}' D^2 (-2e^{-i\delta} - 2) + k_{\theta\theta_0} D^2 \\
& (-2 - 2e^{-i\delta}) + K_{rr}' E^2 (e^{-i\delta} + 1) - K_{rr_1} E^2 (e^{-i\delta} + e^{i\delta}) + k_{\theta\theta}' \\
& D^2 (5 + 2e^{-i\delta} + e^{-2i\delta}) + K_{r,r_1}' E^2 (-e^{-2i\delta} - 1) + k_{\theta,\theta_1}' D^2 (-2e^{-2i\delta} \\
& - 2e^{-i\delta} - 2 - 2e^{i\delta}) + k_{\theta\theta_1} D^2 (-2e^{i\delta} - 2 - 2e^{-i\delta} - 2e^{-2i\delta}) + k_r \theta' \\
& DE (4 + 4e^{-i\delta}) + k_r \theta_1 DE (2 - e^{-i\delta} - 2e^{i\delta} + e^{-2i\delta}) + k_r \theta_1' DE \\
& (e^{-i\delta} - 1 - e^{-2i\delta} + e^{i\delta})
\end{aligned}$$

$$A_{44} = -m \omega^2 + K_{rr_0} E^2 + K_{r'r_0'} E^2 + 4 D^2 k_{\theta, \theta_0'} + k_{\theta\theta_0} D^2 (2 + e^{i\delta} + e^{-i\delta}) - 2 K_{rr'} E^2 + K_{rr_1} E^2 (e^{i\delta} + e^{-i\delta}) + k_{\theta\theta'} D^2 (4 - 2e^{-i\delta} - 2e^{i\delta}) + K_{r'r_1'} E^2 (e^{i\delta} + e^{-i\delta}) + 4 k_{\theta, \theta_1'} D^2 (e^{i\delta} + e^{-i\delta}) + k_{\theta\theta_1} D^2 (2e^{i\delta} + 2e^{-i\delta} + 2 + e^{-2i\delta} + e^{2i\delta}) - 8 k_{r\theta} - 2 k_{r\theta} DE (2 + e^{i\delta} + e^{-i\delta})$$

$$A_{55} = -M \omega^2 + (k_{\theta\theta_0} + k_{\theta',\theta_0'}) (2 - e^{i\delta} - e^{-i\delta}) + k_{\theta\theta'} (4 - 2e^{i\delta} - 2e^{-i\delta}) + (k_{\theta\theta_1} + k_{\theta',\theta_1'}) (2e^{i\delta} - 2 + 2e^{-i\delta} - e^{2i\delta} - e^{-2i\delta})$$

$$A_{56} = k_{\theta\theta_0} (2e^{-i\delta} - e^{-2i\delta} - 1) + k_{\theta',\theta_0'} (2 - e^{-i\delta} - e^{i\delta}) + k_{\theta\theta'} (e^{-i\delta} - e^{-2i\delta} + 1 - e^{i\delta}) + k_{\theta\theta_1} (2 - 2e^{-i\delta} + 2e^{-2i\delta} - e^{i\delta} - e^{-3i\delta}) + k_{\theta',\theta_1'} (2e^{-i\delta} - 2e^{-2i\delta} + 2e^{i\delta} - 2)$$

$$A_{66} = -m \omega^2 + k_{\theta\theta_0} (2 - e^{-i\delta} - e^{i\delta}) + k_{\theta',\theta_0'} (2 - e^{-i\delta} - e^{i\delta}) + (k_{\theta\theta_1} + k_{\theta\theta'} + k_{\theta',\theta_1'}) (2e^{i\delta} + 2e^{-i\delta} - e^{2i\delta} - e^{-2i\delta} - 2)$$

$$A_{77} = -Ma^2 \omega^2 + k_{aa_0} a^2 + k_{aa_1} a^2 (e^{i\delta} + e^{-i\delta})$$

$$A_{78} = k_{aa'} aa'$$

$$A_{88} = -m a'^2 \omega^2 + k_{a'a_0} a'^2 + k_{a'a_1} a'^2 (e^{i\delta} + e^{-i\delta})$$

$$A_{89} = k_{aa'} aa'$$

$$A_{99} = -M b^2 \omega^2 + k_{\beta\beta_0} b^2 + k_{\beta\beta_1} b^2 (e^{i\delta} + e^{-i\delta})$$

$$A_{910} = k_{\beta\beta'} \beta\beta'$$

$$A_{10,10} = -m b'^2 \omega^2 + k_{\beta'\beta_0'} b'^2 + k_{\beta'\beta_1'} b'^2 (e^{i\delta} + e^{-i\delta})$$

$$A_{11,11} = -M c^2 \omega^2 + k_{\gamma\gamma_0} c^2 + k_{\gamma\gamma_1} c^2 (e^{i\delta} + e^{-i\delta})$$

$$A_{11,12} = k_{\gamma\gamma'} cc'$$

$$A_{12,12} = -m c'^2 \omega^2 + k_{\gamma'\gamma_0'} c'^2 + k_{\gamma'\gamma_1'} c'^2 (e^{i\delta} + e^{-i\delta})$$

The determinant (3-23) can be factored into the following blocks:

$$\begin{vmatrix} A_{11} & A_{12} & A_{13} & A_{14} \\ A_{12}^* & A_{22} & A_{23} & A_{24} \\ A_{13}^* & A_{23}^* & A_{33} & A_{34} \\ A_{14}^* & A_{24}^* & A_{34}^* & A_{44} \end{vmatrix} ,$$

$$\begin{vmatrix} A_{55} & A_{56} \\ A_{56}^* & A_{66} \end{vmatrix} , \quad \begin{vmatrix} A_{77} & A_{78} \\ A_{78} & A_{88} \end{vmatrix} , \quad \begin{vmatrix} A_{99} & A_{910} \\ A_{910} & A_{1010} \end{vmatrix} , \quad \begin{vmatrix} A_{11}A_{11} & A_{11}A_{12} \\ A_{11}A_{12} & A_{12}A_{12} \end{vmatrix} ,$$

(3-24)

For all of the blocks except the first one, we can easily find roots

$\omega_j(\delta)$:

$$\omega_4(\delta) = \left\{ \frac{\frac{C_{66}}{m} - \frac{C_{55}}{M} \pm \sqrt{\left(\frac{C_{66}}{m} - \frac{C_{55}}{M}\right)^2 - \frac{4}{Mm}(C_{55}C_{66} - A_{56}^2)}}{2} \right\}^{\frac{1}{2}}$$

$$\omega_5(\delta) = \left\{ \frac{\frac{C_{88}}{m} - \frac{C_{77}}{M} \pm \sqrt{\left(\frac{C_{88}}{m} - \frac{C_{77}}{M}\right)^2 - \frac{4}{Mm}(C_{77}C_{88} - A_{78}^2)}}{2} \right\}^{\frac{1}{2}}$$

$$\omega_6(\delta) = \left\{ \frac{\frac{C_{1010}}{m} - \frac{C_{99}}{M} \pm \sqrt{\left(\frac{C_{1010}}{m} - \frac{C_{99}}{M}\right)^2 - \frac{4}{Mn}(C_{99}C_{1010} - A_{910}^2)}}{2} \right\}^{\frac{1}{2}}$$

$$\omega_7(\delta) = \left\{ \frac{\frac{C_{1212}}{m} - \frac{C_{11}C_{11}}{M} \pm \sqrt{\left(\frac{C_{1212}}{m} - \frac{C_{11}C_{11}}{M}\right)^2 - \frac{4}{Mm}(C_{1212}C_{11}C_{11} - A_{1112}^2)}}{2} \right\}^{\frac{1}{2}}$$

where

$$C_{55} = A_{55} + M\omega^2$$

$$C_{66} = A_{66} + m\omega^2$$

$$C_{77} = A_{77} + M\omega^2$$

$$C_{88} = A_{88} + m\omega^2$$

$$C_{99} = A_{99} + M\omega^2$$

$$C_{1010} = A_{1010} + m\omega^2$$

$$C_{1111} = A_{1111} + M\omega^2$$

and

$$C_{1212} = A_{1212} + m\omega^2$$

(3-25)

The general solution for the 4×4 block of the secular determinant in (3-23) is too complicated to be of much practical value. However, we shall carry out a linear transformation on the ξ_n , ξ_n' , η_n and η_n' coordinates such that

$$\begin{aligned}\xi_n &= x_n + \frac{m}{M_T} (D q_n - E p_n) \\ \xi_n' &= x_n - \frac{M}{M_T} (D q_n - E p_n) \\ \eta_n &= y_n + \frac{m}{M_T} (E q_n + D p_n) \\ \eta_n' &= y_n - \frac{M}{M_T} (E q_n + D p_n).\end{aligned}\quad (3-26)$$

Physically, the x_n and y_n coordinates correspond to translations of the center of mass of the n^{th} repeating unit, q_n corresponds to δr_n , the infinitesimal displacement of the bond r_n , and p_n corresponds to the rotation of the n^{th} repeating unit as a rigid rotator.

When we express the kinetic energy function in terms of these new coordinates, we have

$$T = \frac{1}{2} \sum_n (M_T \dot{x}_n^2 + M_T \dot{y}_n^2 + \mu \dot{q}_n^2 + \mu \dot{p}_n^2) \quad (3-27)$$

where $M_T = M + m$ and $\mu = \frac{Mm}{M + m}$. We can write the valence displacement coordinates as follows:

$$\begin{aligned}\delta r_n &= q_n \\ \delta r_n' &= D (x_{n+1} - x_n) + E (y_{n+1} - y_n) + \frac{m}{M_T} q_{n+1} + \frac{M}{M_T} q_n \\ \delta \theta_n &= \frac{1}{r_0} \left[E (x_n - x_{n-1}) - D (y_n - y_{n-1}) + \left(\frac{M}{M_T} E^2 - \frac{2m + M}{M_T} D^2 \right) p_n - 2 DE q_n - \frac{M}{M_T} p_{n-1} \right] \\ \delta \theta_n' &= \frac{1}{r_0} \left[E (x_{n+1} - x_n) + D (y_{n+1} - y_n) + \frac{2m}{M_T} DE q_{n+1} + \frac{m}{M_T} (D^2 - E^2) p_{n+1} + \left(\frac{m}{M_T} + \frac{2MD^2}{M_T} \right) p_n + \frac{2M}{M_T} DE q_n \right].\end{aligned}\quad (3-28)$$

The potential energy function in terms of these new coordinates is:

$$\begin{aligned}
 V = \frac{1}{2} \sum_n & \left[K_{rr0} q_n^2 + K_{r'r_0} (D^2 x_{n+1}^2 + D^2 x_n^2 - 2 D^2 x_{n+1} x_n + E^2 y_{n+1}^2 + \right. \\
 & E^2 y_{n+1}^2 + E^2 y_n^2 - 2 E^2 y_{n+1} y_n + \frac{m^2}{M_T^2} q_{n+1}^2 + \frac{M^2}{M_T^2} q_n^2 + DE x_{n+1} y_{n+1} - \\
 & 2 DE x_{n+1} q_n + 2 DE x_n y_{n+1} + 2DE x_n y_n + 2 D \frac{m}{M_T} x_{n+1} q_{n+1} - \frac{2Dm}{M_T} \\
 & x_n q_{n+1} + \frac{2DM}{M_T} x_{n+1} q_n - \frac{2DM}{M_T} x_n q_n + 2 E \frac{m}{M_T} y_{n+1} q_{n+1} - 2E \frac{m}{M_T} y_n \\
 & q_{n+1} + 2 E \frac{M}{M_T} y_n q_n + \frac{2M}{M_T^2} q_{n+1} q_n) + 2 K_{rr'} (D q_n x_{n+1} - D q_n x_n + \\
 & E q_n y_{n+1} - E q_n y_n + \frac{m}{M_T} q_n q_{n+1} + \frac{M}{M_T} q_n^2) + 2 K_{rr1} \\
 & q_n q_{n+1} + 2 K_{r'r_1} (D^2 x_{n+1} x_{n+2} - D^2 x_n x_{n+2} - D^2 x_{n+1}^2 + D^2 x_n x_{n+1} + \\
 & DE y_{n+1} x_{n+2} - DE y_n x_{n+2} - DE y_{n+1} x_{n+1} + DE x_{n+1} y_n + \frac{Dm}{M_T} q_{n+1} x_{n+2} - \\
 & \frac{Dm}{M_T} q_{n+1} x_{n+1} + \frac{DM}{M_T} q_n x_{n+2} - \frac{DM}{M_T} q_n x_{n+1} + DE x_{n+1} y_{n+2} - DE x_n y_{n+2} \\
 & - DE x_{n+1} y_{n+1} + DE x_n y_{n+1} + E^2 y_{n+1} y_{n+2} - E^2 y_n y_{n+2} - E^2 y_{n+1}^2 + E^2 \\
 & y_n y_{n+1} + \frac{Em}{M_T} q_{n+1} y_{n+2} - \frac{Em}{M_T} q_{n+1} y_{n+1} + \frac{EM}{M_T} q_n y_{n+2} - \frac{EM}{M_T} q_n y_{n+1} + \\
 & \frac{Dm}{M_T} q_{n+2} x_{n+1} - \frac{Dm}{M_T} q_{n+2} x_n + \frac{Em}{M_T} q_{n+2} y_{n+1} - \frac{Em}{M_T} q_{n+2} y_n + \frac{m^2}{M_T^2} \\
 & q_{n+1} q_{n+2} + \frac{Mm}{M_T^2} q_n q_{n+2} + \frac{Dm}{M_T} q_{n+1} x_{n+1} - \frac{DM}{M_T} q_{n+1} x_n + \frac{EM}{M_T} q_{n+1} \\
 & y_{n+1} - \frac{EM}{M_T} q_{n+1} y_n + \frac{Mm}{M_T^2} q_{n+1}^2 + \frac{M^2}{M_T^2} q_n q_{n+1}) + k \theta \theta_0 \left\{ E^2 x_n^2 + \right. \\
 & E^2 x_{n-1}^2 - 2 E^2 x_n x_{n-1} + D^2 y_n^2 + D^2 y_{n-1}^2 - 2 D^2 y_n y_{n-1} + \frac{M^2}{M_T^2} E^4 \\
 & P_n^2 + \left(\frac{2m+M}{M_T} \right)^2 D^4 P_n^2 - \frac{2M(2m+M)}{M_T^2} D^2 E^2 P_n^2 + 4 D^2 E^2 q_n^2 + \frac{M^2}{M_T^2} P_{n-1}^2 \\
 & - 2 DE x_n y_n + 2DE x_{n-1} y_n + 2 DE x_n y_{n-1} - 2 DE x_{n-1} y_{n-1} + 2 \frac{M}{M_T} E^2 \\
 & P_n x_n - \frac{2(2m+M)}{M_T} D^2 P_n x_n - 2 \frac{M}{M_T} E^2 P_n x_{n-1} + \frac{2(2m+M)}{M_T} D^2 P_n x_{n-1} - \\
 & 4 DE^2 x_n q_n + 4 DE^2 x_{n-1} q_n - 2 \frac{M}{M_T} E x_n P_{n-1} + \frac{2M}{M_T} E x_{n-1} P_{n-1} - 2 D \\
 & \frac{M}{M_T} E^2 P_n y_n + \frac{2(2m+M)}{M_T} D^3 P_n y_n + 2 DE^2 \frac{M}{M_T} P_n y_{n-1} - \frac{2(2m+M)}{M_T} D^3
 \end{aligned}$$

$$\begin{aligned}
& P_n y_{n-1} + 4 D^2 E q_n y_n - 4 D^2 E q_n y_{n-1} + \frac{2MD}{M_T} y_n P_{n-1} - \frac{2MD}{M_T} y_{n-1} P_{n-1} \\
& - 4 DE^3 \frac{M}{M_T} P_n q_n + 4 D^3 E \frac{(2m+M)}{M_T} P_n q_n - 2 \frac{M^2}{M_T^2} E^2 P_n P_{n-1} + 2 \frac{M}{M_T} \\
& \frac{(2m+M)}{M_T} P_n P_{n-1} + 4 \frac{M}{M_T} DE^3 q_n P_{n-1} \Big\} + k_{\theta}, \theta, \theta_0, \left\{ E^2 x_{n+1}^2 + E^2 x_n^2 - \right. \\
& 2 E^2 x_{n+1} x_n + D^2 y_{n+1}^2 + D^2 y_n^2 - 2 D^2 y_{n+1} y_n + \frac{4m^2}{M_T^2} D^2 E^2 q_{n+1}^2 + \\
& \frac{m^2}{M_T^2} (D^2 - E^2)^2 P_{n+1}^2 + \left(\frac{m}{M_T} + \frac{2MD^2}{M_T} \right)^2 P_n^2 + \frac{4m^2}{M_T^2} D^2 E^2 q_n^2 + 2 DE x_{n+1} \\
& y_{n+1} - 2DE x_n y_{n+1} - 2 DE x_{n+1} y_n + 2 DE x_n y_n + \frac{4m}{M_T} DE^2 x_{n+1} q_{n+1} - \\
& \frac{4m}{M_T} DE^2 x_n q_{n+1} + \frac{2m}{M_T} (D^2 E - E^3) (P_{n+1} x_{n+1} - P_{n+1} x_n) + 2E \frac{m}{M_T} P_n x_{n+1} \\
& + 4 \frac{MD^2 E}{M_T} P_n x_{n+1} - 2 \frac{Em}{M_T} P_n x_n - 4 \frac{MD^2 E}{M_T} P_n x_n + 4 \frac{M}{M_T} DE^2 q_n x_{n+1} \\
& - \frac{4M}{M_T} DE^2 x_n q_n + 4 \frac{m}{M_T} D^2 E q_{n+1} y_{n+1} - 4 \frac{m}{M_T} D^2 E y_n q_{n+1} + 2 \frac{m}{M_T} D^3 \\
& P_{n+1} y_{n+1} - \frac{2m}{M_T} DE^2 P_{n+1} y_{n+1} - \frac{2m}{M_T} D^3 P_{n+1} y_n + \frac{2m}{M_T} DE^2 P_{n+1} y_n + \\
& 2 D \frac{m}{M_T} P_n y_{n+1} + 4 \frac{MD^3}{M_T} P_n y_{n+1} - 2 D \frac{m}{M_T} P_n y_{n+1} - 4 \frac{MD^3}{M_T} P_n y_n + \\
& 4 \frac{M}{M_T} D^2 E q_n y_{n+1} - 4 \frac{M}{M_T} D^2 E q_n y_n + \frac{4m^2}{M_T^2} D^3 E q_{n+1} P_{n+1} - \\
& \frac{4m^2}{M_T^2} DE^3 q_{n+1} P_{n+1} + \frac{4m^2}{M_T^2} DE P_n q_{n+1} + 8 \frac{Mm}{M_T^2} D^3 E P_n q_{n+1} + \frac{8Mm}{M_T^2} \\
& D^2 E^2 q_n q_{n+1} + \frac{2m^2}{M_T^2} D^2 P_{n+1} P_n + \frac{4Mm}{M_T^2} D^4 P_{n+1} P_n - \frac{2m^2}{M_T^2} E^2 P_{n+1} P_n - \\
& \frac{4MmD^2 E^2}{M_T^2} P_{n+1} P_n + \frac{4M}{M_T} D^3 E P_{n+1} q_n - \frac{4M}{M_T} DE^3 P_{n+1} q_n \Big\} \\
& + 2 k_{\theta} \theta, \left\{ E^2 (x_n x_{n+1} - x_n^2 - x_{n-1} x_{n+1} + x_n x_{n-1}) - DE (x_{n+1} y_n - \right. \\
& x_{n+1} y_{n-1} - x_n y_n + x_n y_{n-1}) + \left(\frac{M}{M_T} E^3 - \frac{2m+M}{M_T} D^2 E \right) (P_n x_{n+1} - P_n x_n) \\
& - 2 DE^2 (x_{n+1} q_n - x_n q_n) - \frac{ME}{M_T} P_{n-1} x_{n+1} + \frac{ME}{M_T} P_{n-1} x_n + DE (x_n y_{n+1} - \\
& x_n y_n - x_{n-1} y_{n+1} - x_{n-1} y_n) - D^2 (y_n y_{n+1} - y_n^2 - y_{n-1} y_{n+1} + y_{n-1} y_n) + \\
& \left(\frac{M}{M_T} E^2 D - \frac{2m+M}{M_T} D^3 \right) (P_n y_{n+1} - P_n y_n) - 2 D^3 E (q_n y_{n+1} - q_n y_n) - \\
& \frac{M}{M_T} D (P_{n-1} y_{n+1} - P_{n-1} y_n) + \frac{2m}{M_T} DE^2 (q_{n+1} x_n - q_{n+1} x_n - q_{n+1} x_{n-1})
\end{aligned}$$

$$\begin{aligned}
& - \frac{2m}{M_T} D^2 E (q_{n+1} y_n - q_{n+1} y_{n-1}) + \left(\frac{2Mm}{M_T^2} DE^3 - \frac{4m^2 + 2Mm}{M_T^2} D^3 E \right) P_n q_{n+1} - \\
& \frac{4m}{M_T} D^2 E^2 q_n q_{n+1} - \frac{2Mm}{M_T^2} P_{n-1} q_{n+1} + \left(\frac{mD^2 E}{M_T} - \frac{mE^3}{M_T} \right) P_{n+1} x_n - P_{n+1} x_{n-1} \\
& - \left(\frac{mD^3}{M_T} - \frac{m}{M_T} E^2 D \right) (P_{n+1} y_n - P_{n+1} y_{n-1}) + \left(\frac{M}{M_T} E^2 - \frac{2m+M}{M_T} D^2 \right) \left(\frac{m}{M_T} D^2 \right) \\
& \left(\frac{m}{M_T} E^2 \right) P_n P_{n+1} - \frac{2m}{M_T} (D^3 E - E^3 D) P_{n+1} q_n - \frac{Mm}{M_T} (D^2 - E^2) P_{n+1} P_{n-1} + \\
& \left(\frac{mE}{M_T} + \frac{2MD^2 E}{M_T} \right) P_n x_n - P_n x_{n-1} - \left(\frac{mD}{M_T} + \frac{2MD^2}{M_T} \right) (P_n y_n - P_n y_{n-1}) + \left(\frac{m}{M_T} \right. \\
& \left. + \frac{2MD^2}{M_T} \right) \left(\frac{M}{M_T} E^2 - \frac{2m+M}{M_T} D^2 \right) P_n^2 - \left(\frac{2DEm}{M_T} + \frac{4MD^3 E}{M_T} \right) P_n q_n - \frac{M}{M_T} \left(\frac{m}{M_T} \right. \\
& \left. + \frac{2MD}{M_T} \right) P_n P_{n-1} + \frac{2M}{M_T} DE^2 (x_n q_n - x_{n-1} q_n) - \frac{2MD^2 E}{M_T} (q_n y_n - q_n y_{n-1}) + \\
& \frac{2M}{M_T} DE \left(\frac{M}{M_T} E^2 - \frac{2m+M}{M_T} D^2 \right) P_n q_n - \frac{4MD^2 E^2}{M_T} q_n^2 - \frac{2M^2}{M_T^2} DE q_n P_{n-1} \Big\} + \\
& 2k\theta\theta_1 \Big\{ E^2 (x_{n+1} x_n - x_{n-1} x_{n+1} - x_n^2 + x_n x_{n-1}) - DE (x_{n+1} y_n - x_{n+1} y_{n-1} - \\
& x_n y_n + x_n y_{n-1}) + \left(\frac{M}{M_T} E^3 - \frac{2m+M}{M_T} D^2 E \right) (P_n x_{n+1} - P_n x_n) - 2DE^2 \\
& (q_n x_{n+1} - q_n x_n) - \frac{ME}{M_T} (P_{n-1} x_{n+1} - P_{n-1} x_n) - DE (x_n y_{n+1} - y_{n+1} x_{n-1} - \\
& x_n y_n + x_{n-1} y_n) + D^2 (y_{n+1} y_n - y_{n+1} y_{n-1} - y_n^2 + y_n y_{n-1}) - \left(\frac{ME^2 D}{M_T} - \right. \\
& \left. \frac{2m+M}{M_T} D^3 \right) (P_n y_{n+1} - P_n y_n) + 2D^2 E (q_n y_{n+1} - q_n y_n) + \frac{MD}{M_T} (P_{n-1} y_{n+1} - \\
& P_{n-1} y_n) + \left(\frac{M}{M_T} E^3 - \frac{2m+M}{M_T} D^2 E \right) (P_{n+1} x_n - P_{n+1} x_{n-1}) - \left(\frac{ME^2 D}{M_T} - \right. \\
& \left. \frac{2m+M}{M_T} D^3 \right) (P_{n+1} y_n - P_{n+1} y_{n-1}) + \left(\frac{M}{M_T} E^2 - \frac{2m+M}{M_T} D^2 \right)^2 P_n P_{n+1} - \left(\frac{2M}{M_T} DE^3 \right. \\
& \left. - \frac{2m+M}{M_T} D^3 E \right) P_{n+1} q_n - \left(\frac{M^2}{M_T^2} E^2 - \frac{M(2m+M)}{M_T^2} D^2 \right) P_{n+1} P_{n-1} - 2DE^2 (x_n q_{n+1} \\
& - x_{n-1} q_{n+1}) + 2D^2 E (q_n q_{n+1} - y_{n-1} q_{n+1}) - \left(\frac{2M}{M_T} DE^3 - \frac{2m+M}{M_T} D^3 E \right) P_n \\
& q_{n+1} + 4D^2 E^2 q_n q_{n+1} + \frac{2M}{M_T} DE P_{n-1} q_{n+1} - \frac{ME}{M_T} (P_n x_n - P_n x_{n-1}) + \frac{MD}{M_T} \\
& (P_n y_n - P_n y_{n-1}) - \frac{M}{M_T} \left(\frac{M}{M_T} E^2 - \frac{2m+M}{M_T} D^2 \right) P_n^2 + 2 \frac{M}{M_T} DE P_n q_n + \\
& \frac{M^2}{M_T^2} P_n - P_{n-1} \Big\} + 2k\theta\theta' \Big\{ E^2 (x_{n+1} x_{n+2} - x_n x_{n+2} - x_{n+1}^2 + x_n x_{n+1}) + DE (y_{n+1} \\
& x_{n+2} - y_n x_{n+2} - x_{n+1} y_{n+1} - y_n x_{n+1}) + \frac{2m}{M_T} DE^2 (x_{n+2} q_{n+1} - x_{n+1} q_{n+1}) + \frac{m}{M_T}
\end{aligned}$$

$$\begin{aligned}
& (D^2 E - E^3) (P_{n+1} x_{n+2} - P_{n+1} x_{n+1}) + \left(\frac{mE}{M_T} + \frac{2M D^2 E}{M_T} \right) (P_n x_{n+2} - \\
& P_n x_{n+1}) + \frac{2M}{M_T} DE^2 (x_{n+2} q_n - x_{n+1} q_n) + DE (x_{n+1} y_{n+2} - x_n y_{n+2} - \\
& x_{n+1} y_{n+1} + x_n y_{n+1}) + D^2 (y_{n+1} y_{n+2} - y_n y_{n+2} - y_{n+1}^2 + y_n y_{n+1}) + \frac{2m}{M_T} \\
& D^2 E (q_{n+1} y_{n+2} - q_{n+1} y_{n+1}) + \frac{m}{M_T} (D^3 - DE^2) (P_{n+1} y_{n+2} - P_{n+1} y_{n+1}) + \\
& \left(\frac{mD}{M_T} + \frac{2MD^3}{M_T} \right) (P_n y_{n+2} - P_n y_{n+1}) + \frac{2M}{M_T} D^2 E (q_n y_{n+2} - q_n y_{n+1}) + \\
& \frac{2m}{M_T} DE^2 (x_{n+1} q_{n+2} - x_n q_{n+2}) + \frac{2m}{M_T} D^2 E (q_{n+2} y_{n+1} - q_{n+2} y_n) + \\
& 4 \frac{m^2}{M_T^2} D^2 E^2 q_{n+1} q_{n+2} + 2 \frac{m^2}{M_T^2} (D^3 E - DE^3) q_{n+2} P_{n+1} + \left(\frac{2m^2}{M_T^2} DE + \right. \\
& \left. \frac{4m M D^3 E}{M_T^2} \right) P_n q_{n+2} + 4 \frac{Mm}{M_T^2} D^2 E^2 q_n q_{n+2} + \frac{m}{M_T} (D^2 E - E^3) (P_{n+2} \\
& x_{n+1} - P_{n+2} x_n) + \frac{m}{M_T} (D^3 - E^2 D) (P_{n+2} y_{n+1} - P_{n+2} y_n) + \frac{2m^2}{M_T^2} (D^3 E - \\
& DE^3) P_{n+2} q_{n+1} + \frac{m^2}{M_T^2} (D^2 - E^2)^2 P_{n+1} P_{n+2} + \left(\frac{m^2}{M_T^2} + \frac{2Mm D^2}{M_T^2} \right) (D^2 - E^2) \\
& P_n P_{n+2} + \frac{2Mm}{M_T^2} (D^3 E - DE^3) q_n P_{n+2} + \left(\frac{mE}{M_T} + \frac{2MD^2 E}{M_T} \right) (P_{n+1} x_{n+1} - \\
& P_{n+1} x_n) + \left(\frac{mD}{M_T} + \frac{2MD^3}{M_T} \right) (P_{n+1} y_{n+1} - P_{n+1} y_n) + \left(\frac{2m^2}{M_T^2} DE + \frac{4Mm}{M_T^2} D^3 E \right) \\
& P_{n+1} q_{n+1} + \left(\frac{m^2}{M_T^2} + \frac{2Mm}{M_T^2} D^2 \right) (D^2 - E^2) P_{n+1}^2 + \left(\frac{m}{M_T} + \frac{2MD^2}{M_T} \right)^2 P_n P_{n+1} \\
& + \left(\frac{2Mm}{M_T^2} DE + \frac{4M^2 D^3 E}{M_T^2} \right) P_{n+1} q_n + \frac{2M}{M_T} DE^2 (x_{n+1} q_{n+1} - x_n q_{n+1}) + \\
& \frac{2MD^2 E}{M_T} (q_{n+1} y_{n+1} - y_n q_{n+1}) + \frac{4Mm}{M_T^2} D^2 E^2 q_{n+1}^2 + \frac{2Mm}{M_T^2} (D^3 E - DE^3) \\
& q_{n+1} P_{n+1} + \left(\frac{2Mm}{M_T^2} DE + \frac{4M^2}{M_T^2} D^3 E \right) P_n q_{n+1} + \frac{4M^2}{M_T^2} D^2 E^2 q_n q_{n+1} \Big\} \\
& + 2 k_r \theta \left\{ E (q_n x_n - q_n x_{n-1}) - D (y_n q_n - y_{n-1} q_n) + \left(\frac{M}{M_T} E^2 - \frac{2mM}{M_T} D^2 \right) \right. \\
& P_n q_n - 2 DE q_n^2 - \frac{M}{M_T} P_{n-1} q_n + DE (x_n^2 - x_n x_{n-1} - x_n x_{n-1} + x_{n-1}^2) - D^2 \\
& (x_n y_n - x_n y_{n-1} - x_{n-1} y_n + x_{n-1} y_{n-1}) + \left(\frac{M}{M_T} E^2 D - \frac{2m+M}{M_T} D^3 \right) (P_n x_n - \\
& P_n x_{n-1}) - 2 D^2 E (x_n q_n - q_n x_{n-1}) - \frac{M}{M_T} D (P_{n-1} x_n - P_{n-1} x_{n-1}) + E^2
\end{aligned}$$

$$\begin{aligned}
& (y_n x_n - y_n x_{n-1} - x_n y_{n-1} + x_{n-1} y_{n-1}) - DE (y_n^2 + y_{n-1}^2 - 2 y_n y_{n-1}) + \\
& \left(\frac{M}{M_T} E^3 - \frac{2m+M}{M_T} D^2 E \right) (P_n y_n - P_n y_{n-1}) - 2 DE^2 (q_n y_n - q_n y_{n-1}) - \\
& \frac{M}{M_T} E (P_{n-1} y_n - P_{n-1} y_{n-1}) + \frac{m}{M_T} E (q_n x_n - q_n x_{n-1}) - \frac{m}{M_T} D (q_n y_n - \\
& q_n y_{n-1}) + \left(\frac{Mm}{M_T^2} E^2 - \frac{2m^2+Mm}{M_T^2} D^2 \right) P_n q_n - 2 DE \frac{m}{M_T} q_n^2 - \frac{Mm}{M_T^2} P_{n-1} q_n \\
& + \frac{M}{M_T} E (x_n q_{n-1} - x_{n-1} q_{n-1}) - \frac{M}{M_T} D (q_{n-1} y_n - q_{n-1} y_{n-1}) + \left(\frac{M^2}{M_T^2} E^2 \right. \\
& \left. - \frac{2Mm+M^2}{M_T} D^2 \right) P_n q_{n-1} - \frac{2M}{M_T} DE q_n q_{n-1} - \frac{M^2}{M_T^2} P_{n-1} q_{n-1} \Big\} \\
& + 2 k_r \theta' \Big\{ E (x_{n+1} q_n - x_n q_n) + D (y_{n+1} q_n - y_n q_n) + \frac{2m}{M_T} DE q_n q_{n+1} \\
& + \frac{m}{M_T} (D^2 - E^2) P_{n+1} q_n + \left(\frac{m}{M_T} + \frac{2MD^2}{M_T} \right) P_n q_n + \frac{2M}{M_T} DE q_n^2 + DE (x_{n+1}^2 + \\
& x_n^2 - 2x_{n+1} x_n) + D^2 (x_{n+1} y_{n+1} - x_{n+1} y_n - x_n y_{n+1} + x_n y_n) + \frac{2m}{M_T} D^2 E \\
& (x_{n+1} q_{n+1} - x_n q_{n+1}) + \frac{m}{M_T} (D^3 - DE^2) (P_{n+1} x_{n+1} - P_{n+1} x_n) + \\
& \left(\frac{mD}{M_T} + \frac{2MD^3}{M_T} \right) (P_n x_{n+1} - P_n x_n) + \frac{2MD^2 E}{M_T} (q_n x_{n+1} - q_n x_n) + E^2 \\
& (x_{n+1} y_{n+1} - x_n y_{n+1} - y_n x_{n+1} + x_n y_n) + DE (y_{n+1}^2 + y_n^2 - 2 y_{n+1} y_n) + \frac{2m}{M_T} \\
& DE^2 (q_{n+1} y_{n+1} - q_{n+1} y_n) + \frac{m}{M_T} (D^2 E - E^3) (P_{n+1} y_{n+1} - P_{n+1} y_n) + \left(\frac{mE}{M_T} + \right. \\
& \left. \frac{2MD^2 E}{M_T} \right) (P_n y_{n+1} - P_n y_n) + \frac{2M}{M_T} DE^2 (q_n y_{n+1} - q_n y_n) + \frac{m}{M_T} E (q_{n+1} \\
& x_{n+1} - q_{n+1} x_n) + \frac{m}{M_T} D (q_{n+1} y_{n+1} - q_{n+1} y_n) + \frac{2m^2}{M_T^2} DE q_{n+1}^2 + \frac{m^2}{M_T^2} \\
& (D^2 - E^2) P_{n+1} q_{n+1} + \left(\frac{m^2}{M_T^2} + \frac{2MmD^2}{M_T^2} \right) P_n q_{n+1} + 2 \frac{Mm}{M_T^2} DE q_n q_{n+1} + \\
& \frac{M}{M_T} E (q_n x_{n+1} - q_n x_n) + \frac{M}{M_T} D (q_n y_{n+1} - q_n y_n) + \frac{2Mm}{M_T^2} DE q_n q_{n+1} + \\
& \left. \frac{Mm}{M_T^2} (D^2 - E^2) P_{n+1} q_n + \left(\frac{Mm}{M_T^2} + \frac{2M^2}{M_T^2} D^2 \right) P_n q_n + \frac{2M^2}{M_T^2} DE q_n^2 \right\}
\end{aligned}$$

$$\begin{aligned}
& + 2 k_r \theta_1 \left\{ E (x_n q_{n-1} - x_{n-1} q_{n-1}) - D (q_n q_{n-1} - y_{n-1} q_{n-1}) + \left(\frac{M}{M_T} E^2 \right. \right. \\
& - \frac{2m+M}{M_T} D^2) P_n q_{n-1} - 2 DE q_n q_{n-1} - \frac{M}{M_T} P_{n-1} q_{n-1} DE (x_n x_{n+1} - \\
& x_{n-1} x_{n+1} - x_n^2 + x_{n-1} x_n) - D^2 (y_n x_{n+1} - y_{n-1} x_{n+1} - x_n y_n + x_n y_{n-1}) + \\
& \left(\frac{M}{M_T} E^2 D - \frac{2m+M}{M_T} D^3) (P_n x_{n+1} - P_n x_n) - 2 D^2 E (q_n x_{n+1} - q_n x_n) - \\
& \frac{MD}{M_T} (x_{n+1} P_{n-1} - x_n P_{n-1}) + E^2 (x_n y_{n+1} - x_{n-1} y_{n+1} - y_n x_n + x_{n-1} y_n) \\
& - DE (y_n y_{n+1} - y_{n-1} y_{n+1} - y_n^2 + y_{n-1} y_n) + \left(\frac{M}{M_T} E^3 - \frac{2m+M}{M_T} D^2 E \right) \\
& (P_n y_{n+1} - P_n y_n) - 2 DE^2 (q_n y_{n+1} - q_n y_n) - \frac{M}{M_T} E (P_{n-1} y_{n+1} - P_{n-1} y_n) \\
& + \frac{mE}{M_T} (q_{n+1} x_n - q_{n+1} x_{n-1}) - \frac{m}{M_T} D (q_{n+1} y_n - q_{n+1} y_{n-1}) + \left(\frac{Mm}{M_T^2} E^2 - \right. \\
& \left. \frac{2m^2+Mm}{M_T^2} D^2) P_n q_{n+1} - 2 DE \frac{m}{M_T} q_n q_{n+1} - \frac{Mm}{M_T^2} P_{n-1} q_{n+1} + \frac{ME}{M_T} \\
& (x_n q_n - q_n x_{n-1}) - \frac{MD}{M_T} (q_n y_n - y_{n-1} q_n) + \left(\frac{M^2}{M_T^2} E^2 - \frac{2Mm+M^2}{M_T^2} D^2) \right. \\
& \left. P_n q_n - 2 DE \frac{M}{M_T} q_n^2 - \frac{M^2}{M_T^2} P_{n-1} q_n \right\} \\
& + 2 k_r \theta_1' \left\{ E (q_{n+1} x_{n+1} - x_n q_{n+1}) + D (q_{n+1} y_{n+1} - q_{n+1} y_n) + \frac{2m}{M_T} DE \right. \\
& q_{n+1}^2 + \frac{m}{M_T} (D^2 - E^2) P_{n+1} q_{n+1} + \left(\frac{m}{M_T} + \frac{2MD^2}{M_T} \right) P_n q_{n+1} + \frac{2M}{M_T} DE q_n q_{n+1} \\
& + DE (x_{n+1} x_n - x_n^2 - x_{n-1} x_{n+1} x_n x_{n-1}) + D^2 (x_n y_{n+1} - x_n y_n - x_{n-1} y_{n+1} \\
& + x_{n-1} y_n) + \frac{2m}{M_T} D^2 E (q_{n+1} x_n - q_{n+1} x_{n-1}) + \frac{m}{M_T} (D^3 - E^2 D) (P_{n+1} x_n - \\
& P_{n+1} x_{n-1}) + \left(\frac{mD}{M_T} + \frac{2MD^3}{M_T} \right) (P_n x_n - P_n x_{n-1}) + \frac{2MD^2 E}{M_T} (q_n x_n - q_n x_{n-1}) \\
& + E^2 (y_n x_{n+1} - y_n x_n - y_{n-1} x_{n+1} + x_n y_{n-1}) + DE (y_{n+1} y_n - y_n^2 - y_{n-1} y_{n+1} \\
& - y_n y_{n-1}) + \frac{2m}{M_T} DE^2 (y_n q_{n+1} - q_{n+1} y_{n-1}) + \frac{m}{M_T} (D^2 E - E^3) (P_{n+1} y_n - \\
& P_{n+1} y_{n-1}) + \left(\frac{mE}{M_T} + \frac{2MD^2 E}{M_T} \right) (P_n y_n - P_n y_{n-1}) + \frac{2M}{M_T} DE^2 (q_n y_n - q_n y_{n-1}) \\
& + \frac{mE}{M_T} (q_n x_{n+1} - q_n x_n) + \frac{mD}{M_T} (q_n y_{n+1} - q_n y_n) + \frac{2m^2}{M_T^2} DE (q_{n+1} q_n + \\
& \frac{m^2}{M_T^2} (D^2 - E^2) P_{n+1} q_n + \left(\frac{m^2}{M_T^2} + \frac{2MmD^2}{M_T^2} \right) P_n q_n + \frac{2Mm}{M_T^2} DE q_n^2 +
\end{aligned}$$

$$\begin{aligned} & \frac{ME}{M_T} (q_{n-1} x_{n+1} - q_{n-1} x_n) + \frac{MD}{M_T} (q_{n-1} y_{n+1} - q_{n-1} y_n) + \frac{2Mm}{M_T} DE \\ & q_{n+1} q_{n-1} + \frac{Mm}{M_T} (D^2 - E^2) P_{n+1} q_{n-1} + \left(\frac{Mm}{M_T^2} + \frac{2M^2 D^2}{M_T^2} \right) P_n q_{n-1} + \\ & \left. \frac{2M^2}{M_T^2} DE q_n q_{n-1} \right] \}. \end{aligned} \quad (3-29)$$

Putting the expressions for T and V from equations (3-26) and (3-28) into Lagrange's equations, we obtain the following equations of motion:

$$\begin{aligned} & M_T \ddot{x}_k + K_{r,r_0} (2 D^2 x_k - D^2 x_{k-1} - D^2 x_{k+1}) + K_{r,r_1} D^2 (2 x_{k+1} + x_{k-1} - \\ & x_{k+2} - x_{k-2} - 2 x_k) + k_{\theta\theta_0} E^2 (2 x_k - x_{k-1} - x_{k+1}) + k_{\theta'} \theta_0 E^2 (2 x_k - \\ & x_{k+1} - x_{k-1}) + k_{\theta\theta'} E^2 (2 x_{k+1} + 2 x_{k-1} - 2 x_k - x_{k-2} - x_{k+2}) + k_{\theta\theta_1} E^2 \\ & (x_{k+1} + x_{k-1} - x_{k-2} - x_{k+2} - 2 x_k + x_{k-1} + x_{k-1}) + k_{\theta'} \theta_1 E^2 (x_{k+1} + x_{k-1} \\ & - x_{k+2} - x_{k-2} - 2 x_k + x_{k+1} + x_{k-1}) + k_{r\theta} DE (4 x_k - 2 x_{k-1} - 2 x_{k+1}) \\ & + k_{r\theta'} DE (4 x_k - 2 x_{k+1} - 2 x_{k-1}) + k_{r,r_0} DE (2 y_k - y_{k+1} - y_{k-1}) + \\ & k_{\theta\theta_0} DE (-2 y_k + y_{k+1} + y_{k-1}) + k_{\theta'} \theta_0 DE (2 y_k - y_{k+1} - y_{k-1}) - k_{\theta\theta'} \\ & DE (2 y_{k-1} - y_{k-2} - y_k) - k_{\theta\theta_1} DE (2 y_{k-1} - y_{k-2} - y_k) + k_{\theta'} \theta_1 DE \\ & (2 y_{k-1} - y_{k-2} - y_k) - k_{r\theta} D^2 (2 y_k - y_{k-1} - y_{k+1}) + k_{r\theta'} E^2 (2 y_k - y_{k-1} - \\ & y_{k+1}) + k_{r\theta'} (2 y_k - y_{k-1} - y_{k+1}) - k_{r\theta_1} D^2 (2 y_{k-1} - y_{k-2} - y_k) + k_{r\theta_1} \\ & E^2 (2 y_{k+1} - y_{k+2} - y_k) + k_{r\theta_1} D^2 (2 y_{k+1} - y_k - y_{k+2}) + k_{r\theta_1} E^2 \\ & (2 y_{k-1} - y_k - y_{k-2}) + k_{r,r_0} \left(-\frac{Dm}{M_T} q_k - \frac{Dm}{M_T} q_{k+1} + \frac{Dm}{M_T} q_{k-1} - \frac{DM}{M_T} q_k \right) \\ & + K_{rr'} (D q_{k-1} - D q_k) + K_{r,r_1} \left(-\frac{Dm}{M_T} q_{k-1} + \frac{DM}{M_T} q_{k-2} - \frac{DM}{M_T} q_{k-2} - \right. \\ & \left. \frac{DM}{M_T} q_{k-1} + \frac{DM}{M_T} q_{k+1} - \frac{Dm}{M_T} q_{k+2} - \frac{DM}{M_T} q_{k+1} \right) + 2 k_{\theta\theta_0} DE^2 (q_{k+1} - q_k) \\ & + 2 k_{\theta'} \theta_0 DE^2 \left(\frac{m}{M_T} q_k - \frac{m}{M_T} q_{k+1} + \frac{M}{M_T} q_{k-1} - \frac{M}{M_T} q_k \right) + 2 k_{\theta\theta'} \\ & DE^2 \left\{ (q_k - q_{k-1}) + \frac{M}{M_T} (q_k - q_{k+1}) \right\} - 2 k_{\theta\theta_1} DE^2 (q_{k-1} - q_k) + 2 k_{\theta'} \theta_1 \\ & \frac{m}{M_T} DE^2 (q_{k-1} - q_k) + 2 k_{\theta'} \theta_1 \frac{M}{M_T} DE^2 (q_{k-2} - q_{k-1}) + 2 k_{\theta'} \theta_1 \frac{m}{M_T} \end{aligned}$$

$$\begin{aligned}
& DE^2 (q_{k+1} - q_{k+2}) + 2 k_{\theta'} \theta_1' \frac{M}{M_T} DE^2 (q_k - q_{k+1}) + k_r \theta \left\{ E (q_k - \right. \\
& q_{k+1}) - 2 D^2 E (q_k - q_{k+1}) + \frac{m}{M_T} E (q_k - q_{k+1}) + \frac{M}{M_T} (q_{k-1} - q_k) \left. \right\} \\
& + k_r \theta' \left\{ E (q_{k-1} - q_k) + \frac{2m}{M_T} D^2 E (q_k - q_{k+1}) + \frac{2MD^2M}{M_T} (q_{k-1} - q_k) \right. \\
& + \frac{mE}{M_T} (q_k - q_{k+1}) + \frac{ME}{M_T} (q_{k-1} - q_k) \left. \right\} + k_r \theta_1' \left\{ E (q_k - q_{k+1}) + \frac{2m}{M_T} \right. \\
& D^2 E (q_{k+1} - q_{k+2}) + \frac{2MD^2E}{M_T} (q_k - q_{k+1}) + \frac{mE}{M_T} (q_{k-1} - q_k) + \frac{ME}{M_T} \\
& (q_{k-2} - q_{k-1}) \left. \right\} + 2 k_{\theta\theta_0} \left(\frac{M}{M_T} E^2 P_k - \frac{2m+M}{M_T} D^2 P_k - \frac{M}{M_T} E^2 P_{k+1} + \right. \\
& \frac{2m+M}{M_T} D^2 P_{k+1} - \frac{M}{M_T} E P_{k-1} + \frac{M}{M_T} E P_k \left. \right) + k_{\theta'} \theta_0' \left\{ \frac{m}{M_T} (D^2 E - E^3) \right. \\
& (P_k - P_{k+1}) + \left(\frac{Em}{M_T} + \frac{D^2 E}{M_T} \right) P_{k-1} - \frac{Em}{M_T} P_k - \frac{2MD^2E}{M_T} P_k \left. \right\} + k_{\theta\theta'}, \\
& \left\{ \left(\frac{M}{M_T} E^3 - \frac{2m+M}{M_T} D^2 E \right) (P_{k-1} - P_k) - \frac{ME}{M_T} (P_{k-2} - P_{k-1}) + \left(\frac{mE}{M_T} + \right. \right. \\
& \left. \left. \frac{2MD^2E}{M_T} \right) (P_k - P_{k+1}) \right\} + k_{\theta\theta_1} \left\{ \left(\frac{M}{M_T} E^3 - \frac{2m+M}{M_T} D^2 E \right) (P_{k+1} - P_{k+2}) \right. \\
& - \frac{M}{M_T} (P_k - P_{k+1}) \left. \right\} + k_{\theta'} \theta_1' \left\{ \frac{m}{M_T} (D^2 E^3 - E^3) (P_{k-1} - P_k) + \right. \\
& \left(\frac{mE}{M_T} + \frac{2MD^2E}{M_T} \right) (P_{k-2} - P_{k-1}) + \left(\frac{mE}{M_T} + \frac{2MD^2E}{M_T} \right) (P_k - P_{k+1}) \left. \right\} \\
& + k_r \theta \left\{ \left(\frac{M}{M_T} E^2 D - \frac{2m+M}{M_T} D^3 \right) (P_k - P_{k+1}) - \frac{M}{M_T} D (P_{k+1} - P_k) \right\} \\
& + k_r \theta' \left\{ \frac{m}{M_T} (D^3 - DE^2) (P_k - P_{k+1}) + \left(\frac{mD}{M_T} + \frac{2MD^3}{M_T} \right) (P_{k-1} - P_k) \right\} \\
& + k_r \theta_1 \left\{ \left(\frac{M}{M_T} E^2 D - \frac{2m+M}{M_T} D^3 \right) (P_{k-1} - P_k) - \frac{MD}{M_T} (P_{k-2} - P_{k-1}) \right\} \\
& + k_r \theta_1' \left\{ \frac{m}{M_T} (D^3 - E^2 D) (P_{k+1} - P_{k+2}) + \left(\frac{mD}{M_T} + \frac{2MD^2}{M_T} \right) (P_k - P_{k+1}) \right\} = 0
\end{aligned}$$

(3-30a)

$$\begin{aligned}
& M_T \ddot{y}_k + K_r r_0' DE (x_k - \frac{1}{2} x_{k+2} - \frac{1}{2} x_{k-2}) + k_{\theta\theta_0} DE (-2 x_k + x_{k-1} + x_{k+1}) \\
& + k_{\theta'} \theta_0' DE (2 x_k - x_{k-1} - x_{k+1}) - k_{\theta\theta'} DE (2 x_{k+1} - x_{k+2} - x_k) + \\
& k_{\theta'} \theta_1' DE (2 x_{k+1} - x_{k+2} - x_k) - k_r \theta D^2 (2 x_k - x_{k+1} - x_{k-1}) + k_r \theta E^2 \\
& (2 x_k - x_{k-1} - x_{k+1}) + k_r \theta' (2 x_k - x_{k+1} - x_{k-1}) - k_r \theta_1 D^2 (2 x_{k+1} -
\end{aligned}$$

$$\begin{aligned}
& x_{k+2} - x_k) + k_r \theta_1 E^2 (2 x_{k-1} - x_{k-2} - x_k) + k_r \theta_1 D^2 (2 x_{k-1} - x_k - \\
& x_{k-2}) + k_r \theta_1' E^2 (2 x_{k+1} - x_k - x_{k+2}) + K_{r,r_0} E^2 (2 y_k - y_{k+1} - y_{k-1}) \\
& + K_{rr} E^2 (y_{k-1} + y_{k+1} - y_{k-2} - y_{k+2} + 2 y_k + y_{k-1} + y_{k+1}) \\
& + k \theta \theta_0 D^2 (2 y_k - y_{k+1} - y_{k-1}) + k \theta' \theta_0' D^2 (2 y_k - y_{k+1} - y_{k-1}) \\
& - k \theta \theta' D^2 (2 y_{k+1} + 2 y_{k-1} - 2 y_k - y_{k-2} - y_{k+2}) \\
& + k \theta \theta_1 D^2 (2 y_{k+1} + 2 y_{k-1} - y_{k+2} - y_{k-2} - 2 y_k) \\
& + k \theta' \theta_1' D^2 (2 y_{k+1} + 2 y_{k-1} - y_{k+2} - y_{k-2} - 2 y_k) \\
& - k_r \theta DE (4 y_k - 2 y_{k+1} - 2 y_{k-1}) \\
& + k_r \theta' DE (4 y_k - 2 y_{k+1} - 2 y_{k-1}) \\
& - k_r \theta_1 DE (2 y_{k+1} + 2 y_{k-1} - y_{k-2} - y_{k+2} - 2 y_k) \\
& + k_r \theta_1' DE (2 y_{k+1} + 2 y_{k-1} - 2 y_k - y_{k-2} - y_{k+2}) \\
& + K_{r,r_0} \frac{Em}{M_T} (q_{k+1} + q_{k-1}) \\
& + K_{rr} E (q_{k-1} - q_k) + K_{r,r_1} \left\{ \frac{Em}{M_T} (q_{k-1} - q_k) + \frac{EM}{M_T} (q_{k-2} - q_{k-1}) + \right. \\
& \left. \frac{Em}{M_T} (q_{k+1} - q_{k+2}) + \frac{EM}{M_T} (q_k - q_{k+1}) \right\} \\
& + k \theta \theta_0 D^2 E (2 q_k - 2 q_{k+1}) + k \theta' \theta_0' D^2 E \left(\frac{2m}{M_T} q_k - \frac{2m}{M_T} q_{k+1} + \frac{2M}{M_T} \right. \\
& \left. q_{k+1} - \frac{2M}{M_T} q_k \right) + 2 k \theta \theta' \left\{ - D^2 E (q_{k-1} - q_k) - \frac{m}{M} D^2 E (q_{k+1} - q_{k+2}) - \right. \\
& \left. \frac{2MD^2 E}{M_T} (q_k - q_{k+1}) \right\} + 2 k \theta \theta_1 D^2 E (q_{k-1} - q_k + q_{k+1} - q_{k+2}) + 2 k \theta' \theta_1' \\
& D^2 E \left\{ \frac{m}{M_T} (q_{k-1} - q_k) + \frac{M}{M_T} (q_{k-2} - q_{k-1}) + \frac{m}{M_T} (q_{k+1} - q_{k+2}) + \frac{M}{M_T} \right. \\
& \left. (q_k - q_{k+1}) \right\} + k_r \theta \left\{ - D (q_k - q_{k+1}) - 2 DE^2 (q_k - q_{k+1}) - \frac{m}{M_T} D (q_k - \right. \\
& \left. q_{k+1}) - \frac{M}{M_T} D (q_{k-1} - q_k) \right\} + k_r \theta' \left\{ D (q_{k-1} - q_k) + \frac{2m}{M_T} DE^2 (q_k - \right. \\
& \left. q_{k+1}) + \frac{2M}{M_T} DE^2 (q_{k-1} - q_k) + \frac{m}{M_T} D (q_k - q_{k+1}) + \frac{M}{M_T} D (q_{k-1} - q_k) \right\} \\
& + k_r \theta_1 \left\{ - D (q_{k-1} - q_k) - 2 DE^2 (q_{k-1} - q_k) - \frac{m}{M_T} D (q_{k+1} - q_{k+2}) - \right.
\end{aligned}$$

$$\begin{aligned}
& \frac{M}{M_T} D (q_k - q_{k+1}) \Big\} + k_r \theta_1' \Big\{ - D (q_k + q_{k+1}) + \frac{2mDE^2}{M_T} (q_{k+1} - q_{k+2}) \\
& + \frac{2M}{M_T} DE^2 (q_k - q_{k+1}) + \frac{mD}{M_T} (q_{k-1} - q_k) + \frac{M}{M_T} D (q_{k-2} - q_{k-1}) \Big\} + k_{\theta\theta_0} \\
& \Big(\frac{DE^2M}{M_T} P_k + \frac{(2m+M)}{M_T} D^3 P_k + DE^2 \frac{M}{M_T} P_{k+1} - \frac{(2m+M)}{M_T} D^3 P_{k+1} + 2 D^2 E P_k \\
& + \frac{MD}{M_T} P_{k-1} - \frac{MD}{M_T} P_k - 2 DE^2 \frac{M}{M_T} P_k \Big) + k_{\theta'} \theta_0' \Big(\frac{m}{M_T} D^3 P_k - \frac{m}{M_T} DE^2 \\
& P_k - \frac{m}{M_T} D^3 P_{k+1} + \frac{m}{M_T} DE^2 P_{k+1} + \frac{2MD^3}{M_T} P_{k-1} - 2 \frac{MD^3}{M_T} P_k \Big) \\
& + k_{\theta\theta'} \Big\{ \Big(\frac{M}{M_T} E^2 D - \frac{2m+M}{M_T} D^3 \Big) (P_{k-1} - P_k) - 2 D^2 E (P_{k-1} - P_k) - \\
& \frac{M}{M_T} D (P_{k-2} - P_{k-1}) - \frac{2m}{M_T} D^2 E M (P_{k+1} - P_{k+2}) - \Big(\frac{mD}{M_T} + \frac{2MD^2}{M_T} \Big) \\
& (P_k - P_{k+1}) - \frac{2MD^2E}{M_T} (P_k - P_{k+1}) \Big\} + k_{\theta'} \theta_1' \Big\{ \frac{m}{M_T} (D^3 - DE^2) (P_{k-1} - P_k) + \\
& \Big(\frac{mD}{M_T} + \frac{2MD^3}{M_T} \Big) (P_{k-2} - P_{k-1}) + \frac{m}{M_T} (D^3 - E^2 D) (P_{k+1} - P_{k+2}) + \Big(\frac{mD}{M_T} + \\
& \frac{2MD^3}{M_T} \Big) (P_k - P_{k+1}) \Big\} \\
& + k_r \theta \Big\{ \Big(\frac{M}{M_T} E^3 - \frac{2m+M}{M_T} D^2 E \Big) (P_k - P_{k+1}) - \frac{M}{M_T} E (P_{k-1} - P_k) \Big\} \\
& + k_r \theta' \Big\{ \frac{m}{M_T} (D^2 E - E^3) (P_k - P_{k+1}) + \Big(\frac{mE}{M_T} + \frac{2MD^2E}{M_T} \Big) (P_{k-1} - P_k) \Big\} \\
& + k_r \theta_1 \Big\{ \Big(\frac{M}{M_T} E^3 - \frac{2m+M}{M_T} D^2 E \Big) (P_{k-1} - P_k) - \frac{M}{M_T} E (P_{k-2} - P_{k-1}) \Big\} \\
& + k_r \theta_1' \Big\{ \frac{m}{M_T} (D^2 E - E^3) (P_{k+1} - P_{k+2}) + \Big(\frac{mE}{M_T} + \frac{2MD^2E}{M_T} \Big) \\
& (P_k - P_{k+1}) \Big\} = 0 \tag{3-30b}
\end{aligned}$$

$$\begin{aligned}
& \mu \ddot{q}_k + K_r r_{0'} \Big(D \frac{m}{M_T} x_k - \frac{Dm}{M_T} x_{k-1} + \frac{DM}{M_T} x_{k+1} - \frac{DM}{M_T} \Big) + K_{rr'} \Big(D x_{k+1} - \\
& D x_k \Big) + K_r r_{1'} \Big(\frac{Dm}{M_T} x_{k+1} - \frac{Dm}{M_T} x_k + \frac{DM}{M_T} x_{k+2} - \frac{DM}{M_T} x_{k+1} + \frac{Dm}{M_T} x_{k-1} - \\
& \frac{Dm}{M_T} x_{k-2} + \frac{Dm}{M_T} x_k - \frac{DM}{M_T} x_{k-1} \Big) + 2 k_{\theta\theta_0} DE^2 (-x_k + x_{k-1}) + 2 k_{\theta'} \theta_0' \\
& DE^2 \Big(\frac{m}{M_T} x_k - \frac{m}{M_T} x_{k-1} + \frac{M}{M_T} DE^2 x_{k+1} - \frac{M}{M_T} DE^2 x_k \Big) + 2 k_{\theta\theta_1} DE^2 \Big\{ \\
& (-x_{k+1} + x_k) + \frac{M}{M_T} (x_k - x_{k-1}) \Big\} - 2 k_{\theta\theta_1} DE^2 (x_{k+1} - x_k)
\end{aligned}$$

$$\begin{aligned}
& + 2 k_{\theta} \theta_1' DE^2 \left\{ \frac{m}{M_T} (x_{k+1} - y_k) + \frac{M}{M_T} (x_{k+2} - x_{k+1}) + \frac{m}{M_T} (x_{k-1} - \right. \\
& x_{k-2}) + \frac{M}{M_T} (x_k + x_{k-1}) \left. \right\} + k_r \theta \left\{ E (x_k - x_{k-1}) - 2 D^2 E (x_k - x_{k-1}) + \right. \\
& \frac{m}{M_T} E (x_k - x_{k-1}) + \frac{M}{M_T} (x_{k+1} - x_k) \left. \right\} + k_r \theta' \left\{ E (x_{k+1} - x_k) + \frac{2m}{M_T} D^2 E \right. \\
& (x_k - x_{k-1}) + \frac{2MD^2E}{M_T} (x_{k+1} - x_k) + \frac{mE}{M_T} (x_k - x_{k-1}) + \frac{ME}{M_T} (x_{k+1} - x_k) \left. \right\} \\
& + k_r \theta_1 \left\{ E (x_{k+1} - x_k) - 2 D^2 E (x_{k+1} - x_k) + \frac{mE}{M_T} (x_{k-1} - x_{k-2}) + \right. \\
& \frac{ME}{M_T} (x_k - x_{k-1}) \left. \right\} + k_r \theta_1' \left\{ E (x_k - x_{k-1}) + \frac{2m}{M_T} D^2 E (x_{k-1} - x_{k-2}) + \right. \\
& \frac{2MD^2E}{M_T} (x_k - x_{k-1}) + \frac{mE}{M_T} (x_{k+1} - x_k) + \frac{ME}{M_T} (x_{k+2} - x_{k+1}) \left. \right\} + K_r r_0' \\
& \frac{Em}{M_T} (y_{k-1} + y_{k+1}) + K_{rr'} E (y_{k+1} - y_k) + K_r r_1' \left\{ \frac{Em}{M_T} (y_{k+1} - y_k) + \right. \\
& \frac{EM}{M_T} (y_{k+2} - y_{k+1}) + \frac{Em}{M_T} (y_{k-1} - y_{k-2}) + \frac{EM}{M_T} y_k - \frac{EM}{M_T} y_{k-1} \left. \right\} + k_{\theta} \theta_0 \\
& D^2 E (2 y_k - 2 y_{k-1}) \left. \right\} + k_{\theta} \theta_0' D^2 E \left(\frac{2m}{M_T} y_k - \frac{2m}{M_T} y_{k-1} + \frac{2M}{M_T} y_{k+1} - \right. \\
& \frac{2M}{M_T} y_k \left. \right) + 2 k_{\theta} \theta' D^2 E \left\{ (y_k - y_{k+1}) - \frac{m}{M_T} (y_{k-1} - y_{k-2}) - \frac{M}{M_T} \right. \\
& (y_k - y_{k-1}) \left. \right\} + 2 k_{\theta} \theta_1 D^2 E \left\{ (y_{k+1} - y_k) + (y_{k-1} - y_{k-2}) \right\} + 2 k_{\theta} \theta_1' \\
& \left\{ \frac{m}{M_T} (y_{k+1} - y_k) + \frac{M}{M_T} (y_{k+2} - y_{k+1}) + \frac{m}{M_T} (y_{k-1} - y_{k-2}) + \frac{M}{M_T} \right. \\
& (y_k - y_{k-1}) \left. \right\} + k_r \theta \left\{ -D (y_k - y_{k-1}) - 2 DE^2 (y_k - y_{k-1}) - \frac{m}{M_T} D \right. \\
& (y_k - y_{k-1}) - \frac{M}{M_T} D (y_{k+1} - y_k) \left. \right\} + k_r \theta' \left\{ D (y_{k+1} - y_k) + \frac{2m}{M_T} DE^2 \right. \\
& (y_k - y_{k-1}) + \frac{2M}{M_T} DE^2 (y_{k+1} - y_k) + \frac{m}{M_T} D (y_k - y_{k-1}) + \frac{M}{M_T} D \\
& (y_{k+1} - y_k) \left. \right\} + k_r \theta_1 \left\{ -D (y_{k+1} - y_k) - 2 DE^2 (y_{k+1} - y_k) - \frac{m}{M_T} D \right. \\
& (y_{k-1} - y_{k-2}) - \frac{M}{M_T} D (y_k - y_{k-1}) \left. \right\} - k_r \theta_1' \left\{ D (-y_k - y_{k-1}) + \right. \\
& \frac{2m}{M_T} DE^2 (y_{k-1} - y_{k-2}) + \frac{2M}{M_T} DE^2 (y_k - y_{k-1}) + \frac{mD}{M_T} (y_{k+1} - y_k) +
\end{aligned}$$

$$\begin{aligned}
& \left\{ \frac{MD}{M_T} (y_{k+2} - y_{k+1}) \right\} + K_{rr_0} q_k + K_{r'r_0} \left\{ \left(\frac{m^2}{M_T^2} + \frac{M^2}{M_T^2} \right) q_k + \frac{Mm}{M_T^2} q_{k+1} + \right. \\
& \left. \frac{Mm}{M_T} q_{k-1} \right\} + K_{rr'} \left(\frac{m}{M_T} q_{k+1} + \frac{m}{M_T} q_{k-1} + \frac{2M}{M_T} q_k \right) + K_{rr_1} (q_{k+1} + q_{k-1}) \\
& + K_{r'r_1} \left(\frac{m^2}{M_T^2} q_{k+1} + \frac{m^2}{M_T^2} q_{k-1} + \frac{Mm}{M_T^2} q_{k+2} + \frac{Mm}{M_T^2} q_{k-2} + 2 \frac{Mm}{M_T^2} \right. \\
& \left. + \frac{M^2}{M_T} q_{k+1} + \frac{M^2}{M_T^2} q_{k-1} \right) + 4 k_{\theta\theta_0} D^2 E^2 + 4 k_{\theta', \theta_0} D^2 E^2 \\
& \left(\frac{m^2}{M_T^2} q_k + \frac{M^2}{M_T^2} q_k + \frac{2Mm}{M_T^2} q_{k+1} + \frac{2Mm}{M_T^2} q_{k-1} \right) + 4 k_{\theta\theta} D^2 E^2 \\
& \left(- \frac{m}{M_T} q_{k+1} - \frac{m}{M_T} q_{k-1} - \frac{2M}{M_T} q_k \right) + 4 k_{\theta\theta_1} D^2 E^2 (q_{k+1} + q_{k-1}) + \\
& 4 k_{\theta', \theta_1} D^2 E^2 \left(\frac{m^2}{M_T^2} q_{k+1} + \frac{m^2}{M_T^2} q_{k-1} + \frac{Mm}{M_T^2} q_{k+2} + \frac{Mm}{M_T} q_{k-2} + \right. \\
& \left. \frac{2Mm}{M_T^2} q_k + \frac{M^2}{M_T^2} q_{k+1} + \frac{M^2}{M_T^2} q_{k-1} \right) - 2 k_{r\theta} DE \left(2q_k + 2 \frac{m}{M_T} q_k + \right. \\
& \left. \frac{M}{M_T} q_{k+1} + \frac{M}{M_T} q_{k-1} \right) + 2 k_{r'\theta} DE \left(\frac{m}{M_T} q_{k+1} + \frac{m}{M_T} q_{k-1} + \frac{2M}{M_T} q_k + \right. \\
& \left. \frac{2m^2}{M_T^2} q_k + \frac{2Mm}{M_T^2} q_{k-1} + \frac{2Mm}{M_T^2} q_{k+1} + \frac{2M^2}{M_T^2} q_k \right) - 2 k_{r'\theta_1} DE (q_{k+1} + \\
& q_{k-1} + \frac{m}{M_T} q_{k+1} + \frac{m}{M_T} q_{k-1}) + 2 k_{r\theta_1} DE \left(\frac{2m}{M_T} q_k + \frac{M}{M_T} q_{k+1} + \frac{M}{M_T} \right. \\
& q_{k-1} + \frac{m^2}{M_T^2} q_{k+1} + \frac{m^2}{M_T^2} q_{k-1} + \frac{2Mm}{M_T^2} q_k + \frac{2Mm}{M_T^2} q_{k+2} + \frac{2Mm}{M_T^2} q_{k-2} + \\
& \left. \frac{M^2}{M_T^2} q_{k+1} + \frac{M^2}{M_T^2} q_{k-1} \right) + 2 k_{\theta\theta_0} \left\{ - DE^3 \frac{M}{M_T} P_k + D^3 E \frac{2m+M}{M_T} P_k - \right. \\
& \left. \frac{D^3 E (2m+M)}{M_T} P_{k-1} + \frac{M}{M_T} DE^3 P_{k-1} \right\} + 2 k_{\theta', \theta_0} \left(\frac{m^2}{M_T^2} D^3 E P_k - \frac{m^2}{M_T^2} \right. \\
& D^3 E P_k + \frac{m^2}{M_T^2} DE P_{k-1} + \frac{2Mm}{M_T^2} D^3 E P_{k-1} + \frac{M}{M_T} D^3 E P_{k+1} - \frac{M}{M_T} DE^3 \\
& P_{k+1} \left. \right) + 2 k_{\theta\theta_1} \left\{ \left(\frac{Mm}{M_T^2} DE^3 - \frac{2m^2+Mm}{M_T^2} D^3 E \right) P_{k-1} - \frac{Mm}{M_T^2} P_{k-2} - \frac{m}{M_T} \right. \\
& (D^3 E - E^3 D) P_{k+1} - \left(\frac{mDE}{M_T} + \frac{2MD^3 E}{M_T} \right) P_k + \frac{M}{M_T} DE \left(\frac{M}{M_T} E^2 - \frac{2m+M}{M_T} D^2 \right) \\
& P_k - \frac{M^2}{M_T^2} DE P_{k-1} \left. \right\} + k_{\theta\theta_1} \left\{ - \frac{(2m+M)}{M_T} D^3 E P_{k+1} - \left(\frac{2M}{M_T} DE^3 - \right. \right.
\end{aligned}$$

$$\begin{aligned}
& \left\{ \frac{2m+M}{M_T} D^3 E \right\} P_{k-1} + \frac{2M}{M_T} DE P_{k-2} + \frac{2M}{M_T} P_k \left\} + 2k_{\theta'} \theta_1' \left\{ \frac{m^2}{M_T^2} (D^3 E - \right. \right. \\
& DE^3) P_{k-1} + \left(\frac{m^2}{M_T^2} DE + \frac{2mD^3 E}{M_T^2} \right) P_{k-2} + \frac{m^2}{M_T^2} (D^3 E - DE^3) P_{k+1} + \frac{Mm}{M_T^2} \\
& (D^3 E - DE^3) P_{k+2} + \left(\frac{m^2}{M_T^2} DE + \frac{2Mm}{M_T^2} D^3 E \right) P_k + \left(\frac{Mm}{M_T^2} DE + \frac{2M^2 D^3 E}{M_T^2} \right) \\
& P_{k+1} + \frac{Mm}{M_T^2} (D^3 E - DE^3) P_k + \left(\frac{Mm}{M_T^2} DE + \frac{2M^2}{M_T^2} D^3 E \right) P_{k-1} \left\} + k_r \theta \left\{ \right. \\
& \left(\frac{M}{M_T} E^2 - \frac{2m+M}{M_T} D^2 \right) P_k - \frac{M}{M_T} P_{k-1} + \left(\frac{Mm}{M_T^2} E^2 - \frac{m(2m+M)}{M_T^2} D^2 \right) P_k - \\
& \frac{Mm}{M_T^2} P_{k-1} + \left(\frac{M^2}{M_T^2} E^2 - \frac{M(2m+M)}{M_T^2} D^2 \right) P_{k+1} - \frac{M^2}{M_T^2} P_k \left\} + k_r \theta' \left\{ \right. \\
& \frac{m}{M_T} (D^2 - E^2) P_{k+1} + \left(\frac{m}{M_T} + \frac{2MD^2}{M_T} \right) P_k + \frac{m^2}{M_T^2} (D^2 - E^2) P_k + \left(\frac{m^2}{M_T^2} + \right. \\
& \frac{2Mm}{M_T^2} D^2 \right) P_{k-1} + \frac{Mm}{M_T^2} (D^2 - E^2) P_{k+1} + \left(\frac{Mm}{M_T^2} + \frac{2M^2}{M_T^2} D^2 \right) P_k \left\} \right. \\
& + k_r \theta_1 \left\{ \left(\frac{M}{M_T} E^2 - \frac{2m+M}{M_T} \right) P_{k+1} - \frac{M}{M_T} P_k + \left(\frac{Mm}{M_T^2} E^2 - \frac{2m^2+Mm}{M_T^2} D^2 \right) \right. \\
& P_{k-1} - \frac{Mm}{M_T^2} P_{k-2} + \left(\frac{M^2}{M_T^2} E^2 - \frac{2Mm+M^2}{M_T^2} D^2 \right) P_k - \frac{M^2}{M_T^2} P_{k-1} \left\} + k_r \theta_1' \left\{ \right. \\
& \frac{m}{M_T} (D^2 - E^2) P_k + \left(\frac{m}{M_T} + \frac{2MD^2}{M_T} \right) P_{k-1} + \frac{m^2}{M_T^2} (D^2 - E^2) P_{k+1} + \left(\frac{m^2}{M_T^2} \right. \\
& + \frac{2Mm}{M_T^2} D^2 \right) P_k + \frac{Mm}{M_T^2} (D^2 - E^2) P_{k+2} + \left(\frac{Mm}{M_T^2} + \frac{2M^2 D^2}{M_T^2} \right) P_{k+1} \left\} = 0
\end{aligned}$$

(3-30c)

$$\begin{aligned}
& u \ddot{P}_k + k_{\theta\theta_0} \left(\frac{M}{M_T} E^2 x_k - \frac{2m+M}{M_T} D^2 x_k - \frac{M}{M_T} E^2 x_{k-1} + \frac{2m+M}{M_T} D^2 x_{k-1} - \right. \\
& \frac{M}{M_T} E x_{k+1} + \frac{ME}{M_T} x_k \left. \right) + k_{\theta'} \theta_0' \left\{ \frac{m}{M_T} (D^2 E - E^3) (x_k - x_{k-1}) + \frac{Em}{M_T} \right. \\
& x_{k+1} + \frac{2D^2 E}{M_T} x_{k+1} - \frac{Em}{M_T} x_k - \frac{2MD^2 E}{M_T} x_k \left\} + k_{\theta\theta'} \left\{ \left(\frac{M}{M_T} E^3 - \right. \right. \\
& \frac{2m+M}{M_T} D^2 E \right\} (x_{k+1} - x_k) - \frac{ME}{M_T} (x_{k+2} - x_{k+1}) + \left(\frac{mE}{M_T} + \frac{2MD^2 E}{M_T} \right) (x_k - x_{k-1}) \left\} \right. \\
& + k_{\theta\theta_1} \left\{ \left(\frac{M}{M_T} E^3 - \frac{2m+M}{M_T} D^2 E \right) (x_{k+1} - x_k) - \frac{ME}{M_T} (x_{k+2} - x_{k+1}) + \right.
\end{aligned}$$

$$\begin{aligned}
& \left(\frac{M}{M_T} E^3 - \frac{2m+M}{M_T} D^2 E \right) (x_{k-1} - x_{k-2}) - \frac{ME}{M_T} (x_k - x_{k-1}) \Big\} + k_{\theta} \theta_1, \\
& \left\{ \frac{m}{M_T} (D^2 E - E^3) (x_{k+1} - x_k) + \left(\frac{mE}{M_T} + \frac{2M}{M_T} D^2 E \right) (x_{k+2} - x_{k+1}) + \left(\frac{mE}{M_T} + \right. \right. \\
& \left. \left. \frac{2MD^2 E}{M_T} \right) (x_k - x_{k-1}) \right\} + k_r \theta \left\{ \left(\frac{M}{M_T} E^2 D - \frac{2m+M}{M_T} D^3 \right) (x_k - x_{k-1}) - \right. \\
& \left. \frac{M}{M_T} D (x_{k-1} - x_k) \right\} + k_r \theta_1 \left\{ \frac{m}{M_T} (D^3 - DE^2) (x_k - x_{k-1}) + \left(\frac{mD}{M_T} + \right. \right. \\
& \left. \left. \frac{2MD^3}{M_T} \right) (x_{k+1} - x_k) \right\} + k_r \theta_1 \left\{ \left(\frac{M}{M_T} E^2 D - \frac{2m+M}{M_T} D^3 \right) (x_{k+1} - x_k) - \right. \\
& \left. \frac{MD}{M_T} (x_{k+2} - x_{k+1}) \right\} + k_r \theta_1 \left\{ \frac{m}{M_T} (D^3 - E^2 D) (x_{k-1} - x_{k-2}) + \left(\frac{mD}{M_T} \right. \right. \\
& \left. \left. + \frac{2MD^2}{M_T} \right) (x_k - x_{k-1}) \right\} + k_{\theta\theta_0} \left\{ - \frac{DM}{M_T} y_k + \frac{2m+M}{M_T} D^3 y_k + DE^2 \frac{M}{M_T} \right. \\
& y_{k-1} - \frac{(2m+M)}{M_T} D^3 y_{k-1} + 2 D^2 E y_k - 2 D^2 E y_{k-1} + \frac{MD}{M_T} y_{k+1} - \frac{MD}{M_T} y_k \\
& - 2 DE^3 \frac{M}{M_T} y_k \Big\} + k_{\theta} \left\{ \left(\frac{m}{M_T} D^3 y_k - \frac{m}{M_T} DE^2 y_k - \frac{m}{M_T} D^3 y_{k-1} + \right. \right. \\
& \left. \left. \frac{m}{M_T} DE^2 y_{k-1} + \frac{2MD^3}{M_T} y_{k+1} - \frac{2MD^3}{M_T} y_k + k_{\theta} \left(\frac{M}{M_T} E^2 D - \frac{2m+M}{M_T} D^3 \right) \right. \right. \\
& (y_{k+1} - y_k) - 2 D^2 E (y_{k+1} - y_k) - \frac{M}{M_T} D (y_{k+2} - y_{k+1}) - \frac{2mM}{M_T} D^2 E \\
& (y_{k-1} - y_{k-2}) - \left(\frac{mD}{M_T} + \frac{2MD^2}{M_T} \right) (y_k - y_{k-1}) - \frac{2MD^2 E}{M_T} (y_k - y_{k-1}) \\
& + k_{\theta_1} \left\{ \left(\frac{ME^2 D}{M_T} + \frac{2m+M}{M_T} D^3 \right) (y_{k+1} - y_k) + 2 D^2 E (y_{k+1} - y_k) + \frac{MD}{M_T} \right. \\
& (y_{k+2} - y_{k+1}) - \left(\frac{ME^2 D}{M_T} - \frac{2m+M}{M_T} D^3 \right) (y_{k-1} - y_{k-2}) + 2 D^2 E (y_{k-1} - y_{k-2}) \\
& + \frac{MD}{M_T} (y_k - y_{k-1}) \Big\} + k_{\theta} \theta_1 \left\{ \frac{m}{M_T} (D^3 - DE^2) (y_{k+1} - y_k) + \left(\frac{mD}{M_T} + \right. \right. \\
& \left. \left. \frac{2MD^3}{M_T} \right) (y_{k+2} - y_{k+1}) + \frac{m}{M_T} (D^3 - E^2 D) (y_{k-1} - y_{k-2}) + \left(\frac{mD}{M_T} + \frac{2MD^3}{M_T} \right) \right. \\
& (y_k - y_{k-1}) \Big\} + k_r \theta \left\{ \left(\frac{M}{M_T} E^3 - \frac{2m+M}{M_T} D^2 E \right) (y_k - y_{k-1}) - \frac{M}{M_T} E (y_{k+1} \right. \\
& - y_k) \Big\} + k_r \theta_1 \left\{ \frac{m}{M_T} (D^2 E - E^3) (y_k - y_{k-1}) + \left(\frac{mE}{M_T} + \frac{2MD^2 E}{M_T} \right) (y_{k+1} - \right. \\
& y_k) \Big\} + k_r \theta_1 \left\{ \left(\frac{M}{M_T} E^3 - \frac{2m+M}{M_T} D^2 E \right) (y_{k+1} - y_k) - \frac{M}{M_T} E (y_{k+2} - y_{k+1}) \right\}
\end{aligned}$$

$$\begin{aligned}
& + k_r \theta_1' \left\{ \left(\frac{m}{M_T} (D^2 E - E^3) (y_{k-1} - y_{k-2}) + \left(\frac{mE}{M_T} + \frac{2MD^2 E}{M_T} \right) (y_k - y_{k-1}) \right) \right\} \\
& + 2 k_{\theta\theta_0} \left(-DE^3 \frac{M}{M_T} q_k + D^3 E \frac{2m+M}{M_T} q_k - \frac{D^3 E (2m+M)}{M_T} q_{k+1} + \frac{M}{M_T} DE q_{k+1} \right) \\
& + 2 k_{\theta'\theta_0'} \left(\frac{m^2}{M_T^2} D^3 E q_k - \frac{m^2}{M_T^2} DE^3 q_k + \frac{m^2}{M_T^2} DE q_{k+1} + \frac{2Mm}{M_T^2} D^3 E q_{k+1} \right. \\
& + \frac{M}{M_T} D^3 E q_{k-1} - \frac{M}{M_T} DE^3 q_{k-1} \left. \right) + 2 k_{\theta\theta'} \left\{ \left(\frac{Mm}{M_T^2} DE^3 - \frac{2m^2+Mm}{M_T^2} D^3 E \right) q_{k+1} \right. \\
& - \frac{Mm}{M_T^2} q_{k+2} - \frac{m}{M_T} (D^3 E - E^3 D) q_{k-1} - \left(\frac{mDE}{M_T} + \frac{2MD^3 E}{M_T} \right) q_k + \frac{M}{M_T} DE \\
& \left(\frac{M}{M_T} E^2 - \frac{2m+M}{M_T} D^2 \right) q_k - \frac{M^2}{M_T^2} DE q_{k+1} \left. \right\} + k_{\theta\theta_1} \left\{ -\frac{2m+M}{M_T} D^3 E q_{k-1} - \right. \\
& \left(\frac{2M}{M_T} DE^3 - \frac{2m+M}{M_T} D^3 E \right) q_{k+1} + \frac{2M}{M_T} DE q_{k+2} + \frac{2M}{M_T} q_k \left. \right\} + 2 k_{\theta'\theta_1'} \left\{ \frac{m^2}{M_T^2} \right. \\
& (D^3 E - DE^3) q_{k+1} + \left(\frac{m^2}{M_T^2} DE + \frac{2MD^3 E}{M_T^2} \right) q_{k+2} + \frac{m^2}{M_T^2} (D^3 E - DE^3) q_{k-1} + \\
& \frac{Mm}{M_T^2} (D^3 E - DE^3) q_{k-2} + \left(\frac{m^2}{M_T^2} DE + \frac{2Mm}{M_T^2} D^3 E \right) q_k + \left(\frac{Mm}{M_T^2} DE + \frac{2MD^3 E}{M_T^2} \right) \\
& q_{k-1} + \frac{Mm}{M_T^2} (D^3 E - DE^3) q_k + \left(\frac{MmDE}{M_T^2} + \frac{2M^2}{M_T^2} D^3 E \right) q_{k+1} \left. \right\} + k_r \theta \left\{ \left(\frac{ME^2}{M_T} - \right. \right. \\
& \left. \frac{2m+M}{M_T} D^2 \right) q_k - \frac{Mm}{M_T^2} q_{k+1} + \left(\frac{M^2}{M_T^2} E^2 - \frac{M(2m+M)}{M_T^2} D^2 \right) q_{k-1} - \frac{M^2}{M_T^2} q_k \left. \right\} + \\
& k_r \theta' \left\{ \frac{m}{M_T} (D^2 - E^2) q_{k-1} \left(\frac{m}{M_T} + \frac{2MD^2}{M_T} \right) q_k + \frac{m^2}{M_T^2} (D^2 - E^2) q_k + \left(\frac{m^2}{M_T^2} + \right. \right. \\
& \left. \frac{2Mm}{M_T^2} \right) q_{k+1} + \frac{Mm}{M_T^2} (D^2 - E^2) q_{k-1} + \left(\frac{Mm}{M_T^2} + \frac{2M^2}{M_T^2} D^2 \right) q_k \left. \right\} \\
& k_{\theta\theta_0} \left\{ \frac{M^2}{M_T^2} E^4 P_k + \left(\frac{2m+M}{M_T} \right)^2 D^4 P_k + \frac{M^2}{M_T^2} P_k - \frac{M^2}{M_T^2} E^2 P_{k-1} - \frac{M^2}{M_T^2} \right. \\
& E^2 P_{k+1} + \frac{M}{M_T} \frac{2m+M}{M_T} P_{k-1} + \frac{M}{M_T} \frac{2m+M}{M_T} P_{k+1} \left. \right\} + k_{\theta'\theta_0'} \left\{ \frac{m^2}{M_T^2} \right. \\
& (D^2 - E^2) P_k + \left(\frac{m}{M_T} + \frac{2MD^2}{M_T} \right) P_k + \frac{m^2}{M_T^2} D^2 (P_{k+1} + P_{k-1}) + \frac{2MmD^4}{M_T^2} \\
& (P_{k+1} + P_{k-1}) - \frac{m^2}{M_T^2} E^2 (P_{k+1} + P_{k-1}) - \frac{2MmD^2 E^2}{M_T^2} (P_{k+1} + P_{k-1}) \left. \right\} + \\
& k_{\theta\theta'} \left\{ \left(\frac{M}{M_T} E^2 - \frac{2m+M}{M_T} D^2 \right) \left(\frac{m}{M_T} D^2 - \frac{m}{M_T} E^2 \right) (P_{k+1} + P_{k-1}) - \frac{Mm}{M_T^2} \right.
\end{aligned}$$

$$\begin{aligned}
& (D^2 - E^2) (P_{k+2} + P_{k-2}) + 2 \left(\frac{m}{M_T} + \frac{2MD^2}{M_T} \right) \left(\frac{M}{M_T} E^2 - \frac{2m+M}{M_T} D^2 \right) P_k - \\
& \frac{M}{M_T} \left(\frac{m}{M_T} + \frac{2MD^2}{M_T} \right) (P_{k+1} + P_{k-1}) \Big\} + k \theta \theta_1 \left\{ \left(\frac{M}{M_T} E^2 - \frac{2m+M}{M_T} D^2 \right) \right. \\
& (P_{k+1} + P_{k-1}) - \left(\frac{M^2}{M_T^2} E^2 - \frac{M(2m+M)}{M_T^2} D^2 \right) (P_{k+2} + P_{k-2}) - 2 \frac{M}{M_T} \left(\frac{M}{M_T} \right. \\
& E^2 - \frac{2m+M}{M_T} D^2 \Big) P_k + \frac{M^2}{M_T^2} (P_{k-1} + P_{k+1}) \Big\} + k \theta' \theta_1' \left\{ \frac{m^2}{M_T^2} (D^2 - E^2)^2 \right. \\
& (P_{k+1} + P_{k-1}) + \left(\frac{m^2}{M_T^2} + \frac{2Mm}{M_T^2} D^2 \right) (D^2 - E^2) (P_{k+2} + P_{k-2}) + 2 \left(\frac{m^2}{M_T^2} + \right. \\
& \left. \frac{2Mm}{M_T^2} D^2 \right) (D^2 - E^2) P_k + \left(\frac{m}{M_T} + \frac{2MD^2}{M_T} \right)^2 (P_{k+1} + P_{k-1}) \Big\} = 0.
\end{aligned}
\tag{3-30d}$$

Applying the symmetry rule, we can write:

$$\begin{aligned}
x_k &= x_0 e^{i(\omega t + k\delta)} \\
y_k &= y_0 e^{i(\omega t + k\delta)} \\
q_k &= q_0 e^{i(\omega t + k\delta)} \\
P_k &= P_0 e^{i(\omega t + k\delta)}
\end{aligned}
\tag{3-31}$$

where $i = (-1)^{\frac{1}{2}}$.

Substituting equations (3-31) into equations (3-30) and eliminating the common factor $e^{i(\omega t + k\delta)}$, which is not identically zero, we obtain four homogeneous, linear equations for the amplitudes, x_0 , y_0 , q_0 and P_0 . In order for this system of linear equations to have a non-trivial solution, the determinant of the coefficients of the amplitudes must vanish.

This secular determinant has the following form:

$$\begin{vmatrix}
C_{11} & C_{12} & C_{13} & C_{14} \\
C_{12}^* & C_{22} & C_{23} & C_{24} \\
C_{13}^* & C_{23}^* & C_{23} & C_{34} \\
C_{14}^* & C_{24}^* & C_{14}^* & C_{44}
\end{vmatrix} = 0
\tag{3-32}$$

where

$$\begin{aligned}
 C_{11} = & -M_T W^2 + K_{r'r_0'} (2 D^2 - D^2 e^{-i\delta} - D^2 e^{i\delta}) + K_{r'r_1'} D^2 \\
 & (2 e^{-i\delta} + 2 e^{-i\delta} - e^{2i\delta} - e^{-2i\delta} - 2) + k_{\theta\theta_0} E^2 (2 - e^{-i\delta} - e^{i\delta}) \\
 & + k_{\theta'\theta_0'} E^2 (2 - e^{i\delta} - e^{-i\delta}) + k_{\theta\theta_1} E^2 (2 e^{i\delta} + 2 e^{-i\delta} - 2 - \\
 & e^{-2i\delta} - e^{2i\delta}) + k_{\theta\theta_1} E^2 (2 e^{i\delta} + 2 e^{-i\delta} - e^{-2i\delta} - e^{2i\delta} - 2) \\
 & + k_{\theta'\theta_1'} E^2 (2 e^{i\delta} + 2 e^{-i\delta} - e^{-2i\delta} - e^{2i\delta} - 2) + k_{r\theta} DE (4 - \\
 & 2 e^{-i\delta} - 2 e^{i\delta}) + k_{r\theta'} DE (4 - 2 e^{i\delta} - 2 e^{-i\delta}) + k_{r\theta_1} DE \\
 & (2 e^{i\delta} + 2 e^{-i\delta} - e^{-2i\delta} - e^{2i\delta} - 2) + k_{r\theta_1'} DE (2 e^{i\delta} + 2 e^{-i\delta} - \\
 & e^{2i\delta} - e^{-2i\delta} - 2)
 \end{aligned}$$

$$\begin{aligned}
 C_{12} = & K_{r'r_0'} DE (2 - e^{i\delta} - e^{-i\delta}) + k_{\theta\theta_0} DE (e^{i\delta} + e^{-i\delta} - 2) \\
 & + k_{\theta'\theta_0'} DE (2 - e^{i\delta} - e^{-i\delta}) - k_{\theta\theta_1} DE (2 e^{-i\delta} - e^{-2i\delta} - 1) - \\
 & k_{\theta\theta_1} DE (2 e^{-i\delta} - e^{-2i\delta} - 1) + k_{\theta'\theta_1'} DE (2 e^{-i\delta} - e^{-2i\delta} - 1) - \\
 & k_{r\theta} D^2 (2 - e^{-i\delta} - e^{i\delta}) + k_{r\theta'} E^2 (2 - e^{i\delta} - e^{-i\delta}) + k_{r\theta_1} (2 - \\
 & e^{-i\delta} - e^{i\delta}) - k_{r\theta_1} D^2 (2 e^{-i\delta} - e^{-2i\delta} - 1) + k_{r\theta_1} E^2 (2 e^{i\delta} - \\
 & e^{2i\delta} - 1) + k_{r\theta_1'} D^2 (2 e^{i\delta} - 1 - e^{2i\delta}) + k_{r\theta_1'} E^2 (2 e^{-i\delta} - 1 - \\
 & e^{-2i\delta})
 \end{aligned}$$

$$\begin{aligned}
 C_{13} = & K_{r'r_0'} \left(\frac{Dm}{M_T} - \frac{Dm}{M_T} e^{i\delta} + \frac{DM}{M_T} e^{-i\delta} - \frac{DM}{M_T} \right) + K_{rr'} D (e^{-i\delta} - 1) \\
 & + K_{r'r_1'} \left(\frac{Dm}{M_T} e^{-i\delta} + \frac{DM}{M_T} e^{-2i\delta} - \frac{DM}{M_T} e^{-i\delta} + \frac{Dm}{M_T} e^{-i\delta} + \frac{Dm}{M_T} e^{i\delta} - \right. \\
 & \left. \frac{Dm}{M_T} e^{2i\delta} - \frac{Dm}{M_T} e^{i\delta} \right) + 2 k_{\theta\theta_0} DE^2 (-1 + e^{i\delta}) + 2 k_{\theta'\theta_0'} DE^2 \\
 & \left(\frac{m}{M_T} - \frac{m}{M_T} e^{i\delta} + \frac{M}{M_T} e^{-i\delta} - \frac{M}{M_T} \right) + 2 k_{\theta\theta_1} DE^2 \left\{ (1 - e^{-i\delta}) + \right. \\
 & \left. \frac{2M}{M_T} (1 - e^{i\delta}) \right\} - 2 k_{\theta\theta_1} DE^2 (e^{-i\delta} - 1) + 2 k_{\theta'\theta_1'} \left\{ \frac{m}{M_T} DE^2 \right. \\
 & \left. (e^{-i\delta} - 1) + \frac{MD}{M_T} E^2 (e^{-2i\delta} - e^{-i\delta}) + \frac{m}{M_T} DE^2 (e^{i\delta} - e^{2i\delta}) + \frac{M}{M_T} DE^2 \right. \\
 & \left. (1 - e^{i\delta}) \right\} + k_{r\theta} \left\{ E (1 - e^{i\delta}) - 2 D^2 E (1 - e^{i\delta}) + \frac{m}{M_T} E \right.
 \end{aligned}$$

$$\begin{aligned}
& (1 - e^{i\delta}) + \frac{ME}{M_T} (e^{i\delta} - 1) + k_r \theta, \left\{ E (e^{-i\delta} - 1) + \frac{2m}{M_T} D^2 E (1 - e^{i\delta}) \right. \\
& + \frac{2MD^2E}{M_T} (e^{-i\delta} - 1) + \frac{mE}{M_T} (1 - e^{i\delta}) + \frac{ME}{M_T} (e^{-i\delta} - 1) \left. \right\} + k_r \theta_1 \left\{ E \right. \\
& (e^{-i\delta} - 1) - 2 D^2 E (e^{-i\delta} - 1) + \frac{mE}{M_T} (e^{i\delta} - e^{2i\delta}) + \frac{ME}{M_T} (1 - e^{i\delta}) \left. \right\} \\
& + k_r \theta_1, \left\{ E (1 - e^{i\delta}) + \frac{2m}{M_T} D^2 E (e^{i\delta} - e^{2i\delta}) + \frac{2MD^2E}{M_T} (1 - e^{i\delta}) \right. \\
& + \frac{mE}{M_T} (e^{-i\delta} - 1) + \frac{ME}{M_T} (e^{-2i\delta} - e^{-i\delta}) \left. \right\}
\end{aligned}$$

$$\begin{aligned}
C_{14} = k_{\theta\theta_0} & \left(\frac{M}{M_T} E^2 - \frac{2m+M}{M_T} D^2 - \frac{M}{M_T} E^2 e^{i\delta} + \frac{2m+M}{M_T} D^2 e^{i\delta} - \right. \\
& \frac{M}{M_T} E e^{-i\delta} + \frac{M}{M_T} E \left. \right) + k_{\theta',\theta_0}, \left\{ \frac{m}{M_T} (D^2 E - E^3) (1 - e^{i\delta}) + \frac{Em}{M_T} \right. \\
& e^{-i\delta} + \frac{2MD^2E}{M_T} e^{-i\delta} - \frac{Em}{M_T} - \frac{2MD^2E}{M_T} \left. \right\} + k_{\theta\theta'}, \left\{ \left(\frac{M}{M_T} E^3 - \frac{2m+M}{M_T} D^2 E \right) \right. \\
& (e^{-i\delta} - 1) - \frac{ME}{M_T} (e^{-2i\delta} - e^{-i\delta}) + \left(\frac{mE}{M_T} + \frac{2MD^2E}{M_T} \right) (1 - e^{i\delta}) \left. \right\} \\
& + k_{\theta\theta_1} \left\{ \left(\frac{M}{M_T} E^3 - \frac{2m+M}{M_T} D^2 E \right) (e^{-i\delta} - 1) - \frac{ME}{M_T} (e^{-2i\delta} - e^{-i\delta}) + \right. \\
& \left(\frac{M}{M_T} E^3 - \frac{2m+M}{M_T} D^2 E \right) (e^{i\delta} - e^{2i\delta}) - \frac{ME}{M_T} (1 - e^{i\delta}) \left. \right\} + k_{\theta',\theta_1}, \\
& \left\{ \frac{m}{M_T} (D^2 E - E^3) (e^{-i\delta} - 1) + \left(\frac{mE}{M_T} + \frac{2MD^2E}{M_T} \right) (e^{-2i\delta} - e^{-i\delta}) + \right. \\
& \left(\frac{mE}{M_T} + \frac{2MD^2E}{M_T} \right) (1 - e^{i\delta}) \left. \right\} + k_{r\theta} \left\{ \left(\frac{M}{M_T} E^2 D - \frac{2m+M}{M_T} D^3 \right) (1 - e^{i\delta}) \right. \\
& - \frac{M}{M_T} D (e^{i\delta} - 1) \left. \right\} + k_{r\theta'}, \left\{ \frac{m}{M_T} (D^3 - DE^2) (1 - e^{i\delta}) + \left(\frac{mD}{M_T} + \right. \right. \\
& + \frac{2MD^3}{M_T} \left. \right) (e^{-i\delta} - 1) \left. \right\} + k_{r\theta_1} \left\{ \left(\frac{M}{M_T} E^2 D - \frac{2m+M}{M_T} D^3 \right) (e^{-i\delta} - 1) - \right. \\
& \frac{MD}{M_T} (e^{-2i\delta} - e^{-i\delta}) \left. \right\} + k_{r\theta_1'}, \left\{ \frac{m}{M_T} (D^3 - E^2 D) (e^{i\delta} - e^{2i\delta}) + \right. \\
& \left(\frac{mD}{M_T} + \frac{2MD^2}{M_T} \right) (1 - e^{i\delta}) \left. \right\}
\end{aligned}$$

$$\begin{aligned}
C_{22} = K_{r,r_0}, E^2 (2 - e^{i\delta} - e^{-i\delta}) + K_{r,r'}, E^2 (e^{-i\delta} + e^{i\delta} - e^{-2i\delta} - \\
e^{2i\delta} + 2 + e^{-i\delta} + e^{i\delta}) + k_{\theta\theta_0} D^2 (2 - e^{i\delta} - e^{-i\delta}) + k_{\theta',\theta_0}, D^2
\end{aligned}$$

$$\begin{aligned}
& (2 - e^{i\delta} - e^{-i\delta}) - k_{\theta\theta}, D^2 (2 e^{i\delta} + 2 e^{-i\delta} - 2 - e^{-2i\delta} - e^{2i\delta}) \\
& + k_{\theta\theta_1} D^2 (e^{i\delta} + e^{-i\delta} - e^{2i\delta} - e^{-2i\delta} - 2 + e^{-i\delta} + e^{i\delta}) + k_{\theta, \theta_1}, \\
& D^2 (2 e^{i\delta} + 2 e^{-i\delta} - e^{2i\delta} - e^{-2i\delta} - 2) - k_{r\theta} DE (4 - 2 e^{i\delta} - 2 e^{-i\delta}) \\
& + k_{r\theta}, DE (4 - 2 e^{i\delta} - 2 e^{-i\delta}) - k_{r\theta_1} DE (2 e^{i\delta} + 2 e^{-i\delta} - e^{-2i\delta} - \\
& e^{2i\delta} - 2) + k_{r\theta_1}, DE (2 e^{i\delta} + 2 e^{-i\delta} - 2 - e^{-2i\delta} - e^{2i\delta})
\end{aligned}$$

$$\begin{aligned}
C_{23} = & K_{r,r_0}, \frac{Em}{M_T} (e^{-i\delta} - e^{i\delta}) + K_{rr}, E (e^{-i\delta} - 1) + K_{r,r_1}, \frac{Em}{M_T} \\
& \left\{ (e^{-i\delta} - 1) + \frac{EM}{M_T} e^{-2i\delta} - \frac{EM}{M_T} e^{-i\delta} + \frac{Em}{M_T} (e^{i\delta} - e^{2i\delta}) + \frac{EM}{M_T} \right. \\
& \left. - \frac{EM}{M_T} e^{i\delta} \right\} + 2 k_{\theta\theta_0} D^2 E (1 - e^{i\delta}) + 2 k_{\theta, \theta_0}, D^2 E \left(\frac{m}{M_T} - \frac{m}{M_T} \right. \\
& \left. e^{i\delta} + \frac{M}{M_T} e^{-i\delta} - \frac{M}{M_T} \right) + 2 k_{\theta\theta}, \left\{ - D^2 E (e^{-i\delta} - 1) - \frac{m}{M_T} D^2 E \right. \\
& \left. (e^{i\delta} - e^{2i\delta}) - \frac{2MD^2E}{M_T} (1 - e^{i\delta}) \right\} + 2 k_{\theta\theta_1} \left\{ D^2 E (e^{-i\delta} - 1) + \right. \\
& \left. D^2 E (e^{i\delta} - e^{2i\delta}) \right\} + 2 k_{\theta, \theta_1}, D^2 E \left\{ \frac{m}{M_T} (e^{-i\delta} - 1) + \frac{M}{M_T} \right. \\
& \left. (e^{-2i\delta} - e^{-i\delta}) + \frac{m}{M_T} (e^{i\delta} - e^{2i\delta}) + \frac{M}{M_T} (1 - e^{i\delta}) \right\} + k_{r\theta} \left\{ - D \right. \\
& \left. (1 - e^{i\delta}) - 2 DE^2 (1 - e^{i\delta}) - \frac{m}{M_T} D (1 - e^{i\delta}) - \frac{M}{M_T} D (e^{-i\delta} - 1) \right\} \\
& + k_{r\theta}, \left\{ D (e^{-i\delta} - 1) + \frac{2m}{M_T} DE^2 (1 - e^{i\delta}) + \frac{2M}{M_T} DE^2 (e^{-i\delta} - 1) + \right. \\
& \left. \frac{m}{M_T} D (1 - e^{i\delta}) + \frac{M}{M_T} D (e^{-i\delta} - 1) \right\} + k_{r\theta_1} \left\{ - D (e^{-i\delta} - 1) - \right. \\
& \left. 2 DE^2 (e^{-i\delta} - 1) - \frac{m}{M_T} D (e^{i\delta} - e^{2i\delta}) - \frac{M}{M_T} D (1 - e^{i\delta}) \right\} + k_{r\theta_1}, \\
& \left\{ - D (1 - e^{i\delta}) + \frac{2m}{M_T} DE^2 (e^{i\delta} - e^{2i\delta}) + \frac{2M}{M_T} DE^2 (1 - e^{i\delta}) + \right. \\
& \left. \frac{mD}{M_T} (e^{-i\delta} - 1) + \frac{MD}{M_T} (e^{-2i\delta} - e^{-i\delta}) \right\}
\end{aligned}$$

$$\begin{aligned}
C_{24} = & k_{\theta\theta_0} \left\{ - \frac{DE^2M}{M_T} + \frac{(2m+M)}{M_T} D^3 + DE^2 \frac{M}{M_T} e^{i\delta} - \frac{2m+M}{M_T} D^3 e^{i\delta} + \right. \\
& \left. \frac{MD}{M_T} e^{-i\delta} - \frac{MD}{M_T} \right\} + k_{\theta, \theta_0}, \left(\frac{m}{M_T} D^3 - \frac{m}{M_T} DE^2 - \frac{m}{M_T} D^3 e^{i\delta} + \frac{m}{M_T} \right.
\end{aligned}$$

$$\begin{aligned}
& DE^2 e^{i\delta} + \frac{2MD^3}{M_T} e^{-i\delta} - \frac{2MD^3}{M_T} + k_{\theta\theta}, \left\{ \left(\frac{M}{M_T} E^2 D - \frac{2m+M}{M_T} D^3 \right) \right. \\
& (e^{-i\delta} - 1) - 2 D^2 E (e^{-i\delta} - 1) - \frac{M}{M_T} D (e^{-2i\delta} - e^{-i\delta}) - \frac{2mM}{M_T^2} D^2 E \\
& (e^{i\delta} - e^{2i\delta}) - \left(\frac{mD}{M_T} + \frac{2MD^2}{M_T} \right) (1 - e^{i\delta}) - \frac{2MD^2 E}{M_T} (1 - e^{i\delta}) \Big\} \\
& + k_{\theta\theta 1} \left\{ - \left(\frac{ME^2 D}{M_T} + \frac{2m+M}{M_T} D^3 \right) (e^{-i\delta} - 1) + 2 D^2 E (e^{-i\delta} - 1) + \right. \\
& \frac{MD}{M_T} (e^{-2i\delta} - e^{-i\delta}) - \left(\frac{ME^2 D}{M_T} + \frac{2m+M}{M_T} D^3 \right) (e^{i\delta} - e^{2i\delta}) + 2 D^2 E \\
& (e^{i\delta} - e^{2i\delta}) + \frac{MD}{M_T} (1 - e^{i\delta}) \Big\} + k_{\theta, \theta 1}, \left\{ \frac{m}{M_T} (D^3 - DE^2) (e^{-i\delta} \right. \\
& - 1) + \left(\frac{mD}{M_T} + \frac{2MD^3}{M_T} \right) (e^{-2i\delta} - e^{-i\delta}) + \frac{m}{M_T} (D^3 - E^2 D) (e^{i\delta} - \\
& e^{2i\delta}) + \left(\frac{mD}{M_T} + \frac{2MD^3}{M_T} \right) (1 - e^{i\delta}) \Big\} + k_{r\theta} \left\{ \left(\frac{M}{M_T} E^3 - \frac{2m+M}{M_T} D^2 E \right) \right. \\
& (1 - e^{i\delta}) - \frac{M}{M_T} E (e^{-i\delta} - 1) \Big\} + k_{r\theta}, \left\{ \frac{m}{M_T} (D^2 E - E^3) (1 - e^{i\delta}) \right. \\
& + \left(\frac{mE}{M_T} + \frac{2MD^2 E}{M_T} \right) (e^{-i\delta} - 1) \Big\} + k_{r\theta 1} \left\{ \left(\frac{M}{M_T} E^3 - \frac{2m+M}{M_T} D^2 E \right) \right. \\
& (e^{-i\delta} - 1) - \frac{M}{M_T} E (e^{-2i\delta} - e^{-i\delta}) \Big\} + k_{r\theta 1}, \left\{ \frac{m}{M_T} (D^2 E - E^3) \right. \\
& (e^{i\delta} - e^{2i\delta}) + \left(\frac{mE}{M_T} + \frac{2MD^2 E}{M_T} \right) (1 - e^{i\delta}) \Big\} \\
C_{34} = & 2 k_{\theta\theta 0} \left(- DE^3 \frac{M}{M_T} + D^3 E \frac{2m+M}{M_T} + \frac{M}{M_T} D E e^{-i\delta} \right) + 2 k_{\theta, \theta 0}, \\
& \left(\frac{m^2}{M_T^2} D^3 E - \frac{m^2}{M_T^2} DE^3 + \frac{m^2}{M_T^2} D E e^{-i\delta} + \frac{2Mm}{M_T^2} D^3 E e^{-i\delta} + \frac{M}{M_T} D^3 E \right. \\
& e^{i\delta} - \frac{M}{M_T} DE^3 e^{i\delta}) + \\
& 2 k_{\theta\theta}, \left\{ \left(\frac{Mm}{M_T^2} DE^3 - \frac{2m^2+Mm}{M_T^2} D^3 E \right) e^{-i\delta} - \frac{Mm}{M_T^2} D E e^{-2i\delta} - \frac{m}{M_T} \right. \\
& (D^3 E - E^3 D) e^{i\delta} - \left(\frac{mDE}{M_T} + \frac{2MD^2 E}{M_T} \right) + \frac{M}{M_T} D E \left(\frac{M}{M_T} E^2 - \frac{2m+M}{M_T} D^2 \right) \\
& - \frac{M^2}{M_T^2} D E e^{-i\delta} \Big\} + 2 k_{\theta\theta 1} \left\{ - \frac{2m+M}{M_T} D^3 E e^{i\delta} - \left(\frac{2M}{M_T} DE^3 - \frac{2m+M}{M_T} \right. \right. \\
& D^3 E) e^{-i\delta} + \frac{2M}{M_T} D E e^{-2i\delta} + \frac{2M}{M_T} D E \Big\} + 2 k_{\theta, \theta 1}, \left\{ \frac{m^2}{M_T^2} (D^3 E - \right.
\end{aligned}$$

$$\begin{aligned}
& DE^3) e^{-i\delta} + \left(\frac{m^2}{M_T^2} D E + \frac{2MmD^3E}{M_T^2} \right) e^{-2i\delta} + \frac{m^2}{M_T^2} (D^3 E - DE^3) e^{i\delta} \\
& + \frac{Mm}{M_T^2} (D^3 E - DE^3) e^{2i\delta} + \left(\frac{m^2}{M_T^2} DE + \frac{2Mm}{M_T^2} D^3 E \right) + \left(\frac{Mm}{M_T^2} D E + \right. \\
& \left. \frac{2M^2D^3E}{M_T^2} \right) e^{i\delta} + \frac{Mm}{M_T^2} (D^3 E - DE^3) + \left(\frac{Mm}{M_T^2} DE + \frac{2M^2D^3E}{M_T^2} \right) e^{-i\delta} \Big\} \\
& + k_r \theta \left\{ \left(\frac{M}{M_T} E^2 - \frac{2m+M}{M_T} D^2 \right) - \frac{M}{M_T} e^{-i\delta} + \left(\frac{Mm}{M_T^2} E^2 - \frac{m(2m+M)}{M_T^2} D^2 \right) \right. \\
& \left. - \frac{Mm}{M_T^2} e^{-i\delta} + \left(\frac{M^2}{M_T^2} E^2 - \frac{M(2m+M)}{M_T^2} D^2 \right) e^{-i\delta} - \frac{M^2}{M_T^2} \right\} + k_r \theta, \\
& \left\{ \frac{m}{M_T} (D^2 - E^2) e^{i\delta} + \left(\frac{m}{M_T} + \frac{2MD^2}{M_T} \right) + \frac{m^2}{M_T^2} (D^2 - E^2) + \left(\frac{m^2}{M_T^2} + \right. \right. \\
& \left. \left. \frac{2Mm}{M_T^2} D^2 \right) e^{-i\delta} + \frac{Mm}{M_T^2} (D^2 - E^2) e^{i\delta} + \left(\frac{Mm}{M_T^2} + \frac{2M^2}{M_T^2} D^2 \right) \right\} + k_r \theta_1 \\
& \left\{ \left(\frac{M}{M_T} E^2 - \frac{2m+M}{M_T} D^2 \right) e^{i\delta} - \frac{M}{M_T} + \left(\frac{Mm}{M_T^2} E^2 - \frac{2m^2+Mm}{M_T^2} D^2 \right) e^{-i\delta} - \right. \\
& \left. \frac{Mm}{M_T^2} e^{-2i\delta} + \left(\frac{M^2}{M_T^2} E^2 - \frac{2Mm+M^2}{M_T^2} D^2 \right) - \frac{M^2}{M_T^2} e^{-i\delta} \right\} + k_r \theta_1, \left\{ \frac{m}{M_T} \right. \\
& (D^2 - E^2) + \left(\frac{m}{M_T} + \frac{2MD^2}{M_T} \right) e^{-i\delta} + \frac{m^2}{M_T^2} (D^2 - E^2) e^{i\delta} + \left(\frac{m^2}{M_T^2} + \right. \\
& \left. \frac{2Mm}{M_T^2} D^2 \right) + \frac{Mm}{M_T^2} (D^2 - E^2) e^{2i\delta} + \left(\frac{Mm}{M_T^2} + \frac{2M^2D^2}{M_T^2} \right) e^{i\delta} \Big\} \\
C_{33} = & K_{rr0} + K_r r_0, \left\{ \left(\frac{m^2}{M_T^2} + \frac{M^2}{M_T^2} \right) + \frac{Mm}{M_T^2} e^{i\delta} + \frac{Mm}{M_T^2} e^{-i\delta} \right\} + \\
& K_{rr1}, \left(\frac{m}{M_T} e^{i\delta} + \frac{m}{M_T} e^{i\delta} + \frac{2M}{M_T} \right) + K_{rr1} (e^{i\delta} + e^{-i\delta}) + K_r r_1, \\
& \left(\frac{m^2}{M_T^2} e^{i\delta} + \frac{m^2}{M_T^2} e^{-i\delta} + \frac{Mm}{M_T^2} e^{2i\delta} + \frac{Mm}{M_T^2} e^{-2i\delta} + \frac{2Mm}{M_T^2} + \frac{M^2}{M_T^2} \right. \\
& \left. e^{i\delta} + \frac{M^2}{M_T^2} e^{-i\delta} \right) + 4 k_{\theta\theta_0} D^2 E^2 + 4 k_{\theta, \theta_0} D^2 E^2 \left\{ \frac{m^2}{M_T^2} + \frac{M^2}{M_T^2} \right. \\
& \left. + \frac{Mm}{M_T^2} (e^{i\delta} + e^{-i\delta}) \right\} + 4 k_{\theta\theta_1} D^2 E^2 \left(-\frac{m}{M_T} e^{i\delta} - \frac{m}{M_T} e^{-i\delta} - \right.
\end{aligned}$$

$$\begin{aligned}
& \frac{2M}{M_T}) + 4 k_{\theta\theta_1} D^2 E^2 (e^{i\delta} + e^{-i\delta}) + 4 k_{\theta, \theta_1} D^2 E^2 \left\{ \frac{m^2}{M_T^2} e^{i\delta} + \frac{m^2}{M_T^2} e^{-i\delta} + \frac{Mm}{M_T^2} (e^{2i\delta} + e^{-2i\delta}) + \frac{2Mm}{M_T^2} + \frac{M^2}{M_T^2} (e^{i\delta} + e^{-i\delta}) \right\} \\
& + 2 k_r \theta D E \left\{ -2 - 2 \frac{m}{M_T} - \frac{M}{M_T} (e^{i\delta} + e^{-i\delta}) \right\} + 2 k_r \theta_1 D E \\
& \left\{ \frac{m}{M_T} (e^{i\delta} + e^{-i\delta}) + \frac{2M}{M_T} + \frac{2m^2}{M_T^2} + \frac{2Mm}{M_T^2} (e^{-i\delta} + e^{i\delta}) + \frac{2M^2}{M_T^2} \right\} \\
& + 2 k_r \theta_1 D E \left\{ -e^{i\delta} - e^{-i\delta} - \frac{m}{M_T} (e^{i\delta} + e^{-i\delta}) \right\} + 2 k_r \theta_1 D E \\
& \left\{ \frac{2m}{M_T} + \frac{M}{M_T} (e^{i\delta} + e^{-i\delta}) + \frac{m^2}{M_T^2} (e^{i\delta} + e^{-i\delta}) + \frac{2Mm}{M_T^2} + \frac{2Mm}{M_T^2} \right. \\
& \left. (e^{2i\delta} + e^{-2i\delta}) + \frac{M^2}{M_T^2} (e^{i\delta} + e^{-i\delta}) \right\} \\
C_{44} = k_{\theta\theta_0} & \left\{ \frac{M^2}{M_T^2} E^4 + \left(\frac{2m+M}{M_T} \right)^2 D^4 + \frac{M^2}{M_T^2} - \frac{M^2}{M_T^2} E^2 e^{-i\delta} - \frac{M^2}{M_T^2} \right. \\
& E^2 e^{i\delta} + \frac{M}{M_T} \frac{2m+M}{M_T} e^{-i\delta} + \frac{M(2m+M)}{M_T^2} e^{i\delta} \left. \right\} + k_{\theta, \theta_0} \left\{ \frac{m^2}{M_T^2} (D^2 - \right. \\
& E^2) + \left(\frac{m}{M_T} + \frac{2MD^2}{M_T} \right) + \frac{m^2}{M_T^2} D^2 (e^{i\delta} + e^{-i\delta}) + \frac{2Mm}{M_T^2} D^4 (e^{i\delta} + e^{-i\delta}) \\
& - \frac{m^2}{M_T^2} E^2 (e^{i\delta} + e^{-i\delta}) - \frac{2Mm}{M_T^2} D^2 E^2 (e^{i\delta} + e^{-i\delta}) + k_{\theta\theta} \\
& \left\{ \left(\frac{M}{M_T} E^2 - \frac{2m+M}{M_T} D^2 \right) \left(\frac{m}{M_T} D^2 - \frac{m}{M_T} E^2 \right) (e^{i\delta} + e^{-i\delta}) - \frac{Mm}{M_T^2} (D^2 - \right. \\
& E^2) (e^{2i\delta} + e^{-2i\delta}) + 2 \left(\frac{m}{M_T} + \frac{2MD^2}{M_T} \right) \left(\frac{M}{M_T} E^2 - \frac{2m+M}{M_T} D^2 \right) - \frac{M}{M_T} \\
& \left(\frac{m}{M_T} + \frac{2MD^2}{M_T} \right) (e^{i\delta} + e^{-i\delta}) + k_{\theta\theta_1} \left\{ \left(\frac{M}{M_T} E^2 - \frac{2m+M}{M_T} D^2 \right) (e^{i\delta} + \right. \\
& e^{-i\delta}) - \left(\frac{M^2}{M_T^2} E^2 - \frac{M(2m+M)}{M_T^2} D^2 \right) (e^{2i\delta} + e^{-2i\delta}) - \frac{2M}{M_T} \left(\frac{M}{M_T} E^2 - \right. \\
& \frac{2m+M}{M_T} D^2) + \frac{M^2}{M_T^2} (e^{-i\delta} + e^{i\delta}) \left. \right\} + k_{\theta, \theta_1} \left\{ \frac{m^2}{M_T^2} (D^2 - E^2)^2 (e^{i\delta} + \right. \\
& e^{-i\delta}) + \left(\frac{m^2}{M_T^2} + \frac{2Mm}{M_T^2} D^2 \right) (D^2 - E^2) (e^{2i\delta} + e^{-2i\delta}) + 2 \left(\frac{m^2}{M_T^2} + \right.
\end{aligned}$$

$$\frac{2Mm}{M_T^2} D^2 (D^2 - E^2) + \left(\frac{m}{M_T} + \frac{2MD^2}{M_T} \right)^2 (e^{i\delta} + e^{-i\delta}) \}.$$

D. Frequencies of the framework Vibrations

If the molecule is in the crystalline state only a very small number among its fundamentals can give rise to infrared absorption. The fundamentals which can be strong in absorption are only those in which the dipole change in each repeating unit has the same amplitude phase. For a finite chain, the intensity of these vibrations in which repeating units do not have the same amplitude phase can be shown to be very much weaker; for an infinite chain they will have zero intensity. Thus, if there are p characteristic groups in each repeating unit, then according to the above criterion, only those modes for which

$$\delta = \frac{2\pi r}{p} \quad (3-33)$$

(where $r = 0, \dots, p-1$) can be potentially active in absorption. Whether even those will be active depends on the change of dipole moment associated with them.

According to Deeds⁵ the expression for the changing dipole moment parallel to the axis of the chain is given as

$$M_{11} = M_0 e^{i(\omega t - \epsilon\pi)} \cos \left[\frac{1}{2}(N-1)\delta + \epsilon\pi \right] \sin \frac{1}{2} N\delta / \sin \frac{1}{2} \delta \quad (3-34)$$

For changes in the dipole moment perpendicular to the axis of the chain at an angle \mathcal{I} to the initial direction from which rotations are measured, the result of the analysis is that

$$M_{\perp} = \frac{1}{2} M_0 e^{i(\omega t - \epsilon\pi)} \left\{ \cos \left[\frac{1}{2} (N-1) (\delta + \psi) + \epsilon\pi - \mathcal{I} \right] \right. \\ \left. \sin \frac{1}{2} N (\delta + \psi) / \sin \frac{1}{2} (\delta + \psi) + \cos \left[\frac{1}{2} (N-1) (\delta - \psi) + \right. \right. \\ \left. \left. + \epsilon\pi + \mathcal{I} \right] \sin \frac{1}{2} N (\delta - \psi) / \sin \frac{1}{2} (\delta - \psi) \right\} \quad (3-35)$$

where M_0 = the maximum value of the changing dipole moment for a repeating unit,

δ = the amplitude phase difference,

$2\pi\epsilon$ = the phase change of traveling wave on reflection at end of chain ($0 \leq \epsilon \leq 1$),

and ψ = the angular displacement from one repeating unit to the next about the central axis of the chain. If the molecule is planar zigzag, $\psi = \pi$.

The intensity of infrared absorption lines is proportional to $e^{-h\gamma/kT} (M)^2$, where γ is the frequency of the vibration or rotation involved, and M is the change produced in the electric dipole moment.

The molecules under our consideration have $p = 2$ in equation (3-32). Therefore there should be two potentially active fundamentals. They occur when

$$\delta = 0 \quad \text{and} \quad \delta = \pi. \quad (3-36)$$

Fortunately, many of the off-diagonal elements in the secular determinant (3-31) vanish when δ equals 0. When $\delta = 0$, secular determinant (3-31) can be factored into the following blocks:

$$C_{11} \ ; \quad C_{22} \ ; \quad \begin{vmatrix} C_{33} & C_{34} \\ C_{34} & C_{44} \end{vmatrix} \ . \quad (3-37)$$

Therefore, when $\delta = 0$, the roots $\omega_j(\delta)$ of the secular determinant (3-31) are given by:

$$\omega_1(0) = 0 \text{ (translation parallel to axis of chain)} \quad (3-38a)$$

$$\omega_2(0) = 0 \text{ (translation perpendicular to axis of chain)} \quad (3-38b)$$

$$\omega_3(0) = \left\{ \frac{(C_1 + C_2) + \sqrt{(C_1 + C_2)^2 - 4(C_1 C_2 - C_3^2)}}{2\mu} \right\}^{\frac{1}{2}} \quad (3-38c)$$

$$\omega_4(0) = \left\{ \frac{(C_1 + C_2) - \sqrt{(C_1 + C_2)^2 - 4(C_1 C_2 - C_3^2)}}{2\mu} \right\}^{\frac{1}{2}} \quad (3-38d)$$

where

$$C_1 = K_{rr0} + K_{r'r_0'} + 2 K_{rr'} + 2 K_{rr1} + 2 K_{r'r_1'} + 4 k_{\theta\theta_0} D^2 E^2 + 4 k_{\theta'\theta_0'} D^2 E^2 - 8 k_{\theta\theta'} D^2 E^2 + 8 k_{\theta\theta_1} D^2 E^2 + 8 k_{\theta'\theta_1'} D^2 E^2 - 8 k_{r\theta} D E + 8 k_{r'\theta'} D E - 8 k_{r\theta_1} D E + 8 k_{r'\theta_1'} D E$$

$$C_2 = k_{\theta\theta_0} \left\{ E^4 \frac{4M^2}{M_T^2} + \left(\frac{2m+M}{M_T} \right)^2 D^4 + \frac{M^2}{M_T^2} - 2 E^2 \left(\frac{M^2}{M_T^2} \right) + \frac{4Mm+2M^2}{M_T^2} \right\} + k_{\theta'\theta_0'} \left\{ D^2 \left(\frac{3m^2}{M_T^2} + \frac{2M}{M_T} \right) - E^2 \left(\frac{3m^2}{M_T^2} \right) + \frac{4MmD^4}{M_T^2} - \frac{4MmD^2E^2}{M_T^2} + \frac{m}{M_T} \right\} + 2 k_{\theta\theta'} \left\{ \left(\frac{M}{M_T} E^2 - \frac{2m+M}{M_T} D^2 \right) \left(\frac{m}{M_T} D^2 - \frac{m}{M_T} E^2 \right) - \frac{Mm}{M_T^2} (D^2 - E^2) + \left(\frac{m}{M_T} + \frac{2MD^2}{M_T^2} \right) \left(\frac{M}{M_T} E^2 - \frac{2m+M}{M_T} D^2 \right) - \frac{M}{M_T} \left(\frac{m}{M_T} + \frac{2MD^2}{M_T^2} \right) \right\} + 2 k_{\theta\theta_1} \left\{ \left(\frac{M}{M_T} E^2 - \frac{2m+M}{M_T} D^2 \right) - \left(\frac{M^2}{M_T^2} E^2 - \frac{M(2m+M)}{M_T^2} D^2 \right) - \frac{M}{M_T} \left(\frac{M}{M_T} E^2 - \frac{2m+M}{M_T} D^2 \right) + \frac{M^2}{M_T^2} \right\} + 2 k_{\theta'\theta_1'} \left\{ \frac{m^2}{M_T^2} (D^2 - E^2)^2 + \left(\frac{m^2}{M_T^2} + \frac{2Mm}{M_T^2} D^2 \right) (D^2 - E^2) + \left(\frac{m^2}{M_T^2} + \frac{2Mm}{M_T^2} D^2 \right) + \left(\frac{m}{M_T} + \frac{2MD^2}{M_T^2} \right)^2 \right\}$$

$$C_3 = 2 k_{\theta\theta_0} \left(-DE^3 \frac{M}{M_T} + D^3 E \frac{2m+M}{M_T} + D E \frac{M}{M_T} \right) + 2 k_{\theta'\theta_0'} \left(D^3 E \frac{m^2}{M_T^2} - DE^3 \frac{m^2}{M_T^2} + \frac{m^2}{M_T^2} D E + \frac{2Mm}{M_T^2} D^3 E + \frac{M}{M_T} D^3 E - \frac{M}{M_T} DE^3 \right) - 8 k_{\theta\theta'} D^2 E^2 + 2 k_{\theta\theta_1} \left(\frac{M}{M_T} D E + \frac{M}{M_T} - \frac{M}{M_T} DE^3 \right) + 4 k_{\theta'\theta_1'} \left\{ \frac{m^2}{M_T^2} D E (D^2 - \right.$$

$$\begin{aligned}
& E^2) + \left(\frac{m^2}{M_T^2} D E + \frac{2MmD^3E}{M_T^2} \right) + \frac{Mm}{M_T^2} D E (D^2 - E^2) + \left(\frac{Mm}{M_T^2} D E + \frac{2M^2}{M_T^2} \right. \\
& \left. D^3 E \right) \} + k_r \theta \left\{ E^2 \left(\frac{M}{M_T} + \frac{Mm}{M_T^2} + \frac{M^2}{M_T^2} \right) - D^2 \left(\frac{2m+M}{M_T} + \frac{m(2m+M)}{M_T^2} + \right. \right. \\
& \left. \left. \frac{M(2m+M)}{M_T^2} \right) - \frac{M}{M_T} - \frac{Mm}{M_T^2} - \frac{M^2}{M_T^2} \right\} + k_r \theta' \left\{ E^2 \left(-\frac{m}{M_T} - \frac{m^2}{M_T^2} - \right. \right. \\
& \left. \left. \frac{Mm}{M_T^2} \right) + 2 D^2 \left(\frac{m}{M_T} + \frac{M}{M_T} + \frac{m^2}{M_T^2} + \frac{2Mm}{M_T^2} + \frac{M^2}{M_T^2} \right) \right\} + k_r \theta_1 \left\{ \left(\frac{M}{M_T^2} E^2 \right. \right. \\
& \left. \left. - \frac{2m+M}{M_T} D^2 \right) - \frac{M}{M_T} + \frac{Mm}{M_T^2} E^2 - \frac{2m^2+Mm}{M_T^2} D^2 - \frac{Mm}{M_T^2} + \frac{M^2}{M_T^2} E^2 - \right. \\
& \left. \frac{2Mm+M^2}{M_T^2} D^2 - \frac{M^2}{M_T^2} \right\} + k_r \theta_1' \left(\frac{m}{M_T} D^2 - \frac{m}{M_T} E^2 + \frac{m}{M_T} + \frac{2MD^2}{M_T} \right. \\
& \left. + \frac{m^2}{M_T^2} D^2 - \frac{m^2}{M_T^2} E^2 + \frac{m^2}{M_T^2} + \frac{3Mm}{M_T^2} D^2 + \frac{Mm}{M_T^2} E^2 + \frac{Mm}{M_T^2} + \frac{2M^2D^2}{M_T^2} \right).
\end{aligned}$$

When $\delta = \pi$, the off-diagonal elements in the secular determinant (3-31) do not vanish. Therefore, we have used a graphical method to find numerical values for roots $\omega_j(\pi)$. These roots are tabulated for certain specific molecules in Tables VII, VIII, XIII, and XIV.

If we solve the determinant (3-31) when $\delta = \pi$, we obtain the following algebraic secular equation:

$$(\omega^2)^4 + A(\omega^2)^3 + B(\omega^2)^2 + C\omega^2 + D = 0.$$

where

$$\begin{aligned}
A &= - \frac{1}{M_T^2 \mu^2} \left\{ \mu M_T^2 (C_{33} + C_{44}) + M_T \mu^2 (C_{11} + C_{22}) \right\} \\
B &= \frac{1}{M_T^2 \mu^2} \left\{ C_{33} C_{44} M_T^2 - C_{34}^2 M_T^2 - M_T \mu (C_{33} + C_{44}) (C_{11} + C_{22}) \right. \\
&\quad \left. + C_{11} C_{22} \mu^2 - M_T \mu C_{23}^2 - M_T \mu C_{24}^2 - \mu^2 C_{12}^2 - M_T \mu C_{14}^2 \right\}
\end{aligned}$$

$$C = \frac{1}{M_T^2 \mu^2} \left\{ -M_T C_{33} C_{44} (C_{11} + C_{22}) + M_T C_{34}^2 (C_{11} + C_{22}) \right. \\
- \mu C_{11} C_{22} (C_{33} + C_{44}) + M_T C_{23}^2 C_{44} - M_T C_{24}^2 C_{34} + \mu C_{11} C_{23}^2 \\
- M_T C_{24} C_{23} C_{34} + M_T C_{24}^2 C_{33} + \mu C_{24}^2 C_{11} + \mu C_{12}^2 (C_{33} + C_{44}) \\
- \mu C_{13} C_{12} C_{23} + \mu C_{12} C_{24} C_{13} - \mu C_{24} C_{12} C_{14} - M_T C_{14} C_{13} C_{34} \\
\left. + M_T C_{14}^2 C_{33} + \mu C_{14}^2 C_{22} \right\}$$

$$D = \frac{1}{M_T^2 \mu^2} (C_{11} C_{22} C_{33} C_{44} - C_{11} C_{22} C_{34}^2 - C_{11} C_{23}^2 C_{44} + 2 C_{11} C_{23} \\
C_{34} C_{24} - C_{11} C_{33} C_{24}^2 - C_{33} C_{44} C_{12}^2 + C_{12}^2 C_{34}^2 + C_{12} C_{23} C_{13} C_{44} \\
- C_{12} C_{23} C_{34} C_{14} + C_{12} C_{24} C_{34} C_{14} - C_{14} C_{12} C_{23} C_{34} + C_{14} C_{12} C_{24} C_{33} \\
+ C_{22} C_{14} C_{13} C_{34} - C_{14}^2 C_{22} C_{33} - C_{14} C_{23} C_{13} C_{24} + C_{14}^2 C_{23}^2)$$

and

$$C_{11} = 4 K_r r_0 D^2 - 8 K_r r_1 D^2 + 4 k_{\theta\theta_0} E^2 + 4 k_{\theta' \theta_0'} E^2 - 8 k_{\theta\theta'} E^2 \\
- 8 k_{\theta\theta_1'} E^2 - 8 k_{\theta' \theta_1'} E^2 + 8 k_{r\theta} DE + 8 k_{r\theta'} DE - 8 k_{r\theta_1} DE - 8 k_{r\theta_1'} DE$$

$$C_{12} = 4 K_r r_0 DE - 4 k_{\theta\theta_0} DE + 4 k_{\theta' \theta_0'} DE + 4 k_{\theta\theta'} DE + 4 k_{\theta\theta_1'} DE \\
- 4 k_{\theta' \theta_1'} DE - 4 k_{r\theta} D^2 + 4 k_{r\theta'} E^2 + 4 k_{r\theta'} + 4 k_{r\theta_1} D^2 - 4 k_{r\theta_1} \\
E^2 - 4 k_{r\theta_1'} D^2 - 4 k_{r\theta_1'} E^2$$

$$C_{13} = 2 K_r r_0 D \left(\frac{m}{M_T} - \frac{M}{M_T} \right) - 2 K_r r_1 D \left(\frac{m}{M_T} - \frac{M}{M_T} \right) \\
- 4 k_{\theta\theta_0} DE^2 + 4 k_{\theta' \theta_0'} DE^2 \left(\frac{m}{M_T} - \frac{M}{M_T} \right) + 4 k_{\theta\theta'} DE^2 \left(1 + \frac{M}{M_T} \right) \\
- 4 k_{\theta\theta_1'} DE^2 - 8 k_{\theta' \theta_1'} DE^2 \left(\frac{m}{M_T} - \frac{M}{M_T} \right) + 2 k_{r\theta} (E - 2 D^2 E + \\
\frac{Em}{M_T} - \frac{ME}{M_T}) + 2 k_{r\theta'} E (-1 + \frac{2m}{M_T} D^2 - \frac{2M}{M_T} D^2 + \frac{m}{M_T} - \frac{M}{M_T}) \\
+ 2 k_{r\theta_1} E (-1 + 2 D^2 - \frac{m}{M_T} + \frac{M}{M_T})$$

$$C_{14} = 2 k_{\theta\theta_0} \left(\frac{M}{M_T} E^2 - \frac{2m+M}{M_T} D^2 + \frac{M}{M_T} E \right) + 2 k_{\theta' \theta_0'} \left(\frac{m}{M_T} (D^2 E - \\
E^3) - \frac{Em}{M_T} - \frac{2MD^2 E}{M_T} + 2 k_{\theta\theta'} \left(\frac{2m+M}{M_T} D^2 E - \frac{M}{M_T} E^3 - \frac{ME}{M_T} + \frac{mE}{M_T} \right) \right.$$

$$\begin{aligned}
& + \frac{2MD^2E}{M_T}) + 4 k_{\theta\theta_1} \left(\frac{(2m+M)}{M_T} D^2 E - \frac{M}{M_T} E^3 - \frac{ME}{M_T} \right) + 2 k_{\theta'\theta_1'} \\
& \left(\frac{m}{M_T} E^3 - \frac{m}{M_T} D^2 E + \frac{2mE}{M_T} + \frac{4MD^2E}{M_T} \right) + 2 k_{r\theta} \left(\frac{M}{M_T} E^2 D - \frac{2m+M}{M_T} D^3 \right. \\
& \left. + \frac{M}{M_T} D \right) + 2 k_{r\theta'} \left(\frac{m}{M_T} D^3 - \frac{m}{M_T} DE^2 - \frac{mD}{M_T} - \frac{2MD^3}{M_T} \right) + 2 k_{r\theta_1} \\
& \left(\frac{2m+M}{M_T} D^3 - \frac{M}{M_T} E^2 D - \frac{MD}{M_T} \right) + 2 k_{r\theta_1'} \left(\frac{m}{M_T} E^2 D - \frac{m}{M_T} E^2 D - \right. \\
& \left. \frac{m}{M_T} D^3 + \frac{mD}{M_T} + \frac{2MD^2}{M_T} \right)
\end{aligned}$$

$$\begin{aligned}
C_{22} = & 4 K_{r'r_0'} E^2 - 4 K_{rr'} E^2 + 4 k_{\theta\theta_0} D^2 + 4 k_{\theta'\theta_0'} D^2 + 8 k_{\theta\theta'} D^2 \\
& - 8 k_{\theta\theta_1} D^2 - 8 k_{\theta'\theta_1'} D^2 - 8 k_{r\theta} DE + 8 k_{r\theta'} DE + 8 k_{r\theta_1} DE \\
& - 8 k_{r\theta_1'} DE
\end{aligned}$$

$$\begin{aligned}
C_{23} = & -2 K_{rr'} E + 2 K_{r'r_1'} \frac{Em}{M_T} \left(-1 + \frac{2EM}{M_T} - \frac{Em}{M_T} \right) + 4 k_{\theta\theta_0} D^2 E \\
& + 4 k_{\theta'\theta_0'} D^2 E \left(\frac{m}{M_T} - \frac{M}{M_T} \right) + 4 k_{\theta\theta'} D^2 E \left(1 + \frac{m}{M_T} - \frac{2M}{M_T} \right) \\
& - 8 k_{\theta\theta_1} D^2 E + 8 k_{\theta'\theta_1'} D^2 E \left(-\frac{m}{M_T} + \frac{M}{M_T} \right) + 2 k_{r\theta} \left(-D - 2DE^2 \right. \\
& \left. - \frac{m}{M_T} D + \frac{M}{M_T} D \right) + 2 k_{r\theta'} \left(-D + \frac{2m}{M_T} DE^2 - \frac{2M}{M_T} DE^2 + \frac{m}{M_T} D - \frac{M}{M_T} D \right) \\
& + 2 k_{r\theta_1} \left(D + 2DE^2 + \frac{m}{M_T} D - \frac{M}{M_T} D \right) + 2 k_{r\theta_1'} \left(-D - \frac{2m}{M_T} DE^2 - \right. \\
& \left. \frac{m}{M_T} D + \frac{MD}{M_T} \right)
\end{aligned}$$

$$\begin{aligned}
C_{24} = & 2 k_{\theta\theta_0} D \left(-\frac{ME^2}{M_T} + \frac{(2m+M)D^2}{M_T} - \frac{M}{M_T} \right) + 2 k_{\theta'\theta_0'} D \left(\frac{m}{M_T} D^2 - \right. \\
& \left. \frac{m}{M_T} E^2 - \frac{2M}{M_T} D^2 \right) + 2 k_{\theta\theta'} D \left(\frac{M}{M_T} E^2 - \frac{2m+M}{M_T} D^2 + 2DE - \frac{M}{M_T} + \right. \\
& \left. \frac{2Mm}{M_T^2} DE - \frac{m}{M_T} - \frac{2MD}{M_T} - \frac{2MDE}{M_T} \right) + 4 k_{\theta\theta_1} D \left(\frac{M}{M_T} E^2 + \frac{2m+M}{M_T} D^2 - \right. \\
& \left. 2DE + \frac{M}{M_T} \right) + 4 k_{\theta'\theta_1'} D \left(\frac{m}{M_T} E^2 - \frac{m}{M_T} D^2 + \frac{m}{M_T} + \frac{2MD^2}{M_T} \right) + 2 k_{r\theta} E \\
& \left(\frac{M}{M_T} E^2 - \frac{2m+M}{M_T} D^2 + \frac{M}{M_T} \right) + 2 k_{r\theta'} E \left(\frac{m}{M_T} D^2 - \frac{m}{M_T} E^2 - \frac{m}{M_T} - \frac{2MD^2}{M_T} \right)
\end{aligned}$$

$$\begin{aligned}
& + 2 k_r \theta_1 E \left(\frac{2m+M}{M_T} D^2 - \frac{M}{M_T} E^2 - \frac{M}{M_T} \right) + 2 k_r \theta_1' E \left(\frac{m}{M_T} E^2 - \right. \\
& \left. \frac{m}{M_T} D^2 + \frac{m}{M_T} + \frac{2MD^2}{M_T} \right) \\
C_{33} = & K_{rr0} + K_{r'r_0'} \left(\frac{m^2}{M_T^2} + \frac{M^2}{M_T^2} - \frac{2Mm}{M_T^2} + 2 K_{rr'} \left(\frac{M}{M_T} - \frac{m}{M_T} \right) - \right. \\
& 2 K_{rr1} - 2 K_{r'r_1'} \left(\frac{m^2}{M_T^2} + \frac{M^2}{M_T^2} - \frac{2Mm}{M_T^2} \right) + 4 k_{\theta\theta_0} D^2 E^2 + 4 k_{\theta'} \theta_0' \\
& D^2 E^2 \left(\frac{m^2}{M_T^2} + \frac{M^2}{M_T^2} - \frac{2Mm}{M_T^2} \right) + 8 k_{\theta\theta'} D^2 E^2 \left(\frac{m}{M_T} - \frac{M}{M_T} \right) - 8 k_{\theta\theta_1} \\
& D^2 E^2 - 8 k_{\theta'} \theta_1' D^2 E^2 \left(\frac{m^2}{M_T^2} + \frac{M^2}{M_T^2} - \frac{2Mm}{M_T^2} \right) - 4 k_r \theta DE \left(1 + \frac{m}{M_T} \right. \\
& \left. - \frac{M}{M_T} \right) + 4 k_r \theta' DE \left(\frac{M}{M_T} + \frac{m^2}{M_T^2} - \frac{m}{M_T} - \frac{2Mm}{M_T^2} + \frac{M^2}{M_T^2} \right) + 4 k_r \theta_1 DE \\
& \left(1 + \frac{m}{M_T} \right) + 4 k_r \theta_1' DE \left(\frac{m}{M_T} - \frac{M}{M_T} - \frac{m^2}{M_T^2} + \frac{2Mm}{M_T^2} - \frac{M^2}{M_T^2} \right) \\
C_{34} = & 2 k_{\theta\theta_0} DE \left(- \frac{M}{M_T} E^2 + \frac{2m+M}{M_T} D^2 - \frac{M}{M_T} \right) + 2 k_{\theta'} \theta_0' DE \left(\frac{m^2}{M_T^2} D^2 - \right. \\
& \frac{m^2}{M_T^2} E^2 - \frac{m^2}{M_T^2} - \frac{2Mm}{M_T^2} D^2 - \frac{M}{M_T} D^2 + \frac{M}{M_T} E^2 \left. \right) + 2 k_{\theta\theta'} DE \left(\frac{2m^2+Mm}{M_T^2} D^2 \right. \\
& \left. - \frac{Mm}{M_T^2} E^2 - \frac{Mm}{M_T^2} + \frac{m}{M_T} D^2 - \frac{m}{M_T} E^2 - \frac{2MD^2}{M_T} + \frac{M^2}{M_T^2} E^2 - \frac{2Mm+M^2}{M_T^2} D^2 \right. \\
& \left. + \frac{M^2}{M_T^2} \right) + 4 k_{\theta\theta_1} DE \left(\frac{M}{M_T} E^2 + \frac{2M}{M_T} \right) + 4 k_{\theta'} \theta_1' DE \left(\frac{m^2}{M_T^2} E^2 - \frac{m^2}{M_T^2} D^2 \right. \\
& \left. + \frac{m^2}{M_T^2} + \frac{3Mm}{M_T^2} D^2 - \frac{Mm}{M_T^2} E^2 - \frac{Mm}{M_T^2} - \frac{2M^2 D^2}{M_T^2} + k_r \theta \left(\frac{M}{M_T} E^2 - \right. \right. \\
& \frac{2m+M}{M_T} D^2 + \frac{M}{M_T} + \frac{Mm}{M_T^2} E^2 - \frac{2m^2+Mm}{M_T^2} D^2 + \frac{Mm}{M_T^2} - \frac{M^2}{M_T^2} E^2 + \frac{2Mm+M}{M_T^2} D^2 \\
& \left. - \frac{M^2}{M_T^2} \right) + k_r \theta' \left(\frac{m}{M_T} E^2 - \frac{m}{M_T} D^2 + \frac{m}{M_T} + \frac{2MD^2}{M_T} + \frac{m^2}{M_T^2} D^2 - \frac{m^2}{M_T^2} E^2 \right. \\
& \left. - \frac{m^2}{M_T^2} - \frac{3Mm}{M_T^2} D^2 + \frac{Mm}{M_T^2} E^2 + \frac{Mm}{M_T^2} + \frac{2M^2}{M_T^2} D^2 \right) + k_r \theta_1 \left(\frac{2m+M}{M_T} D^2 \right. \\
& \left. - \frac{M}{M_T} E^2 - \frac{M}{M_T} - \frac{Mm}{M_T} E^2 + \frac{2m^2+Mm}{M_T^2} D^2 - \frac{Mm}{M_T^2} + \frac{M^2}{M_T^2} E^2 - \frac{2Mm}{M_T^2} D^2 \right.
\end{aligned}$$

$$\begin{aligned}
& + \frac{M^2}{M_T^2}) + k_r \theta_1' \left(\frac{m}{M_T} D^2 - \frac{m}{M_T} E^2 - \frac{m}{M_T} - \frac{2MD^2}{M_T} - \frac{m^2}{M_T^2} D^2 + \right. \\
& \left. \frac{m^2}{M_T^2} E^2 + \frac{m^2}{M_T^2} + \frac{3Mm}{M_T^2} D^2 - \frac{Mm}{M_T^2} E^2 - \frac{Mm}{M_T^2} - \frac{2M^2 D^2}{M_T^2} \right) \\
C_{44} = & k_{\theta\theta_0} \left\{ \frac{M^2}{M_T^2} E^4 + \left(\frac{2m+M}{M_T} \right)^2 D^4 + \frac{M^2}{M_T^2} + \frac{2M^2}{M_T^2} E^2 - \frac{2(2Mm+M^2)}{M_T^2} \right\} \\
& + k_{\theta'\theta_0'} \left(\frac{m}{M_T} + \frac{2MD^2}{M_T} - \frac{m^2}{M_T^2} D^2 - \frac{4Mm}{M_T^2} D^4 + \frac{m^2}{M_T^2} E^2 + \frac{4Mm}{M_T^2} D^2 E^2 \right) \\
& - 2 k_{\theta\theta'} \left\{ \left(\frac{M}{M_T} E^2 - \frac{2m+M}{M_T} D^2 \right) \left(\frac{m}{M_T} D^2 - \frac{m}{M_T} E^2 \right) + \frac{Mm}{M_T^2} (D^2 - E^2) \right. \\
& + \left(\frac{m}{M_T} + \frac{2MD^2}{M_T} \right) \left(\frac{M}{M_T} E^2 - \frac{2m+M}{M_T} D^2 \right) - \frac{M}{M_T} \left(\frac{m}{M_T} + \frac{2MD^2}{M_T} \right) \left. \right\} - 2 k_{\theta\theta_1} \\
& \left\{ \left(\frac{M}{M_T} E^2 - \frac{2m+M}{M_T} D^2 \right) + \left(\frac{M^2}{M_T^2} E^2 - \frac{2Mm+M^2}{M_T^2} D^2 \right) + \frac{M}{M_T} \left(\frac{M}{M_T} E^2 - \right. \right. \\
& \left. \left. \frac{2m+M}{M_T} D^2 \right) + \frac{M^2}{M_T^2} \right\} - 2 k_{\theta'\theta_1'} \left\{ \frac{m^2}{M_T^2} (D^2 - E^2)^2 - \left(\frac{m^2}{M_T^2} + \right. \right. \\
& \left. \left. \frac{2Mm}{M_T^2} D^2 \right) (D^2 - E^2) - \left(\frac{m^2}{M_T^2} + \frac{2Mm}{M_T^2} D^2 \right) (D^2 - E^2) + \left(\frac{m}{M_T} + \frac{2MD^2}{M_T} \right)^2 \right. \\
& \left. \left. \right\} \right.
\end{aligned}$$

(3-39)

D. Numerical Calculations

In this section we shall calculate the actual frequencies of the framework vibrations involving coordinates x , y , p , and q for polyvinyl chloride and polyacrylonitrile. We shall use the constants and the force constants listed in Tables V, VI, XI and XII. The vibrational frequencies, $\bar{\nu}$, in cm^{-1} , are obtained from the roots of the algebraic secular equations (3-38) and (3-39) by the use of the relation $\bar{\nu} = \frac{\omega}{2\pi C}$.

For polyvinyl chloride we have found the following frequencies of the framework vibrations involving the coordinates, x, y, p and q.

When $\delta = 0$

$$\bar{\nu}_1(0) = 1188 \text{ cm.}^{-1}$$

$$\bar{\nu}_2(0) = 475 \text{ cm.}^{-1}$$

When $\delta = \pi$, the equation (3-39) becomes:

$$(\omega^2)^4 - 4.615 \times 10^{28} \times (\omega^2)^3 - 6.251 \times 10^{56} (\omega^2)^2 - 1.748 \times 10^{84} \omega^2 + 0.0426 \times 10^{112} = 0 \quad (3-40)$$

By putting the left-hand side of the equation (3-40) equal to K, we can plot a graph K versus ω^2 . We have obtained the graph shown in Figure 7 for polyvinyl chloride. We notice that two roots of the algebraic equation (3-40) in the 1-2000 cm.^{-1} range are:

$$\omega_3^2(\pi) = 7.5 \times 10^{28}$$

$$\omega_4^2(\pi) = 0.035 \times 10^{28}$$

Accordingly, when $\delta = \pi$

$$\bar{\nu}_3(\pi) = 1269 \text{ cm.}^{-1}$$

$$\bar{\nu}_4(\pi) = 93 \text{ cm.}^{-1}$$

For polyacrylonitrile, we have found the following frequencies of the framework vibrations involving the coordinates x, y, p, and q.

When $\delta = 0$

$$\bar{\nu}_1(0) = 1185 \text{ cm.}^{-1}$$

$$\bar{\nu}_2(0) = 648 \text{ cm.}^{-1}$$

When $\delta = \pi$, the equation (3-39) becomes:

$$(\omega^2)^4 - 4.601 \times 10^{28} (\omega^2)^3 - 6.264 \times 10^{56} (\omega^2)^2 - 1.734 \times 10^{84} \omega^2 + 0.0421 \times 10^{112} = 0 \quad (3-41)$$

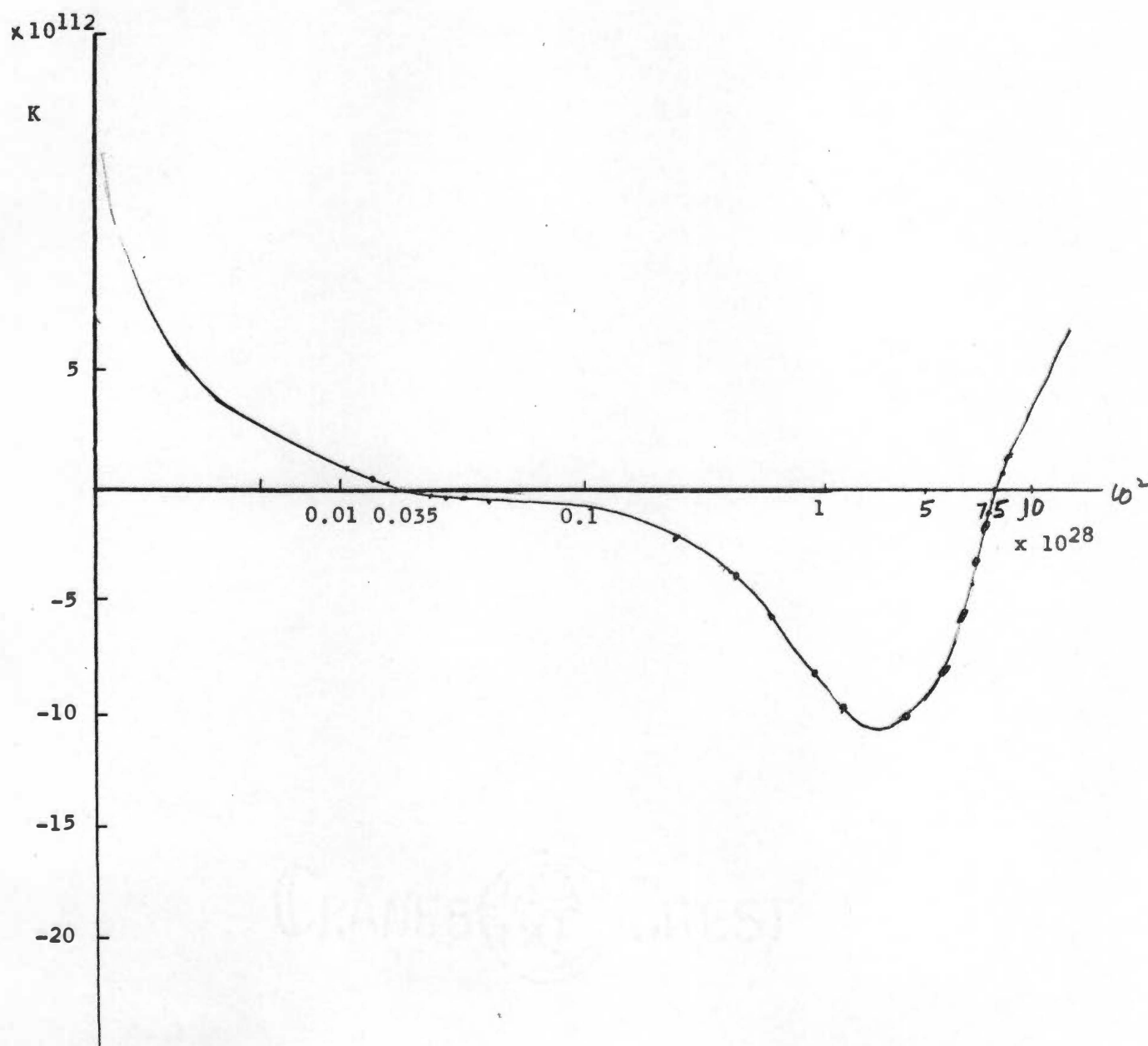


Figure 7. The Roots of the Algebraic Equation (3-40) in 1-2000 cm.^{-1} Range.

By putting the left-hand side of the equation (3-41) equal to K, we can plot a graph K versus ω^2 . For polyacrylonitrile, we have obtained the graph similar to what we obtained for polyvinyl chloride. Thus, we have obtained two roots of the algebraic equation (3-41) in the 1-2000 cm.^{-1} range as

$$\omega_3^2 = 5.74 \times 10^{28}$$

$$\omega_4^2 = 0.031 \times 10^{28}.$$

Accordingly, when $\delta = \pi$,

$$\bar{\nu}_3(\pi) = 1214 \text{ cm.}^{-1}$$

$$\bar{\nu}_4(\pi) = 98 \text{ cm.}^{-1}.$$

CHAPTER IV

VIBRATIONAL ANALYSIS OF POLYVINYL CHLORIDE

A. General Considerations

Vinyl chloride¹⁰ can be produced by the dehydrohalogenation of ethylene chloride. Vinyl chloride polymerizes readily in the presence of peroxides to a hard brittle resin in which the units are linked regularly in a head-to-tail fashion. In order to achieve a complete assignment of the infrared and Raman spectra of a molecule, some knowledge of its structure or possible structures is necessary. Otherwise, a complete determination of selection rules and normal modes is not possible. If the structure is not known with certainty, it nevertheless serves as a useful starting point for the analysis. The structure of polyvinyl chloride is presumed to be based on a head-to-tail arrangement of the $-\text{CH}_2\text{CH}(\text{Cl})-$ monomer units. The chemical structure could therefore be written $(-\text{CH}_2\text{CHCl}-)_n$. The X-ray diffraction pattern of oriented specimens, however, shows¹¹ that the fundamental repeat distance along the chain axis is about 5 Å. This suggests¹¹ that, although the carbon chain backbone is a planar zigzag, the chlorine atoms are alternately on opposite sides of the plane of the carbon chain. Thus, the crystallographic repeating unit consists of two monomer units. This suggested structure of polyvinyl chloride is shown schematically in Figure 8. The C_2 axes coincide with the two-fold axes of the CH_2 groups, the mirror planes σ_v coincide with the planes of the CHCl groups, and the glide plane σ_g is the plane of the carbon backbone. In analyzing

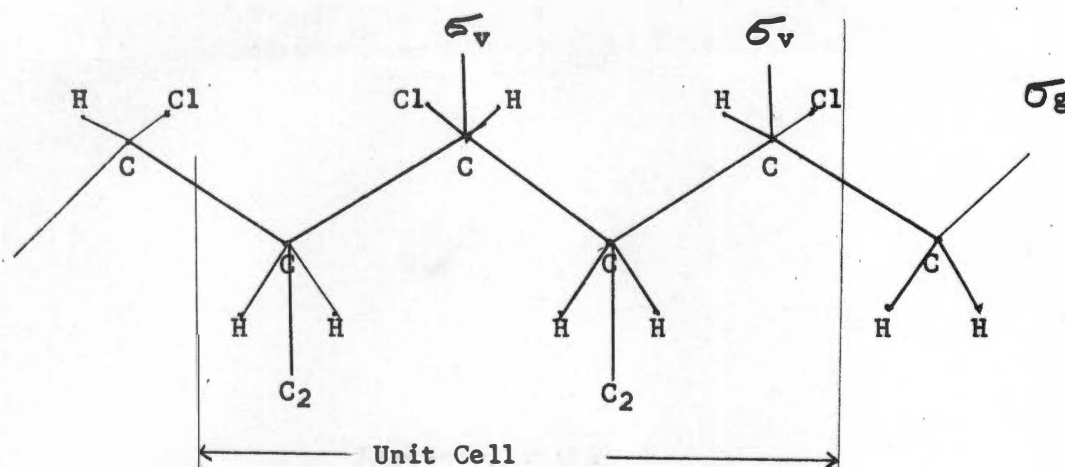


Figure 8. Structure of Polyvinyl Chloride.

the infrared spectrum, it is also important to know what proportion of the sample is crystalline. We already discussed in Chapter III the differences in the spectra of the crystalline and amorphous polymers.

Infrared spectra in the region of $300\text{--}1500\text{ cm.}^{-1}$ have been reported for polyvinyl chloride by Thompson and Tarkington.^{12,13} Polarized infrared studies on oriented polyvinyl chloride in the region of about 800 to 3000 cm.^{-1} have been obtained by Elliott, Ambrose, and Temple.¹⁴ Infrared spectra in the extended range of 70 to 3000 cm.^{-1} have been obtained by Krimm and Liang.¹⁵ The one-dimensional space group for the polyvinyl chloride structure shown in Figure 6 has a factor group isomorphic to the point group C_{2v} . Therefore we can obtain the symmetry species, characters, and selection rules which are shown in Table III.

TABLE III

CHARACTER TABLE, SYMMETRY SPECIES, AND SELECTION RULES FOR
POLYVINYL CHLORIDE

C_{2v}	E	C_2	σ_v	σ_g	IR	R
A_1	1	1	1	1	a	a
A_2	1	1	-1	-1	f	a
B_1	1	-1	1	-1	a	a
B_2	1	-1	-1	1	a	a

a = active; f = forbidden

B. Frequencies of Framework Vibrations

In order to make numerical calculations, we need to know the equilibrium configuration of polyvinyl chloride. The necessary constants are listed in Table IV.

TABLE IV

THE EQUILIBRIUM CONFIGURATION OF POLYVINYL CHLORIDE

Reference	C-C Bond Distance (Å)	C-H Bond Distance (Å)	C-Cl Bond Distance (Å)	C-C-C Angle	Cl-C-H Angle
Syrkin and Dyatkina ¹⁶	1.54	1.071	1.69	109°28' (Assumed)	110°30'
Muller ¹⁷	1.54-1.55			114°	
Bauer ¹⁸	1.50	1.08			
Dieke and Kistiakowsky ¹⁹		1.1			
Pauling and Brockway ²⁰	1.53-1.54	1.09 ± 0.03		111°	111°30'
Assumed here	1.54	1.071	1.69	111°30'	109°28'

From the data in Table IV and the well-known masses of the hydrogen, carbon and chlorine atoms, we can calculate the constants we need. The results are given in Table V.

TABLE V
CONSTANTS USED IN THIS ANALYSIS

Symbol	Description	Value
m_H	mass of hydrogen atom	1.6732×10^{-24} gm.
m_C	mass of carbon atom	19.9230×10^{-24} gm.
m_{Cl}	mass of chlorine atom	59.103×10^{-24} gm.
$m = m_C + 2 m_H$	mass of CH_2 group	23.2694×10^{-24} gm.
$M = m_C + m_H + m_{Cl}$	mass of $CHCl$ group	80.593×10^{-24} gm.
$M_T = m + M$	total mass of one repeating unit	103.2694×10^{-24} gm.
$\mu = \frac{Mm}{M_T}$	reduced mass of one repeating unit	18.123×10^{-24} gm.
θ	$(CH_2) - (CHCl) - (CH_2)$ angle	101°
θ'	$(CHCl) - (CH_2) - (CHCl)$ angle	101°
r_0	$(CH_2) - (CHCl)$ bond distance	1.65 \AA

Using known force constants from similar molecules, we shall make a complete assignment of the infrared active fundamental band sets in the polyvinyl chloride spectra. A set of force constants which works well for some other molecules^{5,21} is listed in Table VI.

TABLE VI
A SET OF FORCE CONSTANTS

Nominal Force Constant		In Units of 10^5 Dynes/Cm.
$K_{rr_0} \approx K_{r'r'_0}$	=	4.44
$k_{\theta\theta_0} \approx k_{\theta'\theta'_0}$	=	0.35
$k_{\phi\phi_0} \approx k_{\phi'\phi'_0}$	=	0.311
$k_{aa_0} \approx k_{a'a'_0}$	=	4.8
$k_{aa1} \approx k_{a'a'_1}$	=	0.34
$k_{\beta\beta_0} \approx k_{\beta'\beta'_0}$	=	12
$k_{\beta\beta1} \approx k_{\beta'\beta'_1}$	=	1.06
$k_{\gamma\gamma_0} \approx k_{\gamma'\gamma'_0}$	=	15
$k_{\gamma\gamma1} \approx k_{\gamma'\gamma'_1}$	=	0.167
K_{C-Cl}	=	3.64
K_{C-H}	=	4.79
$k_{\theta\theta_0}$ (for Cl-C-H angle)	=	0.58

The numerical calculations in section D of Chapter III lead us to assign the infrared active fundamental band sets for the framework vibrations as shown in Table VII.

C. The Frequency Assignment of Infrared Spectrum of Polyvinyl Chloride

We shall interpret the assignments made in section B of this chapter and complete assignments for other band sets.

In the $100\text{--}200\text{ cm.}^{-1}$ region, there occur three weak infrared band sets. It is believed that these band sets are due mainly to framework

TABLE VII
INFRARED FREQUENCY ASSIGNMENT FOR THE FRAMEWORK VIBRATIONS
OF THE POLYVINYL CHLORIDE

Observed Frequency in cm.^{-1}	Intensity	Calculated Frequency in cm.^{-1}	Assignment	Coordinates Involved
102	vw^a	93	chain bending when $\delta = \pi$	x, y, p, q
160	w^b	197	torsional when $\delta = \pi$	ζ
182	w }			
430	w	410	(HCCl) rocking	α
487	w	475	chain bending when $\delta = 0$	p, q
693	m	725	(CH ₂) rocking	α'
833	w	819	(HCCl) twisting	β
963	m	950	(CH ₂) twisting	β'
1096	m	1036	(HCCl) wagging	γ
1125	vw	1188	chain stretching when $\delta = 0$	p, q
1235	vw	1269	chain stretching when $\delta = \pi$	x, y, p, q

^a vw = very weak.

^bw = weak.

vibrations. Using the force constant²¹ $k_{\theta\theta_0} = 0.311 \times 10^5$ dynes/cm. (for the cyclic chain molecules), we have calculated possible frequency of torsional vibration. It turned out to be at 294 cm.^{-1} . Therefore we have adjusted the value of $k_{\theta\theta_0}$ so that we may have the frequency of

torsional vibration at 197 cm^{-1} . The adjusted value of $k_{\theta\theta_0}$ is $0.15 \times 10^5 \text{ dynes/cm}$.

From the result we obtained in section D of Chapter III we have assigned to chain bending vibration (when $\delta = \pi$) the band at 102 cm^{-1} . These assignments are different from those given by Krimm and Liang.¹⁵

A comparison of the spectra of $\text{CH}_3\text{CH}_2\text{Cl}$,²² $\text{CH}_3\text{CHClCH}_3$ ²³ suggests that the C-Cl stretching frequencies lie approximately in the region between 600 and 700 cm^{-1} while the C-Cl bending frequencies are found at about 300 to 400 cm^{-1} . From this we have assigned to C-Cl bending vibrations the bands at 315 and 363 cm^{-1} . We have assigned C-Cl stretching modes for the two bands at 615 and 635 cm^{-1} .

Our numerical calculations have led us to assign to (CH_2) rocking mode the band at 693 cm^{-1} and to (CH_2) twisting vibration the band at 963 cm^{-1} . These assignments agree with those given by the author in the analysis of cyclic chain molecules.²¹ We notice that assignments are different from those given by Krimm and Liang.¹⁵ It was suggested by Krimm and Liang that the band at 635 cm^{-1} arises from interactions in the crystalline regions of the polymer or due to rotational isomers of the polymer chain which are present in the amorphous region. But our calculation leads to the prediction that the band at 635 cm^{-1} is also assigned to C-Cl bending vibration. This assignment is also supported by Mizushima and Shimanouchi.²⁴

The bands at 430 and 480 cm^{-1} were assigned by Krimm and Liang to the degenerate chain bending modes $\gamma-(\pi/2)$ and $\gamma-(3\pi/2)$. But our numerical calculations in Section D of Chapter IV which is based on a

new transformation (3-26) has led us to believe that we should assign to chain bending mode when $\delta = 0$ the band at 487 cm.^{-1} . We have assigned to (HCCl) rocking vibration the band at 430 cm.^{-1} .

From our calculations we expect a band set at 735 cm.^{-1} which should be assigned to the (CH₂) wagging vibration. But this mode does not seem to be assignable to any band in the spectrum. It is clear that the spectrum of a deuterated polymer would be most helpful on this point.

In the $800\text{--}1200 \text{ cm.}^{-1}$ region, where no strongly infrared active fundamentals of characteristic groups are expected, infrared band sets are believed to be due mainly to framework vibrations. Our theory developed in section C of Chapter IV has proved to be most valuable on this point. The results of our numerical calculations in section D of Chapter IV and the results obtained from the expressions (3-25) show clearly that the band at 833 cm.^{-1} should be assigned to (HCCl) twisting vibration when $\delta = 0$, the band at 1096 cm.^{-1} should be assigned to (HCCl) wagging vibrations when $\delta = 0$. Furthermore, they show that the bands at 1125 and 1235 cm.^{-1} should be assigned to chain stretching vibrations when $\delta = 0$ and $\delta = \pi$ respectively. Krimm and Liang¹⁵ could not assign to any vibrational mode the band at 1235 cm.^{-1} .

Our calculations confirmed the assignment of the band at 1197 cm.^{-1} to a (CH) wagging vibration which was predicted by Krimm and Liang with less certainty. The fact that the band set covering the frequency range $1140\text{--}1250 \text{ cm.}^{-1}$ is weak in the infrared but strong in the Raman spectrum lends support to the assignment of this band set.

There is little doubt about the assignments of the strongly infrared active band sets from the detailed analyses of small molecules.²⁵ The strong band at 1427 cm^{-1} is undoubtedly caused by the (CH_2) stretching mode, although it is at a somewhat lower frequency than the corresponding mode at about 1460 cm^{-1} in polyethylene.²⁶ By analogy with the polyethylene case, we may assign the 1352 cm^{-1} band to the (CH_2) wagging mode. The two bands at 1330 and 1250 cm^{-1} are most probably assignable to the two (CH) bending modes. It is well-established that the band at 1250 cm^{-1} corresponds to the (CH) bending mode.

For the assignments of C-Cl modes, it is probable that they are mixed with the framework vibrations. We notice that the (CCl) wagging mode is forbidden by the selection rules.

The four expected CH and CH_2 stretching vibrations are undoubtedly to be assigned to the four high frequency bands at 2820 , 2849 , 2920 , and 2967 cm^{-1} . By analogy with the corresponding modes at 2853 and 2925 cm^{-1} in polyethylene²⁶ and normal paraffin,⁵ we can assign the 2849 cm^{-1} band to the symmetric (H-C-H) stretching vibration and the 2920 cm^{-1} to the unsymmetric (H-C-H) stretching mode.

A complete assignment of the infrared spectrum of the polyvinyl chloride is listed in Table VIII.

TABLE VIII
FREQUENCY ASSIGNMENTS OF THE INFRARED SPECTRUM OF THE
POLYVINYL CHLORIDE

Observed Frequency in cm^{-1}	Intensity	Calculated Frequency in cm^{-1}	Assignment Given in this Analysis	Assignment Given by Krimm and Liang ¹⁵
102	vw^a	93	chain bending when $\delta = \pi$	$(\pi/2)^b$
160	w	197	torsional when $\delta = \pi$	$(3\pi/2)$
182	w			
315	vw	328	(C-Cl) bending	$\delta_w(\text{CCl})$
363	w			$\delta(\text{CCl})$
430	w	411	(HCCl) rocking	$\rho_- (3\pi/2)$
615	s	658	(C-Cl) stretching	$\rho(\text{CCl})$
635	s			$\rho(\text{CCl})$
693	m	725	(CH ₂) rocking	$\rho(\text{CCl})$
833	w	819	(HCCl) twisting	$\rho_+ (\pi/2)$
963	m	950	(CH ₂) twisting	$\rho_+ (3\pi/2)$
1096	m	1036	(HCCl) wagging	$\rho_+ (0)$
1125	vw	1188	chain stretching when $\delta = 0$	$\rho_+ (\pi)$
1197	w	1194	(CH) wagging	$\delta_w(\text{CH})$
1235	vw	1269	chain stretching when $\delta = \pi$	
1250	s	1249	(CH) wagging	$\delta(\text{CH})$
1330	m	1337	(CH) bending	$\delta(\text{CH})$
1352	vw	1379	(CH ₂) wagging	$\delta_w(\text{CH}_2)$
1427	s	1468	sym. H-C-H bending	$\delta(\text{CH}_2)$
2820	vw	2819	(CH) stretching	$\rho(\text{CH})$

TABLE VIII (CONTINUED)

Observed Frequency in cm^{-1}	Intensity	Calculated Frequency in cm^{-1}	Assignment Given in this Analysis	Assignment Given by Krimm and Liang ¹⁵
2849	w	2865	sym. C-H stretching	γ_s (CH ₂)
2920	m	2925	unsym. C-H stretching	γ_a (CH ₂)
2967	w	2972	(CH) stretching	γ (CH)

^aw = weak; vw = very weak; s = strong.

^b γ = stretching; δ = bending; γ_r = rocking; γ_w = wagging;
 γ_t = twisting; s = symmetric; a = antisymmetric.

CHAPTER V

VIBRATIONAL ANALYSIS OF POLYACRYLONITRILE

A. General Considerations

Acrylonitrile is made from either ethylene or acetylene as a starting point.¹⁰ Acrylonitrile long has been used as a co-monomer in the synthesis of synthetic rubbers and plastics. When polymerized alone, it forms a solid resin which is composed of linear polymers. The solution of this resin can be spun into threads, which led to the introduction in 1948 of a new synthetic fiber known as Orlon. This fiber is especially resistant to deterioration by weathering and sunlight and finds extensive use for fabrics for outdoor use. Acrilan and Dynel are other trade names for this polymer.

The infrared spectrum of polyacrylonitrile in the rocksalt region has been studied by Harms²⁷ and Burlant.²⁸ The infrared spectrum of polyacrylonitrile in the 70-3000 cm^{-1} range was obtained by Krimm and Liang.²⁹

The structure of polyacrylonitrile is presumed to be based on a head-to-tail arrangement of $-\text{CH}_2\text{CH}(\text{CN})-$ monomer units. The configuration has been thought to be an atactic one, the irregular arrangement of the CN groups being inferred from the quality of the X-ray diffraction pattern.³⁰ However, it is now believed that the structure is actually isotactic, but in a helical conformation. Since the $\text{C}\equiv\text{N}$ bond has been investigated thoroughly, we may apply the theory developed in Chapter IV to find the vibrational modes of polyacrylonitrile. That is, we treat

the $C\equiv N$ group as an instantaneously rigid rotator in finding normal modes of $(N\equiv C-CH)$ characteristic group.

The one dimensional space group of the structure of polyacrylonitrile has a factor group isomorphic with the point group C_{2v} . Therefore we can obtain the symmetry species, characters, and selection rules which are shown in Table III.

B. Frequencies of Framework Vibrations

In order to make numerical calculations, we need to know the equilibrium configuration of the polyacrylonitrile molecule. The necessary constants are listed in Table IX.

TABLE IX

THE EQUILIBRIUM CONFIGURATION OF POLYACRYLONITRILE^{25,16}

C-C Bond Distance (Å)	C-H Bond Distance (Å)	C≡N Bond Distance (Å)	C-C-C Angle	C-N-C-H Angle
1.54	1.071	1.15	109°28'	110°

From the data in Table IX and the well-known masses of the hydrogen, carbon, and nitrogen atoms, we can calculate the constants we need. The results are given in Table X.

From the results we obtained in section D of Chapter III, and the numerical values obtainable from the expressions (3-25), we may assign the fundamental band sets to the framework vibrations of polyacrylonitrile.

TABLE X
CONSTANTS USED IN THE ANALYSIS OF POLYACRYLONITRILE

Symbol	Description	Value
m_H	mass of hydrogen	1.6732×10^{-24} gm.
m_C	mass of carbon	19.9230×10^{-24} gm.
m_N	mass of nitrogen	23.258×10^{-24} gm.
$m = m_C + 2 m_H$	mass of CH_2 group	23.2694×10^{-24} gm.
$M = 2 m_C + m_H + m_N$	mass of $(NCCH)$ group	64.577×10^{-24} gm.
$M_T = m + M$	total mass of one repeating unit	87.846×10^{-24} gm.
$u = \frac{Mm}{M+m}$	reduced mass of one repeating unit	17.15×10^{-24} gm.
θ_0	C-C-C angle	101°
θ'	C-C-H angle	110°
r_0	$(CH_2)-(NCCH)$ bond distance	1.65 \AA

The assignments of the infrared active fundamental band sets are shown in Table XII. The set of force constants used here is listed in Table XI.

C. The Frequency Assignments of Infrared Spectrum of Polyacrylonitrile

We shall interpret the assignments made in section B of this chapter and complete assignments for other band sets. The result of our calculations in section D of Chapter IV leads us to assign the 86 cm.^{-1} band to a chain bending vibration when $\delta = \pi$. This assignment is different from

TABLE XI
A SET OF FORCE CONSTANTS

Nominal Force Constant		In Units of 10^5 Dynes/Cm.
$k_{rr_0} \approx k_{r'r'_0}$	=	4.44
$k_{\theta\theta_0} \approx k_{\theta'\theta'_0}$	=	0.35
$k_{\theta\theta_0} \approx k_{\theta'\theta'_0}$	=	0.311
$k_{aa_0} \approx k_{a'a'_0}$	=	4.8
$k_{aa_1} \approx k_{a'a'_1}$	=	0.34
$k_{\beta\beta_0} \approx k_{\beta'\beta'_0}$	=	12
$k_{\beta\beta_1} \approx k_{\beta'\beta'_1}$	=	1.06
$k_{\gamma\gamma_0} \approx k_{\gamma'\gamma'_0}$	=	15
$k_{\gamma\gamma_1} \approx k_{\gamma'\gamma'_1}$	=	0.167
k_{C-C-N}	=	4.50
k_{C-H}	=	4.79
$k_{\theta\theta_0}$ (for $N\equiv C-C-H$ group)	=	0.55

TABLE XII

 INFRARED FREQUENCY ASSIGNMENTS FOR THE FRAMEWORK VIBRATIONS
 OF POLYACRYLONITRILE

Observed Frequency in cm.^{-1}	Intensity	Calculated Frequency in cm.^{-1}	Assignment	Coordinates Involved
86	w	98	chain bending when $\delta = \pi$	x, y, p, q
675	w	648	chain bending when $\delta = 0$	p, q
778	m	725	(CH ₂) rocking	α'
862	vw	803	(HCCN) twisting	β
1044	(sh)	950	(CH ₂) twisting	β'
1073	s	1024	(HCCN) wagging	γ
1115 1175	(sh) (sh)	1185	chain stretching when $\delta = 0$	p, q
1227	mw	1214	chain stretching when $\delta = \pi$	x, y, p, q
1359 1375	ms (sh)	1379	(CH ₂) wagging	γ
1447	vs	1468	sym. H-C-H bending	internal co- ordinates of (CH ₂) group
2870	m	2865	sym. C-H stretching	internal co- ordinates of (CH ₂) group
2940	vs	2925	unsym. C-H stretching	internal co- ordinates of (CH ₂) group

the one given by Krimm and Liang. It is believed that this band set is due mainly to framework vibrations.

Most of the CH_2 modes can be readily assignable as in the previous studies of other polymers. The σ bands at 2940, 2870, and 1447 cm^{-1} are undoubtedly to be assigned to unsymmetric C-H stretching, symmetric C-H stretching and symmetric C-H bending, respectively.

The π band at 1359 cm^{-1} is assigned to (CH_2) wagging vibration. The corresponding modes for polyethylene,²⁶ polyvinyl chloride and polyvinylidene chloride,¹⁵ polystyrene³¹ and polyvinyl alcohols³² all are observed near the same frequency.

Assignments of $\text{C}\equiv\text{N}$ modes are given by Krimm and Liang²⁹ and Herzberg.²⁵

A complete assignment of the observed bands is shown in Table XIII, together with our calculated values.

In the 800–1250 cm^{-1} region, where no strongly infrared active fundamentals are expected, except the 1073 band, infrared band sets are believed to be due mainly to the framework vibrations. The results of our calculations in section D of Chapter III show clearly that there ought to be five frequencies there. However, the assignment of the 1073 band is doubtful. It is probable that this is one of the combination bands, since many of the weak bands in the spectrum can be assigned as overtones or combinations of the fundamentals. The assignment of the 1375 cm^{-1} band is different from the one given by Krimm and Liang. The results of our calculations in section D of Chapter III shows that the 1227 cm^{-1} band should be assigned to the chain stretching vibration, al-

though Krimm and Liang argued that it should be assigned to (CH₂) twisting mode. On this point more experimental investigations are needed, with deuterated compounds.

TABLE XIII

FREQUENCY ASSIGNMENTS OF INFRARED SPECTRUM OF THE POLYACRYLONITRILE

Observed Frequency in cm. ⁻¹	Intensity	Calculated Frequency in cm. ⁻¹	Assignment Given in this Analysis	Assignment Given by Krimm and Liang ¹⁵
86	mw	98	chain bending when $\delta = \pi$	8 (CH ₂)- δ_w (CH ₂)
127	vs		(CN) wagging	δ_w (CN)
259	ms	267	(C-CN) wagging	δ_w (C-CN)
430	w		(CN) bending	δ (CN)
532	m	489	(C-CN) bending	δ (C-CN)
675	w	648	chain bending when $\delta = 0$	δ_w (CN) + δ (C-CN)
778	m	725	CH ₂ rocking	δ_r (CH ₂) γ (C-CN)
862	vw	803	(HCCN) twisting	2 x δ (CN)
1044	(sh)	950	(CH ₂) twisting	γ + (0)
1073	s	1024	(HCCN) wagging	γ + (π)
1115 1175	(sh) (sh)	1185	chain stretching when $\delta = 0$	(C-CN) + δ_w (C-CN) + δ_w (CN) = 1171?
1227	mw	1214	chain stretching when $\delta = \pi$	δ_t (CH ₂)
1247	s	1249	(CH) wagging	δ_w (CH)
1310	w	1337	(CH) bending	δ (CH)

TABLE XIII (CONTINUED)

Observed Frequency in cm. ⁻¹	Intensity	Calculated Frequency in cm. ⁻¹	Assignment Given in this Analysis	Assignment Given by Krimm and Liang ¹⁵
1359	ms	1379	(CH ₂) wagging	δ_w (CH ₂) (CH ₃) group?
1375	(sh)			
1447	vs	1468	(CH ₂) bending	δ (CH ₂) bending
2237	vs		(CN) stretching	ν (CN) stretching
2810	vw	2819	(CH) stretching	
2870	m	2865	sym. H-C-H stretch- ing	
2940	vs	2925	unsym. H-C-H stretch- ing	

CHAPTER VI

SUMMARY AND CONCLUSIONS

For a complete utilization of molecular spectral data, it is necessary to make a mathematical study of the vibrations, and often also of the rotations, of the molecules. It is believed that the procedures described in this dissertation provide a systematic method for analyzing the vibrations of large molecules. Actually, rotations turn out to be special forms of normal modes of vibration in this method of treatment.

The theoretical analysis has been facilitated by:

- (i) Use of the Multiple Origin Method. This effects a great simplification in the kinetic energy function and leaves the vibrational secular determinant in symmetrical form.
- (ii) Use of group theory. The theory of groups gives insight into the use of symmetry to break up complicated problems into easier ones. It also provides selection rules and indicates the kinds of interactions which occur.
- (iii) Extension of the method, originally developed by Lagrange,³³ in which it is assumed that the normal modes in a chain-type structure are standing waves formed by the superposition of traveling waves progressing along the chain. The dependence of normal frequencies upon the amplitude phase difference is obtained.
- (iv) Introduction of a new transformation, based on physical considerations. This new transformation enables us to reduce the

secular determinant of the framework vibrations into soluble form for the type of molecule considered here.

The results obtained in this dissertation may be summarized as follows:

(1) Although Shaffer⁹ has developed a general method for analyzing unsymmetrical three-particle systems, there are difficulties in applying his method to actual molecules. In section B of Chapter III, a new approach of analyzing unsymmetrical three-particle systems was attempted and found to be successful in obtaining the fundamental frequencies for such a characteristic group.

(2) The determination of the fundamental frequencies of the framework vibrations is quite complicated for the molecules considered here. In section C of Chapter IV, the framework vibrations of a planar zigzag chain molecule were analyzed in detail. It was found that the orientation of displacement coordinates ξ_n, η_n, ζ_n , which works well for chain molecules containing two identical characteristic groups per unit cell, such as normal paraffin and polyethylene, is inappropriate for chain molecules containing two different characteristic groups, such as polyvinyl chloride and polyacrylonitrile. A new orientation of displacement coordinates $\xi_n, \eta_n, \zeta_n, \xi'_n, \eta'_n, \zeta'_n$ was introduced and found to be useful in analyzing the framework vibrations of planar zigzag chain molecules containing two different characteristic groups. It appears that there is no practical straightforward mathematical method to reduce the secular determinant of the framework vibrations into a soluble analytic form. However, various transformations based on physical considerations have been tried. The

new transformation (3-26) was found to reduce the determinant into a soluble form. Furthermore, the new coordinates obtained by the transformation (3-26) have physical significance.

(3) In Chapters IV and V new assignments of the infrared active fundamental band sets in polyvinyl chloride and polyacrylonitrile have been made on the basis of the rigorous theory developed in Chapter III. Some of the frequency assignments given by Krimm and Liang^{15,29} are different from the corresponding assignments given here. It appears that Krimm and Liang made frequency assignments on the basis of calculated values of polyethylene.²⁶ We should expect that the vibrational analyses of polyvinyl chloride and polyacrylonitrile are different from the analysis of polyethylene, since polyvinyl chloride and polyacrylonitrile have two different characteristic groups in each repeating unit while polyethylene has two identical characteristic groups in each repeating unit. The results of this dissertation make our assignments seem more plausible. This emphasizes the importance of detailed mathematical analyses of specific molecules.

(4) From the analyses of normal paraffin⁵ and cyclic chain molecules,²¹ the infrared band sets in the $1\text{--}200\text{ cm.}^{-1}$ region are believed to be due to torsional framework vibrations. Using the force constant $k_{\theta\theta_0} = 0.31 \times 10^5$ dynes/cm. to calculate a predicted frequency of the torsional framework vibration, we have found it to be at 296 cm.^{-1} for polyacrylonitrile and 287 cm.^{-1} for polyvinyl chloride. Since there are no band sets at those frequencies for those molecules, we have adjusted the force constant $k_{\theta\theta_0}$ to be $k_{\theta\theta_0} = 0.151 \times 10^5$ dynes/cm. so that we may assign

the band at 197 cm.^{-1} to the torsional framework vibration when $\delta = 0$. This new force constant $k_{\theta\theta_0} = 0.151 \times 10^5 \text{ dynes/cm.}$ and the assignments of the normal frequencies involved in the motion of ξ, η, ξ', η' would give useful information to guide experimental study of chain molecules, particularly in determining the field of force, the equilibrium configuration, symmetry and specific heats of the molecules. This torsional mode is unobservable in such molecules as the normal paraffins, so that the torsional force constant could not be determined for them, although it should be very similar to that obtained here.

A great deal of theoretical and experimental work remains to be done. The theoretical part will consist of carrying out a study including more interactions between framework and internal motions and between various neighbors, and study of the modes of helical chains, since it seems that this is a likely type of conformation. The experimental part will consist of making spectra of deuterated molecules in order to help establish the correct assignment of the various band sets.

This dissertation is a necessary first step in understanding some of the properties of some very important synthetic fibers. It is hoped that future extensions of this work will make it possible to understand the behavior of all sorts of extended molecules and fibers.

BIBLIOGRAPHY

BIBLIOGRAPHY

1. Crawford, B. L., Jr. and Brinkley, S. R., Jr., J. Chem. Phys., 9, 69 (1941).
2. Long, H. C., Ph. D. Dissertation, The Ohio State University, 1948.
3. Pliskin, W. A., Ph. D. Dissertation, The Ohio State University, 1949.
4. Kidder, R. E., Ph. D. Dissertation, The Ohio State University, 1950.
5. Deeds, W. E., Ph. D. Dissertation, The Ohio State University, 1951.
6. Eckart, C., Phys. Rev., 47, 552 (1935).
7. Dennison, D. M., Rev. Mod. Phys., 3, 280 (1931).
8. Yates, R. C., Phys. Rev., 36, 555 (1930).
9. Shaffer, W. H. and Schuman, R. P., J. Chem. Phys., 12, 506 (1944).
10. Noller, C. R., Chemistry of Organic Compounds. Philadelphia and London: W. B. Saunders Company, 1951.
11. Fuller, C. S., Chem. Rev., 26, 143 (1940).
12. Thompson, H. W. and Torkington, P., Proc. Roy. Soc., A184, 21 (1945).
13. Thompson, H. W. and Torkington, P., Trans. Faraday Soc., 41, 246 (1945).
14. Elliott, A., Ambrose, E. J., and Temple, R. B., J. Chem. Phys., 16, 877 (1948).
15. Krimm, S. and Liang, C. Y., J. Polymer Sci., 22, 95 (1956).
16. Syrkin, Y. K. and Dyatkina, M. E., Structure of Molecules and the Chemical Bond. New York: Interscience Publications, Inc., 1950.
17. Muller, A., Proc. Roy. Soc. (London), A120, 437 (1928).
18. Bauer, S. H., J. Chem. Phys., 4, 407 (1936).
19. Dieke, G. H. and Kistiakowsky, G. B., Phys. Rev., 45, 4 (1934).
20. Pauling, L. and Brockway, L. O., J. Am. Chem. Soc., 59, 1223 (1937).
21. Suh, S. K., M. S. Thesis, The University of Tennessee, 1959.

22. Daasch, L. W., Liang, C. Y. and Nielsen, J. Rud, J. Chem. Phys., 22, 1293 (1954).
23. Landolt-Bornstein, Zahlenwerte and Functionen, I, Springer, Berlin, 1951.
24. Mizusima and Shimanouchi, J. Chem. Phys., 26, 970 (1957).
25. Herzberg, G., Molecular Spectra and Molecular Structure II.. Infrared and Raman Spectra of Polyatomic Molecules. New York: D. Van Nostrand Company, Inc.
26. Liang, C. Y., Krimm, S. and Sutherland, G. B. B. M., J. Chem. Phys., 25, 549 (1956).
27. Harms, D., Anal. Chem., 25, 1140 (1953).
28. Burlant, W. J. and Parsons, J. L., J. Polymer Sci., 22, 249 (1956).
29. Krimm, S. and Liang, C. Y., J. Polymer Sci., 31, 513 (1958).
30. Bunn, C. W., Fibres from Synthetic Polymers, R. Hill, Ed., Elsevier, Amsterdam, 1953, p. 229.
31. Liang, C. Y. and Krimm, S., J. Polymer Sci., 27, 241 (1958).
32. Krimm, S., Liang, C. Y. and Sutherland, G. B. B. M., J. Polymer Sci., 22, 227 (1956).
33. Lagrange, J. L., Mécanique Analytique, Paris: DeSaint, 1788, Tome I.