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Gabriel Kron

Citation: [The Journal of Chemical Physics](#) **14**, 19 (1946); doi: 10.1063/1.1724056

View online: <http://dx.doi.org/10.1063/1.1724056>

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Electric Circuit Models for the Vibration Spectrum of Polyatomic Molecules

GABRIEL KRON*

General Electric Company, Schenectady, New York

(Received August 20, 1945)

Electrical circuits are developed to determine the normal frequencies and normal modes of vibration of polyatomic molecules having arbitrary configurations. The networks for each molecule are set up without equations from physical considerations alone and may be solved by an a.c. network analyzer, by numerical methods, or by digital (punch card, etc.) calculating machines. The networks also allow the establishment of the resultant secular equations of the molecule by simple inspection. The potential function considered is either a general quadratic form of the displacements, or it may correspond to the customary "valence-force" system employing stretching, bending, and twisting of the valence bonds and valence angles. A companion paper contains network analyzer tests on the CO_2 , OCS , and ethyl alcohol molecules by the "valence-force" model. Both the normal frequencies and normal modes of vibration check satisfactorily with known results within the accuracy of the instruments.

PART I. GENERALIZATION POSTULATES

Mathematical Models¹

TO account for the fundamental frequencies of the infra-red and Raman spectra, the chemist devised several types of mathematical models:

- (1) The nuclei execute harmonic vibrations requiring a quadratic potential energy function.
- (2) The nuclei execute anharmonic vibrations requiring cubic and quartic, etc., terms in addition to the quadratic terms in the potential function.
- (3) The "central force" model assumes forces only along the lines connecting the nuclei.
- (4) The "valence force" model associates with the valence bonds appropriate mechanical properties such as stretching and twisting of the bonds, bending of the angles between two bonds or between two planes containing the bonds.
- (5) The general model contains a mixture of the quadratic and the valence force models.

Physical Models

Since the analytical study of the above types of models becomes increasingly complex with

increasing numbers of atoms or radicals, attempts were made to introduce mechanical models.² To represent the valence force model, the atoms were replaced by weights, the bonds between them by springs (or beams), and the angular bending between two bonds was given by the bending of the beams themselves. Such mechanical models, however, do not lend themselves to satisfactory measurements nor do they allow the variation of the various weights and elastic coefficients by the necessary small steps.

On the other hand, electric circuit models set up on an a.c. network analyzer can be adjusted to variations by rather small steps and allow easy measurement of both the normal frequencies and the modes of vibration not only of the valence force but of any type of model as long as it is linear. In the absence of a network analyzer, the electric circuits may be solved

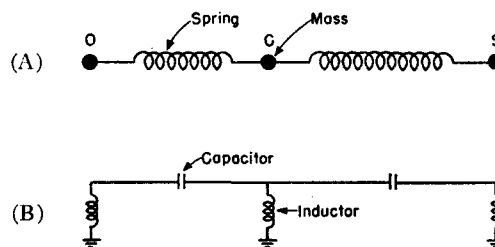


FIG. 1. Masses and springs with one degree of freedom. (A) The OCS molecule. (B) Its electrical analog.

* Consulting engineer.

¹ The writer wishes to acknowledge his indebtedness to Dr. R. M. Fuoss, Sterling Professor of Chemistry, Yale University for several discussions and for his encouragement to pursue the electric-circuit model study of complex molecules. Also he wishes to thank Drs. S. Dushman, J. P. Blewett, and R. P. Johnson, of the Research Laboratory of the General Electric Company, for their comments and encouragement.

² D. E. Teets and D. H. Andrews, *J. Chem. Phys.* **3**, 175 (1935); Murray, Deitz, and Andrews, *ibid.* **3**, 180 (1935).

numerically³ by hand or by punch-card methods. The circuits also allow the setting up of the resultant secular equations by simple inspection.

Systems with One Degree of Freedom

It has been known for over a century that a mass is analagous to an inductance and a spring to a capacitor. Let, for instance, the OCS molecule be considered, Fig. 1. The three masses representing the three atomic nuclei lie in a straight line along the x axis and are connected by two springs that represent the bonds between the nuclei. The electrical model consists of two capacitors connected to the ground by three inductors. If all the three masses vibrate along the x direction at one of their natural frequencies, in the model oscillatory electric currents of the same frequency flow. Then

- (1) The voltages across the inductors represent the displacement of the corresponding masses in the x direction.
- (2) The currents in the inductors represent the forces acting on the masses.

Two important limitations of this conventional electrical model should be noted.

(1) *Each mass must vibrate along one direction only, namely along the x axis.*

Actually in the OCS molecule the nuclei also vibrate at right angles to the x axis, but the electrical model is unable to represent that type of motion. In more general molecules each mass may have six degrees of freedom, namely three translational motions along the x , y , and z axes and three rotational motions around them. The conventional electrical model completely fails there.

(2) *Each valence bond also must lie along the x axis.*

If the angle at C is different from 180 degrees, the conventional electrical model again fails. Of course, in general molecules the bonds extend in every direction.

Systems with Several Degrees of Freedom

It is the purpose of this paper to develop electrical circuits that represent the vibration properties of nuclei that have six degrees of

freedom. They are connected by valence bonds that extend in space along arbitrary directions and are endowed with arbitrary properties.

A mechanical system which is rather similar to that of vibrating molecules is a spatial frame structure of beams. Equivalent circuits for such a frame structure have already been developed in another publication.⁴ However, *a frame structure is not an exact analog of the chemist's molecule*. In some respects it is too general and in other respects it lacks many of the properties with which the molecules are endowed. For instance, in the molecular model there is no uniform bending along the length of a bond and any bending at the junctions takes place in a plane only. On the other hand, the chemist assumes cross-product stretching between two bonds, a concept that does not occur in a structural frame.

The equations of a simplified beam that can be stretched, twisted, and bent at the junctions will be developed here anew from fundamentals in a manner that will enable it to acquire properties that a physical beam does not possess. For that purpose it will be necessary to decompose each beam into several composite beams, each of the latter possessing only one particular property such as a stretching or an angular bending, etc. Each bond will then be a summation of several of such properties and each molecule will be a summation of several of such beams.

Three Principles to Establish Models for Physical Systems

The mathematical model of a physical system is a set of symbols arranged in the form of equations, while the physical model considered here is a set of stationary electrical coils (resistors, inductors, and capacitors) arranged in a configuration that spatially is analogous to the original system. For simple systems these models are also simple, but for complex configurations, such as a polyatomic molecule, both types of models soon become unmanageable and one gets lost in a maze of mathematical symbols or electrical coils.

However, in going from simpler to more com-

³ Gabriel Kron, "Numerical Solution of Ordinary and Partial Differential Equations by Means of Equivalent Circuits," J. App. Phys. **16**, 172-186 (March, 1945).

⁴ Gabriel Kron, "Tensorial Analysis and Equivalent Circuits of Elastic Structures," J. Frank. Inst. **238**, 399-442 (December, 1944).

plex physical systems, it is possible to follow certain guiding principles that bound the course of reasoning in a narrow channel and establish along the flow guideposts to direct a straight-line progress. These principles must run a parallel course for either type of model and must have a one-to-one correspondence. They have already proved indispensable in establishing models for complex engineering systems representable either by sets of algebraic or by sets of partial differential equations.

To establish a *mathematical* model for a complex physical system it has been postulated that⁶

"The set of equations of a complex system composed of several units, each with n degrees of freedom, are the same as the set of equations of a simple system composed of units, each with one (or a small number of) degrees of freedom except that each scalar symbol in the latter set is replaced by an appropriate tensor."

A tensor is a scalar, one-rowed matrix, rectangular or cubic matrix, in general an n -dimensional matrix, which obeys certain definite laws of transformation. A tensor is considered as the mathematical equivalent of a physical entity with n degrees of freedom (such as a bond between two nuclei) and as such it is represented (for purposes of manipulation) by a single mathematical symbol.

The parallel principle for establishing an electrical (physical) model is postulated as follows:

"The equivalent circuit of a complex system composed of units with n degrees of freedom is the same as the equivalent circuit of a simple system composed of units with one (or a few) degrees of freedom, except that each coil in the latter model is replaced by an appropriate n -wire transmission system."

The n -wire transmission line contains in general as many coils as the corresponding tensor contains components. (See Fig. 4.) The transmission line is the electrical equivalent of a physical entity with n degrees of freedom and as such it is represented (for purposes of manipulation) by a single electrical symbol, that of a coil.

(It is not intended to restrict the physical model to stationary coils and to stationary transmission lines, nor to restrict it to the use of electrical coils.)

⁶ Gabriel Kron, "Equivalent Circuits of the Elastic Field," J. App. Mech. **A11**, 146-61 (September, 1944).

The connecting link between the two parallel postulates is a third postulate:

"Only a tensor equation (an equation in which each symbol is a tensor) is representable by a physical model. *Vice versa*, all physical systems (or rather their models) can be mathematically represented correctly only by tensor equations."

This last postulate denies the possibility of constructing a *physical* model (an equivalent circuit) for any haphazard set of mathematical equations claiming to describe the behavior of a physical system. The equations must be in a definite tensorial form to correspond term by term to a model. This postulate denies the existence of even a *mental* model (the type engineers like to use, such as "cutting" of flux lines) dictated by a set of non-tensor equations. (The non-existence of a *geometrical* model for a non-tensor equation is commonly understood.)

Since the physical system to be analyzed presently consists of elementary springs and masses whose conventional equations are already in a tensorial form, the third postulate will play only a subsidiary role in the following. (It plays a crucial role, however, in the model representation of partial differential equations along curvilinear coordinates or of moving and rotating mechanical and electromechanical systems.) The main emphasis will be on the first and second postulates to help establish comparatively simple equations and comparatively simple networks for the otherwise very complex molecular phenomena.

The Course of Procedure

These postulates suggest the following course of procedure to establish either the equations or the equivalent circuits of a complex physical system.

(1) Divide the system into its component units. The collection of units will be called the "primitive" system.

(2) Since the units themselves are rather complex, rotate and re-adjust each of the latter along its simplest possible reference frame (without destroying, of course, its essential unity).

(3) Set up the equations, or the equivalent circuits, of each of the simplified units as if all the others were absent.

(4) Re-adjust and rotate each of the simplified units into the form in which it actually occurs in the system, either by a matrix of transformation (in the mathematical model) or by an actual rotation (in the physical model). That is, re-establish the primitive system of the model.

(5) Reconnect the units (the primitive system) into the resultant system either by a matrix of transformation or by an analogous actual interconnection of the equivalent circuits.

By the use of the concept of "interconnection" in the form of a matrix of transformation, the intricate relations due to the simultaneous presence of several units are automatically taken care of without further thought.

In really complex systems, as in organic molecules, the subdivisions may continue through several successive steps, introducing thereby "multiply compound" tensors, that is, tensors in which each component itself is a compound tensor (whose components are again tensors) and "multiply compound" networks, that is, networks in which each coil itself stands for a whole network each coil in which again represents, say, an n -wire transmission line.

Units to be Assumed

Since it is customary to assume often a mixture of the several types of models possible, the following six types of units of a molecule will be studied here individually.⁶

(1) Mass of a nucleus. Occurs in all models. (See Fig. 2.)

(2) Stretching of a bond between two nuclei. Occurs in both central and valence force models and it also represents the square term in a quadratic form (Fig. 3).

(3) Cross-product between two bonds. Occurs in the quadratic potential model (Fig. 5).

(4) Bending of the angle between two valence bonds in the absence of torsion. Occurs in the valence bond models (Fig. 7).

(5) Torsion of a bond.

(6) Bending of the angle between two valence bonds in the presence of torsion (Fig. 9).

There are several other units possible which are not treated here. For instance,

(7) Cross-product between two angles.

(8) Bending of the angle between a bond and a plane containing several bonds.

(9) Bending of the angle between two planes.

When no torsion is present, each component of a unit has three degrees of freedom, namely, translations along the x , y , and z axes. In the presence of torsion, three additional degrees of freedom appear, namely rotations around the x , y , and z axes, denoted here by p , q , and r .

Determination of Normal Frequencies

While the examples in the present paper express the equations and the electric model along Cartesian coordinates, the same general procedure applies when other types of coordinates are used, such as "internal" or "symmetry" coordinates. In a more convenient reference frame the network model may split into several independent networks.

The solution of the secular equations is well known. The electrical network gives the desired information by the following steps:

(1) Insert a constant frequency generator between any one of the junction points and the ground.

(2) Assume an arbitrary frequency of oscillations ω and adjust the value of coils (representing the masses) accordingly.

(3) Measure the generator current.

As ω varies, the generator current will also vary. Now *the series of value of ω at which the generator current becomes zero represent the normal frequencies of the molecule.* Also, the corresponding absolute potentials at the junctions (assuming the ground at zero potential) represent the particular modes of vibration.

With zero generator current the electrical power stored in the network oscillates between the inductors and capacitors, requiring no extraneous source to maintain the oscillations.

It may happen that for one normal frequency several modes are possible. In such cases placing the generator to a different junction produces a different type of mode. The measured potentials supply sufficient equations to determine each of the degenerate modes.

It should be noted that the generator frequency is not varied as the frequency of the system varies. The networks are of the type

⁶ G. Herzberg, *Infrared and Raman Spectra for Polyatomic Molecules* (D. Van Nostrand Company, New York, 1945).

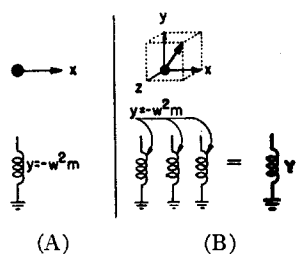


FIG. 2. Equivalent circuit of a particle. (A) One-dimensional motion. (B) Three-dimensional motion.

that require the generator frequency to remain constant and the inductors representing the masses to be adjustable.

The measured normal frequency may be improved by Rayleigh's principle in the following way:

(1) Calculate the electrical power for the measured voltage distribution in all the ground coils, assuming ω as unknown. This power is the kinetic energy.

(2) Calculate the power in the rest of the network. This power is the elastic energy.

The equality of the two energies determines a more correct ω .

PART II. THE PRIMITIVE SYSTEM

A Particle

The kinetic energy of a particle oscillating along the x axis is $T = \frac{1}{2}mx^2$. The equation of force is

$$F = m d^2x/dt^2 = -\omega^2 mx = Yx. \quad (1)$$

Expressing force as current and displacement as voltage, the equation of the electrical analog is $I = YE$. Its admittance is represented by a grounded inductor, Fig. 2(A).

When the particle vibrates along all three directions, its equation is $\mathbf{F} = \mathbf{Y} \cdot \mathbf{x}$ or $\mathbf{I} = \mathbf{Y} \cdot \mathbf{E}$ where the admittance matrix is

$$\mathbf{Y} = -\omega^2 \mathbf{m} = \begin{matrix} & \begin{matrix} x & y & z \end{matrix} \\ \begin{matrix} x \\ y \\ z \end{matrix} & \begin{bmatrix} -\omega^2 m & & \\ & -\omega^2 m & \\ & & -\omega^2 m \end{bmatrix} \end{matrix}. \quad (2)$$

The equivalent circuit is given in Fig. 2(B). In analogy with representing a tensor (or matrix) by a bold face letter, a compound coil will be represented by a coil drawn in heavy lines.

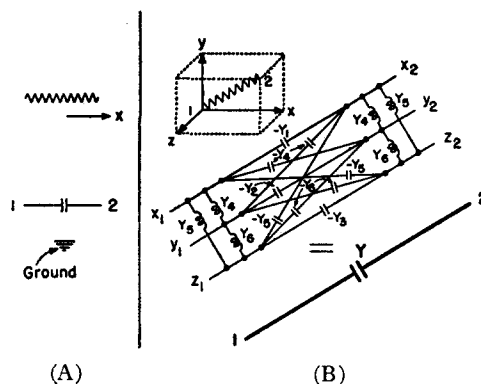


FIG. 3. Equivalent circuit of a tension spring. (A) One-dimensional motion. (B) Three-dimensional motion (Eq. (7)).

A similar matrix (along axes $\mathbf{p}, \mathbf{q}, \mathbf{r}$) may be set up to represent the moment of inertia of a particle. It is customary to neglect it, however, in molecular vibration studies.

Stretching of a Bond

A restoring force between two particles acting along the connecting line may be represented by a spring. Rotating the spring along the x axis (Fig. 3(A)), its potential energy is

$$V = \frac{1}{2}k(x_2 - x_1)^2. \quad (3)$$

Differentiating with respect to x_1 and x_2 in succession, its equation is $\mathbf{F} = \mathbf{Y} \cdot \mathbf{x}$ or $\mathbf{I} = \mathbf{Y} \cdot \mathbf{E}$ where the admittance matrix

$$\mathbf{Y} = \begin{matrix} & \begin{matrix} x_1 & x_2 \end{matrix} \\ \begin{matrix} x_1 \\ x_2 \end{matrix} & \begin{bmatrix} k & -k \\ -k & k \end{bmatrix} \end{matrix}. \quad (4)$$

Its equivalent circuit is shown in Fig. 3(A). It is a three-terminal (two-junction pair) network, or a transmission line, in which the two ground coils happen to be zero because of the accidental equality of the four k 's in \mathbf{Y} .

Let the spring be rotated to its original position whose direction cosines are l, m , and n . The matrix of transformation is

$$\mathbf{A} = \begin{matrix} & \begin{matrix} 1 & 2 \end{matrix} \\ \begin{matrix} 1 \\ 2 \end{matrix} & \begin{bmatrix} A_1 & \\ & A_1 \end{bmatrix} \end{matrix} \quad \mathbf{A}_1 = \begin{matrix} & \begin{matrix} x' & y' & z' \end{matrix} \\ \begin{matrix} x' \\ y' \\ z' \end{matrix} & \begin{bmatrix} l & m & n \end{bmatrix} \end{matrix}. \quad (5)$$

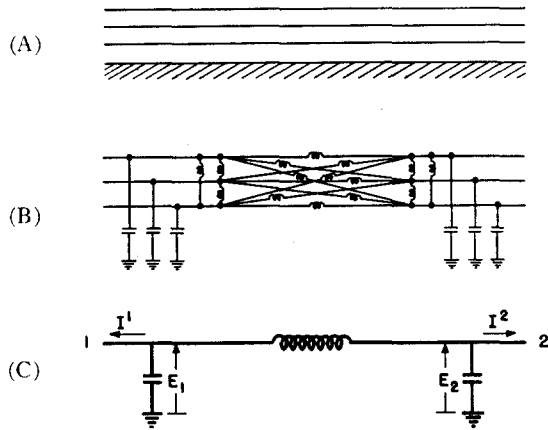


FIG. 4. Equivalent circuit of an n -wire transmission system. (A) N -wire transmission line. (B) Its equivalent circuit. (C) Compound transmission line.

The resultant equation is $\mathbf{I}' = \mathbf{Y}'\mathbf{E}'$ where

$$\mathbf{Y}' = \mathbf{A}_t \mathbf{Y} \mathbf{A} = \begin{array}{c} \begin{array}{cc} 1 & 2 \\ \hline 1 & k & -k \\ 2 & -k & k \end{array} \end{array}, \quad (6)$$

$$\mathbf{k} = \begin{array}{c} \begin{array}{ccc} x & y & z \\ \hline x & l^2 & lm & ln \\ y & ml & m^2 & mn \\ z & nl & nm & n^2 \end{array} \end{array} \times \mathbf{k} = \begin{array}{c} \begin{array}{ccc} x & y & z \\ \hline x & Y_1 & Y_4 & Y_5 \\ y & Y_4 & Y_2 & Y_6 \\ z & Y_5 & Y_6 & Y_3 \end{array} \end{array}. \quad (7)$$

The resultant circuit is shown in Fig. 3(B). Its establishment is given in the next section.

Equivalent Circuit of an N -Wire Transmission Line

A symmetrical matrix may be looked upon, for the present purpose, to represent the impedance matrix of an n -wire transmission line, Fig. 4(B). (There are other possible interpretations.) The equivalent circuit of such a line (Fig. 4(B)) may be established from \mathbf{Y} by the following steps:

(1) The mutual admittances are represented by a coil between the respective terminals. A positive "coil" is an inductor, a negative "coil" is a capacitor.

(2) The sum of each column, taken with opposite signs, is replaced by a coil between the respective terminal and the ground.

Such an n -wire transmission system is represented symbolically by the conventional transmission line diagram drawn in heavy lines (Fig.

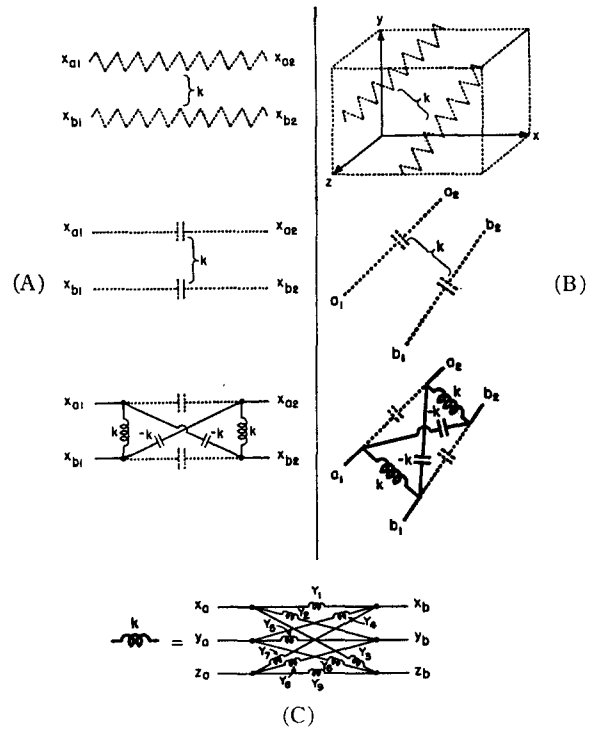


FIG. 5. Equivalent circuit of a cross-product. (A) One-dimensional motion. (B) Three-dimensional motion. (C) Equivalent circuit of a compound coil k (Eq. (9)).

4(C)), the "compound transmission line." In many cases considered in this paper the ground coils are absent.

The Cross-Product Terms

A cross-product term between two bonds in the potential energy, such as $\frac{1}{2}k\Delta r_{12}\Delta r_{34}$, represents a mutual spring constant between two springs (Fig. 5(A)) and is analogous to the mutual coupling between two parallel transmission lines.

Let the two springs both be rotated along the x direction, still with the mutual coupling between them. The potential energy of the latter is

$$V = \frac{1}{2}k(x_{a2} - x_{a1})(x_{b2} - x_{b1}). \quad (8)$$

Differentiating, the admittance matrix is

$$\mathbf{Y} = \begin{array}{c} \begin{array}{cc|cc} & x_{a1} & x_{a2} & x_{b1} & x_{b2} \\ \hline x_{a1} & & & & \\ x_{a2} & & k & -k & \\ x_{b1} & k & -k & & \\ x_{b2} & -k & k & & \end{array} \end{array}. \quad (9)$$

The equivalent circuit of the coupling between two transmission lines consists of *four identical coils* k as shown in Fig. 5(A), two of them differing only in sign.

Let now the first spring be rotated along a line with direction cosines l_a, m_a, n_a , and the other spring along a different line with direction cosines l_b, m_b, n_b (Fig. 5(B)). The resultant matrix of transformation is

$$\mathbf{A} = \begin{array}{c} \begin{array}{cc|cc} a_1 & a_2 & b_1 & b_2 \\ \hline x_{a1} & \mathbf{A}_a & & \\ x_{a2} & & \mathbf{A}_a & \\ \hline x_{b1} & & & \mathbf{A}_b \\ x_{b2} & & & \end{array} \end{array} \quad \begin{array}{c} \begin{array}{ccc} x' & y' & z' \\ \hline l_a & m_a & n_a \\ \hline \end{array} \\ \mathbf{A}_a = \mathbf{x} \\ \begin{array}{ccc} x' & y' & z' \\ \hline l_b & m_b & n_b \\ \hline \end{array} \\ \mathbf{A}_b = \mathbf{x} \end{array} \quad (10)$$

Multiplying Eq. (9) by Eq. (10) as $\mathbf{A}_i \mathbf{Y}_a$, the resultant is

$$\mathbf{Y}' = \begin{array}{c} \begin{array}{cc|cc} a_1 & a_2 & b_1 & b_2 \\ \hline a_1 & & \mathbf{k} & -\mathbf{k} \\ a_2 & & -\mathbf{k} & \mathbf{k} \\ \hline b_1 & \mathbf{k}_t & -\mathbf{k}_t & \\ b_2 & -\mathbf{k}_t & \mathbf{k}_t & \end{array} \end{array} \quad (11)$$

$$\mathbf{k} = \mathbf{y}_a \begin{array}{c} \begin{array}{ccc} x_b & y_b & z_b \\ \hline l_a l_b & l_a m_b & l_a n_b \\ m_a l_b & m_a m_b & m_a n_b \\ n_a l_b & n_a m_b & n_a n_b \end{array} \end{array} \times k$$

$$\begin{array}{c} \begin{array}{ccc} x_b & y_b & z_b \\ \hline x_a & Y_1 & Y_2 & Y_3 \\ y_a & Y_4 & Y_5 & Y_6 \\ z_b & Y_7 & Y_8 & Y_9 \end{array} \end{array} \quad (12)$$

The transpose of \mathbf{k} is denoted as \mathbf{k}_t .

In the electrical network the cross-product term \mathbf{k} is represented by four equal "compound" coils (Fig. 5(C)) just as is the single transmission line coupling. The compound coil \mathbf{k} is given in Fig. 5(C).

Bending of Valence Angles

The force resisting an angular change between two valence bonds may be replaced, in the absence of torsion in the molecule, by an angular

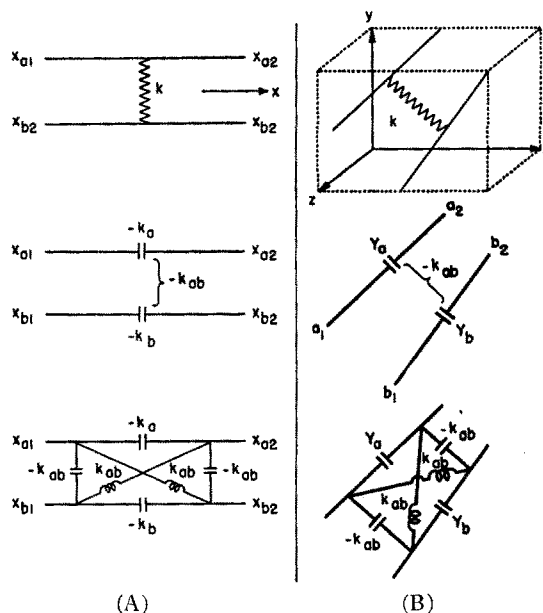


FIG. 6. Equivalent circuit of an angular spring between two distant bars. (A) One-dimensional motion. (B) Three-dimensional motion.

spring connecting two bars having no rigidity. Let the two bars, a and b , with the angular spring, be rotated along the x axis (Fig. 6(A)). The angle by which one of the bars is displaced is $(y_{a2} - y_{a1})/L_a$; hence the potential energy stored

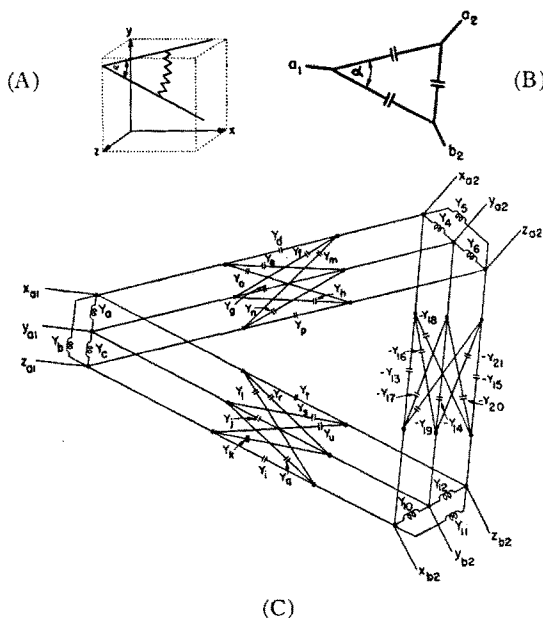


FIG. 7. Equivalent circuit of an angular spring between two neighboring bars. (A) Angular spring. (B) Compound network. (C) Actual network (Table I).

in the spring is

$$V = \frac{1}{2}k \left[\frac{y_{a2} - y_{a1}}{L_a} - \frac{y_{b2} - y_{b1}}{L_b} \right]^2. \quad (13)$$

Differentiating, the admittance matrix is

$$Y = \begin{array}{c} \begin{array}{cc} & \begin{array}{cccc} y_{a1} & y_{a2} & y_{b1} & y_{b2} \end{array} \\ \begin{array}{c} y_{a1} \\ y_{a2} \\ y_{b1} \\ y_{b2} \end{array} & \begin{array}{|c|c|c|c|} \hline k_a & -k_a & -k_{ab} & -k_{ab} \\ \hline -k_a & k_a & k_{ab} & -k_{ab} \\ \hline -k_{ab} & k_{ab} & k_b & -k_b \\ \hline k_{ab} & -k_{ab} & -k_b & k_b \\ \hline \end{array} \end{array}, \quad (14)$$

where $k_a = k/L_a^2$; $k_b = k/L_b^2$; and $k_{ab} = k/L_a L_b$.

The equivalent circuit of the angular spring is two-coupled transmission lines, Fig. 6(A). The coupling has a sign opposite to that in Fig. 5(A).

In place of the directions of the bars themselves, let the directions of the lines *perpendicular* to the bars and lying in their plane be considered and let their direction cosines be denoted by l_a , m_a , n_a , and l_b , m_b , n_b , respectively. The resultant transformation matrix A is the same as in Eq. (10) except on the left-hand side the unit vector x is replaced by y . The resultant Y' is by $A_t Y A$.

$$Y = \begin{array}{c} \begin{array}{cc} & \begin{array}{cccc} a_1 & a_2 & b_1 & b_2 \end{array} \\ \begin{array}{c} a_1 \\ a_2 \\ b_1 \\ b_2 \end{array} & \begin{array}{|c|c|c|c|} \hline k_a & -k_a & -k_{ab} & k_{ab} \\ \hline -k_a & k_a & k_{ab} & -k_{ab} \\ \hline -k_{ab} & k_{ab} & k_b & -k_b \\ \hline k_{ab} & -k_{ab} & -k_b & k_b \\ \hline \end{array} \end{array} = \begin{array}{c} \begin{array}{cc} a & b \\ \hline a & Y_a & Y_{ab} \\ \hline b & Y_{ab} & Y_b \end{array} \end{array}, \quad (15)$$

$$k_{ab} = \begin{array}{c} \begin{array}{cc} x & y & z \\ \hline x & l_a l_b & l_a m_b & l_a n_b \\ \hline y & m_a l_b & m_a m_b & m_a n_b \\ \hline z & n_a l_b & n_a m_b & n_a n_b \end{array} \end{array} \frac{k}{L_a L_b}. \quad (16)$$

k_a (and k_b) are the same as k_{ab} with all "b" subscripts replaced by "a" (or "a" replaced by "b").

The compound electrical network is given in Fig. 6(B). It is the same as Fig. 4(B) except that the mutual coils k_{ab} have opposite signs.

Angle between Two Neighboring Bonds

When the two bonds forming a valence angle are connected together (Fig. 7(A)), then one of the junctions disappears. The connection matrix connecting two junctions a_1 and b_1 into one

junction is

$$A = \begin{array}{c} \begin{array}{cc} a_1' & a_2' & b_2' \\ \hline a_1 & 1 & \\ \hline a_2 & & 1 \\ \hline b_1 & 1 & \\ \hline b_2 & & 1 \end{array} \end{array}, \quad (17)$$

$$1 = \begin{array}{c} \begin{array}{cc} x & y & z \\ \hline x & 1 & \\ \hline y & & 1 \\ \hline z & & 1 \end{array} \end{array}. \quad (18)$$

By the law of transformation $Y' = A_t Y A$, the resultant admittance matrix is

$$Y'' = \begin{array}{c} \begin{array}{cc} & \begin{array}{ccc} a_1' & a_2' & b_2' \end{array} \\ \begin{array}{c} a_1' \\ a_2' \\ b_2' \end{array} & \begin{array}{|c|c|c|} \hline k_a + k_b - k_{ab} - k_{abt} & -k_a + k_{abt} & -k_b + k_{ab} \\ \hline -k_a + k_{ab} & k_a & -k_{ab} \\ \hline -k_b + k_{abt} & -k_{abt} & k_b \\ \hline \end{array} \end{array}. \quad (19)$$

The equivalent circuit is given in Fig. 7 and in Table I. In two dimensions, $n_a = n_b = 0$.

Torsion of a Bond

The treatment of the torsion of a bond is analogous to that of stretching except that the variables and unit vectors \mathbf{x} , \mathbf{y} , \mathbf{z} are replaced by \mathbf{p} , \mathbf{q} , \mathbf{r} . The potential energy is $V = \frac{1}{2}k(p_2 - p_1)^2$. When the bond lies along x , its \mathbf{Y} is given in Eq. (4) and when lying in a general direction, its \mathbf{Y} is given in Eq. (6). The equivalent circuits are similar to Fig. 3.

It should be noted that the previously developed circuits cannot be interconnected with the circuit representing torsion, or rather there would be no interconnection between them. The bending of valence angles in the presence of torsion, newly treated in the next section, allows the interconnection of the \mathbf{x} , \mathbf{y} , \mathbf{z} and \mathbf{p} , \mathbf{q} , \mathbf{r} axes.

Bending and Torsion of Valence Angles

In the presence of torsion the single angular spring with a force constant k connecting two

TABLE I. Admittances of coils in Fig. 7(C).

$Y_1 = k \frac{l_a^2}{L_a^2}$	$Y_7 = k \frac{l_b^2}{L_b^2}$	$Y_{13} = k \frac{l_a l_b}{L_a L_b}$	$Y_{19} = k \frac{l_b n_a}{L_a L_b}$
$Y_2 = k \frac{m_a^2}{L_a^2}$	$Y_8 = k \frac{m_b^2}{L_b^2}$	$Y_{14} = k \frac{m_a m_b}{L_a L_b}$	$Y_{20} = k \frac{m_a n_b}{L_a L_b}$
$Y_3 = k \frac{n_a^2}{L_a^2}$	$Y_9 = k \frac{n_b^2}{L_b^2}$	$Y_{15} = k \frac{n_a n_b}{L_a L_b}$	$Y_{21} = k \frac{m_b n_a}{L_a L_b}$
$Y_4 = k \frac{l_a m_a}{L_a^2}$	$Y_{10} = k \frac{l_b m_b}{L_b^2}$	$Y_{16} = k \frac{l_a m_b}{L_a L_b}$	
$Y_5 = k \frac{l_a n_a}{L_a^2}$	$Y_{11} = k \frac{l_b n_b}{L_b^2}$	$Y_{17} = k \frac{l_b m_a}{L_a L_b}$	
$Y_6 = k \frac{m_a n_a}{L_a^2}$	$Y_{12} = k \frac{m_b n_b}{L_b^2}$	$Y_{18} = k \frac{l_a n_b}{L_a L_b}$	
$Y_a = Y_4 + Y_{10} - Y_{16} - Y_{17}$	$Y_h = -Y_6 + Y_{21}$	$Y_o = -Y_5 + Y_{19}$	
$Y_b = Y_5 + Y_{11} - Y_{18} - Y_{19}$	$Y_i = -Y_{11} + Y_{19}$	$Y_p = -Y_3 + Y_{15}$	
$Y_c = Y_6 + Y_{12} - Y_{18} - Y_{19}$	$Y_j = -Y_8 + Y_{14}$	$Y_q = -Y_{10} + Y_{17}$	
$Y_d = -Y_1 + Y_{13}$	$Y_k = -Y_{12} + Y_{21}$	$Y_r = -Y_{10} + Y_{16}$	
$Y_e = -Y_4 + Y_{17}$	$Y_l = -Y_7 + Y_{13}$	$Y_s = -Y_{12} + Y_{20}$	
$Y_f = -Y_4 + Y_{16}$	$Y_m = -Y_5 + Y_{18}$	$Y_t = -Y_{11} + Y_{18}$	
$Y_g = -Y_2 + Y_{14}$	$Y_n = -Y_6 + Y_{20}$	$Y_u = -Y_9 + Y_{15}$	

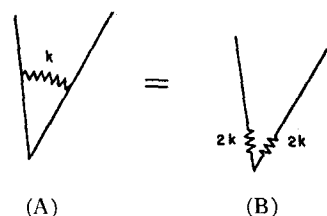


FIG. 8. Replacement of angular spring by two beams with torsion. (A) Angular spring. (B) Two beams.

bars has to be replaced by two springs in series, each with a force constant $2k$, Fig. 8. Each spring now resists the angular change of a single bar so that each bar can be treated independently of the other.

It should be noted that when several angles originate on a bond, the bond is considered as composed of several bars in parallel, each bar being associated with a different angle and a different angular force constant k . (There may also be two more bars belonging to the same bond, relating to a stretching and a twisting force constant.)

Let the bond be rotated along the x axis (Fig. 9(A)). The angle by which the bar is displaced is $(y_2 - y_1)/L - r_1$, where r_1 is the angular rotation of end 1 around the z axis. The potential energy in the spring is

$$V = \frac{1}{2}(2k) \left(\frac{y_2 - y_1}{L} - r \right)^2. \quad (20)$$

Differentiating, the admittance matrix is

$$\mathbf{Y} = \begin{matrix} & \begin{matrix} y_1 & y_2 & r_1 \end{matrix} \\ \begin{matrix} y_1 \\ y_2 \\ r_1 \end{matrix} & \begin{bmatrix} \frac{2k}{L^2} & -\frac{2k}{L^2} & \frac{2k}{L} \\ -\frac{2k}{L^2} & \frac{2k}{L^2} & -\frac{2k}{L} \\ \frac{2k}{L} & -\frac{2k}{L} & 2k \end{bmatrix} \end{matrix}. \quad (21)$$

Its equivalent circuit, Fig. 9(A), now contains ground coils.

Let the bond be rotated into its actual position and let the following directions be defined:

(1) The direction cosine of the line *perpendicular* to the bond and lying in the plane of the two bonds (the plane of the bending) be l_1 , m_1 , n_1 .

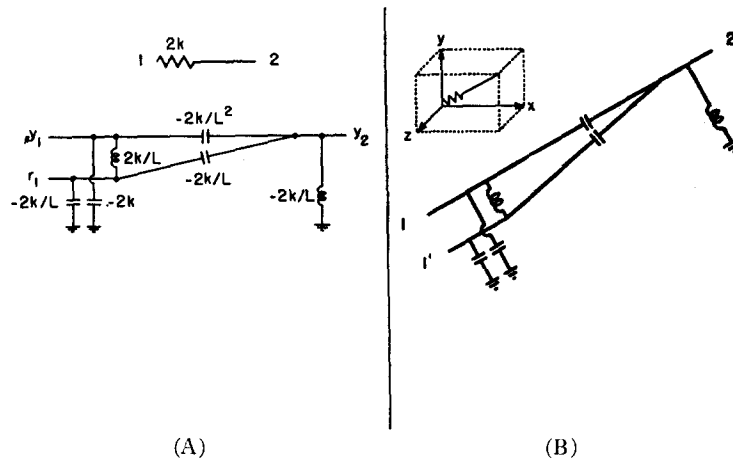


FIG. 9. Beam equivalent of an angular spring in the presence of torsion.
(A) One-dimensional motion. (B) Three-dimensional motion.

(2) The direction cosine of the line *perpendicular* to the plane of the two bonds be l_2, m_2, n_2 .

The transformation matrix is

$$\begin{array}{c}
 \begin{array}{c|c|c}
 1 & 2 & 1_r \\
 \hline
 y_1 & \mathbf{A}_1 & \\
 y_2 & & \mathbf{A}_1 \\
 r_1 & & \mathbf{A}_2
 \end{array} \\
 \mathbf{A} =
 \end{array}
 \begin{array}{c}
 \begin{array}{c|c|c}
 x & y & z \\
 \hline
 l_1 & m_1 & n_1 \\
 \hline
 p_1 & q_1 & r_1 \\
 \hline
 l_2 & m_2 & n_2
 \end{array} \\
 \mathbf{A}_1 = y \\
 \mathbf{A}_2 = r_1
 \end{array}
 \quad (22)$$

The resultant \mathbf{Y} is

$$\mathbf{Y} = \begin{array}{c} 1 \\ 2 \\ 1_r \end{array} \begin{array}{c|c|c} 1 & 2 & 1_r \\ \hline \frac{2k_1}{L^2} & -\frac{2k_1}{L^2} & \frac{2k_{12}}{L} \\ \hline -\frac{2k_{12t}}{L^2} & \frac{2k_1}{L^2} & -\frac{2k_{12}}{L} \\ \hline \frac{2k_{12t}}{L} & -\frac{2k_{12t}}{L} & 2k_{22} \end{array} \quad (23)$$

$$\mathbf{k}_{12} = \begin{array}{c} p \\ q \\ r \end{array} \begin{array}{c|c|c} x & y & z \\ \hline l_1 l_2 & l_1 m_2 & l_1 n_2 \\ \hline m_1 l_2 & m_1 m_2 & m_1 n_2 \\ \hline n_1 l_2 & n_1 m_2 & n_1 n_2 \end{array} \quad (24)$$

\mathbf{k}_1 (and \mathbf{k}_2) are the same as \mathbf{k}_{12} with all "2" subscripts replaced by "1" (or "1" replaced by "2"). Its equivalent circuit is shown in Figs. 9 (B) and 10 and in Tables II and III.

PART III. THE RESULTANT SYSTEM

The Resultant Physical Model

Let the four-atom molecule of Fig. 11(A) be considered. Its primitive system is shown in Fig. 11(B). There exist a cross-product term between the two distant bonds f and i , and a valence angle α between two neighboring bonds. The potential energy of the system is

$$V = \frac{1}{2} [k_{ab}(\Delta r_{ab})^2 + k_{bc}(\Delta r_{bc})^2 + k_{ad}(\Delta r_{ad})^2 + k(\Delta r_{ad})(\Delta r_{bc}) + k_\alpha(\Delta \alpha)^2] \quad (25)$$

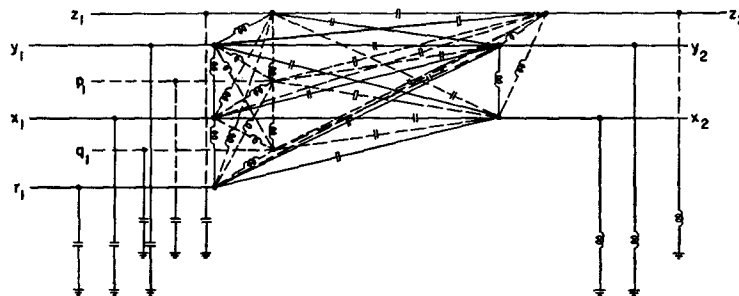


FIG. 10. Equivalent circuit of a beam. (Tables III and IV.) End 1 rigid, end 2 free to rotate.

TABLE II. Admittances of coils on Fig. 11 lying between various junctions.

$x_1 \rightarrow y_1 = Y_4$		$y_2 \rightarrow z_2 = Y_6$	$x_2 \rightarrow y_2 = Y_4$	$r_1 \rightarrow x_2 = -Y_{23}$
$z_1 = Y_5$	$y_1 \rightarrow z_1 = Y_6$		$z_2 = Y_5$	$y_2 = -Y_{24}$
$p_1 = Y_{19}$	$p_1 = Y_{25}$	$z_1 \rightarrow p_1 = Y_{26}$		$z_2 = -Y_{21}$
$q_1 = Y_{22}$	$q_1 = Y_{20}$	$q_1 = Y_{27}$	$p_1 \rightarrow q_1 = Y_{16}$	
$r_1 = Y_{23}$	$r_1 = Y_{24}$	$r_1 = Y_{21}$	$r_1 = Y_{17}$	$q_1 \rightarrow r_1 = Y_{12}$
$x_2 = -Y_1$	$x_2 = -Y_4$	$x_2 = -Y_5$	$x_2 = -Y_{19}$	$x_2 = -Y_{22}$
$y_2 = -Y_4$	$y_2 = -Y_2$	$y_2 = -Y_6$	$y_2 = -Y_{25}$	$y_2 = -Y_{20}$
$z_2 = -Y_5$	$z_2 = -Y_6$	$z_2 = -Y_3$	$z_2 = -Y_{26}$	$z_2 = -Y_{27}$
ground $\rightarrow x_1 = -(Y_{19} + Y_{22} + Y_{23})$			ground $\rightarrow x_2 = Y_{19} + Y_{22} + Y_{23}$	
$y_1 = -(Y_{25} + Y_{20} + Y_{24})$			$y_2 = Y_{25} + Y_{20} + Y_{24}$	
$z_1 = -(Y_{26} + Y_{27} + Y_{21})$			$z_2 = Y_{26} + Y_{27} + Y_{21}$	
$p_1 = -(Y_7 + Y_{10} + Y_{11})$				
$q_1 = -(Y_{10} + Y_8 + Y_{12})$				
$r_1 = -(Y_{11} + Y_{12} + Y_9)$				

Each expression in V represents a unit in the primitive system.

The resultant electrical model, Fig. 12(B), is built up from the compound coils, Fig. 12(A), in a manner analogous to the interconnection of the units of the original system. The step from the compound coils to the actual coils consists of

interconnecting all analogous x , y , z or p , q , r terminals separately as shown in Fig. 13.

The physical interpretation of the network is as follows:

(1) Relating to each *particle*

(a) The voltage from a terminal to ground gives the total displacement

TABLE III. Definition of admittances in Table II.

$Y_1 = 2k \frac{l_1^2}{L^2}$	$Y_7 = 2k \frac{l_2^2}{L^2}$	$Y_{13} = 2k \frac{l_2^2}{L^2}$	$Y_{19} = 2k \frac{l_1 l_2}{L}$	$Y_{25} = 2k \frac{m_1 l_2}{L}$
$Y_2 = 2k \frac{m_1^2}{L^2}$	$Y_8 = 2k \frac{m_2^2}{L^2}$	$Y_{14} = 2k \frac{m_2^2}{L^2}$	$Y_{20} = 2k \frac{m_1 m_2}{L}$	$Y_{26} = 2k \frac{n_1 l_2}{L}$
$Y_3 = 2k \frac{n_1^2}{L^2}$	$Y_9 = 2k \frac{n_2^2}{L^2}$	$Y_{15} = 2k \frac{n_2^2}{L^2}$	$Y_{21} = 2k \frac{n_1 n_2}{L}$	$Y_{27} = 2k \frac{n_1 m_2}{L}$
$Y_4 = 2k \frac{l_1 m_1}{L^2}$	$Y_{10} = 2k \frac{l_2 m_2}{L^2}$	$Y_{16} = 2k \frac{l_2 m_2}{L^2}$	$Y_{22} = 2k \frac{l_1 m_2}{L}$	
$Y_5 = 2k \frac{l_1 n_1}{L^2}$	$Y_{11} = 2k \frac{l_2 n_2}{L^2}$	$Y_{17} = 2k \frac{l_2 n_2}{L^2}$	$Y_{23} = 2k \frac{l_1 n_2}{L}$	
$Y_6 = 2k \frac{m_1 n_1}{L^2}$	$Y_{12} = 2k \frac{m_2 n_2}{L^2}$	$Y_{18} = 2k \frac{m_2 n_2}{L^2}$	$Y_{24} = 2k \frac{m_1 n_2}{L}$	

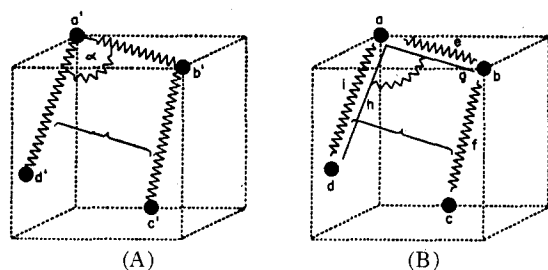


FIG. 11. Assumed molecular system $XYZW$. (A) Resultant system. (B) Primitive system.

(linear or angular) of the particle in the corresponding direction.

- (b) The current between a terminal and a ground gives the resultant force or torque acting on the particle in the corresponding direction

(2) Relating to each *valence bond*

- (a) The difference of potential between two terminals gives the change in the length or angular position of the bond in the corresponding direction.
- (b) The current between two terminals gives the corresponding force in the bond.

(3) Relating to the *total system*

- (a) The total power in the ground coils representing the masses gives the total kinetic energy of the vibrating system.

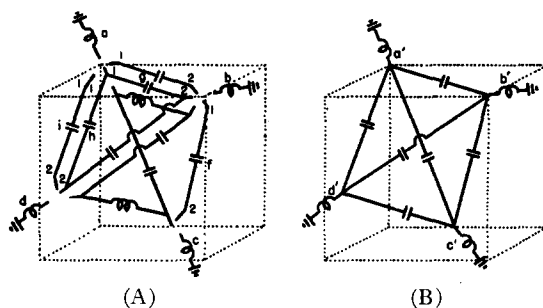


FIG. 12. Electric circuit model. (A) Primitive system. (B) Resultant system.

- (b) The total power in the rest of the network gives the total potential energy stored in the vibrating system.

The Resultant Mathematical Model

The units of the mathematical model consist of the \mathbf{Y}' matrices of the four masses (Eq. (2)), three stretching springs (Eq. (6)), one cross-product term (Eq. (11)), and one angular spring (Eq. (15)), all rotated in their proper spatial positions. These matrices are arranged along the diagonal line of a compound \mathbf{Y}' (Eq. (26)) with thirteen rows and columns representing the equations of the primitive system $\mathbf{I} = \mathbf{Y}\mathbf{E}$, namely thirty-nine scalar equations.

The interconnected system of Fig. 12(B) has

	a	b	c	d	e ₁	e ₂	f ₁	f ₂	g ₁	g ₂	h ₂	i ₁	i ₂
a	$-\omega^2 m_a$												
b		$-\omega^2 m_b$											
c			$-\omega^2 m_c$										
d				$-\omega^2 m_d$									
e ₁					\mathbf{Y}_e	$-\mathbf{Y}_e$							
e ₂					$-\mathbf{Y}_{et}$	\mathbf{Y}_e							
f ₁							\mathbf{Y}_f	$-\mathbf{Y}_f$				\mathbf{Y}_{fi}	$-\mathbf{Y}_{fi}$
f ₂							$-\mathbf{Y}_f$	\mathbf{Y}_f				$-\mathbf{Y}_{fi}$	\mathbf{Y}_{fi}
g ₁									\mathbf{Y}_{g1}	\mathbf{Y}_{g4}	\mathbf{Y}_{g5}		
g ₂									\mathbf{Y}_{g4t}	\mathbf{Y}_{g2}	\mathbf{Y}_{g6}		
h ₂									\mathbf{Y}_{g5t}	\mathbf{Y}_{g6t}	\mathbf{Y}_{g3}		
i ₁							\mathbf{Y}_{fit}	$-\mathbf{Y}_{fit}$				\mathbf{Y}_i	$-\mathbf{Y}_i$
i ₂							$-\mathbf{Y}_{fit}$	\mathbf{Y}_{fit}				$-\mathbf{Y}_i$	\mathbf{Y}_i

(26)

only five junctions, hence four-junction pairs. If each of the new junction pairs is selected so as to include the ground, the relation between the voltages (displacements) of the primitive and the resultant system is the matrix of transformation **A**, Eq. (27).

$$A' = \begin{matrix} & \begin{matrix} a' & b' & c' & d' \end{matrix} \\ \begin{matrix} a \\ b \\ c \\ d \\ e_1 \\ e_2 \\ f_1 \\ f_2 \\ g_1 \\ g_2 \\ h_2 \\ i_1 \\ i_2 \end{matrix} & \begin{bmatrix} \mathbf{I} & & & \\ & \mathbf{I} & & \\ & & \mathbf{I} & \\ & & & \mathbf{I} \\ \mathbf{I} & & & \\ & \mathbf{I} & & \\ & & \mathbf{I} & \\ & & & \mathbf{I} \\ \mathbf{I} & & & \\ & \mathbf{I} & & \\ & & & \mathbf{I} \\ \mathbf{I} & & & \\ & & & \mathbf{I} \end{bmatrix} \end{matrix}, \quad (27)$$

$$Y'' = \begin{matrix} & \begin{matrix} a & b & c & d \end{matrix} \\ \begin{matrix} a \\ b \\ c \\ d \end{matrix} & \begin{bmatrix} Y_e + Y_{g1} + Y_i - \omega^2 m_a & Y_{fit} - Y_e + Y_{g4} & -Y_{fit} & Y_{g5} - Y_i \\ Y_{fi} - Y_{et} + Y_{g4t} & Y_e + Y_f + Y_{g2} - \omega^2 m_b & -Y_f & -Y_{fi} + Y_{g6} \\ -Y_{fi} & -Y_{ft} & Y_f - \omega^2 m_c & Y_{fi} \\ Y_{g5t} - Y_i & -Y_{fit} + Y_{g6t} & Y_{fit} & Y_{g3} + Y_i - \omega^2 m_d \end{bmatrix} \end{matrix}. \quad (28)$$

Vice versa, the electric circuit model may be established from the secular equation by the reverse steps of those given previously. The two

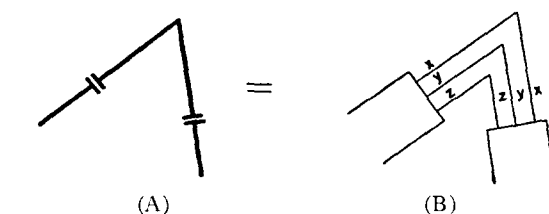


FIG. 13 Interconnection of coils. (A) Interconnection of compound coils. (B) Interconnection of actual coils.

where **I** is the unit matrix of Eq. (18). The admittance matrix of the resultant system is by **A'****Y'****A'**.

The equations **I''** = **Y''E''** represent the twelve secular equations of the molecule.

Relations between the Two Models

The secular equations **I** = **YE** may be established by a simple inspection of the electric circuit model of Fig. 12(B). In particular, **Y''** is established as follows.

(1) The mutual admittance terms are the coils connecting corresponding terminals.

(2) The main diagonal terms are the sum of the admittances entering each junction, taken with opposite sign.

methods of setting up the electrical model may serve as a check on the correctness of the network.