I THE MEASUREMENT OF SMALL, COMMERCIAL-FREQUENCY, ALTERNATING POTENTIALS.

II THE NORMAL FREQUENCIES OF VIBRATION FOR SYSTEMS OF POINT PARTICLES HAVING TETRAHEDRAL AND OCTAHEDRAL SYMMETRY.

Thesis by

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I THE MEASUREMENT OF SMALL, COMMERCIAL-FREQUENCY, ALTERNATING POTENTIALS.

ABSTRACT

A mechanical rectifier for use at commercial frequencies has been constructed. Accidental electromotive forces have been so far eliminated that it can be used with a sensitive direct current galvanometer as a detecting instrument. Four galvanometers have been tried and the results are described. With the most sensitive galvanometers used, the sensitivities of the system at 50 cycles were 0.05 microvolts (without the critical damping resistance) and 0.00004 microamperes.

The use of a vibration galvanometer and of the mechanical rectifier with a low-frequency vacuum-tube amplifier has been investigated. An input potential 0.001 of that corresponding to the noise level of the amplifier can be detected. This combination is then about 100 times as sensitive as an amplifier with the same noise level used with a telephone receiver.

§1 Introduction. The Measurement of Small Alternating Potentials.

Measurements of direct currents of the order of 10^{-10} amperes of direct potentials of the order of 10^{-7} volts, and of commercial frequency alternating currents of the order of 10^{-8} amperes are now made in ordinary laboratory practice with relatively simple apparatus now on the market. Current measurements may be pushed to far greater sensitivity by the use of certain recently developed vacuum tubes.

In contrast to this, measurements of alternating potentials are limited to about 10^{-6} volts in ordinary practice. Many mechanical systems should theoretically give rise to such potentials, the study of which is often of considerable interest. As an aid to the investigation of such problems, we have attempted to increase the sensitivity of measurements of alternating potentials.

Two lines of attack have been followed: (a) a mechanical rectifier for use with an alternating current input and feeding into a direct current galvanometer has been designed, and (b) a vacuum-tube amplifier operating into a tuned detecting instrument has been studied.

§2 Mechanical Rectifiers.

Mechanical rectifiers of the general type of synchronous commutators have long been used in commercial practice. There are, however, two inherent difficulties in design which have prevented their laboratory use.

The first of these is due to the friction and varying resistance of the brushes. This gives rise to varying and unknown electromotive forces in the commutator itself in addition to fluctuations in the current being rectified. As it is well known that the frictional electromotive forces producted by closing a knife switch produce large deflections in a sensitive galvanometer, it is evident that this type of rectifier is not well suited to use with such instruments.

The second difficulty is due to the potential difference between the two ends of a commutator bar when that bar is moving so as to cut the earth's magnetic field.

Although Dannatt and Holt[1] have described an improved commutator with special brushes which was used successfully with a milliammeter, this type of rectifier did not seem, on preliminary investigation, as promising as the following type.

The general idea involved is that a set of contact points, operated by a cam on the shaft of a synchronous motor and making contact with another set of points as does a galvanometer key, without slipping, should be free from potentials or varying resistances due to such slipping. By mounting the contacts on a face plate rotatable about the shaft, phase adjustment may be secured.

Sharp and Crawford[2] designed and tested such a synchronous reversing key with which they were able to use a microammeter. The movable contacts were mounted on the free end of a flexible strip which was moved by a follower mounted on it and bearing on a cam turned by a synchronous motor. The fixed contacts and fixed end of the flexible strip were mounted on a disk rotatable about the cam. The contacts were platinum. Neither description nor photographs were explicit enough to permit duplication of their apparatus or a discussion of possible defects, but the difficulties inherent in the commutator type are evidently absent.

In the first model designed for this investigation, the contact points were all mounted on a Bakelite disk, each movable point being individually actuated by an attached wedge pressed against a cam by a spiral spring. This arrangement was unsatisfactory because of the severe friction and heating at the cam, and had also various minor defects.

In the final form adopted (Fig. 1 and 2) the cam turns in a bushing, which, of course, moves in a circle. The normal components are resolved by two sets of slides at right angles. The movable contact points are mounted on the outer sliding block which moves linearly .

§3 Description of the Rectifier Used.

The face plate, stand, base and other similar parts are of brass. In all bearing surfaces, one member is Tobin bronze, the other, drill rod. All parts of the electrical circuit are copper, the insulating bushings are Redmanol, and the insulating washers, mica.

The 1/4" steel shaft turning in a bronze bushing terminates in a bronze circular cam 1/2" in diameter by 9/32" thick set 0.015" off center and balanced. The cam accurately fits the hole in a 5/8" square steel slider with grooved edges. This steel slider, which takes up the sideways motion of the cam, moves in a rectangular hole in a second, bronze slider 13/16" by 1" by 1/4" thick which moves vertically. Four contact points are carried on the horizontal, 13/16", faces of the bronze slider. There are four 1/4" square lugs on its ends which have holes fitting the 1/8" steel rods supported by brass blocks pinned and screwed to the face plate. No play can be felt in this chain of bearings.

The contacts are 9/32" by 9/32" hollow copper cylinders into which Redmanol has been pressed. A steel rod is screwed into the Redmanol for fastening and a mica washer insulates the copper from the bronze.

The second set of four contact points, similarly constructed,

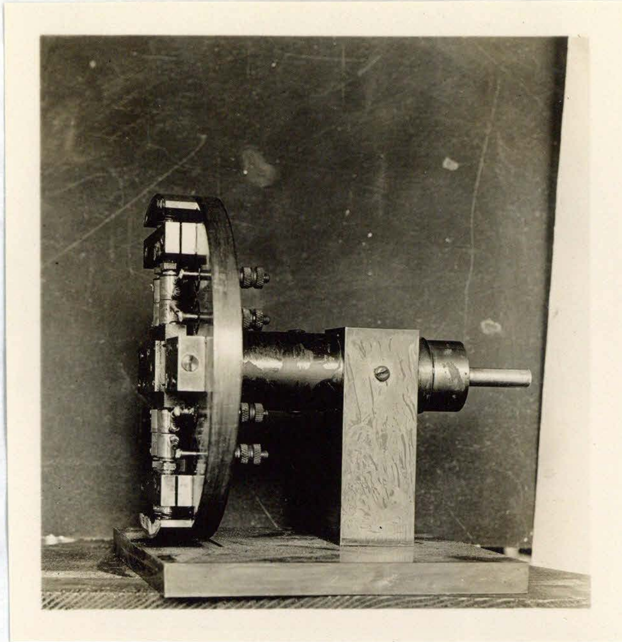

Fig 1
Side view of rectifier

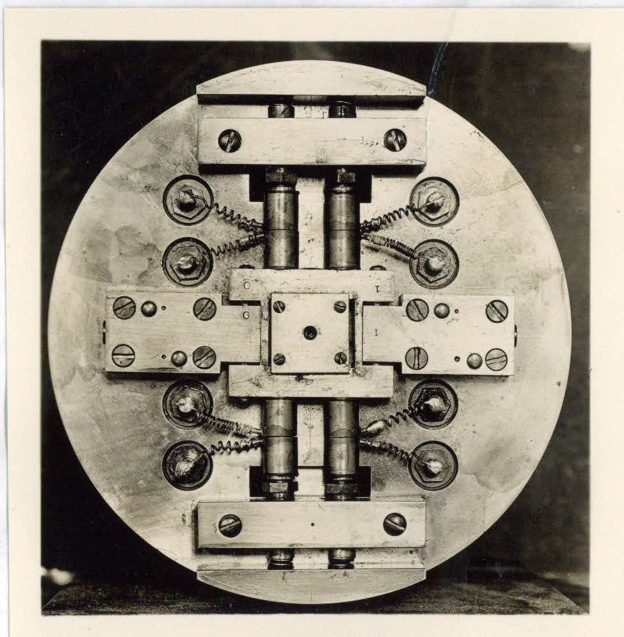

Fig 2
Front view of rectifier

are mounted on the ends of 1/8" steel rods 1/2" long which slide without play in bronze bushings. The other ends of the rods are enlarged so that they come to definite positions against the bushings. These bushings screw through brass blocks, split and provided with a screw for tightening, which are screwed and pinned to the face plate. Against the enlarged ends of the rods, steel spiral springs set in holes in another block push.

Connection to the contact points is made by soldering a copper spiral to a copper rod driven into a #60 hole in the side of each contact point near the surface of contact. The other end of the spiral is soldered to the end of a copper binding post projecting through a Redmanol plug pressed into a hole in the face plate.

The face plate, 4 7/32" diameter by 5/16" thick, has a 1 5/8" projecting boss on the back which provides a long bearing turning on a taper supported by the upright. Set screws through the boss prevent the face plate's turning except when desired.

The 1/4 horsepower synchronous motor (much larger than neccessary) turns 3000 revolutions per minute on 50 cycle current. It is enclosed in a shield made of 18 alternate layers of 0.018 Armco iron and sheet copper, the iron being brought out and bolted to give a continuous magnetic circuit.

A flexible coupling with a fiber disk insulates the motor from the rectifier.

§4 Adjustment of the Rectifier.

By screwing the bushings in which the rods carrying the outer contact points slide, the apparatus is adjusted visually and tactually until contact seems to occur in the middle of the stroke. A constant error of not to exceed 5% may be expected from this setting. If greater precision is desired, a dry cell may be so connected that the alternating current output feeds into a millivoltmeter, and the contacts then adjusted to give zero deflection. The contact points must be cleaned occasionally with alcohol.

To make the phase adjustment, alternating current is fed in and the face plate rotated until zero deflection is obtained. The face plate is then set normal to this position.

§5 Behavior of the Rectifier with Various Galvanometers.

The behavior of the rectifier with four galvanometers of different characteristics has been investigated. Both circuit and face plate are grounded when in use.

With a Leeds and Northrup pointer galvanometer 2320-d, coil resistance 1000 ohms, period 3 seconds, direct current sensitivity 0.5microamperes per millimeter scale division, the alternating current sensitivity is 0.6 microamperes per millimeter scale division. It was measured by taking 2 volts from a transformer and stepping down through a potential divider. The deflections are linear with the current, steady, and reverse accurately if the face plate is turned through 180 degrees. The motor shield is unnecessary with this galvanometer.

With a Leeds and Northrup type P reflecting galvanometer 2239-a, coil resistance 124 ohms, period 10 seconds, direct current sensitivity 0.011 microamperes per millimeter deflection at one meter, the alternating current sensitivity is 0.018 microamperes per millimeter. It was measured by stepping 110 volts down through a potential divider. A transformer in the vicinity caused considerable disturbance. The deflections are linear with the current, steady, and reverse accurately if the face plate is turned through 180 degrees. Without the motor shield, the zero shifts about 3 millimeters when the face plate is rotated.

With a Leeds and Northrup type HS reflecting galvanometer 2285-a, coil resistance 18.4 ohms, period 8.3 seconds, direct current sensitivity without critical damping resistance 0.033 microvolts per millimeter, the alternating current sensitivity is 0.048 microvolts per millimeter, measured as in the previous case. The deflections are approximately linear with the current and are steady to about 1 millimeter. The motor shields are essential and even with them, the shift of zero point is about 5 millimeters when the face plate is rotated. Both the HS galvanometers are easily disturbed if a line, even of twisted wire, carrying an ampere or so gets near the input leads. Part of the zero deflection may be due to other things in the vicinity rather than to the motor.

With a Leeds and Northrup type HS reflecting galvanometer 2285-f, coil resistance 915 ohms, period 21.1 seconds, direct current sensitivity 2.8×10^{-5} microamperes per millimeter, the alternating current sensitivity is 3.3×10^{-5} microamperes per millimeter, measured as in the two preceding cases. The deflections are approximately linear with the current, and as steady as in direct current measurements. There is a zero shift of some 5 centimeters when the face plate is rotated, which appears to be affected by the room lights and similar disturbances, with the motor shielded. Measurements with this instrument were difficult because of the long period and severe over-damping.

§6 Discussion.

This rectifier has the advantages over the vibration galvanometer of greater sensitivity and automatic tuning to the proper frequency, but requires a power source, either mechanical or electrical, of the same frequency as the effect to be measured. Over the alternating current galvanometer, there are the advantages of independence of the circuit constants (except insofar as they affect the damping), of the possibility of using mechanical rather than electrical power, and of using an auxiliary with a standard instrument, rather than an expensive, separate one. Measurements of phase are impossible with the vibration galvanometer alone, and are difficult with the alternating current galvanometer, but are quite simple with this rectifier.

§7 Limitations on Voltage Amplification at Commercial Frequencies.

The problem may be put in the form, what is the smallest potential which may be impressed on the input of an amplifier and yet cause an observable effect in the output of that amplifier. When a telephone receiver is used as the detecting instrument, one hears, after a certain amount of amplification has been used, noise in the receiver even though there is no input at all. The smallest detectable input is then that which when amplified is just observable against the background of noise already present.

The noise present in amplifiers is due to a variety of causes. First, there are disturbances due to external conditions, e.g., microphonic noises and pick-up from light circuits. Second, there are those originating in the circuits external to the tubes, due to oscillating circuits, leaks across condensers or resistances, etc. These two may be eliminated by proper design and location of the amplifier, although it frequently requires some study to accomplish this in a particular case. Finally, noise originates within the tubes themselves because of leaks across insulation, production of positive ions in the residual gas, and certain other effects, most serious of which is the particulate nature of the electrons. By reason of this particulate nature, electricity passes through the tube as individual particles, and hence statistically, rather than as a continuous fluid. The statistical fluctuations in the flow are fluctuations of current and, with sufficient amplification, appear as noise. All other internal tube noises can be reduced to imperceptible amounts, but this effect, being dependent on the nature of electricity itself, cannot be reduced. It can be partially avoided by the use of very high amplification in the first tube, but there are stability limits for such amplification, and moreover, the conditions for attaining it are incompatible with those for eliminating other tube noises. Until a way out of this difficulty is found, the limit of detectable input is the order of this irreducible noise, about 10^{-6} volts. If an amplifier could be constructed without a first stage, the problem might be solved, but so far, no progress has been made in this direction.

Since the noise is distributed over all frequencies, the probable energy in any particular frequency band at any time is itself infinitesimal if the frequency band is. If the input is monofrequentic, and other noise frequencies are filtered out, it should be possible to detect inputs much smaller than 10^{-6} volts. However, it seems that as the sensitivity of a detecting device is increased, so also is its period of response. If we integrate the noise over an infinite period, it attains infinite amplitude at every frequency. Hence the period, and the sensitivity, of the detecting instrument cannot be extended indefinitely, for a new limiting phenomenon has appeared.

§8 Description of the Amplifier.

For an investigation of this sort, it is not necessary to use the somewhat troublesome circuits and tubes used to reduce the noise as far as possible, for any noise level will do as well. The amplifier used consisted of as many Western Electric 102-D tubes as could be used in the particular test, resistance coupled with 1 microfarad coupling condensers, 200,000 ohm coupling resistances, 270 volt B batteries and 500,000 ohm grid leaks. 0.015 microfarad filter condensers shunted each coupling resistance. The amplifier and B batteries were enclosed in a 16-gauge sheet-iron box. The noise level corresponded to an input of about 5×10^{-4} volts.

A special output transformer designed to operate between a Western Electric 102-D tube and a 1000 ohm galvanometer was loaned us by the Seismological Laboratory and was used in this work.

§9 Use of the Amplifier with Tuned Instruments.

At commercial frequencies, electrical tuning is not practicable and the only device of this sort used was the filter condensers shunting the coupling resistances. These serve to remove any high-frequency disturbances.

If the output from an amplifier be fed into a vibration galvanometer, and the light beam from that galvanometer be allowed to so impinge on a photoelectric cell attached to the input that the width of the light beam on the cell changes with a small change in the position of the galvanometer mirror, then any signal given the amplifier will be regenerated by this optical system. Such an optical system was tried, but was unsatisfactory because of the great effect of very slight jars and the like which set the galvanometer to vibrating.

A Leeds and Northrup alternating current galvanometer 2470 was also tried, current for actuating the field and potential for the input both being taken from a 110-volt line. With such a galvanometer, it is necessary that the inductive reactance of the circuit of which its coil is a part predominate over the capacitive reactance if the instrument is to be stable. But it is also necessary that the total reactance be nearly zero if it is to be sensitive. The reactance was a function of the primary circuit of the output transformer, i.e., of an amplifier delivering a heavy and fluctuating current, and was therefore not constant. If, then, enough capacity were included in the circuit to give the instrument satisfactory sensitivity, it shortly became unstable. Because of this difficulty, no further work was done with this type of galvanometer.

A Leeds and Northrup vibration galvanometer 2350-a was tried, using a 20-cycle, 0.005-volt input from an earth inductor coil, stepped down, when necessary, through a potential divider. With two stages of amplification, the galvanometer was perfectly steady and gave 1 millimeter deflection at 1 meter for an input of 6×10^{-6} volts. When two more stages were added, the fluctuations became serious. An input of 2×10^{-7} volts could be detected, but only by immediate comparison with the zero position. The deflections were nearly linear with any number of stages, but the system is not suitable for, in general, other than null measurements, because of the inconstant sensitivity.

Very similar results were obtained with a Leeds and Northrup type P galvanometer 2239-a in conjunction with the rectifier described in the first part of this thesis. With one stage of amplification, the galvanometer was steady and the system had a sensitivity of 7.5×10^{-6} volts input per millimeter deflection. With three stages of amplification, this galvanometer was so unsteady that only about 2×10^{-7} volts input could be detected.

If the type P galvanometer were replaced by a type HS 2285-a, the same limit was reached, but with only two stages of amplification. In all cases, if higher amplification than that noted above were used, either the amplifier blocked, or the galvanometer became too unsteady to read. With any number of tubes, the unsteadyness observed remained both qualitatively and quantitatively the same if no input was used, and hence appears to have been due solely to disturbances generated within the amplifier.

§10 Discussion.

From these data, it appears that the use of tuned instruments makes it possible to read easily a voltage 0.01 of that corresponding to the noise level of the amplifier, and to detect 0.001 of that voltage. It will be noticed that there is no gain in sensitivity when the amplifier is such as we have used, over the sensitivity of the galvanometers used directly, but, even here, there is the advantage of requiring very little power. Such a system could be used directly, e.g., on polarizable cells.

We may extrapolate these results and predict that with an amplifier whose noise level is that corresponding to 10^{-6} volts, it should be possible to detect at least 10^{-8} volts.

§11 References.

1. C. Dannatt and N. Holt "A Precision Average Voltmeter for Power Frequencies" World Power vol. 7 (1927) p. 241

2. Sharp and Crawford "Some Recent Developments in Exact Alternating Current Measurements" Proc.A.I.E.E. vol.29 part 2 (1910) p. 1518

II THE NORMAL FREQUENCIES OF VIBRATION FOR SYSTEMS OF POINT PARTICLES HAVING TETRAHEDRAL AND OCTAHEDRAL SYMMETRY.

ABSTRACT

By treating symmetrical systems of point particles as non-holonomic systems, the work involved in solving for the normal frequencies is lessened. The case of central forces is treated for both XY_4 and XY_6. The results obtained for XY_4 agree with those of previous investigators, but those for XY_6 do not.

§1 Introduction.

Recent texts on analytical dynamics in general treat non-holonomic systems only sufficiently to show how they may be converted into holonomic ones in special cases. The general equations for non-holonomic systems are little more complicated than those for holonomic, and may actually be easier to solve because of higher symmetry. To attain this higher symmetry, it may be expedient in some cases to put ordinarily holonomic systems into non-holonomic form. Such is the case in the systems considered below.

§2 The Lagrangian Equations when the Number of Coordinates Exceeds the Number of Degrees of Freedom.[1,2,3]

Since Hamilton's principle in its usual form

$$\delta\int_{t_1}^{t_2} L(q_1 \cdots q_{3n}\, \dot{q}_1 \cdots \dot{q}_{3n}\, t)\,dt = 0 \qquad (1)$$

does not depend on the coordinates chosen for the discussion of a problem, it will hold whether the system is holonomic or not. The equation

$$\int_{t_1}^{t_2}\left\{\sum_{i=1}^{3n}\left(\frac{\partial L}{\partial q_i} - \frac{d}{dt}\frac{\partial L}{\partial \dot{q}_i}\right)\delta q_i\right\} dt = 0 \qquad (2)$$

follows from equation (1) without regard to the interdependence of the coordinates. If these coordinates are related by the m equations of constraint

$$_jf(q_1 \cdots q_{3n}\, t) = 0 \qquad (j = 1, 2, \cdots m) \qquad (3)$$

we may eliminate m coordinates and their derivatives from L, or instead, we may formally remove their interdependence by multiplying the variations of the equations of constraint (3) by undetermined functions λ_j and adding these to equation(2) to give

$$\int_{t_1}^{t_2}\left\{\sum_{i=1}^{3n}\left(\frac{\partial L}{\partial q_i} - \frac{d}{dt}\frac{\partial L}{\partial \dot{q}_i} + \sum_{j=1}^{m}\lambda_j\frac{\partial\, _jf}{\partial q_i}\right)\delta q_i\right\} dt = 0 \qquad (4)$$

We may now, by the usual reasoning, write the 3n equations

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{q}_i} - \frac{\partial L}{\partial q_i} = \sum_{j=1}^{m}\lambda_j\frac{\partial\, _jf}{\partial q_i} \qquad (i = 1, 2, \cdots 3n) \qquad (5)$$

which, together with the m equations of constraint (3) determine the values of the 3n coordinates and m undetermined multipliers.

In addition to the usual type of geometric conditions, any known integrals of the equations of motion may be used as constraints.

3 Infinitesimal Oscillations about Equilibrium for an Isolated System of n Point Particles.

For such a system, L is not a function of the time and is equal to T minus V, where T is the kinetic and V the potential energy of the system. The six integrals of linear and angular momentum[4], which will all be taken equal to zero in the cases we shall consider, provide six equations of constraint. To describe the system, we shall use n sets of rectangular Cartesian coordinates, derivable from one another by translation, with origins at the positions of the n particles when the system is in an equilibrium configuration.

The potential energy may be expanded in a Maclaurin's series in 3n variables about this equilibrium configuration, where it will be assigned the value zero. Third and higher powers will be neglected. The condition that $\partial V/\partial q_i = 0$ in the equilibrium configuration does not follow in general from the equations of motion (5) for these partial derivatives are related, not to the total force along the corresponding coordinate, but only to that part of it due to reactions included in L as distinguished from reactions included in the constraints. If, however, an equilibrium configuration of the system remains an equilibrium configuration in the absence of the constraints, or if the constraints exert no forces in the equilibrium configuration, or again, if the constraints do not determine the equilibrium configuration, but only the permitted displacements, then <u>in that configuration</u> $\partial V/\partial q_i = 0$[5] and these partial derivatives are the negatives not only of that part of the forces due to reactions included in L, but also of the total forces along the corresponding coordinates. In the systems of interest, then, the coefficients of the first powers in the Maclaurin's series expantion are individually zero and the potential energy is given by

$$2V = \sum_{i=1}^{3n} \sum_{j=1}^{3n} b_{ij}\, q_i\, q_j \qquad (6)$$

The vanishing of the first powers can also be deduced by a direct consideration of the forces. Consider any component of force on the i th particle, say Q_i. This will be the sum of components of forces due to various internal and external reactions. Each of these may be separately expanded in a Maclaurin's series about the equilibrium position and these series added term by term. Then $Q_i = Q_{io} + \sum_{j=1}^{3n} Q_{ij}\, q_j + \cdots$. Since the q's are zero in the equilibrium configuration, $Q_i = Q_{io} = 0$ there, and hence $Q_{io} = 0$ for all configurations. If as is true in the systems of interest, the forces that make up Q_{io} arise solely from reactions included in V, then $\partial V/\partial q_i = 0$.

Since the kinetic energy of this system is the sum of the kinetic energies of the particles composing it, and since the coordinates for each particle are orthogonal, no cross products will appear[6]. Therefore

$$2T = \sum_{i=1}^{3n} a_i\, \dot{q}_i^{\,2} \qquad (7)$$

where the a's are constants.

The equations of constraint are, for the cases of interest, homogeneous, linear functions of the coordinates.

$${}_jf(q_1 \cdots q_{3n}) = \sum_{i=1}^{3n} {}_jf_i\, q_i = 0 \qquad (j = 1,2,\cdots 6) \quad (8)$$

The undetermined multipliers may be written as ${}_o\lambda_j + {}_1\lambda_j$ where ${}_o\lambda_j$ is the constant value of λ_j in the equilibrium configuration.

Since the equations of motion (5) must be satisfied when the variables and their derivatives are all zero, the ${}_o\lambda$'s are all zero and we have

$$\left.\begin{aligned} a_i \ddot{q}_i + \sum_{j=1}^{3n} b_{ij}\, q_j &= \sum_{r=1}^{6} {}_1\lambda_r\, {}_rf_i & \qquad (i = 1,2,\cdots 3n) \\ \sum_{i=1}^{3n} {}_rf_i\, q_i &= 0 & \qquad (r = 1,2,\cdots 6) \end{aligned}\right\} \qquad (9)$$

To solve, let

$$q_i = A_i e^{\mu t}$$
$$_1\lambda_i = -M_i e^{\mu t} \tag{10}$$

Then

$$(a_i\mu^2 + b_{ii})A_i + \sum_{\substack{j=1\\ j\neq i}}^{3n} b_{ij} A_j + \sum_{r=1}^{6} {}_r f_i M_i = 0 \qquad (i = 1,2,\cdots 3n)$$
$$\sum_{i=1}^{3n} {}_r f_i A_i = 0 \qquad (r = 1,2,\cdots 3n) \tag{11}$$

The condition for the coexistance of equations (11) is that the determinant Δ of the coefficients of the A's and M's vanish. Δ is a $(3n+6)$th order axisymmetric determinant with six rows and six columns of constants and is of the $(3n-6)$th degree in the variable μ^2. The variable is confined to the 3n non-zero elements of the principle diagonal. In the systems we shall consider, the symmetry is such that the terms of Δ may be arranged to form a "block circulant",

$$\begin{vmatrix} E & F & G \\ G & E & F \\ F & G & E \end{vmatrix} = 0$$

where E, F, and G are square arrays of the $(n+2)$th order. Δ may then be factored into three determinants, each of the $(n+2)$th order, by taking the sum of the k th rows of E, F, and G to be the k th row of one factor and the sum of the k th row of E, ω times the k th row of F, and ω^2 times the k th row of G to be the other two, where ω is successively each of the two complex cube roots of unity.[7]

§4 Normal Frequencies for Systems of Type XY_4 in a Regular Tetrahedron.

We locate the equilibrium positions of the five particles in a set of rectangular Cartesian coordinates as follows: 1 at 000, 2 at aaa, 3 at $\bar{a}\bar{a}a$, 4 at $a\bar{a}\bar{a}$, 5 at $\bar{a}a\bar{a}$. Using five new sets of coordinates obtained by translation as indicated in §3, the coordinates after displacement of the particles from equilibrium are: x_0, y_0, z_0 for 1; x_1, y_1, z_1 for 2; etc. We denote the mass of 1 by

m_0, that of any peripheral particle by m_1; the force constant associated with a force between the central and any peripheral particle along the line joining them by k_{01}, that similarly associated with a force between two peripheral particles by k_{12}; the angle between the line from the center to a corner and any edge to that corner by θ ($\cos\theta = 1/\sqrt{3}$), that between the projection of an edge on a parallel coordinate plane and an axis in that plane by φ ($\cos\varphi = 1/\sqrt{2}$). We further denote the ratio of the force due to the interaction between the central and any peripheral particle when the system is in an equilibrium configuration, to the distance between them in that configuration by b, and the analogous ratio concerning two peripheral particles by h. ($b = -4h$)

The kinetic and potential energies for infinitesimal displacements and velocities are then as given by the following equations.

$$2T = m_0(\dot{x}_0^2+\dot{y}_0^2+\dot{z}_0^2)+m_1(\dot{x}_1^2+\dot{y}_1^2+\dot{z}_1^2+\dot{x}_2^2+\dot{y}_2^2+\cdots+\dot{z}_4^2)$$

$$\begin{aligned}
2V = {} & (k_{01}/3)\Big[(x_1+y_1+z_1-x_0-y_0-z_0)^2+(-x_2+y_2-z_2+x_0-y_0+z_0)^2 \\
& \quad +(-x_3-y_3+z_3+x_0+y_0-z_0)^2+(x_4-y_4-z_4-x_0+y_0+z_0)^2\Big] \\
& +(2b/3)\Big\{\Big[(x_1-x_0)^2+(x_2-x_0)^2+(x_3-x_0)^2+(x_4-x_0)^2+(y_1-y_0)^2+(y_2-y_0)^2 \\
& \quad +(y_3-y_0)^2+(y_4-y_0)^2+(z_1-z_0)^2+(z_2-z_0)^2+(z_3-z_0)^2+(z_4-z_0)^2\Big] \\
& \quad -\Big[(x_1-x_0)(y_1-y_0)+(x_1-x_0)(z_1-z_0)+(y_1-y_0)(z_1-z_0) \\
& \quad +(x_0-x_2)(y_2-y_0)+(x_0-x_2)(z_0-z_2)+(y_2-y_0)(z_0-z_2) \\
& \quad +(x_0-x_3)(y_0-y_3)+(x_0-x_3)(z_3-z_0)+(y_0-y_3)(z_3-z_0) \\
& \quad +(x_4-x_0)(y_0-y_4)+(x_4-x_0)(z_0-z_4)+(y_0-y_4)(z_0-z_4)\Big]\Big\} \\
& +(k_{12}/2)\Big[(x_1+z_1-x_2-z_2)^2+(x_1+y_1-x_3-y_3)^2+(y_1+z_1-y_4-z_4)^2 \\
& \quad +(y_2-z_2-y_3+z_3)^2+(x_2-y_2-x_4+y_4)^2+(x_3-z_3-x_4+z_4)^2\Big] \\
& +(b/8)\Big\{\Big[(x_1-z_1-x_2+z_2)^2+(x_1-y_1-x_3+y_3)^2+(y_1-z_1-y_4+z_4)^2 \\
& \quad +(y_2+z_2-y_3-z_3)^2+(x_2+y_2-x_4-y_4)^2+(x_3+z_3-x_4-z_4)^2\Big] \\
& \quad +2\Big[(x_1-x_4)-(x_2-x_3)-(y_1-y_2)-(y_3-y_4)-(z_1-z_3)-(z_2-z_4)\Big]
\end{aligned} \tag{12}$$

There are also the six equations of constraint obtained from the integrals of linear and angular momentum.

$$
\begin{aligned}
m_0x_0+m_1(x_1+x_2+x_3+x_4) &= 0\\
m_0y_0+m_1(y_1+y_2+y_3+y_4) &= 0\\
m_0z_0+m_1(z_1+z_2+z_3+z_4) &= 0\\
y_1+y_2-y_3-y_4-z_1+z_2+z_3-z_4 &= 0\\
x_1+x_2-x_3-x_4-z_1+z_2-z_3+z_4 &= 0\\
x_1-x_2-x_3+x_4-y_1+y_2-y_3+y_4 &= 0
\end{aligned}
\qquad (13)
$$

When the Lagrangian determinantal equation discussed in § 2 is set up and solved, we find four distinct roots. The corresponding frequencies follow, the figure in parentheses being the multiplicity.

$$4\pi^2\nu_1^2(1)=(k_{01}+4k_{12})/m_1$$ strong

$$4\pi^2\nu_2^2(2)=(k_{12}-b/4)/m_1 \qquad (14)$$

$$4\pi^2\nu_{3,4}^2(3) = \frac{1}{m_1}\left\{A \pm\sqrt{A^2-\frac{m_0+4m_1}{6m_0}(4k_{01}k_{12}-5k_{01}b-8k_{12}b-2b^2)}\right\}$$

$$A = \frac{4m_1+m_0}{6m_0}(k_{01}-2b)+k_{12}+b/12+k_{01}/3$$

§ 5 Normal Frequencies for Systems of Type XY_6 in a Regular Octahedron.

The general procedure is identical with that of §4. The particles are located as follows: 1 at 000, 2 at a00, 3 at 0a0, 4 at $\bar{a}00$, 5 at $0\bar{a}0$, 6 at 00a, and 7 at $00\bar{a}$. There is one additional force constant, k_{24}, associated with a force between two opposite peripheral particles, and an additional ratio, j, involving the reactions and distances of two opposite peripheral particles. For this system, $\cos\theta = 1/\sqrt{2}$, and $b = -4h-2j$.

The kinetic and potential energies for infinitesimal displacements and velocities are given by the following equations.

$$
\begin{aligned}
2T &= m_0(\dot{x}_0^2+\dot{y}_0^2+\dot{z}_0^2)+m_1(\dot{x}_1^2+\dot{y}_1^2+\dot{z}_1^2+\dot{x}_2^2+\dot{y}_2^2+\cdots+\dot{z}_6^2) \\
2V &= k_{01}\left[(x_1-x_0)^2+(x_3-x_0)^2+(y_2-y_0)^2+(y_4-y_0)^2+(z_5-z_0)^2+(z_6-z_0)^2\right] \\
&\quad +b\left[(x_2-x_0)^2+(x_4-x_0)^2+(x_5-x_0)^2+(x_6-x_0)^2+(y_1-y_0)^2+(y_3-y_0)^2\right. \\
&\qquad \left.+(y_5-y_0)^2+(y_6-y_0)^2+(z_1-z_0)^2+(z_2-z_0)^2+(z_3-z_0)^2+(z_4-z_0)^2\right] \\
&\quad +(k_{12}/2)\left[(x_1-y_1-x_2+y_2)^2+(x_1-z_1-x_5+z_5)^2+(x_1+y_1-x_4-y_4)^2\right. \\
&\qquad +(x_1+z_1-x_6-z_6)^2+(y_2-z_2-y_5+z_5)^2+(x_2+y_2-x_3-y_3) \\
&\qquad +(y_2+z_2-y_6-z_6)^2+(x_3-z_3-x_6+z_6)^2+(x_3-y_3-x_4+y_4) \\
&\qquad \left.+(x_3+z_3-x_5-z_5)^2+(y_4+z_4-y_5-z_5)^2+(y_4-z_4-y_6+z_6)\right] \\
&\quad +(h/2)\left[(x_1+y_1-x_2-y_2)^2+(x_1-z_1-x_6+z_6)^2+(x_1-y_1-x_4+y_4)^2\right. \\
&\qquad +(x_1+z_1-x_5-z_5)^2+(y_2+z_2-y_5-z_5)^2+(x_2-y_2-x_3+y_3)^2 \\
&\qquad +(y_2-z_2-y_6+z_6)^2+(x_3+z_3-x_6-z_6)^2+(x_3+y_3-x_4-y_4)^2 \\
&\qquad \left.+(x_3-z_3-x_5+z_5)^2+(y_4-z_4-y_5+z_5)^2+(y_4+z_4-y_6-z_6)^2\right] \\
&\quad h\left[(x_2-x_5)^2+(x_5-x_4)^2+(x_4-x_6)^2+(x_6-x_2)^2+(y_1-y_6)^2+(y_6-y_3)^2\right. \\
&\qquad \left.+(y_3-y_5)^2+(y_5-y_1)^2+(z_1-z_2)^2+(z_2-z_3)^2+(z_3-z_4)^2+(z_4-z_1)^2\right] \\
&\quad k_{24}\left[(x_1-x_3)^2+(y_2-y_4)^2+(z_5-z_6)^2\right] \\
&\quad j\left[(x_2-x_4)^2+(x_5-x_6)^2+(y_1-y_3)^2+(y_5-y_6)^2+(z_1-z_3)^2+(z_2-z_4)^2\right]
\end{aligned} \tag{15}
$$

As in the preceding system, there are six equations of constraint.

$$
\begin{aligned}
m_0x_0+m_1(x_1+x_2+x_3+x_4+x_5+x_6) &= 0 \\
m_0y_0+m_1(y_1+y_2+y_3+y_4+y_5+y_6) &= 0 \\
m_0z_0+m_1(z_1+z_2+z_3+z_4+z_5+z_6) &= 0 \\
y_5-y_6-z_2+z_4 &= 0 \\
x_5-x_6-z_1+z_3 &= 0 \\
x_2-x_4-y_1+y_3 &= 0
\end{aligned} \tag{16}
$$

From these we obtain, as in §4, the frequencies. In this case, however, there are six distinct roots in the determinant.

$$4\pi^2\nu_1^2(1) = (k_{01}+4k_{12}+2k_{24})/m,$$
$$4\pi^2\nu_2^2(3) = (2k_{12}-2h)/m,$$
$$4\pi^2\nu_3^2(3) = (k_{12}+h-2j)/m, \tag{17}$$
$$4\pi^2\nu_4^2(2) = (k_{01}+k_{12}+2k_{24}+3h)/m,$$
$$4\pi^2\nu_{5,6}^2(3) = \frac{1}{m_0 m_1^2}\left\{A \pm \left[A^2 + m_0 m_1^2(m_0+6m_1)(-k_{01}k_{12}+3k_{01}h+2k_{01}j+4\{2h+j\}\{k_{12}+h\})\right]^{1/2}\right\}$$
$$A = \frac{m_1}{2}(m_0+2m_1)k_{01}+\frac{3}{2}k_{12}-\frac{1}{2}(m_0+16m_1)h-(m_0+4m_1)j$$

§6 Discussion.

Dennison[8], Schaefer[9], Radakovic[10], and Urey and Bradley[11] have investigated the former of the two systems discussed in this paper. In all cases they set up the potential energy in terms of as many coordinates as there are degrees of freedom. This requires the the solution of a ninth degree ninth order determinantal equation instead of the two seventh order third degree determinantal equations used in this investigation. Since their ninth degree equation has only four unequal roots, it could be solved by straightforward methods, but the labor involved is so great as to make the use of special methods nescessary. The advantages of the method here used are not very great in this case.

Equations 14 are in agreement with those obtained by the above-mentioned workers, but their interpretation of b as proportional to $\partial V/\partial r_i$, where r_i is the distance between the central and a peripheral particle, in a certain system of coordinates, is incorrect, since by applying the analysis of §3, it may be shown that these coefficients are resultant forces which vanish, not forces due to particular interactions which do not vanish.

Application of equations 14 to data on various molecules supposed to have this structure has been made by the investigators given above and by others. The agreement, better than one per cent for the tetrachlorides of carbon, silicon, titanium, and tin, is better than would be expected from the approximations made in applying this analysis to real molecules.

Redlich, Kurz, and Rosenfeld[13] have treated the octahedral system, setting up the equations of motion from the standpoint of forces rather than potentials. They have overlooked the interaction due to changes in the angles of application of the forces when the molecule is distorted. Equations 17 reduce to theirs if b is set equal to zero.

There is at present insufficient experimental data to permit a test of equations 17. If only four frequencies were found experimentally, k_{24} and j could be assumed zero to a first approximation and the other three constants evaluated. k_{12} and h could then be used to compute the constants of the Morse function and k_{24} and j obtained from it. New values of k_{12} and h could then be calculated, and so on.

7 References.

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