The Journal of Chemical Physics

A Mechanical Analyzer for the Solution of Secular Equations and the Calculation of Molecular Vibration Frequencies

D. P. MacDougall and E. Bright Wilson Jr.

Citation: The Journal of Chemical Physics **5**, 940 (1937); doi: 10.1063/1.1749967
View online: http://dx.doi.org/10.1063/1.1749967
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/5/12?ver=pdfcov
Published by the AIP Publishing

at over a hundred points and the integrations are performed graphically with the aid of a planimeter. When $\lambda_2=3$, $\mu_2=1.0$ (i.e. $r_{c2}=0$) the integrands become infinite and it is necessary to carry out the integrations analytically in this region. The accuracy of the numerical integrations is considerably decreased by a partial cancellation of positive and negative contributions to the integrals. However, we believe that we have obtained sufficient accuracy for the purposes of this paper. The following is a summary of the numerical values of the second derivatives of the integrals which we used:

(Numbers in units of e^2/a_0 for $R=2.0a_0$)

$$L''(aa,\,bc)=0.029921,\quad L''(bb,\,ac)=0.052345,$$
$$L''(ab,\,ac)=0.033504,\quad L''(ab,\,bc)=0.000248,$$
$$L''(ac,\,ac)=0.021646,\quad L''(aa,\,cc)=0.058286,$$
$$L''(aa,\,ac)=0.059021,\quad K''(a,\,bc)=0.035949,$$
$$K''(b,\,ac)=0.058053,\quad J''(R_{ac})=0.073263,$$
$$G''(R_{ac})=0.061640,\quad I''(R_{ac})=0.122104.$$

We wish to express our appreciation to the American Philosophical Society for financial aid throughout the course of this work.

DECEMBER, 1937 JOURNAL OF CHEMICAL PHYSICS VOLUME 5

A Mechanical Analyzer for the Solution of Secular Equations and the Calculation of Molecular Vibration Frequencies

D. P. MacDougall and E. Bright Wilson, Jr.
Mallinckrodt Chemical Laboratory, Harvard University, Cambridge Massachusetts

(Received September 18, 1937)

A set of coupled harmonic oscillators has been constructed, so designed that it can be used to solve the numerical secular equations occurring in the theory of the vibration of polyatomic molecules and in other problems. Each oscillator consists of a shaft with cross arms carrying weights to increase the moment of inertia and springs to provide restoring force. The unit is free to rotate about the axis of the shaft, except for the restoring force of the springs. The various units are connected to one another by additional springs. In operation the springs and weights are adjusted to values which represent the coefficients of the secular equation to be solved, the whole device is driven by an eccentric of variable speed, and the frequencies of resonance, representing the roots of the equation, are measured.

Kettering, Shutes and Andrews[1] introduced the method of analyzing the vibrational spectra of polyatomic molecules by the use of vibrating models consisting of steel balls representing the atoms, connected by springs representing the valence bonds. By vibrating such a model with a motor and eccentric system, the frequencies of resonance of the model can be picked up and measured. Despite the many advantages which this method possesses, it also has certain limitations. It is difficult, for example, to construct a model sufficiently close to the ideal of point masses and weightless springs, especially since the springs must be rigidly attached to the balls and must be capable of resisting tension, compression, bending, and in some cases torsion. For each of these multiple duties the spring must have the proper force constant. The most serious limitation, however, is the lack of flexibility of the apparatus. A model must be built, not only for each molecule, but also for each set of trial values of the various force constants, since the springs are not adjustable. Furthermore, there are many types of potential function which cannot be reproduced by such a model because of geometrical limitations—springs may get in one another's way, for example.

Because of the great power of the Andrews' method, it seemed important to devise a mechanical analyzer that would preserve the advantages and overcome the difficulties mentioned above. In order to achieve this end, the geometrical analogy between the molecule and the model was discarded, since what is really desired is a mechanical system having the same potential and kinetic energies (except for a scale factor) as the molecule. A set of coupled harmonic oscillators forms such a system if the coupling is of the proper form.

[1] Kettering, Shutes and Andrews, Phys. Rev. 36, 531 (1930); F. Trenkler, Physik. Zeits. 36, 162 (1935), etc.

Description of Apparatus

The apparatus finally built consists of units, each unit being essentially a harmonic oscillator. A unit consists of a horizontal shaft mounted so that it can rotate in two ball bearings. Perpendicular to this shaft are a number of Duralumin rods which pass through holes in the shaft provided with set screws to hold the rods in place. These rods are parallel to one another and each is grooved from end to end. One of them carries a brass weight on either side of the shaft. These weights give the oscillator unit a moment of inertia which is readily adjustable since the weights may be slid in and out along the rods and held at any point by a set screw. There are also several sizes of weights. See Fig. 1.

Another cross rod, at the end, is used to provide an adjustable restoring force for the unit, this being accomplished by connecting to it two springs the other ends of which are attached to fixed points, one on each side. See Fig. 2.

Such a unit behaves like a harmonic oscillator if the shaft is rotated slightly from the equilibrium position determined by the springs at the end. Gravity has no effect since the two weights are balanced. The frequency of vibration will depend on the position and size of the weights (the moment of inertia of the system about the shaft) and on the restoring force of the springs, which is adjusted by changing the position of the springs on the cross rod.

The complete machine consists of a number of such units (we have actually used five) mounted with their shafts parallel to one another and connected by coupling springs. See Fig. 3. These coupling springs connect one unit with another as desired, using the extra cross rods as shown

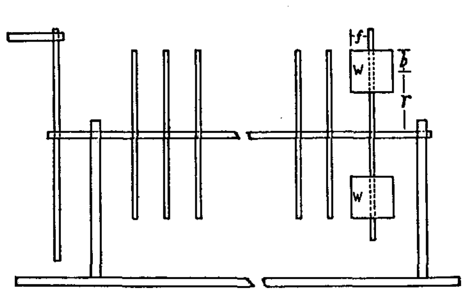

FIG. 1. Side view of one oscillator unit without springs.

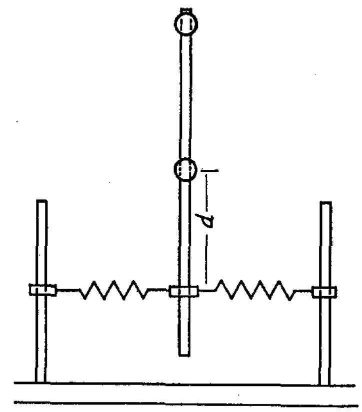

FIG. 2. End view of one oscillator unit showing "positive" springs.

in Fig. 4. Each unit may be connected with any other (or several other) units, with either positive or negative coupling coefficients. The springs are attached to the rods by means of small connectors which slide on the rods and are held at any point by set screws. These make the effective restoring forces adjustable; they also hold the springs slightly to one side so that crossed springs (Fig. 4a) do not touch each other.

Finally, springs may be connected from the projecting top piece of an end rod to the base below the end of the shaft. Such a spring, called a "negative" spring, (Fig. 5) tends to unstabilize the usual equilibrium position, in contrast to the effect of the "positive" springs illustrated in Fig. 2. They are only used when the coupling springs provide more restoring force to the single unit than is desired. The springs have been wound on a lathe from steel piano wire, most of them from wire 0.037″ in diameter.

The whole mechanism is driven by a light spring which connects one of the cross rods with an eccentric driven through a variable speed reducer with a friction drive, connected to an electric motor. The method of operation, after the constants have been set, is to vary the speed of the driving mechanism until a speed is reached which produces a maximum oscillation of the units. This is a resonance frequency of the machine and at that frequency the units undergo a normal oscillation. The frequency is measured with a stopwatch and a revolution counter on the eccentric shaft.

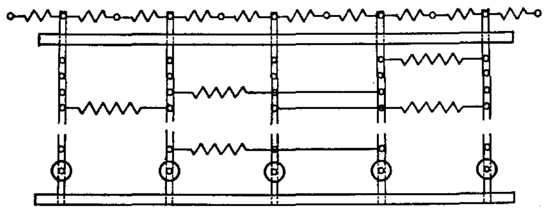

FIG. 3. Top view of five unit machine with arbitrary spring connections.

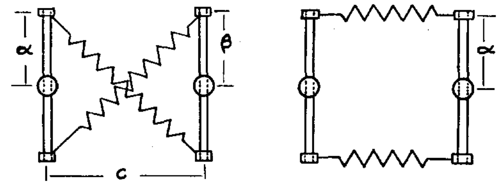

FIG. 4. View along two shafts showing coupling springs. (a) Coupling coefficient positive. (b) Coupling coefficient negative.

Principle

The kinetic energy of a system such as the one described above is

$$2T=\sum_{i=1}^{N} I_i\dot{\theta}_i^2, \tag{1}$$

where I_i is the moment of inertia of the ith unit, θ_i is the angular displacement of the ith unit from its equilibrium position, and N is the number of units. The potential energy is given by

$$2V=\sum_{i,\ j=1}^{N} a_{ij}\theta_i\theta_j, \tag{2}$$

in which the constants a_{ij} are determined by the springs. Thus, for $i\neq j$, the magnitude of a_{ij} is determined by the stiffness and position of the springs connecting the units i and j, while the sign of a_{ij} is determined by the mode of connection of these springs (Fig. 4(a) or (b)). The magnitude of a_{ii} is determined by the totality of restoring force due to all the springs attached to unit i, including those connecting it to other units. If the contribution of the coupling springs (a_{ij}) is too small, enough restoring force may be introduced by the use of "positive" springs (Fig. 2) to bring a_{ii} up to the desired values; if the coupling springs contribute too much to a_{ii}, enough may be subtracted by the use of "negative" springs (Fig. 5) to lower a_{ii} to the desired value.

The resonance frequencies of a system with these expressions for the kinetic and potential energies is obtained[2] by the solution of the secular equation:

$$\begin{vmatrix} a_{11}-I_1\lambda & a_{12} & a_{13} & \cdots & a_{1N} \\ a_{21} & a_{22}-I_2\lambda & a_{23} & \cdots & a_{2N} \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ a_{N1} & a_{N2} & a_{N3} & \cdots & a_{NN}-I_N\lambda \end{vmatrix}=0, \tag{3}$$

in which $\lambda=4\pi^2\nu^2$, ν being a resonance frequency. Consequently, since the machine may be set with any desired values of the coefficients a_{ij} and I_i, it is evident that a measurement of the resonance frequencies is in effect a mechanical solution of Eq. (3).

Application to Molecular Vibrations

In treating the vibrations of molecules, the secular Eq. (3) is obtained as part of the procedure for calculating the normal frequencies and modes of vibration. The quantities a_{ij} have the same significance as before; namely, they are the coefficients of the quadratic terms in $2V$. The quantities I_i are the coefficients in the kinetic energy expression $2T$ but they are not, in the case of molecules, moments of inertia. Their exact molecular significance depends upon the coordinates used to express $2T$ and $2V$.

The simplest coordinate system is one consisting of the Cartesian coordinates of each atom, measured from the equilibrium positions of each atom. In this system the quantities I_i are simply the masses of the atoms. The angles θ_1, θ_2, etc. of the model are to be correlated with the coordinates x_1, y_1, z_1, x_2, y_2, z_2, etc. It should be emphasized that each unit on the machine (and therefore each θ_i) is to be correlated with one coordinate of the molecule and not with one atom. Cartesian coordinates possess the advantage of giving the kinetic energy a simple form. It is usually fairly easy, also, to express the potential energy in terms of such coordinates. The disadvantage of Cartesian coordinates is that the secular equation in terms of them has $3n$

[2] This follows from the standard theory of small vibrations. See Jeans, *Theoretical Mechanics* (Ginn and Co., 1907), p. 348.

rows and columns (n being the number of atoms) and consequently $3n$ units are needed. Six of the roots (for nonlinear molecules) will be zero because of the six motions of translation and rotation.

If $3n-6$ internal coordinates, such as interatomic distances and angles, are used, the rows of the secular equation and the units of the machine are reduced in number to $3n-6$, but it is usually much harder to obtain the expression for the kinetic energy. Frequently such coordinates give the potential energy a very simple form. However, only such coordinates can be used on this machine which throw the kinetic energy into a form without cross terms $\dot{\theta}_i\dot{\theta}_j$.

If the molecule has any symmetry, this may be used to factor the secular equation and then each factor may be solved separately on the machine. There are two ways of doing this in general. One method uses $3n$ coordinates of some sort which are so chosen that they have the same symmetry as the normal coordinates and at the same time give the kinetic energy the necessary diagonal form (Eq. (1)). These coordinates are usually very convenient to obtain and use. However, distributed among the various factors of the secular equation, there will be six roots of value zero, so that some at least of these factors will be of higher degree than is necessary.

In order to eliminate these zero roots one may use $3n-6$ internal coordinates of some sort, having the symmetry properties of the normal coordinates and the property of transforming the kinetic energy into the proper diagonal form. So-called *symmetry coordinates*[3] are such a set of coordinates and are useful if factors up to the maximum capacity of the machine are to be solved. If the factors to be solved are of lower degree than the number of units, it is usually simpler to use the other choice of coordinates ($3n$ in number). Whenever the symmetry is used to factor the equation, group theory is of great utility, especially for more complicated molecules involving degeneracy.

Operation

In order to solve any particular example of Eq. (3) by means of the machine, the springs and weights are adjusted to give the proper values of a_{ij} and I_i, according to the following procedure:

If a pair of springs is connected between the ith and jth units as in Fig. 4(b), the contribution to $2V$ is $2K\alpha^2(\theta_i-\theta_j)^2$, or $a_{ij}=a_{ji}=-2K\alpha^2$, where K is the Hooke's law constant of the springs in dynes/cm and α is the length of the lever arm as shown in Fig. 4(b). There is also a contribution of $2K\alpha^2$ to a_{ii} and a_{jj}.

If a pair of springs is connected as shown in Fig. 4(a),

$$a_{ij}=a_{ji}=2K\alpha\beta\left(1-\frac{l}{g}+\frac{c^2l}{g^3}\right),$$

where α, β, and c are as shown in the figure, $g=(c^2+(\alpha+\beta)^2)^{\frac{1}{2}}$ and l is the length of the unstretched spring. There is a contribution

$$-2K\left[\alpha\beta-\alpha\beta\frac{l}{g}-\frac{\alpha^2c^2l}{g^3}\right] \text{ to } a_{ii}$$

and a contribution

$$-2K\left[\alpha\beta-\frac{\alpha\beta l}{g}-\frac{\beta^2c^2l}{g^3}\right] \text{ to } a_{jj}.$$

If a pair of "positive" springs are connected between the ith unit and fixed rods as shown in Fig. 2, they contribute an amount $+Kd^2$ to a_{ii}.

When it is necessary to reduce the restoring force on the ith unit, a "negative" spring is connected as shown in Fig. 5. This *subtracts* an amount $(Kst\delta)/u$ from a_{ii}, where s and t are as shown in the figure, $u=s+t$, and δ is the

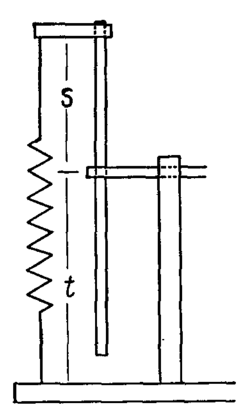

FIG. 5. Side view of end of one unit, showing "negative" spring in place.

[3] J. B. Howard and E. B. Wilson, Jr., J. Chem. Phys. **2**, 630 (1934).

amount which the spring has been extended from its unstretched length.

The force constants of the springs were determined with an accuracy of 0.2 to 0.3 of 1 percent by hanging a weight of suitable size on the end of the spring and measuring the frequency of oscillation of the pendant weight, from which $K=4\pi^2\nu^2(M+\frac{1}{3}m)$, if ν is the frequency of oscillation, M the mass of the weight hung on the spring and m the mass of the spring. Most of the springs used had a force constant of about 10^5 dynes/cm. Since a_{ij} varies as the square of the distance of the point of attachment of the spring from the axis, it is obvious that a wide range of values can be obtained with a single set of springs.

The moments of inertia of the various units are adjusted to the proper value by fixing the weights (w in Fig. 1) at the proper positions, taking into account the moment of inertia of the shaft, spring arms, etc. The weights make a contribution: $I=2M(r^2+b^2/3+f^2/4)$. M is the mass of one of the pair of weights; r, b, and f are as shown in Fig. 1. The weights used range from 200 grams to 1000 grams.

Since it is impossible to adjust springs and weights so as to obtain molecular magnitudes, some convenient scale factor is introduced. Hence the resonance frequencies of the machine bear a known relation to the frequencies of the equivalent molecule.

It is impossible to make the spring arms absolutely inflexible. The flexibility of the spring arms corresponds to a slight weakening in the springs, increasing as the distance from the axis increases according to the equation: $K_{\text{effective}}=K(1-\gamma\alpha^3)$. γ is determined by measuring the flexure of the spring arm for a known force. This correction is small, amounting only to 3–4 percent at the ends of the spring arms.

As the "negative" springs are somewhat cumbersome to adjust, it is fortunate that in many cases it is possible to eliminate them altogether. If we make the substitution $\lambda'=\lambda+\lambda_0$ in Eq. (3), we obtain a new determinantal equation, the solutions of which are each greater by λ_0 than the corresponding ones of the original equation. In addition, we note that each a_{ii} has been increased by an amount $I_i\lambda_0$. In principle then, we can always eliminate the necessity for "negative" springs by making λ_0 sufficiently large. If the secular equation being solved has one or more zero roots (translation or rotation), the machine will also display modes of motion of zero frequency with the result that it has no stable equilibrium position. This difficulty may be overcome by the use of the substitution just described, which increases all the frequencies. It might also be mentioned here that the usual transformations which leave the value of a determinant unchanged or multiply it by a number, such as multiplying a given row and a given column by a number or adding rows and columns, may often be applied to Eq. (3) to give a determinant which is more convenient to set up on the machine.

The normal frequencies of this machine range from one to ten cycles per second, so that it is a simple matter to observe the amplitudes and phase relationships of the motions of the various units when the machine is in resonance, and thus to obtain the normal mode of vibration corresponding to each frequency.

Accuracy

The five unit instrument at present in use has been tested in a number of ways. The quantitative results, except in especially unfavorable circumstances, have been within about one percent of the calculated values. One series of tests was made in which the symmetrical motions of formaldehyde were studied and these showed that even in such simple applications the labor of using the mechanical method was less than that required to solve the problem analytically.