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A Potentiometric Secular Equation Computer*

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An electrical computer for solving secular equations is described. The technique makes use of the linear equations from which the secular equation is derived. Each of the linear equations is successively represented by a potentiometric circuit. A series of successive approximations is carried out to arrive at the desired solutions.

INTRODUCTION

SECULAR equations make their appearance both in connection with the electronic and vibrational energies of molecules. With respect to electronic energy, the secular equation results from the use of the linear variation method for getting approximate electronic wave functions. Resonance energy calculations represent a particular case of this. With respect to vibrational energy, the secular equation is involved in the classical determination of the normal modes of vibration and fundamental vibration frequencies of a polyatomic molecule.

The manual labor involved in solving secular equations has prompted several investigators to seek time saving devices that yield solutions with a fair degree of accuracy. Several mechanical devices have been designed for the determination of vibration frequencies of molecules.[1-3] Weights and springs are interconnected to represent either directly or indirectly the vibrating molecule. More recently an electrical network analyzer has been adapted for this purpose.[4] Inductance and capacitances represent masses and force constants. The resonant frequencies of the electrical circuit then correspond to those of the molecular vibration. An electrical device has the advantage over its mechanical counterpart in being easier to interconnect for a complicated situation and easier to measure for the result.

A secular equation always has associated with it a set of simultaneous linear equations, the solution of which is equivalent to the solution of the secular equation. These linear equations are homogeneous. For the closely related problem of solving non-homogeneous simultaneous linear equations, various mechanical and electrical calculators have been constructed.[5-8] These electrical calculators have been useful in treating infra-red and mass spectrometry data in analytical work. However, they are not well adapted for the present purpose since for each different value of the energy or frequency most all of the coefficients would need to be reset. The calculator to be described is of this same type but with the incorporation into the circuits of a pair of potentiometers which takes care of the various energy or frequency values.

MATHEMATICAL CONSIDERATIONS

The secular equation in its most general form may be written:

$$\begin{vmatrix} H_{11}-ED_{11} & H_{12}-ED_{12} & \cdots & H_{1n}-ED_{1n} \\ H_{21}-ED_{21} & H_{22}-ED_{22} & \cdots & H_{2n}-ED_{2n} \\ \cdot & \cdot & \cdot & \cdot \\ H_{n1}-ED_{n1} & H_{n2}-ED_{n2} & \cdots & H_{nn}-ED_{nn} \end{vmatrix} = 0, \quad (1)$$

where in the quantum mechanical linear variation function problem the H_{ij} are matrix components of the Hamiltonian operator, the D_{ij} are matrix components of unity, and E is the energy. There will be n corresponding rows and columns if there are n functions in the linear variation, and there will result n values of the parameter E. In the molecular vibration problem the H_{ij} are

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[1] C. F. Kettering, L. W. Shutts, and D. H. Andrews, Phys. Rev. **36**, 531 (1930).

[2] D. H. Andrews and J. W. Murray, J. Chem. Phys. **2**, 634 (1934).

[3] D. P. MacDougall and E. B. Wilson, Jr., J. Chem. Phys. **5**, 940 (1937).

[4] G. Kron, J. Chem. Phys. **14**, 19, (1946); G. K. Carter and G. Kron, J. Chem. Phys. **14**, 32 (1946); R. H. Hughes and E. B. Wilson, Jr., Rev. Sci. Inst. **18**, 103 (1947).

[5] J. B. Wilbur, J. Frank. Inst. **222**, 715 (1936).

[6] T. D. Morgan and F. W. Crawford, Oil Gas J. **43**, 100–105 (August 26, 1944).

[7] C. E. Berry, D. E. Wilcox, S. M. Rock, and H. W. Washburn, J. App. Phys. **17**, 262 (1946).

[8] C. C. Eaglesfield, J. App. Phys. **17**, 1125 (1946).

coefficients in the quadratic form expressing the potential energy in terms of coordinates, the D_{ij} are coefficients in the quadratic form for the kinetic energy in terms of velocities, and E equals $4\pi^2\nu^2$ where ν takes on the n values of the fundamental vibration frequency.

Associated with the secular Eq. (1) is a set of n homogeneous simultaneous linear equations:

$$(H_{11}-ED_{11})C_1+(H_{12}-ED_{12})C_2+\cdots$$
$$+(H_{1n}-ED_{1n})C_n=0,$$
$$(H_{21}-ED_{21})C_1+(H_{22}-ED_{22})C_2+\cdots$$
$$+(H_{2n}-ED_{2n})C_n=0,\quad (2)$$
$$\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot$$
$$(H_{n1}-ED_{n1})C_1+(H_{n2}-ED_{n2})C_2+\cdots$$
$$+(H_{nn}-ED_{nn})C_n=0.$$

This set of equations has a non-trivial solution only if the determinant of the coefficients of the variables is zero. The secular equation states just this condition. Solution of Eqs. (2) is, therefore, equivalent to solution of the secular equation, but goes further in giving relative values of the variables, C_i, which in the linear variation method are the coefficients of the wave functions and in the vibration problem give the form of the normal modes of vibration.

Solution of the linear Eqs. (2) can be carried out by a series of successive approximations such as are used in solving non-homogeneous linear equations.[6,7] This procedure is similar to the relaxation method of Southwell.[9]

If one of the correct values for E is placed in Eqs. (2) these equations become dependent so that only $n-1$ C_i's can be determined, and these only relative to the nth C_i. The n equations can then be considered as equations in $n-1$ C_i variables and the energy parameter E as the nth variable. The method then consists in first fixing one of the C_i's, say C_1, at some arbitrary convenient value. E is given an arbitrary value somewhere in the neighborhood of a value expected as a solution. The first equation is then solved for C_2; all other C_i's except C_1 and C_2 are zero unless previous information as to their probable values is at hand. Using this value of C_2 and the same values of C_1 and E, the second equation is then solved for C_3. This is continued through the sequence of C_i's, thus obtaining a value of C_n

[9] R. V. Southwell, *Relaxation Methods in Engineering Science* (Oxford Univ. Press, Cambridge, England, 1940).

from the $n-1$st equation. The nth equation is then used to solve for a better value of E. This cycle of operations is repeated a few times until further changes in the E and C_i's are within the desired error, these final values then constituting a solution. By starting with appropriately chosen E's, the procedure will converge to the various characteristic values of E and the corresponding C_i's.

ELECTRICAL CIRCUIT

Consider the linear Eqs. (2) in the form:

$$H_{11}C_1+H_{12}C_2+\cdots+H_{1n}C_n$$
$$=E(D_{11}C_1+D_{12}C_2+\cdots+D_{1n}C_n),$$
$$\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad (3)$$
$$H_{n1}C_1+H_{n2}C_2+\cdots+H_{nn}C_n$$
$$=E(D_{n1}C_1+D_{n2}C_2+\cdots+D_{nn}C_n).$$

The left-hand side may be represented electrically in the manner described by Berry, Wilcox, Rock, and Washburn.[7] A single product term, such as $H_{11}C_1$, is obtained by setting a potentiometer to represent the value of one factor, the voltage tapped off being applied to a second potentiometer which is set to the other factor. The potential from the second potentiometer is then proportional to the product of the two factors. The summation of terms is obtained by connecting the potentials representing products through a set of "addition resistors" to a common point. This common point has then a potential which is the average of the several product potentials and is, therefore, proportional to their sum.

The right-hand side of an equation of set (3) differs in form from the left-hand side by having multiplication by E. This is accomplished by having an extra addition resistor, in the form of a potentiometer, which is connected to ground potential and with a sliding contact to tap off a fraction E of the average potential representing the sum of terms.

When the equation is satisfied the two potentials representing the right and left sides, respectively, will be equal. This situation may be determined with the aid of any null detector commonly used in potentiometric work.

In any given problem the setting of the potentiometers representing the H_{ij}'s and D_{ij}'s may result in a value of E beyond the range of the E

potentiometer. To take care of this possibility the equations are considered in the form (4):

$$A(H_{11}C_1+H_{12}C_2+\cdots+H_{1n}C_n)$$
$$= B(D_{11}C_1+D_{12}C_2+\cdots+D_{1n}C_n),$$
$$\cdots \cdots \cdots \cdots \cdots \cdots \cdots \quad (4)$$
$$A(H_{n1}C_1+H_{n2}C_2+\cdots+H_{nn}C_n)$$
$$= B(D_{n1}C_1+D_{n2}C_2+\cdots+D_{nn}C_n).$$

The sides of each equation are now symmetrical and are represented electrically in the same manner as the right side of an equation of set (3). E is obviously the ratio B/A. The full positive range of E may be obtained in two steps. If A is set to its maximum value (considered as unity), B will be equal to E and will cover the range from 0 to 1 (on an arbitrary scale). If B is set to unity, the various values of A from 1 to 0 will correspond to E varying from 1 to infinity. In practice, to avoid confusion, A and B potentiometers are labeled $1/E$ and E, respectively, it being understood that the potentiometer not being varied must be kept at its maximum setting.

The calculator as actually constructed is shown in Fig. 1. It will handle up to six linear equations or a sixth degree secular equation. Figure 2 shows the circuit for the case of two equations with two variables. The extension to more equations is apparent. The calculator involves a bank of seventy-two 100-ohm wire-wound radio volume controls for the H's and D's, thirty-six for each. There are six 100-ohm potentiometers to represent the six C's in a given equation. A reversing switch for each C potentiometer allows for plus and minus signs for the C's. The addition resistors, R, are each approximately 100,000 ohms and are carefully matched to each other by taking series pairs of properly chosen 50,000-ohm resistors. The E potentiometers (E and $1/E$) are 100,000 ohms and are not necessarily matched to the addition resistors but must be matched to each other.

A twelve-pole six-position gang switch, serving as an *Equation Selector*, permits switching any particular set of six H's and six D's of a given equation to the addition resistors. A four-pole two-position gang switch, as a *Function Selector*, serves to connect the *Null Detector* either for balancing an equation or for connecting it together with a *Standard Potentiometer* for the
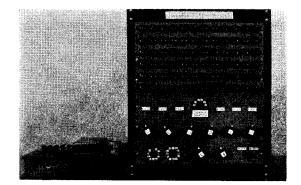

FIG. 1. Secular equation computer.

purpose of measuring final values of C's and E or $1/E$ of a solution or for setting the original values of the H's and D's. A one-pole ten-position gang switch serving as a *CE Selector* connects the standard potentiometer and detector (when the function selector is set at "standard") to any of the six C potentiometers or two E potentiometers for the purpose of measuring each individually. This selector also has a contact connected to ground to make possible a check on the balance between positive and negative sides of the power source, and a contact marked "$H-D$" to connect the *HD Selector*. This H and D selector is a one-pole twelve-position gang switch which with the aid of the equation selector makes it possible to set or measure any one of the seventy-two H_{ij}'s or D_{ij}'s.

All circuit elements are mounted on the panel illustrated except the power source, null detector, and standard potentiometer. The circuit was designed for either a.c. or d.c. operation but so far only d.c. has been used. The power source consists of two 2-volt storage cells of large capacity connected in series, the common connection being taken as zero potential. On both the $+2$ v and -2 v sides are placed rheostats to allow for making the magnitude of the voltage on both sides of zero identical. As the C potentiometers are varied or the signs are reversed, there will be differences in the current drained from the battery and the zero may shift with respect to the midpoint between the two extreme potentials. This variation is partially compensated by introducing fixed 100-ohm resistors, C', at the sign switches to cause a current drain from one cell when the corre-

sponding C potentiometer causes a drain from the other cell. This will not take care of a variable drain caused by current drawn from a C potentiometer by its attached H and D potentiometers. A complete zero balance adjustment is accomplished by varying one of the rheostats so as to balance the null detector, when the CE selector is set on the zero or ground contact mentioned above. This adjustment can be made conveniently once in each cycle of the successive approximations.

The null detector is a box-type lamp and scale galvanometer, and the standard potentiometer is a slide wire accurate to 0.1 percent. It should be noticed that the standard potentiometer and an equal series resistance are connected directly across the total voltage supplied to the C potentiometers. A zero setting on the potentiometer then corresponds exactly to the midpoint between the two extreme potentials and the full-scale setting is exactly equal to the ,maximum positive potential applied to the C's. There is, therefore, no need to standardize the potential measurement since relative values are sufficient.
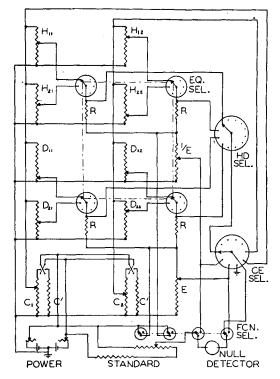

FIG. 2. Circuit diagram of the secular equation computer.

OPERATIONAL ROUTINE

1. *Arrange the mathematical problem in a form convenient for the calculator.* Since the scale on the measuring potentiometer runs from 0 to 1000 and the full-scale reading on the various component potentiometers matches a full-scale setting of the measuring potentiometer, the units for expressing the H's and D's are conveniently chosen so the maximum H_{ij} and the maximum D_{ij} are 1000 or shortly under.

2. *Set each of the H and D potentiometers to their appropriate values.* To do this, have the function selector on "Standard," the sign switches on "$+$," and the C potentiometers at their maximum values. With the CE selector on "zero" and the standard set to 0, adjust the balancing rheostat at the power source. This zero balance would be expected to remain the same during setting of the H's and D's, but should be occasionally checked as a precaution. Now set the CE selector to "$H-D$," the equation selector to the first equation, and the HD selector to H_1. With the standard set to the numerical value for H_{11}, adjust the H_{11} potentiometer to balance as shown by the null detector. Next with the HD selector set to H_2, the H_{12} potentiometer may be set, etc.

3. *Set the E or 1/E potentiometer to an assumed approximate value.* The function selector gang switch on the "Standard" position connects the maximum positive voltage across the E and $1/E$ potentiometers so that here again full-scale on these correspond to full-scale on the standard. However, for this purpose it is preferable to divide the standard reading by 1000 to make the maximum value unity. The CE selector is set on "E" or "$1/E$" and the corresponding potentiometer balanced.

4. *Proceed to balance the equations successively until all are balanced simultaneously.* A typical step in this procedure would be carried out as follows. The function selector is set on "Balance." Any one C or E potentiometer is varied to balance a given equation chosen by the equation selector. The settings of the CE and HD selectors and the standard potentiometer are immaterial during this operation, but since the zero must be checked occasionally it saves time to have the CE selector on "Zero" and the standard set to 0

so that by merely flipping the function selector to "Standard" the zeroing rheostat may be adjusted to balance. In balancing a given equation a particular C potentiometer might be required to go beyond its range. If it must go through zero the corresponding sign switch is flipped. If a value beyond the maximum is required, that particular potentiometer is left at maximum setting and other C's are later reduced in value. "Cut-and-try" methods are useful in obtaining rapid convergence to a solution. It may turn out that changing a given potentiometer either more or less than that corresponding to balance is preferable to an exact balance. The order of balancing of the equations may be varied at will. Also it is unnecessary to vary one particular variable in balancing a particular equation. The only requirement is that at the end of the successive approximations all equations are balanced simultaneously within the error inherent in the problem or in the calculator.

5. *Read the values of the C's and E which constitute the solution.* This is done with the standard potentiometer. The function selector is set on "Standard" and the CE selector is set on "E" and "$1/E$" to determine these. To measure the C's first throw all sign switches to the positive direction after recording which are negative. The zero must be readjusted. Then each of the C's are read by setting the CE selector to the appropriate C and setting the standard potentiometer to obtain a null.

6. *Search for other solutions, if desired.* The solutions for maximum and minimum values of E are most easily obtained. Solutions for intermediate E's are obtained quickly if reasonably good initial values of E and the C's are used. A more definite procedure to follow is to solve secular equations of successively increasing degree from the second degree up to the maximum. This involves no change in the settings of the H's and D's, but merely keeping certain C's zero and disregarding a corresponding number of equations. Since the $n+1$ E values which are solutions for an $(n+1)$st degree secular equation are interleaved with the n roots of a preceding nth degree secular equation,[10] it is possible to

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[10] L. Pauling and E. B. Wilson, Jr., *Introduction to Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1935), p. 188.

TABLE I. Signs of matrix elements and of E.

	H	D	E	Operation
1	$+$	$+$	$+$	Set up directly
2	$+$	$-$	$-$	Reverse signs of D and E
3	$-$	$+$	$-$	Reverse signs of H and E
4	$-$	$-$	$+$	Reverse signs of H and D
5	$+$	$+$	$-$	Substitute for E to get type 1
6	$+$	$-$	$+$	Reverse signs to get type 5 and
7	$-$	$+$	$+$	substitute for E
8	$-$	$-$	$-$	

make an estimate of the former from the latter.

POSITIVE AND NEGATIVE SIGNS

In the design of the calculator there appears to be a limitation on the algebraic signs that can be used for the H's, D's, and E's. Although sign switches are provided for taking care of both positive and negative C's, no such provision is made for possible negative H's, D's, and E's, although with a more complicated circuit that would have been possible. As will be shown, however, the calculator can, in principle, handle all possible combinations of signs, but in practice certain combinations may be inconvenient.

Consider first the situations where all H's have like signs, all D's have like sign, and all E's have like sign. Eight possible combinations are shown in Table I. In the first four combinations the sign of an H_{ij} is the same as that of the corresponding product ED_{ij}. These cases can be handled by merely reversing the signs of certain pairs as indicated. The justification for this is that it amounts to no more than a possible change in sign of the secular determinant which is zero anyway. The E's obtained as solutions must be given the appropriate sign depending upon whether or not it was reversed in setting up the problem on the calculator. In the last four combinations in the table the sign of an H_{ij} is the opposite of the sign of the product ED_{ij}. The quantity $H_{ij} - ED_{ij}$ is then a sum of two positive numbers or a sum of two negative numbers. The circuit as designed will handle only differences rather than sums. However, the following algebraic substitution in the original secular equation will put the problem in a suitable form. Consider case 5 to which the last three can be transformed by reversal of signs. Now let $E = E' - E_0$ such

that E' is positive and variable, E_0 being a positive constant greater than the maximum absolute value of E. Then

$$H_{ij} - E D_{ij} = H_{ij} + E_0 D_{ij} - E' D_{ij} = H_{ij}' - E' D_{ij}$$

where each $H_{ij}' = H_{ij} + E_0 D_{ij}$ is calculated for an arbitrarily chosen $E_0 \geq |E|_{max}$ and then set on the secular equation calculator instead of the original H_{ij}. The terms are all now of type 1.

Secular equations having matrix components of mixed sign types 1 to 4 may require merely a change in sign of some rows and columns of the secular equation determinant. The corresponding C's would then come out with reversed signs. If this is not possible or convenient the following trick may be used. Any term of type 4 mixed with type 1 or of type 3 mixed with type 2 can be set up as for positive H and D, but when used in balancing a linear equation the corresponding C sign switch is reversed. This procedure requires care in changing the appropriate sign switches each time a new equation is switched into the circuit. Mixtures of sign types 5 to 8 are treated in the same way but with the preliminary substitution for $E = E' - E_0$ as above.

The most general type of mixture of signs may be handled as follows: Consider the four possibilities where E is positive. (E is the same throughout a given secular equation for a given solution. If E is negative a similar procedure applies.) Let $E = E' - E_0$ where again E' and E_0 are positive, but now $E' \geq E_0$. This substitution converts terms of type 6 and 7 into 4 and 1, respectively, if $E_0 > |H_{ij}/D_{ij}|_{max}$ where the maximum is for all terms of types 6 and 7. This substitution does not change the type of terms of types 1 and 4 and so gives a secular equation of only types 1 and 4 which can be handled by the method given in the preceding paragraph. If the maximum ratio $|H_{ij}/D_{ij}|$ is very large, there might be difficulty in getting accurate solutions. There is no need to worry about a zero D_{ij} causing an infinite ratio since such a term could be considered to be directly of type 1 or 4.

ACCURACY

Errors inherent in the electrical circuit include lack of ability to set the potentiometers precisely, loading effects on potentiometers, lack of perfect balance in the addition resistors, contact resistances, and lack of balance between positive and negative voltages from the power supply. The 1000-ohm radio volume controls used for the H's and D's have each about 300 turns of wire making it impossible to set a given value to better than 0.3 percent of the maximum. Helical potentiometers would be preferable, but were not considered for this application since part of the aim in building the calculator was to minimize expenditure consistent with reasonable accuracy. For the C potentiometers 0.3 percent precision in setting was not critical inasmuch as in problems of this type a given percent error in the C's will result in a somewhat smaller percent error in the E. The 100,000-ohm E potentiometer can be set to 0.1 percent.

There are large loading effects on the C potentiometers since the effective resistance of twelve 1000-ohm H and D potentiometers connected in parallel is 83 ohms, even smaller than the 100 ohms of the C potentiometer to which they are attached through the sliding contact. Current drain through the H's and D's causes a non-linearity in the setting of the C's but no difficulty arises since measurement of the actual potential is always made under the loaded condition. The loading effect on the H and D potentiometers is negligible, the current drain through a 100,000-ohm addition resistor affecting the potential at the sliding contact by less than 0.2 percent. The E potentiometers have no load when balance is obtained.

The addition resistors were matched to within a maximum deviation from the mean of less than 0.2 percent, and the two E potentiometers were found to check within 0.1 percent. Possible error caused by lack of balance of positive and negative voltages has been eliminated by the zero adjustment described earlier. No difficulties with contact resistances have been encountered.

The error in the final solution is expected to be of the order of 0.5 percent of the full scale reading for the E or $1/E$ and at best 1 percent of the maximum value for each C. Perhaps the best way of indicating accuracy of solution is to compare solutions obtained with the calculator with those already known for a given secular equation. Such an example is the following.

AN EXAMPLE

The example chosen for illustration is that of the determination of resonance among the two Kekulé and three Dewar structures of benzene.[11,12]

Although this fifth degree secular equation is easily reduced through considerations of symmetry to a product of three first degree and one second degree equation, it is used here in its unreduced form as a test of the calculator since the solutions are accurately known.

The secular equation as set up by Pauling and Wheland may be written in simpler form by dividing the equation by $(3\alpha/2)^5$ and defining a new parameter, $E = -(Q-W)/(3\alpha/2)$, where W is the energy, Q the coulombic integral, and α the exchange integral. The result is:

$$\begin{vmatrix} 1-E & 1-E/4 & 1-E/2 & 1-E/2 & 1-E/2 \\ 1-E/4 & 1-E & 1-E/2 & 1-E/2 & 1-E/2 \\ 1-E/2 & 1-E/2 & -E & 1-E/4 & 1-E/4 \\ 1-E/2 & 1-E/2 & 1-E/4 & -E & 1-E/4 \\ 1-E/2 & 1-E/2 & 1-E/4 & 1-E/4 & -E \end{vmatrix} = 0.$$

This equation appears to be in suitable arrangement for the calculator, the H_{ij}'s and D_{ij}'s being all positive and having maximum values of unity. However, it is known that the correct solutions are $E = 2/3[(13)^{\frac{1}{2}} - 1]$, 0, $-4/3$, $-4/3$, $-2/3[(13)^{\frac{1}{2}} + 1]$. Only the positive solutions would be found if the problem were set up on the calculator in this form. By substituting $E = 4 - 4E'$ and dividing each row of the secular equations by -4 the resulting equation is such that

$$\|H_{ij}\| = \begin{bmatrix} 3/4 & 0 & 1/4 & 1/4 & 1/4 \\ 0 & 3/4 & 1/4 & 1/4 & 1/4 \\ 1/4 & 1/4 & 1 & 0 & 0 \\ 1/4 & 1/4 & 0 & 1 & 0 \\ 1/4 & 1/4 & 0 & 0 & 1 \end{bmatrix},$$

$$\|D_{ij}\| = \begin{bmatrix} 1 & 1/4 & 1/2 & 1/2 & 1/2 \\ 1/4 & 1 & 1/2 & 1/2 & 1/2 \\ 1/2 & 1/2 & 1 & 1/4 & 1/4 \\ 1/2 & 1/2 & 1/4 & 1 & 1/4 \\ 1/2 & 1/2 & 1/4 & 1/4 & 1 \end{bmatrix}.$$

[11] L. Pauling and G. W. Wheland, J. Chem. Phys. **1**, 362 (1933).

[12] H. Eyring, J. Walter, and G. E. Kimball, *Quantum Chemistry* (John Wiley and Sons, Inc., New York, 1944), pp. 249–254.

TABLE II.

	E	C_1	C_2	C_3	C_4	C_5
Correct	0.5658	(1000)*	1000	434	434	434
Calc.	0.560	1000	1000	407	411	422
Correct	1.0000	(1000)	−1000	0	0	0
Calc.	1.00	1000	−1000	0	0	0
Correct	1.3333	0	0	(754)	−754	0
Calc.	1.32	0	0	754	−755	0
Correct	1.3333	0	0	(650)	(−908)	258
Calc.	1.325	0	0	650	−908	255
Correct	1.7676	(1000)	1000	−768	−768	−768
Calc.	1.76	1000	1000	−782	−750	−762

* Parentheses indicate C values arbitrarily chosen equal to the value on the computer.

All E' values are positive. Table II shows values of E' and the C's as found by the calculator as compared with those obtained algebraically.

The third and fourth solutions constitute a twofold degeneracy. Since in such a case any linear combination of the wave functions also is a solution with the same energy, it is obvious that any number of different sets of C's could have been found. The two sets of C's shown in the table were obtained using previous knowledge that certain C's could be set equal to zero.

The accuracy of the calculations is about that expected.

COMPARISON OF CALCULATORS

The only other calculator particularly adapted to secular equations is the network analyzer which has, in principle, the advantage that the solutions are obtained directly rather than through successive approximations. Such an advantage is of minor importance since the time required to obtain convergence to a solution using the potentiometer computer is somewhat smaller than the time required to set up the problem. To set all seventy-two H's and D's for a given secular equation takes less than an hour. To obtain a particular solution then takes only a few minutes in most cases.

A serious limitation of the network analyzer is that there can be no off-diagonal D_{ij}'s. The potentiometric computer will handle any case of non-orthogonality and also problems with assymmetrical H_{ij} and D_{ij} matrices should they be of

any interest. The setting of a given H_{ij} in the potentiometric computer, which involves merely adjusting a potentiometer, is much simpler than connecting together several standardized condensers or coils as in the network analyzer.

The potentiometric secular equation computer can also solve non-homogeneous linear equations by setting the E and $1/E$ potentiometers at

unity, using H_{ij}'s to represent positive matrix components and D_{ij}'s to represent negative matrix components, and keeping one C_i at unity, the corresponding H's and D's representing the constant terms in the equations.

Multilayer Gas Adsorption on Composite Surfaces

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The equation of Brunauer, Emmett, and Teller (BET) for the adsorption of a gas on a free plane homogeneous surface is extended to the case of a mixture of two such surfaces, in an attempt to explain the observed deviations below one monolayer. The resulting equation may be greatly simplified for the case that the adsorption energy parameter, c, for each component surface, is large with respect to unity, as is usually the case in low temperature adsorptions of nitrogen, argon, etc. This approximate form of the equation is applied to the nitrogen isotherm on an inorganic salt and gives substantially better agreement with experiment than does the simple BET equation. The region of agreement between the experimental and BET isotherms is discussed on the basis of a two-component surface, and conditions are given under which one might obtain *two* distinct regions of the isotherm which are fitted by the BET equation by the use of two sets of parameters. It is suggested that it is the lower of these two regions which gives rise to the occasionally observed "saturation adsorption" values corresponding to only small fractions of a monolayer.

INTRODUCTION

FOR gas adsorption in the range below about 0.8 monolayer it is commonly observed that the theoretical isotherm of Brunauer, Emmett, and Teller[1,2] (BET) for a free plane homogeneous surface, based on the rectilinear plot fitting best in the neighborhood of one monolayer, predicts too low an adsorption. A typical example of this behavior is shown in Fig. 1 for the nitrogen adsorption isotherm at 78°K on an inorganic salt; Fig. 2 gives the corresponding rectilinear plot. The departure from the theoretical curve is usually attributed[3] to an inhomogeneity of the

surface, which leads to preferential adsorption on those areas which have high energies of adsorption, and which therefore justly belong to higher values of the energy parameter,[4] c, than that given by the best fit near one monolayer—i.e., on the more "uniform" part of the surface. Most calorimetric data[3,5] for adsorptions below one monolayer lend support to this interpretation, as do also the abnormally large c values obtained, for example, by Armbruster[6] and co-workers at very low relative pressures in the low temperature adsorption of inert gases on metals.

If surface inhomogeneity is indeed responsible for these low adsorption discrepancies, it poses an

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[1] S. Brunauer, P. H. Emmett, and E. Teller, J. Am. Chem. Soc. 60, 309 (1938).

[2] An excellent review of the theory is contained in Brunauer's book, *The Adsorption of Gases and Vapors, Vol. I, Physical Adsorption* (Princeton University Press, Princeton, 1943), p. 151 *et seq.*

[3] Reference 2, pp. 158, 335.

[4] The energy parameter, c, is given by Brunauer, Emmett, and Teller as $c = \exp(E_1 - E_L)/RT$, where E_1 and E_L are, respectively, the energy of adsorption into the first layer and the energy of liquefaction.

[5] See, for example, W. D. Harkins and G. E. Boyd, J. Am. Chem. Soc. 64, 1145 (1942); W. D. Harkins and G. Jura *ibid.* 66, 919 (1944), Fig. 8.

[6] M. H. Ambruster, J. Am. Chem. Soc. 64, 2545 (1942); M. H. Armbruster and J. B. Austin, *ibid.* 66, 159 (1944).