$$Bt = 2\pi - \frac{\pi^2 F}{3} - 2\pi\left(1 - \frac{\pi F}{3}\right)^{1/2}$$

$$= 6.28318 - 3.2899F - 6.28318\,(1 - 1.0470F)^{1/2} \quad (11)$$

The last term in equation (9) is zero when $F = 0$ and increases as F increases. Hence, for any value of F, equation (11) gives too high a value of Bt, the error being zero when $F = 0$. Now, at a value of $F = 0.85$, equations (8) and (11) give values of Bt agreeing to within 0.005, corresponding to a variation of F at this point of less than 0.001. Hence equation (11) was used for values of F from 0 to 0.85 and equation (8) for values from 0.86 to 1. The results are shown in Table I. The errors in Bt are less than those corresponding to a variation of 0.001 in the value of F.

TABLE I

TABLE FOR INTERPRETING EXPERIMENTAL RESULTS IN TERMS OF THE PARTICLE DIFFUSION EQUATION

F	Bt	F	Bt	F	Bt	F	Bt
0	0	0.25	0.0623	0.50	0.301	0.75	0.905
0.01	0.00009	.26	.0678	.51	.316	.76	.944
.02	.00036	.27	.0736	.52	.332	.77	.985
.03	.00076	.28	.0797	.53	.348	.78	1.028
.04	.00141	.29	.0861	.54	.365	.79	1.073
.05	.00219	.30	.0928	.55	.382	.80	1.120
.06	.0032	.31	.0998	.56	.400	.81	1.171
.07	.0044	.32	.1070	.57	.419	.82	1.224
.08	.0057	.33	.1147	.58	.438	.83	1.280
.09	.0073	.34	.1226	.59	.458	.84	1.340
.10	.0091	.35	.1308	.60	.479	.85	1.404
.11	.0111	.36	.1391	.61	.500	.86	1.468
.12	.0132	.37	.1485	.62	.522	.87	1.543
.13	.0156	.38	.1577	.63	.545	.88	1.623
.14	.0183	.39	.167	.64	.569	.89	1.710
.15	.0210	.40	.177	.65	.594	.90	1.80
.16	.0241	.41	.188	.66	.620	.91	1.91
.17	.0274	.42	.199	.67	.647	.92	2.03
.18	.0309	.43	.210	.68	.675	.93	2.16
.19	.0346	.44	.222	.69	.703	.94	2.32
.20	.0386	.45	.234	.70	.734	.95	2.50
.21	.0428	.46	.246	.71	.765	.96	2.72
.22	.0473	.47	.259	.72	.798	.97	3.01
.23	.0520	.48	.273	.73	.832	.98	3.41
.24	.0570	.49	.287	.74	.868	.99	4.11

On the Use of Structures as an Aid in Understanding Π-Electron Spectra

By WILLIAM T. SIMPSON

The possibility of obtaining symmetry species from known transformation properties of the squares of trial wave functions is investigated. Application to structures follows from the association of structures with wave functions squared. Observed electronic term values are arranged in a diagonal matrix which is then transformed into non-diagonal form. Base vectors in the transformed coördinate system are interpreted with respect to structures. It is pointed out that the energy matrix in non-diagonal form lends itself to various applications.

Introduction

The HLSP or valence bond method[1] provides a particular quantum mechanical basis for an understanding of the role played by structures (also called mesomeric forms, resonance forms, paper structures, etc.) but certain objections arise. In large molecules the wave functions which, according to the valence bond scheme, correspond to the principal or unexcited structures make only small contributions.[2] Moreover, the valence bond scheme as usually employed involves the neglect of quantities which are certainly large and does not ordinarily take into account the so-called σ-bonds. One wonders, in view of the practical uses to which structures can be put, if there is not some fundamental justification for an approach other than the valence bond method, which also involves the use of structures. In the next paragraphs several rather striking examples of the utility of structures will be cited.

It is found that the 2600 Å. band in benzene is in all probability $A_{1g} \rightarrow B_{2u}$[3] and this is exactly what one expects if the transition is considered to take place between ψ_g and ψ_e where

$$\psi_g = 2^{-1/2}(\psi_1 + \psi_2),\ \psi_e = 2^{-1/2}(\psi_1 - \psi_2)$$

and ψ_1^2 has the transformation properties of one Kekulé structure, ψ_2^2 of the other.[4] It is important to note that structures are taken as corresponding to ψ^2's.

The transition moment integral in the language of wave functions (squared) related to structures is

$$\int \psi_g\, \vec{q}\, \psi_e\, d\tau = \frac{1}{2}\,[\int \psi_1^2\, \vec{q}\, d\tau - \int \psi_2^2\, \vec{q}\, d\tau]$$

so that the electric moment implied by a distribution of charge transforming like one Kekulé structure must be different from that implied for the other than the transition be allowed. That the electric moments are in fact equal may be seen in pictorial fashion from the Kekulé structures

(1) Recent treatments have been given by D. P. Craig, Proc. Roy. Soc. (London), A200, 272 (1950), and M. Simonetta and V. Schomaker, J. Chem. Phys., 19, 649 (1951).

(2) A. Pullman, Doctoral Thesis, Univ. of Paris, 1946.

(3) See for example F. M. Garforth, J. chim. phys., 45, 6 (1948).

(4) This is demonstrated in Part 1.

It is convenient to take the center of the molecule as origin. If para disubstitution is introduced
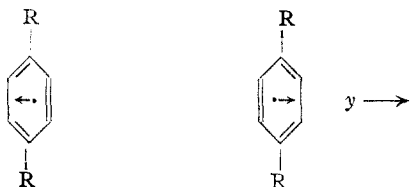
it is seen that the electric moments generated must necessarily be in opposite directions along the y axis.[5] The difference of the moments no longer vanishes and the perturbed 2600 Å. transition becomes allowed (y), which is required by more conventional arguments based on group theory.[6] This method of predicting polarization using structures is of course not restricted to benzene but can be applied whenever it is possible to describe the states between which the transition takes place as the sum and difference of two trial wave functions each related to a structure.

Another example of the application of structures arises in a study of the triphenylmethane dyes.[7] The general dye is
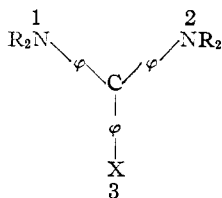
where the numbers serve to indicate the position of the charge. For example if –X is –NR$_2$ (and R– is Me) the dye is crystal violet
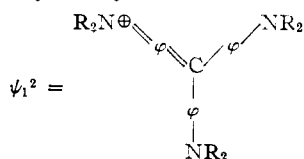
The particular structure illustrated transforms like $\psi_1{}^2$ where the subscript indicates the position of the charge. The strong band at 5700 Å. found in crystal violet can be associated[8] with a transition to a degenerate upper level[4]

$$\psi_1 + \psi_2 + \psi_3 \longrightarrow \psi_1 - \psi_2, 2\psi_3 - \psi_1 - \psi_2$$
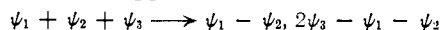
The degeneracy of the upper level is removed when –X becomes, for example, –OMe; and two bands appear, appropriately polarized, one at 5900 Å., the other at 4700 Å.

There are numerous examples of the utility of structures which are so common as to pass almost unnoticed. For instance it is sometimes not

(5) Imagine, for example, that the substituents, R, repel the respective adjacent double bonds.

(6) See for example S. H. Wollman, J. Chem. Phys., **14**, 123 (1946).

(7) G. N. Lewis and J. Bigeleisen, THIS JOURNAL, **65**, 2102 (1943).

(8) The association is of course not mandatory. However even the possibility of making the association is regarded as being highly suggestive.

realized that the writing out of the conventional structures is an indispensable prerequisite to molecular orbital calculations. The approaches to the color of cyanine dyes by L. G. S. Brooker and to the color of triphenylmethane dyes by G. E. K. Branch make a most extensive and fruitful use of structures, and in a way which need not be considered to be quantum mechanical in the sense of the HLSP method.

It is the object of this paper to give a method for combining quantal and group theoretical ideas with work with structures of an empirical nature (mesomerism). The result is a scheme which is not inconsistent with quantum mechanics but which is quantum mechanical only by implication.

The plan is to start with observed electronic energies for a given system, regarding them as diagonal elements of the energy matrix in a Heisenberg representation. Then instead of making the prohibitively difficult transformation to the Schrödinger representation (which is fully pictorial, with base vectors the positions of all the particles) one makes a transformation to an intermediate representation characterized by the property that the base vectors are associated with structures. This new representation is called the *structure representation*. It has certain of the qualities of the Schrödinger scheme in that to a degree there is a "shape" or configuration aspect; hence there is greater opportunity for the exercise of quantum mechanical and chemical intuition than with the Heisenberg scheme. Matrix elements in the structure representation can be used to systematize data for families of related molecules and to act as a basis for predicting unknown matrix elements.

The present paper is divided into two parts. The first is devoted to the relationship between species of levels and structures and hence to polarizations of bands. The second part deals with the matrix transformation theory and hence with the question of transition energies.

Part I

Symmetry Species from Structures.—In this part it will be shown how symmetry species are obtained for states constructed from certain hypothetical trial functions (as used in the linear variation method in quantum mechanics). The functions are never themselves explicitly stated but are defined only to the extent that their squares transform like structures, which are considered as given. For example, given the structures for formamidinium ion
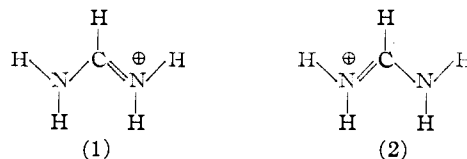
and assuming (1) transforms like $\psi_1{}^2$, (2) like $\psi_2{}^2$, then to which species do the state wave functions belong which can be made from ψ_1 and ψ_2? The answer to this question cannot strictly be given, but in a rather direct fashion species can be obtained which can be used to predict polarizations of bands. If a transition takes place between states of species

Γ_i and Γ_j then the direct product species $\Gamma_i\Gamma_j$ gives the polarization. If we are forced incorrectly to use $\Gamma_i\Gamma_k$ and $\Gamma_j\Gamma_k$ as representing the states (and assuming no degeneracy) then $\Gamma_i\Gamma_k\Gamma_j\Gamma_k = \Gamma_i\Gamma_j$ will again give the polarization, by virtue of $\Gamma_k\Gamma_k = \Gamma_0$ the identity representation. We shall see that the use of structures, and hence of the transformation properties of trial wave functions squared, may bring in spurious species as Γ_k above.

Briefly, the symmetry species are obtained in the same fashion as for trial ψ's, with the use of[9]

$$<\psi_i>^\Gamma = \sum_R \chi^\Gamma(R)R\psi_i$$

Here R is an operation of the group, $\chi^\Gamma(R)$ is the character belonging to the species Γ and the operation R. $<\psi_i>^\Gamma$ is, in this paper, called a *fragment*. The usual procedure is to link up trial ψ's with species through the calculation of the non-vanishing fragments and this procedure is adapted to the use of structures. Thus, as will be proved in Appendix I, one infers species from the non-vanishing fragments

$$<(i)>^\Gamma = \sum_R \chi^\Gamma(R)R(i)$$

The parentheses around (i) denote a structure, so with regard to transformation properties we have the relation (which provides the connection with quantum mechanics)

$$(i) = \psi_i^2$$

Calculation of Fragments.—We shall now show how species are obtained generally, by considering several representative cases. First we treat formamidinium ion and allyl radical

(3)　　　　　　　　　(4)
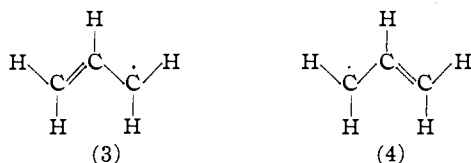
Each of these molecules is considered to belong to C_{2v} with the character table

C_{2v}		E	C_2	σ_v	σ_v'
z	A_1	1	1	1	1
	A_2	1	1	−1	−1
x	B_1	1	−1	1	−1
y	B_2	1	−1	−1	1

The σ_v operation is taken to be reflection in the plane of the molecule, hence the x direction is the long direction of the molecule.

For formamidinium ion the non-vanishing fragments are

$$(1) + (2) \quad A_1$$
$$(1) - (2) \quad B_1$$

so that from ψ_1 and ψ_2 two states having the species A_1 and B_1 can be formed, and the transition $A_1 \rightarrow B_1$ is allowed (x).

For allyl radical we find

$$(3) + (4) \quad A_1 = B_2B_2$$
$$(3) - (4) \quad B_1 = A_2B_2$$

and $A_1 \rightarrow B_1$ allowed (x). However the odd π-electron makes the *wave function* $\psi_3 + \psi_4$ belong to B_2 while $\psi_3 - \psi_4$ belongs to A_2. Thus the polarization is given by

$$B_2A_2 = B_2B_2A_2B_2 = A_1B_1$$

The species A_1 and B_1 are spurious, but lead to the correct prediction with respect to polarization. A similar situation arises in the case of certain non-alternant hydrocarbons, such as the hypothetical molecule pentalene.[10]

Before taking up the next example, benzene, we need to recall that mixing between ψ's which are not equivalent is accidental, so that for the present purposes we can consider non-equivalent ψ's (and non-equivalent structures) separately. Equivalence is defined as: ψ_i and ψ_j are equivalent if for some R $R\psi_i = \psi_j$. Let us now start from the Kekulé structures for benzene and include also a particular type of ionic structure

(1)　　　(2)　　　(3)　　　(4)
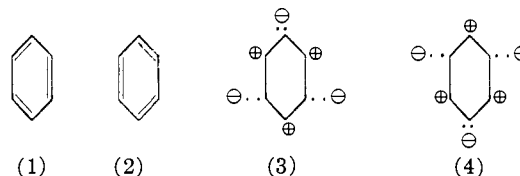
The Kekulé structures are equivalent, as are the two ionic structures. Starting from the character table for D_{6h} we find for the Kekulé structures

$$(1) + (2) \quad A_{1g}$$
$$(1) - (2) \quad B_{2u}$$

and for the ionic structures

$$(3) + (4) \quad A_{1g}$$
$$(3) - (4) \quad B_{1u}[11]$$

This means that altogether there can be formed from ψ_1, ψ_2, ψ_3 and ψ_4 states belonging to A_{1g} (two states), B_{1u} and B_{2u}. There is a theoretical difficulty which cannot be disposed of easily but which is not a practical difficulty. That is, suppose from the Kekulé structures the real species are $A_{1g}\Gamma_k$, $B_{2u}\Gamma_k$, while from the ionic structures the species are $A_{1g}\Gamma_l$, $B_{1u}\Gamma_l$, where $\Gamma_l \neq \Gamma_k$. Then the polarization for, say, $A_{1g}\Gamma_k \rightarrow B_{1u}\Gamma_l$ will not be given correctly. It seems to be necessary to make use of more conventional quantum-mechanical approaches, such as the HLSP method in order to guard against this contingency.

As a final illustration we consider a case for which there is degeneracy. The approach here is adapted from a procedure developed by Dr. T. J. Webb.[12] The central idea is to form the fragments as before, using not the characters, but the elements of the matrices of the irreducible representations. Thus in place of $\chi^\Gamma(R)$ we use $\chi^\Gamma_{mn}(R)$, where we might, for example, consistently use the elements in the 1st row $(m = 1)$ and 2nd column $(n = 2)$ of a particular set of matrices representing a particular Γ.

Consider the case of crystal violet

(9) See for example H. Eyring, J. Walter and G. E. Kimball, "Quantum Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 188.
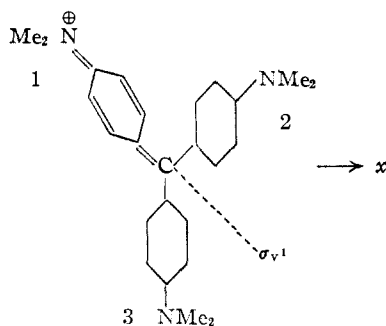
(10) D. P. Craig and A. Maccoll. *J. Chem. Soc.*, 964 (1949).

(11) Note that only one member of the set of equivalent structures is required; and that, considering a set of equivalent structures, there are as many species represented as there were linearly independent structures given (non-degenerate case).

(12) Private communication.

where, as before, the number represents the structure with the charge on the indicated nitrogen. Assuming C_{3v} symmetry we use the following "character table":

C_{3v}	E	$\sigma_v{}^1$	$\sigma_v{}^2$	$\sigma_v{}^3$	C_3	C_3'
z Γ_0	1	1	1	1	1	1
Γ_1	1	-1	-1	-1	1	1
x $\Gamma_2{}^{11}$	1	$1/2$	$1/2$	-1	$-1/2$	$-1/2$
$\Gamma_2{}^{12}$	0	$-\sqrt{3/2}$	$\sqrt{3/2}$	0	$\sqrt{3/2}$	$-\sqrt{3/2}$
$\Gamma_2{}^{22}$	1	$-1/2$	$-1/2$	1	$-1/2$	$-1/2$
y $\Gamma_2{}^{21}$	0	$-\sqrt{3/2}$	$\sqrt{3/2}$	0	$-\sqrt{3/2}$	$\sqrt{3/2}$

and find

$$(1) + (2) + (3) \quad \Gamma_0$$
$$(1) - (2) \quad \Gamma_2{}^{11}$$
$$2(3) - (1) - (2) \quad \Gamma_2{}^{21}$$

so that Γ_0 and Γ_2 (doubly degenerate) each occurs once. Incidentally, if (1), say, were not transformed into itself by any R of the group there would be as many linearly independent ψ's formed as operations of the group, which is the same as the total number of "species" (degenerate n-tuples counted as n species). In the present case three "species" are represented (using this method of counting which differentiates between $\Gamma_2{}^{11}$ and $\Gamma_2{}^{21}$) corresponding to the fact that we started from three equivalent structures, in complete analogy with the non-degenerate case.

We now have a method for inferring species (possibly spurious, but nonetheless useful ones) from a given set of structures, but there remains the question of proving the method. This is done for the case of no degeneracy in Appendix I.

Part II

The Structure Representation.—In this part a discussion is given of the question of attempting to make predictions[13] about transition energies as well as polarizations. A preliminary problem is to obtain a correspondence between what is observed for a given molecule and the structure-theoretical formalism which has been partly developed in Part I and is to be further explained below. To illustrate and *define* the solution of this preliminary problem the simple case of benzene is treated. In deciding "what is observed" we limit ourselves to transitions believed to involve $2p_\pi$ electronic excitation with no change in principal quantum number. To make the illustration simple only the first two singlet electronic states are considered.

(13) It has frequently been said that applications of structures are made "after the fact." It is the aim here to point out one way in which it may be possible to reverse the procedure.

What is observed, then, are the energies O and E_1 corresponding, respectively, to the species A_{1g} and B_{2u}. The zero of energy is thus taken to be the true ground state energy of the molecule ($E_0 = 0$). The spectroscopic terms are written in a matrix, called the observed energy matrix

$$\mathbf{E} = \begin{pmatrix} 0 & 0 \\ 0 & E_1 \end{pmatrix}$$

The eigenvectors representing the states are $\begin{pmatrix} 1 \\ 0 \end{pmatrix}_{A_{1g}}$, and $\begin{pmatrix} 0 \\ 1 \end{pmatrix}_{B_{2u}}$. An orthogonal transformation gives

$$\mathbf{S}^{-1}\,\mathbf{E}\,\mathbf{S} = \mathbf{E}' = \begin{pmatrix} E_1/2 & -E_1/2 \\ -E_1/2 & E_1/2 \end{pmatrix}$$

where $\quad \mathbf{S}^{-1} = \begin{pmatrix} 2^{-1/2} & 2^{-1/2} \\ 2^{-1/2} & -2^{-1/2} \end{pmatrix}$

$\mathbf{E}'$ represents the energy in the *primed* coördinate system, the structure representation. The eigenvectors after the transformation are the columns of $\mathbf{S}^{-1}$

$$\begin{pmatrix} 2^{-1/2} \\ 2^{-1/2} \end{pmatrix}_{A_{1g}}, \text{ and } \begin{pmatrix} 2^{-1/2} \\ -2^{-1/2} \end{pmatrix}_{B_{2u}}$$

It is now possible to assume that the base vectors in the primed system $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$ and $\begin{pmatrix} 0 \\ 1 \end{pmatrix}$ correspond to the states ψ_1 and ψ_2 where (1) is one Kekulé structure, (2) the other. This procedure is given validity by the discussion in Part I.[14] The $\mathbf{E}'$ off-diagonal elements give the interaction between the primed base vectors or, loosely, the Kekulé structures, while the diagonal elements are the energies of the structures.

The transformation is uniquely determined by the requirement that the energies of the Kekulé structures (diagonal elements of $\mathbf{E}'$) must be equal. We have seen a particular way in which "what is observed" for benzene is fitted into the structure formalism. It should be noted that within the meaning of the words defined here, it is strictly true that the ground state of benzene is the sum of two ψ's corresponding to structures. The matrix transformation theory is not perturbation theory but exact. It is used in preference to a wave-mechanical formulation partly to emphasize the fact that the many electron ψ's are not known.[15]

It is seen that ideally there are as many states considered as structures, symmetry relations between structures lead to a unique $\mathbf{S}$,[16] and the structures have the proper transformation properties to give the correct observed symmetries. These conditions are stated within the framework of the

(14) It should be borne in mind that here Kekulé structures are the squares of unknown wave functions whose sum transforms like A_{1g}, whose difference transforms like B_{2u}. If one attempts to draw two such entities, he succeeds in producing drawings which bear a remarkable resemblance to Kekulé structures.
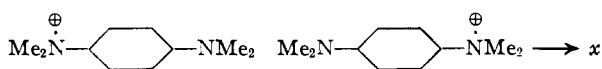
(15) A many electron ψ function seems to be aesthetically undesirable for use in dealing semi-empirically with spectroscopic problems involving so few data. Thus an n-electron ψ implies the possibility of predicting the probability that n electrons are simultaneously at n selected positions.

(16) Actually, the assumption is made that symmetry relations between elements of $\mathbf{E}'$ can be inferred from the transformation properties of structures or wave functions squared. It should be noted that between members of a complete set of equivalent structures and equivalent corresponding wave functions there is a unique one to one correspondence.

preliminary problem, that of obtaining a correspondence between the structure-theoretical approach and what is observed. There is the further and more important problem of applications to be discussed next.
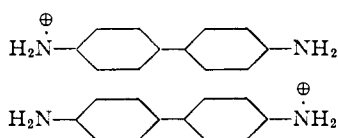
Methods of Application.—It is not the purpose of this paper to prove that the methods outlined are fruitful; but rather to suggest a formalism which is quantitative in nature, not at variance with quantum mechanics and which may be fruitful.

The first method of application stems entirely from the considerations of Part I. One starts from frequently used or conventional structures and attempts to predict polarizations of bands. An example is the $A_{1g} \rightarrow B_{2u}$ classification of the 2600 Å. benzene band based on a consideration of the Kekulé structures. Another is an indication that the visible band of Wurster's Blue should be

$$\overset{\oplus}{\text{Me}_2\text{N}}\text{—}\langle\;\rangle\text{—NMe}_2 \quad \text{Me}_2\text{N—}\langle\;\rangle\text{—}\overset{\oplus}{\text{NMe}_2} \longrightarrow x$$

polarized x. (Besides the group theoretical methods of Part I, here one can apply the expression for the transition moment given in the Introduction).

Several other methods of application hinge upon the requirement that the formalism shall have been applied successfully to a given molecule (that the "preliminary problem" in the sense of the last section shall have been solved). Perhaps the most promising method lies in the capacity, formally, to predict stationary state energy shifts which accompany small changes in the given molecule. The main point is that it is often quite difficult to guess what the effect of the structural change will be on the energy levels, but considerably easier to estimate expected changes in the energies, diagonal and off-diagonal, in the primed coördinate system, *i.e.*, the structure representation. For example, visible absorption in the radical of benzidine

$$\overset{\oplus}{\text{H}_2\text{N}}\text{—}\langle\;\rangle\text{—}\langle\;\rangle\text{—NH}_2$$

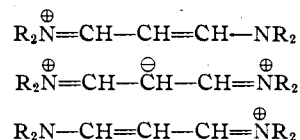$$\text{H}_2\text{N—}\langle\;\rangle\text{—}\langle\;\rangle\text{—}\overset{\oplus}{\text{NH}_2}$$

(which lies at a longer wave length than that for (Wurster's Blue) might be described as arising from a splitting due to the interaction of the functions related to the structures given above. This interaction (which involves an electron transfer over a considerable distance) should probably be smaller than the related interaction in Wurster's Blue, and hence the off-diagonal matrix elements (in the primed representation) describing the benzidine radical should be smaller than those for Wurster's Blue. Starting from the Wurster's Blue $\mathbf{E}'$ one guesses a new $\mathbf{E}'$, diagonalizes it and obtains a predicted direction of change in transition energy.

A similar method which also requires that the formalism shall have been applied successfully to a given molecule consists in the adoption of certain elements of $\mathbf{E}'$ for the given molecule in constructing $\mathbf{E}'$ for a related molecule. This process will be illustrated with reference to amidinium ions and higher homologs. Consider $R_2\overset{\oplus}{N}$=CH—NR$_2$, R_2N

—CH=$\overset{\oplus}{N}R_2$ a substance which absorbs at $\sim$2000 Å. (x) (the polarization has not actually been determined experimentally, but is assumed to have been determined as x in which case the structure-theoretical formalism can be applied). Then if $\Delta E = 2\alpha$.

$$\mathbf{E} = \begin{pmatrix} -\alpha & 0 \\ 0 & +\alpha \end{pmatrix} \text{ and } \mathbf{E}' = \begin{pmatrix} 0 & -\alpha \\ -\alpha & 0 \end{pmatrix}$$

The first higher homolog

$$R_2\overset{\oplus}{N}\text{=CH—CH=CH—NR}_2$$

$$R_2\overset{\oplus}{N}\text{=CH—}\overset{\ominus}{C}H\text{—CH=}\overset{\oplus}{N}R_2$$

$$R_2N\text{—CH=CH—CH=}\overset{\oplus}{N}R_2$$

is then considered to be represented approximately by

$$\mathbf{E}' = \begin{pmatrix} 0 & -\alpha & 0 \\ -\alpha & 0 & -\alpha \\ 0 & -\alpha & 0 \end{pmatrix}$$

Diagonalization of this matrix leads to the prediction that for the transition from the ground to first excited state $\Delta E < 2\alpha$. Essentially this application was made by Herzfeld and Sklar,[17] who considered they were using the HLSP or valence bond method. It seems preferable to reserve these names for the quantum-mechanical treatment[1] in which matrix elements are "rigorously" obtained.

Still a third approach, which essentially requires the assumption of a successful preliminary application of the formalism for a given molecule, consists in the determination of the polarization of a transition which becomes allowed when the given molecule is perturbed. The example given at the beginning of this paper of para disubstitution making the 2600 Å. band in benzene allowed (y) illustrates the procedure. It should be noted that group theoretical methods, with all reference to structures omitted, are here sufficient; but the use of structures makes the application easy as well as pictorial.

Uniqueness and Other Questions.—In order that the method may be applied to a given molecule for which the term values and species are known we require: (A) that the number of structures be equal to the number of observed levels, (B) that a unique S can be found, and (C) that the structures transform properly.

With regard to (A), if there are too many structures they can sometimes be lumped together. Thus in the example given earlier for the triphenylmethane dyes, the structures were distinguished by the position of the charge, while Kekulé mesomerism in the benzenoidal phenyls was ignored. If there are too few structures then some energy levels must be ignored. If there are too many structures, one possibility is to regard the energy matrix $\mathbf{E}'$ as being only approximate but giving the lower levels more accurately. Instead of being an analog of a Heisenberg representation treatment the method then more closely resembles the Ritz variation method treatment in quantum mechanics. The matrix

(17) K. F. Herzfeld and A. L. Sklar, *Rev. Modern Phys.*, **14**, 294 (1942).

$$\mathbf{E'} = \begin{pmatrix} 0 & -\alpha & 0 \\ -\alpha & 0 & -\alpha \\ 0 & -\alpha & 0 \end{pmatrix}$$

given above for R_2N=CH—CH=CH—NR_2 might yield a good value for $E_1 - E_0$ but a poor value for $E_2 - E_0$. This is to be understood as accompanying a Ritz type of calculation. We turn now to requirement (B).

If there are n structures and n levels, then the existence of a unique S requires that there be $n(n + 1)/2 - n$ subsidiary conditions.[18] Thus if we apply the formalism to naphthalene, with the three structures

(1)   (2)   (3)
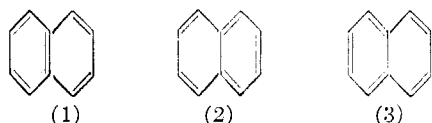
(and assume three states of appropriate symmetry have been identified from the spectrum) we need three subsidiary conditions. Two conditions are required by symmetry, namely, $E_{12}' = E_{13}'$, $E_{22}' = E_{33}'$ so that a unique S cannot be found. However, if we assume $E_{11}' = E_{22}'$ then a particular method of transforming the experimentally given E is immediately determined. The E' so determined is a rigorous representation of the energy but must be regarded as one corresponding to a special (although perfectly possible)[19] relation between (1) and the pair (2) and (3). Naphthalene is discussed in more detail in Appendix II, where a transformation of the observed energy matrix to non-diagonal form is made.

With regard to the requirement (C) that the structures transform properly, application of the methods described in Part I will show in any given case (where the state species are determined by experiment) whether or not certain structures can be employed; or will determine for a given set of structures which state species have to be observed, or selected from among the species observed. The need for satisfying (C) is crucial.

Concluding Remarks.—It seems desirable to emphasize that the word *structure* is used in two ways. In Part I, structure usually refers to the diagrams that are drawn according to the rules of chemical valence theory; but in Part II it stands for the squares of the trial functions associated with primed base vectors. Thus for formamidinium ion the sum and difference of the structures in the sense of Part I have to give the species A_1 and B_1. In place of the structures used before one might take

(1)   (2)
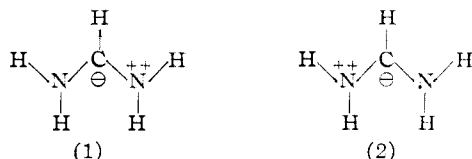
(18) There are $n(n + 1)/2$ elements on and above the diagonal of $\mathbf{E'}$ (which is symmetric) and we know only n term values. If we do not know the first term value we can still retain this arbitrariness in $\mathbf{E'}$.

(19) If for a given set of functions, ψ_1, ψ_2 and ψ_3, $E_{11}' \neq E_{22}'$ then add constx $(\psi_2 + \psi_3)$ to ψ_1 to give a new function still of the required symmetry (and hence still capable of being represented by (1)).

Although (1) and (2) are written according to rules of valence, still, on the basis of chemical intuition, they would be called "far-fetched." It is also possible to draw structures for benzene to take the place of the Kekulé forms but these too would be far-fetched. A restriction to reasonable structures (in the sense of Part I) is required, although it may be difficult to formulate.

We can now appreciate what condition must obtain in order that the present theory be fruitful. The condition is that it shall develop after a large number of applications that the Part I structures can be identified with the Part II structures. The writer believes that on the basis of already existing examples (some of which are described in the Introduction) this identification can be made. Nevertheless the proof has to be completely inductive, so it seems undesirable to pass judgment at this time. It would be interesting if the condition were not fulfilled, for this would indicate that structures cannot be fitted into a calculus of observable quantities dealing with electronic energy levels.

It should be mentioned that application to other than π-electron spectra might be foreseen; with the feature of working in a primed representation retained, but with new criteria for defining a particular S to take the place of structures. An interesting possibility is to diagonalize a part of the observed transition moment matrix. When applied to π-electron spectra this procedure may give something very much like the structure representation but in a manner which is independent of the concept of structure in the sense of Part I. To illustrate briefly, consider formamidinium ion again, with

$$\mathbf{E} = \begin{pmatrix} 0 & 0 \\ 0 & E_1 \end{pmatrix} \text{ and } \mathbf{X} = \begin{pmatrix} 0 & x_{01} \\ x_{01} & 0 \end{pmatrix}$$

where x_{01} is the observed $0 \to 1$ transition moment. Taking $x_{00} = x_{11} = 0$ is equivalent to measuring the electric moment of the ion from the center. In the primed representation these quantities are

$$\mathbf{E'} = \begin{pmatrix} E_1/2 & -E_1/2 \\ -E_1/2 & E_1/2 \end{pmatrix} \text{ and } \mathbf{X'} = \begin{pmatrix} x_{01} & 0 \\ 0 & -x_{01} \end{pmatrix}$$

The energy matrix is the same as in the structure representation but in addition through the use of $\mathbf{X'}$ it is possible quantitatively to classify the primed base vectors with respect to electron distribution. Note that the equal and opposite electric moments of the base vectors are suggestive of interpretation with respect to structures.

Acknowledgment.—The writer wishes particularly to acknowledge the influence of the work of Professor G. E. K. Branch and of Dr. L. G. S. Brooker as communicated through their published research and in many stimulating conversations.

Appendix I

Species from Squares of Wave Functions.—The object is to show that the non-vanishing fragments constructed from structures give species for states which are constructed from the corresponding trial functions. Assuming with respect to transformation properties that (i) $= \psi_1^2$ we may turn our attention in the following to ψ's and their squares. The problem of spurious species will arise as a natural part of the proof. The case of degeneracy is not considered and all ψ's are taken as equivalent, with ψ_i considered as a representative.

(1).—We shall investigate the transformation properties of the non-vanishing fragments

$$<\psi_i^2>^{\Gamma\alpha} = \sum_R \chi^{\Gamma\alpha}(R)R\psi_i^2$$

Greek subscripts are used for species associated with ψ^2's, arabic with ψ's. First consider the product, transforming like $\Gamma_a\Gamma_b$

$$<\psi_i>^{\Gamma_a} <\psi_i>^{\Gamma_b} = \sum_R \chi^{\Gamma_a}(R)R\psi_i \sum_S \chi^{\Gamma_b}(S)S\psi_i$$

The general term $R\psi_iS\psi_i$ is either of the form $\pm\psi_j\psi_k$ or $\pm \psi_j^2$ so that the product is a sum of squared terms [s], and cross terms [c]

$$<\psi_i>^{\Gamma_a} <\psi_i>^{\Gamma_b} = [s] + {}^*[c]$$

It will now be shown that the squared terms alone transform like the entire product (like $\Gamma_a\Gamma_b$). Assume a particular operation of the group T with, for example

$$T <\psi_i>^{\Gamma_a} <\psi_i>^{\Gamma_b} = - <\psi_i>^{\Gamma_a} <\psi_i>^{\Gamma_b}$$

Then $T[s] = - [s]$ and $T[c] = -[c]$ separately, because a squared term cannot be transformed into a cross-term.

Now let us take $\Gamma_\alpha = \Gamma_a\Gamma_b$ and note that quite independently of the argument just given, but from a property of fragments

$$<\psi_i^2>^{\Gamma\alpha} = \sum_R \chi^{\Gamma\alpha}(R)R\psi_i^2$$

belongs to the species Γ_α. Thus for each pair Γ_a and Γ_b there is a sum [s] which transforms in the same way as (and hence, apart from a constant factor, equals) the fragment $<\psi_i^2>^{\Gamma\alpha}$.

From the construction of all the $< \psi_i^2 >^{\Gamma\alpha}$ we can infer something about the Γ_a and Γ_b. If no fragment can be formed from ψ_i^2 for the particular species Γ_β and $\Gamma_c\Gamma_d = \Gamma_\beta$, then at least one of Γ_c and Γ_d must be missing.

(2).—Now we use the results of paragraph one to show more formally the connection between *product species* obtained from the squares of functions (like Γ_α) and species obtained from functions themselves (like Γ_a). Let us use the fact that the set of equivalent ψ^2's has the same number of elements as the set of equivalent corresponding ψ's and note that for the case of no degeneracy this must be the same as the number of species. Then we have the result that the set of species as obtained in the usual way from the ψ's

$$S_1 = \{\Gamma_a, \Gamma_b, \ldots, \Gamma_n\}$$

has the same number of elements as the set obtained from the ψ^2's

$$S_2 = \{\Gamma_\alpha, \Gamma_\beta, \ldots, \Gamma_\nu\}$$

This second set is by paragraph one also equal to the set of product species

$$\{\Gamma_a\Gamma_a, \Gamma_a\Gamma_b, \Gamma_a\Gamma_c, \ldots, \Gamma_b\Gamma_a, \Gamma_b\Gamma_b, \Gamma_b\Gamma_c, \ldots, \Gamma_n\Gamma_n\}$$

(the set property $\{a, a\} = \{a\}$ is used throughout) and so contains the identity, Γ_0. If S_1 contains Γ_0 then S_2 contains the n distinct species $\{\Gamma_0\Gamma_a, \Gamma_0\Gamma_b, \Gamma_0\Gamma_c, \ldots, \Gamma_0\Gamma_n\}$ so that S_2 *is the same* as S_1.

We conclude that if Γ_0 is represented among the true species then the construction of all the non-vanishing fragments from structures or ψ^2's gives all the species that would have been obtained in the conventional way from the unsquared ψ's.

Moreover if S_1 does not contain Γ_0 then there must be at least one Γ_p such that Γ_p times each member of S_1 gives S_2. If structures are used instead of wave functions for the enumeration of species through the calculation of the non-vanishing fragments, Γ_p is neglected; but, as explained in Part I, polarizations are given correctly.

Appendix II

An Example, Naphthalene.—This example is to be considered as a further illustration of the solution of the "preliminary problem": obtaining a correspondence between what is observed and the structure theoretical formalism. Application of the methods outlined in Part I shows that from the structures

(1)   (2)   (3) $x \longrightarrow$
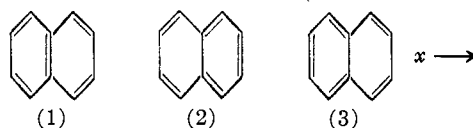
one can obtain the fragments and species

(1)	A_{1g}
(2) + (3)	A_{1g}
(2) − (3)	$B_{3u}(x)$

We now construct a matrix in the structure representation which depicts the first two A_{1g} and the first B_{3u} observed levels as arising from interactions among (1), (2) and (3). The observations for naphthalene are still somewhat controversial. The $\mathbf{E}$ of singlet observed energies has the diagonal elements (e.v.) $[0, 3.85, 4.18, 5.57, \ldots,]$.[20] According to Schnepp and McClure[21] the $0 \to 3.85$ band is definitely forbidden and is probably either $A_{1g} - A_{1g}$ or $A_{1g} - B_{1g}$, and the $0 \to 4.18$ band is polarized x. We are less concerned at this point with naphthalene than with the example afforded by naphthalene. Let us then assume that the $0 \to 3.85$ band is $A_{1g} - A_{1g}$ so that

$$\mathbf{E} = \begin{pmatrix} t & 0 & 0 \\ 0 & 3.85 + t & 0 \\ 0 & 0 & 4.18 + t \end{pmatrix}$$

We choose the zero of energy so that $E_{11}' = E_{22}' = E_{33}' = 0$ (see the brief discussion of naphthalene in Part II) and using trace invariance in similarity transformations obtain

$$t = -2.68 \ (61.7 \text{ kcal./mole})$$

$$\mathbf{E} = \begin{pmatrix} -2.68 & 0 & 0 \\ 0 & 1.17 & 0 \\ 0 & 0 & 1.50 \end{pmatrix}$$

Now we look for an $\mathbf{S}$ with $\mathbf{S}^{-1}\mathbf{E}\,\mathbf{S} = \mathbf{E}'$ and such that

$$E_{11}' = E_{22}' = E_{33}' = 0, E_{12}' = E_{13}'$$

as required by symmetry and the extra assumption discussed in Part II. We can put symmetry into $\mathbf{S}^{-1}$ directly

$$\mathbf{S}^{-1} = \begin{pmatrix} A & (1\text{-}A^2)^{1/2} & 0 \\ 2^{-1/2}(1\text{-}A^2)^{1/2} & -2^{-1/2}A & 2^{-1/2} \\ 2^{-1/2}(1\text{-}A^2)^{1/2} & -2^{-1/2}A & -2^{-1/2} \end{pmatrix}$$

Recall that the columns of $\mathbf{S}^{-1}$ each represent a state of naphthalene. It is helpful to think of the first and second columns as linear combinations of

$$\begin{pmatrix} 0 \\ 2^{-1/2} \\ 2^{-1/2} \end{pmatrix} \text{ and } \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} A_{1g}$$

which are kept normalized and orthogonal. Applying the defining equation for $\mathbf{S}$ and equating, say, the elements $(\mathbf{S}^{-1}\mathbf{E}\mathbf{S})_{11}$ and $\mathbf{E}_{11}' = 0$ we find $A = 0.552$ so that

$$\mathbf{E}' = \begin{pmatrix} 0 & -1.25 & -1.25 \\ -1.25 & 0 & -1.50 \\ -1.25 & -1.50 & 0 \end{pmatrix}$$

Attention is called to the fact that $-t$ has certain of the properties of "resonance energy" and is of a reasonable value. Also, note that the contributions $((\mathbf{S}^{-1}_{11})^2$ for the ground state) of (1), (2) and (3) are, respectively, 0.30, 0.35 and 0.35. One might use these contributions in attempting to predict bond distances but the results do not differ appreciably from predictions based on the assumption of equal contributions of the three structures. The above suggested applications are of course only intuitive, but the quantity t may have value even when considered from a rigorous standpoint.

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(20) M. Kasha and R. V. Nauman, *J. Chem. Phys.*, **17**, 516 (1949).

(21) Private communication. But see J. R. Platt, *ibid.*, **19**, 1418 (1951).