ELECTRON LEVELS IN POLYATOMIC MOLECULES HAVING RESONATING DOUBLE BONDS[1]

KARL F. HERZFELD

Department of Physics, Catholic University of America, Washington, D. C.

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The first part of this paper discusses in general terms the electron levels of molecules in which resonance between double bonds occurs. It is pointed out that there exists, for every such resonance problem, an analogue of coupled mechanical oscillators or more generally of coupled A.C. circuits. The importance of the nodes is emphasized and it is made plausible that the energy increases with the number of nodes.

The second part is concerned with the effect of electronegative substitution on the absorption frequency connected with electron transitions. This effect is ascribed to the migration of electrons into the resonating system. The general formulas are given. It is shown that in polyenes the effect is very sensitive to the position of substitution; the shift can be to the red or to the violet.

In benzene, the shift is always to the red; in multiple substitution, the theory predicts approximate additivity which is confirmed by the data. The theoretical calculation of the frequency shift for fluorobenzene and phenol agrees fairly well with the facts.

I. GENERAL CONSIDERATION OF MOLECULES HAVING RESONANCE

A. Visible and ultraviolet absorption spectra of organic molecules

Such absorptions, at not too high temperatures, are due to transitions from the ground state to an electronically excited state. The problem arises therefore as to the nature of the excited states. In molecules which contain only single bonds, the excited states are closely related to the excited states of individual atoms. For most atoms occurring in organic molecules, the excited states lie so high that the first resulting absorption is in the far ultraviolet. This is the case in the simple hydrocarbons (30) (region around 1500 A.) and the alcohols (30) (region around 1600 A.). In the alkyl halides Price (20) has found a Rydberg series, corresponding to atomic excitation, but this absorption moves from 1600 A. for methyl chloride to 2900 A. for methyl bromide and 3600 A. for methyl iodide, corresponding to the shift in the ionization potentials of the halides.

We shall not consider these spectra further but turn to those associated with double bonds. A double bond consists of two parts, the normal single bond, in which the wave functions of two paired electrons—one from each atom—

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Several of the statements made in the abstract and the talk on the subject of the second half of this paper turned out later to be erroneous.

thoroughly overlap, and a so called π–π bond, made up of two π electrons or unsaturation electrons (Mulliken) or mobile electrons (Lennard-Jones), one in each atom. These electrons are approximately in unexcited atomic p functions, with the axis normal to the bond. The electron distribution (ψ function) is shown schematically in figure 1. The ψ function of a p atomic state has opposite signs on opposite sides of the nucleus, which fact is indicated in the figure by the shadowing, and therefore two arrangements are possible. At the left, the two functions point the same way and therefore add up in the central portion, where they overlap. Therefore, the electron density is relatively large between the two nuclei, and this negative charge provides the extra additional bonding between the nuclei (Penney (19)). On the right is shown the case where the two wave functions point in the opposite direction and therefore cancel out in the region where they overlap. In this case there is little negative charge between the two positive ions and the uncompensated repulsion between the positive ions makes this state antibonding.

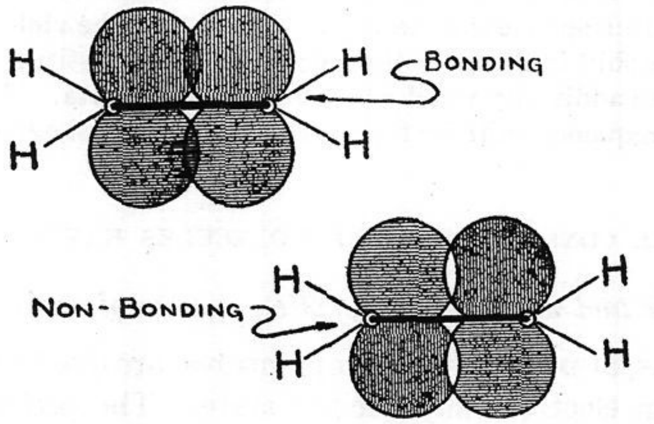


FIG. 1. π–π bond in ethylene

The atomic state with axis in the x direction is for carbon, nitrogen, oxygen, and fluorine a $2p$ state given by a hydrogen-like wave function

$$\psi = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{5/2} x\cdot\exp - \frac{Zr}{2a_0} \tag{1}$$

for sulfur, silicon, and chlorine the $3p$ state

$$\psi = \frac{1}{81}\sqrt{\frac{2}{\pi}}\left(\frac{Z}{a_0}\right)^{5/2}\left(6 - \frac{Zr}{a_0}\right) x\cdot\exp - \frac{Zr}{3a_0} \tag{1'}$$

where Z is the effective nuclear charge and a_0 the Bohr radius. The electron spins (of angular momentum $\frac{1}{2}\frac{h}{2\pi}$ each) may be antiparallel, so that they compensate and give a singlet state; this is the case for the bonding combination of wave functions. Or the spins may be parallel, when they add up and give a triplet state (three orientations), which occurs in the antibonding case.

The spectrum of an isolated double bond is experimentally (30) often still in the far ultraviolet (C_2H_4, 1750 A.; formic acid, 1550 A.; on the other hand acetone, 3300 A.). Most molecules giving absorption in the visible or near ultraviolet have conjugated double bonds, so that resonance phenomena become important, and this will be the subject considered from now on. To understand such resonance a mechanical analogue will be considered next.

B. Mechanical resonance

Consider four particles of equal mass (unity) arranged in a line, each of which is tied to its equilibrium position by a spring of force H. Then they can oscillate independently, and all have the same frequency ν, given by

$$4\pi^2\nu^2 = H \tag{2}$$

Now provide a weak spring h between any two neighbors. Then the whole system is coupled, and moves as a whole; there are four modes of vibration, shown with their frequencies in figure 2. Attention is drawn to the fact that the first mode of lowest frequency has no node, the next one has one node, the third one has two nodes, and the last one has three nodes. The results are derived from the equations of motion:

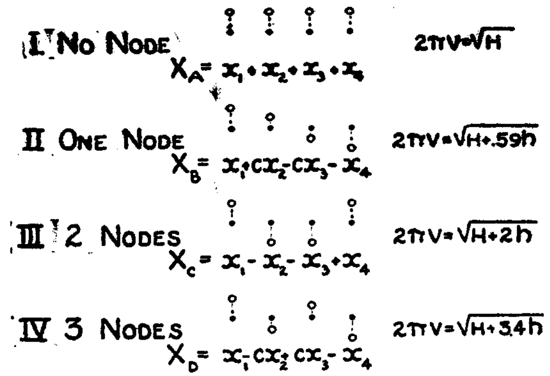


FIG. 2. Modes of vibration for four particles of equal mass arranged in a line

$$\begin{aligned}
&\frac{d^2 x_1}{dt^2} + Hx_1 + h(x_1 - x_2) = 0\\
&\frac{d^2 x_2}{dt^2} + Hx_2 + h(x_2 - x_1) + h(x_2 - x_3) = 0\\
&\frac{d^2 x_3}{dt^2} + Hx_3 + h(x_3 - x_2) + h(x_3 - x_4) = 0\\
&\frac{d^2 x_4}{dt^2} + Hx_4 + h(x_4 - x_3) = 0
\end{aligned} \tag{3}$$

These equations lead to the "secular equation"

$$\begin{vmatrix} H+h-\lambda & -h & 0 & 0 \\ -h & H+2h-\lambda & -h & 0 \\ 0 & h & H+2h-\lambda & -h \\ 0 & 0 & -h & H+h-\lambda \end{vmatrix} = 0 \tag{4}$$

which has four roots for λ, $\lambda = 4\pi^2\nu^2$. To each such root belongs one mode of vibration. However, the task of solving the equation is simplified by guessing at the form of the motion, e.g., for the first mode $x_1 = x_2 = x_3 = x_4$; if this is put into equations 3 it immediately leads to $\lambda = H$. Since the second and fourth mode shows $x_3 = -x_2$, the equations 3 are reduced to the form

$$\begin{aligned} -\lambda x_1 + (H+h)x_1 - hx_2 &= 0 \\ -\lambda x_2 + (H+2h)x_2 - hx_1 + hx_2 &= 0 \end{aligned} \tag{5}$$

which easily gives for the second mode

$$\lambda = 4\pi^2\nu^2 = H + h(2 - \sqrt{2}) \tag{6}$$

$$\frac{x_2}{x_1} = \sqrt{2} - 1,\ x_2 = -x_3,\ x_4 = -x_1$$

and for the fourth mode

$$\lambda = 4\pi^2\nu^2 = H + h(2 + \sqrt{2}) \tag{6'}$$

$$\frac{x_2}{x_1} = -(\sqrt{2} + 1),\ x_2 = -x_3,\ x_4 = -x_1$$

The remaining third mode can also be easily found by setting $x_1 = x_4$, $x_2 = x_3$. Each of the four independent modes of vibration shown in figure 2 can be described by one "normal coördinate," which will be called here X_1, X_2, X_3, X_4. These normal coördinates are given by a linear combination of the momentary deflection of all four points,—these deflections being called here x_1, x_2, x_3, x_4. This statement is true not only if the points move in one of the four modes of vibration shown in figure 2, but also if they move in as general a way as is possible for the system, which general motion can be represented as a superposition of these four modes of vibration.

The equations are

$$\begin{aligned} X_1 &= b_1[x_1 + x_2 + x_3 + x_4] \\ X_2 &= b_2[x_1 + (\sqrt{2} - 1)x_2 - (\sqrt{2} - 1)x_3 - x_4] \\ X_3 &= b_3[x_1 - x_2 - x_3 + x_4] \\ X_4 &= b_4[x_1 - (\sqrt{2} + 1)x_2 + (\sqrt{2} + 1)x_3 - x_4] \end{aligned} \tag{6''}$$

$$b_1^2[1 + 1 + 1 + 1] = 4b_1^2 = 1$$

$$b_2^2[1 + (\sqrt{2} - 1)^2 + (\sqrt{2} - 1)^2 + 1] = (8 - 4\sqrt{2})b_2^2 = 1$$

$$b_3^2[1 + 1 + 1 + 1] = 4b_3^2 = 1$$

$$b_4^2[1 + (\sqrt{2} + 1)^2 + (\sqrt{2} + 1)^2 + 1 = (8 + 4\sqrt{2})b_4^2 = 1$$

If the system moves in one of the modes pictured in figure 2, all the X's except one are zero (e.g., if it moves in mode 3, X_1, X_2, and X_4 are zero).

Attention should be drawn to the fact that the coefficients given above are the ones which have been calculated previously in equations 6 and 6′. For the general case of a system of n coupled oscillators, one has n normal coördinates $X_1 \cdots X_n$, which are given by

$$X_s = \sum_j c_j^s x_j$$

where the coefficients can be calculated by methods similar to those employed above (see Appendix I).

Exactly the same equations as the ones discussed now are also valid for a system of electrical circuits without resistance, coupled capacitively. If there is, in addition, inductive coupling, the secular equation of the type of equation 4 is replaced by one of the type

$$\begin{vmatrix} H_{11} - S_{11}\lambda & H_{12} - S_{12}\lambda \cdots & H_{1n} - S_{1n}\lambda \\ H_{21} - S_{21}\lambda & H_{22} - S_{22}\lambda \cdots & H_{2n} - S_{2n}\lambda \\ \cdots\cdots & \cdots\cdots & \cdots\cdots \\ H_{n1} - S_{n1}\lambda & H_{n2} - S_{n2}\lambda & H_{nn} - S_{nn}\lambda \end{vmatrix} = 0 \qquad (4')$$

Here the S_{jj} are self-inductances and the S_{jk} mutual inductances.

C. Wave function and energy of resonating systems

In the case before us, one ignores generally the in-plane bonds and deals with the π–π bonds only. Consider now a group of two CH_2 and two CH radicals, ignoring the unpaired electrons which will form the three single bonds when the groups are brought together to form $CH_2{=}CH{-}CH{=}CH_2$. We direct our attention to the four unpaired p electrons, one in each atom, which will be involved in the π–π bond formation. As long as the four groups are far apart, the electrons have the same energy, so that we have four states of equal energy, one in each atom, or for the system as a whole, a fourfold degenerate state. If we now bring the groups closer, there will be interaction between the four states of equal energy, i.e., an effect analogous to coupling in the mechanical or electrical circuit case discussed above. The fourfold degenerate state will be split up, and instead of four states of equal energy we shall have in this case, four states with four different energies.

The amount of splitting will increase the larger the coupling, i.e., the closer the atoms come together. It is this splitting of degenerate states by resonance which is the subject treated here. In the case of n carbon atoms, the result of the split is n (or less) energy states. In a solid metal, which is built up of a very large number of like atoms brought together, the levels lie so close that one gets a practically continuous "conduction band."

The task now before us falls into two parts: (*1*) to find formally the correct wave function, and (*2*) to calculate the energy.

The wave function of the whole molecule is always built up—in the approximation in most frequent use—as a linear combination of wave functions of certain "elements" on which the theory is based. These elements are either valence-bond structures or the individual atomic wave functions. The atomic wave functions enter in all cases, either directly or indirectly, into the construction of the wave function of these "elements" of the theory. In every case, however, the unmodified wave functions of the π electrons in isolated atoms have been used. This in itself is surely inexact, since the presence of the other atoms acts as perturbation. If an atom is subject to a perturbing field which does not introduce new places of infinite potential energy, its perturbed wave function can always be represented exactly by a series development into unperturbed wave functions. But it does not seem quite clear how this should be done in a molecule. If one grants, however, the use of the unperturbed atomic wave functions, the question arises as to how to make up the wave function of the whole molecule.

Two different approaches are in use; both have a naive and a sophisticated form. The first method, the valence-bond or Heitler–London–Pauling–Slater (HLPS) method, uses as elements the different valence-bond structures of the whole molecule; then the proper wave functions are linear combinations of the wave function of these valence-bond structures, and the computation problem is to find the correct coefficients.

In the naive form, only non-ionic valence-bond structures (for neutral molecules) are considered, and usually only those of low energy. In the sophisticated form, ionic structures are included, but for neutral molecules no atom loses or gains more than one electron. That is so because only two π electrons with the same axis of the dumbbell can be in the same atom (they have to have antiparallel spins).

The molecular orbital method (Lennard-Jones–Mulliken–Hückel) considers one-electron orbitals of the whole molecule, made up linearly of the atomic π functions of all the atoms having such electrons. The resulting molecular orbital is then the wave function for an electron which is considered as running through the whole molecule. These one-electron molecular orbitals for the whole molecule are then treated in the same way in which atomic one-electron states are treated in an atom, e.g., in a lithium atom, one has one $1s$, one $2s$, three $2p$, one $3s$, etc. one-electron atomic orbitals. In the ground state of the lithium atom, the three electrons are located in the lowest possible states, not more than two to a state. The ground state of the lithium atom has therefore two electrons in $1s$ and one electron in $2s$. By analogy, the benzene molecule has six molecular orbitals; in the ground state there are two electrons in each of the three lowest states. Excitation consists in having one or more electrons transferred to higher orbitals.

In the naive valence-bond method, ionic states were excluded; in the naive molecular orbital method, the effect of repulsion between electrons on the wave function is not considered, and therefore, more than one π electron arrives "by accident" oftener at the same atom than should be the case. This can be partly remedied by complete antisymmetrization (6, 25) which, however, complicates the calculation greatly.

Assuming that the wave functions are known, the calculation of the energy is straightforward; however, in practice it might become impossible for large molecules, owing to the great number of terms in the expression. For fairly exact calculations with antisymmetrized molecular orbitals, the Wurster salts (5) and biphenyl (11) seem to present the limit attainable without calculating machines.

The problem which does present theoretical difficulties is that of finding the wave functions. The general problem of the proper wave functions for the electrons which form the π–π bonds is formally the same as for the electrons forming the single bonds. An excellent critical discussion of the methods used has been given by Van Vleck and Sherman (32; see also 33). The presentation in this section follows their discussion.

Actually it is not necessary to calculate the wave functions before one can get the energy values. One proceeds in the following manner: Write the compound wave function:

$$\Psi_s = \sum_j c_j^{(s)} \psi_j \tag{7}$$

Here Ψ_s is the wave function of the whole molecule (HLSP method) in the s^{th} state or the wave function of the s^{th} molecular orbital (MO method), while ψ_j is the wave function of the j^{th} valence-bond structure (HLSP) or of the π state in the j^{th} atom (MO).

The $c_j^{(s)}$ are coefficients, and their calculation would permit writing the wave function to be used.

If H is the Hamiltonian function of the whole molecule, one defines the numbers:

$$H_{kj} = \int \psi_k^* H \psi_j \, d\tau \tag{8}$$

$$S_{kj} = \int \psi_k^* \psi_j \, d\tau \tag{8'}$$

Then one can express the energy in general as a quadratic function of the c. If one now looks for the lowest possible energy state and for the next higher states with wave functions normal to that of the lowest state, one gets equations of the form

$$\sum_j c_j^s (H_{kj} - S_{kj}E) = 0 \tag{9}$$

which can only be solved if the determinant

$$\begin{vmatrix} H_{11} - S_{11}E & H_{1n} - S_{1n}E \\ H_{n1} - S_{n1}E & H_{nn} - S_{nn}E \end{vmatrix} = 0 \tag{10}$$

This provides the n energy values E_s directly, and when they are known, the c values can be found from equation 9.

Often the following approximation is made:

$$S_{jj} = 1 \qquad S_{kj} = 0 \qquad k \neq j$$

That means that the overlap between wave functions of neighboring valence structures or neighboring atoms is neglected. For the in-plane bonds, such a neglect cannot be justified. In π–π bonds, however, and for the molecular orbital method, the error is much smaller. The determinant is then simplified and takes a form on which much mathematical work has been done: namely,

$$\begin{vmatrix} H_{11} - E & H_{12} \cdots & H_{1n} \\ H_{21} & H_{22} - E & \cdots \\ \cdots\cdots & \cdots\cdots & \cdots\cdots \\ H_{n1} & H_{n2} \cdots & H_{nn} - E \end{vmatrix} = 0 \qquad (10')$$

It should be pointed out again that all the different energy values E_s found by solving equation 10 or 10′ arise from the resonance splitting of the same (if only like atoms are concerned) unexcited atomic p states, and the transitions considered here occur only between levels arising in this way from the same atomic level.

From the mathematical standpoint, the solution of such an equation as 10 or 10′, which might be of high order, gives trouble, while the wave functions are afterwards found by a straightforward but tedious calculation of determinants and minors. It is, however, more enlightening to reverse the process and consider first the task of finding the proper wave functions. The calculation of the energies—one for each wave function— is then straightforward, but can become in practice almost impossible owing to the large number of terms.

The task of finding suitable wave functions for symmetrical molecules can be shortened by group theory. However, group theory itself is rather complicated and can be replaced in some cases by inspection and inspired guess work. For this purpose, one first shows that for every problem of quantum-theoretical resonance, there is a mechanical or electrical analogue. Assume that one has a quantum problem which requires a solution of a secular equation

$$\begin{vmatrix} H_{11} - \lambda & H_{12} \cdots & H_{n1} \\ H_{21} & H_{22} - \lambda \cdots\cdots & \\ \cdots\cdots & \cdots\cdots & \cdots\cdots \\ H_{n1} & & H_{nn} - \lambda \end{vmatrix} = 0 \qquad (10'')$$

or, in short,

$$| H_{ij} - S_{ij}\lambda | = 0$$

The solutions λ are the energy values E of the states resulting from the resonance splitting.

The mechanical analogue consists of a system of n particles of unit mass. The j^{th} particle is tied to an equilibrium position by a spring of restoring force constant $H_{jj} + \sum_{k \neq j} H_{jk}$, and tied to the k^{th} particle by a spring of restoring force constant $-H_{jk}$. This mechanical system will have n independent modes of vibration. For each mode of vibration, the motion of the whole system can be expressed by a "normal coördinate" which is a linear combination of the motions of the individual particles. To each mode of vibration corresponds one wave function, made up linearly of the wave functions of the elements used (valence-bond structures or single atomic wave functions.) Numerically the same coefficients which appear in the equation expressing the normal coördinate by the coördinates of the individual mechanical particles appear also in the equation which connects the correct wave function with the wave functions of the structure elements.

If only neighboring particles are connected by coupling springs, i.e., if in the resonance problem only neighboring atoms interact, each mode of vibration will show "nodes." In the corresponding wave function, a node means that there is in the molecular orbital a change of sign between the two atomic functions of the neighboring atoms considered. If a node falls on an atom, the wave function of that atom does not appear in the particular molecular orbital. In general the mode of vibration of lowest frequency (the wave function of the lowest molecular orbital) will have no node. All possible numbers of nodes, up to a maximum n', will appear in *one* mode of vibration (one molecular orbital). If no degeneracy exists, that is, if no two modes of vibration have the same frequency (no two orbitals the same energy), n', the maximum number of nodes, is equal to $n - 1$, the number of particles minus 1, and each number of nodes between 0 and $n - 1$ occurs in one mode of vibration and only one. If degeneracy exists, there will be more than one mode of vibration having the same number of nodes, but they will be differently arranged in these different modes. The maximum number of nodes occurring will then be less than $n - 1$ (see Appendices II and III).

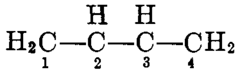
If it is possible to guess at the modes of vibration and, with the help of that guess, calculate with not too much trouble the modes of vibration and frequencies of the mechanical analogue as was done in Section I,B, this gives immediately the wave functions and energies (E instead of $4\pi^2\nu^2$).

This guessing is easier, the simpler and more symmetrical the mechanical system. For this reason, the method is particularly useful in the molecular orbital method, where the elements from which the correct wave function is built are the atomic one-electron p functions. These are the same for all carbon atoms and only different for other atoms like nitrogen, oxygen, and sulfur which might occur—usually at the periphery of the molecule. Most of the H_{ii} values are then equal.

D. Examples

This procedure for finding the wave functions will now be illustrated by some examples.

(*1*) *Butadiene* (*9, 10, 13*) (*figure 3*): There is a skeleton



$$\mathrm{H_2}\underset{1}{\mathrm{C}}-\overset{\mathrm{H}}{\underset{2}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{3}{\mathrm{C}}}-\underset{4}{\mathrm{C}}\mathrm{H_2}$$

with one atomic π state and one π electron in each carbon atom (the latter are numbered 1, 2, 3, 4). It is assumed that only neighbors interact. The case is therefore exactly analogous to the mechanical example discussed in Section I.

B and shown in figure 2. The wave functions of the molecular orbitals are, in order of ascending energy:

$$\begin{array}{ll} M_1\psi_1 = p_1 + p_2 + p_3 + p_4 & \text{No node} \\ M_2\psi_2 = p_1 + cp_2 - cp_3 - p_4 & \text{One node} \\ M_3\psi_3 = p_1 - p_2 - p_3 + p_4 & \text{Two nodes} \\ M_4\psi_4 = p_1 - c'p_2 + c'p_3 - p_4 & \text{Three nodes} \end{array}$$

Here p_j is the atomic π function of the j^{th} atom, M are normalization constants of the same character as the b's of Section I, B; the values of the constants c and c' are again $\sqrt{2} - 1$ and $\sqrt{2} + 1$. (For molecules of arbitrary n, the constants c can be best calculated by considering the analogous mechanical motion as a standing wave.) One sees that the wave function is (with respect to the center of the molecule) even or odd, depending on whether the number of nodes is even or odd. This is the background for Mulliken's statement that in polyenes the states are alternately even or odd.

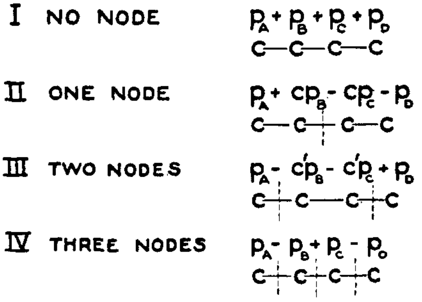


FIG. 3. Molecular orbitals for butadiene

$$\underset{A}{\mathrm{H_2C}}=\underset{B}{\mathrm{C}}-\underset{C}{\mathrm{C}}=\underset{D}{\mathrm{CH_2}}$$

(*2*) *Benzene* (*6*, *25*) (*see figure 4*): There are six significant atomic π states, one in each carbon atom, and therefore six molecular orbitals must arise from the resonance splitting. The molecular orbital of lowest energy has no nodes; there is only one such state, and from symmetry the coefficients of all the atomic wave functions are the same.

$$M_1\psi_1 = p_1 + p_2 + p_3 + p_4 + p_5 + p_6$$

The largest number of nodes possible is three, and there is only one possible arrangement (the other imaginable arrangement would have the nodes go through all six carbon atoms, and then all coefficients would be zero and there would be no wave function). Therefore the molecular orbital of highest energy is:

$$M_6\psi_6 = p_1 - p_2 + p_3 - p_4 + p_5 - p_6$$

That leaves four states to be accounted for by one or two nodes, so that the orbitals having one or two nodes must either both be doubly degenerate or one triply degenerate and the other simple. As a matter of fact, both are doubly degenerate. The proper positions of the nodes are shown in figure 4, and the wave functions are:

$$\begin{array}{ll} \text{One node:} & M_2\psi_2 = p_2 + p_3 - p_5 - p_6 \\ & M_3\psi_3 = p_1 + c(p_2 + p_6) - p_4 - c(p_3 + p_5) \\ \text{Two nodes:} & M_4\psi_4 = p_2 - p_3 + p_5 - p_6 \\ & M_5\psi_5 = p_1 + p_4 - c'(p_2 + p_3 + p_5 + p_6) \end{array}$$

c and c' can again be calculated by considering the motion of the mechanical analogue as a standing wave problem.

As will be shown elsewhere, this method can be applied to rather complicated molecules.

E. The total number of molecular states

There is no direct connection between the number of valence-bond structures used in the Heitler–London–Pauling–Slater method and the number of one-electron molecular orbitals found by the MO method. On the other hand, the total number of molecular states arising, according to the MO method, is the same as the *total* number of valence structures.

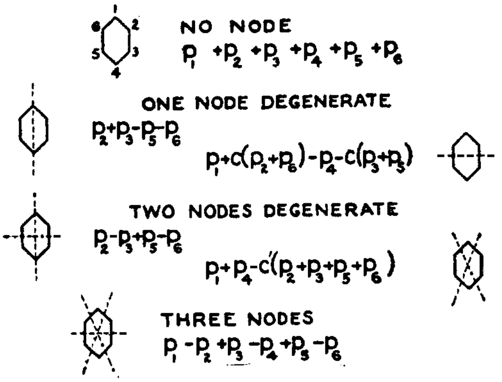


FIG. 4. Molecular orbitals for benzene

While no general proof of this statement has been given, it will be illustrated below for butadiene. Of course, many of these molecular states are of no experimental importance because they lie higher than atomic excited states, or require the excitation of several electrons.

There are twenty valence structures of butadiene which are in the singlet state: namely, two non-ionic states, the usual one and one other, where one double bond connects the two inner, one the two outer carbon atoms; twelve singly ionized structures (four positions for the positive ion, and in each case three positions for the negative ion), with a double bond connecting the two neutral atoms; six doubly ionized structures $\left(\frac{4 \times 3}{2}\right.$ positions for the positive ions$\left.\right)$.

The molecular orbital method fills four molecular orbitals with four electrons.

This also gives twenty molecular states: namely, six states in which two orbitals contain two electrons each and the other two orbitals are empty (four orbitals available for the first electron pair, and in each case three orbitals then available for the second pair; but this counts each state twice). The ground state belongs to this group. Twelve molecular states in which one orbital is occupied by two electrons, two orbitals by one electron each, and one orbital is empty (any one of the four orbitals might be occupied by an electron pair, and in each case the empty orbital might be any one of the remaining three). The first excited state is in this group. Two states in which there is one electron in each orbital. These states differ only by the way the spins are paired.

No general formula for the total number of singlet states has been developed.

II. THE EFFECT OF SUBSTITUTION ON THE WAVE NUMBER OF ELECTRONIC TRANSITIONS

A. General considerations

Mulliken (15, 16, 17) has treated the effect of substitution on the electron levels of polyenes. If a hydrogen atom is replaced by a methyl group, Mulliken treats the latter as having the structure $C{\equiv}H_3$, so that a new double bond is added in the proper position (hyperconjugation). The results agree well with experiment.

Sklar (24) has considered the effect of substitution on the intensity of the forbidden transition at 2600 A. in benzene. He uses the molecular orbital method and draws attention to the consequences of the migration of charges into the benzene ring. His method, however, can also be used to explain the wavelength shift and to calculate it in first approximation. This is not limited to benzene, but can be applied to other molecules having resonating π–π bonds.

We shall call the resonating molecule or ion in which the substitution is made the "resonating system R" and the substituent X. We assume that there are no π–π bonds in the substituent. Call φ_j the j^{th} unoccupied orbital in the unsubstituted resonating system, W_j its energy (negative), ζ the occupied π orbital of proper orientation in the substituent, and W its energy. Call H_{R} the Hamiltonian of the unsubstituted resonating system, including the effects of all electrons contained therein, and H_{X} the Hamiltonian of the substituent after removal of one π electron. Abbreviate:

$$\omega_j = W_j + \int \varphi_j H_{\text{X}} \varphi_j \, d\tau \qquad \omega = W + \int \zeta H_{\text{R}} \zeta \, d\tau$$

$$2\rho_j = \int \varphi_j (H_{\text{R}} + H_{\text{X}}) \zeta \, d\tau + S_j (W_j + W)$$

$$S_j = \int \varphi_j \zeta \, d\tau \tag{13}$$

We assume $|\omega| > |\omega_j|$ (ortho–para-directing substitution).

Here ω_j, ω are the energies of the orbitals in R and in the substituent as modified by the Coulomb contribution of the other partner, S_j the overlap between resonating system orbital and substituent orbital, and ρ_j the exchange integral. If Λ_j^2 signifies the fraction of an electron from the substituent migrating into orbital j and b^2 the amount remaining, then the normalization condition is:

$$\sum_j \Lambda_j^2 + 2\sum_j \Lambda_j b S_j + b^2 = 1 \tag{14}$$

The energy of an electron from the substituent, which is allowed to be distributed between the substituent and the unoccupied orbitals of the resonating group, is

$$\sum_j \Lambda_j^2 \omega_j + 2\sum_j \Lambda_j\, b\rho_j + b^2\omega$$

and the energy change due to migration is

$$U = \sum_j \Lambda_j^2\omega_j + 2\sum_j \Lambda_j\, b\rho_j + b^2\omega - \omega \tag{15}$$

The summation goes over the unfilled orbitals of the resonating system. In equation 15 the term $2\Sigma\Lambda_k\Lambda_j \int \varphi_k H_X \varphi_j \, d\tau$ has been left out, for reasons given by Sklar. (We write Λ_j for Sklar's a_j and believe that Λ_j^2 is a better measure for migration than Sklar's λ_j^2.) If one minimizes U taking care of the normalization condition (expression 14), one finds, neglecting terms in Λ^3 and higher powers:

$$\Lambda_j = \frac{\rho_j - \omega S_j}{\omega - \omega_j} \tag{16}$$

This applies to unfilled states of the system, but is independent of what other states are filled. Introducing equation 16 in equation 15, one finds for the energy change in any state of the molecule:

$$U = \sum_j (\omega - \omega_j)\Lambda_j^2 \tag{17}$$

The terms have the opposite sign from the one which one would at first expect.

Consider now the shift in the wave number of a given electron transition. In the ground state of the resonating radical, all orbitals are filled up to a certain number n $\left(\text{in neutral molecules, } N = \frac{n}{2}\right)$. Therefore electrons from the substituent migrate into all the empty orbitals, $j > n$.

$$U_g = +\sum_{j>n} (\omega - \omega_j)\Lambda_j^2 \tag{17$'$}$$

If now one electron is excited into the orbital $m > n$, this orbital (or half of it) is excluded from migration, but an orbital n has become free. Therefore, for the excited state

$$U_e = \Lambda_n^2(\omega - \omega_n) + \sum_{j>n} (\omega - \omega_j)\Lambda_j^2 - \Lambda_m^2(\omega - \omega_m) \tag{17$''$}$$

and the shift in wave numbers due to substitution has the value

$$\Delta\nu = \frac{1}{ch}(U_s - U_g) = \Lambda_n^2 \frac{\omega - \omega_n}{hc} - \Lambda_m^2 \frac{\omega - \omega_m}{hc} \tag{18}$$

$$\Lambda_j^2 (\omega - \omega_j) = \frac{1}{\omega - \omega_j}(\rho_j - S_j \omega)^2 \tag{18'}$$

In other words, the effect of substitution on the energy difference of an electron transition is due to the fact that, upon excitation, a migrating electron has been pushed out of the excited orbital but instead has been allowed to migrate into a previously filled, lower orbital.

The heat of ionization (taken positively) of an electron from the j^{th} orbital is changed through substitution by the amount

$$+ (\omega - \omega_j)\Lambda_j^2$$

B. Effect of the position of substitution and of the state of excitation

We limit ourselves here to substitution of a substituent X on a carbon atom, and assume that the distance between the substituent and the carbon atom is independent of the place of substitution. It is further assumed that this distance is the same in the ground state and in the excited state of the molecule. Overlap integrals between atoms which are not nearest neighbors are neglected. It is then possible to introduce some integrals which depend only on the nature of the substituent, but not on its position or the particular molecular orbital of the resonating system.

Write the wave function of the j^{th} molecular orbital of the resonating system in the form (see 32 and 33; here φ is used instead of ψ to indicate that φ is not the wave function of the whole substituted system):

$$\varphi_j = \sum_k c_k^{(j)} p_k \tag{19}$$

p_k being the atomic π function of the k^{th} carbon atom of the resonating system.

Then (see reference 13), if the substitution is made on the s^{th} carbon atom:

$$S_j = c_s^{(j)} S \tag{20}$$

$$S = \int p_s \zeta \, d\tau \tag{20'}$$

$$\rho_j = c_s^{(j)}[\rho' + \tfrac{1}{2}S(W + W_j)] \tag{21}$$

$$2\rho' = \int p_s (H_R + H_X) \zeta \, d\tau \tag{21'}$$

The assumption made in equation 21 is that the exchange energy integrals can also be neglected except between nearest neighbors.

Therefore one gets

$$\Lambda_j = c_s^{(j)} \frac{\rho' + \frac{1}{2}S(W - 2\omega + W_j)}{\omega - \omega_j} \tag{22}$$

$W - \omega$ is independent of j and depends on the place of substitution only if R is an ion and H_R has a Coulomb part.

Therefore it is useful to introduce a further abbreviation:

$$\rho = \rho' + \tfrac{1}{2}S(W - 2\omega) \tag{23}$$

$$\Lambda_j = c_s^{(j)} \frac{\rho + \frac{1}{2}SW_j}{\omega - \omega_j} \tag{23'}$$

As long as the values of Λ are sufficiently small, the effects of more than one substitution ought to be additive.

C. Application to polyenes

If these formulae are applied to polyene molecules or methine dyes containing N carbon atoms, one has

$$c_s^{(j)} = \frac{1}{M_j} \cos\left[\left(\frac{N+1}{2} - s\right)\frac{\pi j}{N}\right] \qquad j \text{ even} \tag{24}$$

$$= \frac{1}{M_j} \sin\left[\left(\frac{N+1}{2} - s\right)\frac{\pi j}{N}\right] \qquad j \text{ odd}$$

$$0 \leqq j \leqq N - 1,\ s \text{ running from 1 to } N$$

The last full orbital is $j = \frac{N}{2} - 1$; the first excited one is $j = \frac{N}{2}$ (N is even). Designate the former by the index g, the latter by the index e.

The ionization potential of the ground state is changed by

$$\frac{2}{3N}\left[1 - (-1)^s \sin \pi \frac{2s - 1}{N}\right]^2 \frac{(\rho + \frac{1}{2}SW_g)^2}{\omega - \omega_g} \tag{25}$$

and that of the excited state by

$$\frac{1}{N} \frac{\left(\rho + \frac{S}{2} W_e\right)^2}{\omega - \omega_e} \tag{25'}$$

Equation 25′ means that the migration into the excited orbital is independent of the position of the substituent. The question whether, upon substitution at the first carbon atom, the ionization potential of the ground state or that of the excited state is more affected depends on the question whether

$$\frac{2}{3}\left(1 + \sin\frac{\pi}{N}\right)^2 \frac{1}{|\omega - \omega_g|} \quad \text{or} \quad \frac{1}{\omega - \omega_e}$$

is larger (if the effect of SW_j in the numerator is neglected).

The frequency shift is given by

$$\Delta\nu = \frac{1}{hcN}\left\{\frac{(\rho + \frac{1}{2}SW_g)^2}{\omega - \omega_g} \frac{2}{3}\left[1 - (-1)^s \sin \pi \frac{2s - 1}{N}\right]^2 - \frac{(\rho + \frac{1}{2}SW_e)^2}{\omega - \omega_e}\right\} \tag{25''}$$

Equation 25 has interesting consequences, which will be illustrated by an example. Abbreviate for the moment

$$\Delta\nu_1 = \frac{1}{hc}\frac{(\rho + \frac{1}{2}SW_g)^2}{\omega - \omega_g}\frac{2}{3N}$$

$$\Delta\nu_2 = \frac{1}{hc}\frac{(\rho + \frac{1}{2}SW_e)^2}{\omega - \omega_e}\frac{1}{N}$$

and apply the formula to $N = 6$. Then,

$$s = 1, 6 \quad \Delta\nu = \Delta\nu_1\left(1 + \sqrt{\frac{3}{2}}\right) - \Delta\nu_2$$

$$s = 2, 5 \quad \Delta\nu = -\Delta\nu_2$$

$$s = 3, 4 \quad \Delta\nu = \Delta\nu_1\left(1 - \sqrt{\frac{3}{2}}\right) - \Delta\nu_2$$

In general, the factor of the first term disappears if $\frac{N}{2}$ is odd, $\frac{N}{4} + \frac{1}{2}$ even, for $s = \frac{N}{4} + \frac{1}{2}$ and the corresponding atom $s' = N + 1 - s$. It is interesting that, if one sums up the wave-number shifts one gets by substituting in turn on all carbon atoms, one finds:

$$\Sigma\Delta\nu = \frac{1}{hc}\frac{(\rho + \frac{1}{2}SW_g)^2}{\omega - \omega_g} - \frac{1}{hc}\frac{(\rho + \frac{1}{2}SW_e)^2}{\omega - \omega_e}$$

D. *Application to benzene and derivatives*

(1) Experimental data

In this section the experimental data for the wave number of the 0–0 transition in the vapor state are collected (table 1), since only these can be used for comparison. Even these transitions contain, besides the electronic energy difference, the difference in zero-point energies in the excited and ground states, summed up over all vibration frequencies. It is hoped here that, while the zero-point energies themselves are affected by substitution, the differences might not be affected sufficiently to matter, so that the change in the wave number of the 0–0 transition upon substitution might be taken as change in the electronic transition.

(2) General theoretical considerations

The 2600 A. band arises in benzene if one electron is taken out of orbital 3 and transferred to orbital 5 (see Section I,D,(2)). The coefficients c of the atomic p function in the two orbitals are practically the same except for the normalization factors (called σ by Sklar). One has

$$c^g = \frac{1}{\sqrt{1.20}\cdot\sqrt{3}} = 0.53; \qquad c^e = \frac{1}{\sqrt{0.72}\cdot\sqrt{3}} = 0.68$$

One can then not say offhand that the shift must always be to the red. One can, however, expect that the substitutions which give a large red shift will also be effective auxochromes. Table 2 compares the red shift from table 1 with the values of Δf, the increase of transition probability for monosubstituted benzenes (24). A general parallelism is noted, except for the different positions of CH_3 and F.

(3) Additivity

It has been noted previously that for polysubstituted benzenes there should not be the pronounced dependence of the effect on the position of substitution which exists in the intensity (auxochromic effect), but that the red shift of substituents should be approximately additive. The data in table 3 are approximately in agreement with this statement.

TABLE 1

Monosubstituted benzenes

FORMULA	ν (0–0)	$\Delta\nu$	REFERENCE
C_6H_6	38,089		(30)
$C_6H_5CH_3$	37,484	−605	(30)
C_6H_5F	37,818	−271	(31)
C_6H_5Cl	37,052	−1037	(30)
C_6H_5Br	36,996	−1093	(30)
C_6H_5CN	36,516	−1573	(30)
C_6H_5OH	36,350	−1739	(30)
$C_6H_5NH_2$	34,034	−4055	(30)

TABLE 2

Comparison of red shift with auxochromic efficiency

COMPOUND	$C_6H_5CH_3$	C_6H_5F	C_6H_5OH	$C_6H_5NH_2$
$-\Delta\nu$ from table 1	605	271	1739	4055
$\Delta f \times 10^4$	12	100	170	200

There are, however, deviations: first of all, the position of substitution does make a difference; para substitution gives in general a larger red shift than ortho or meta substitution. It is consistent with this fact that the shift in 1,2,4-trichlorobenzene is larger than in 1,3,5-trichlorobenzene.

Two explanations for the effect of the position and for the deviation from additivity come to mind. The reason may be experimental, insofar as ν $(0 \rightarrow 0)$ is not the pure electron jump but contains also the difference in zero-point energies (Section II,D,(1)). On the theoretical side it may be noted that ω_j (equation 13) contains the effect of the Coulomb force, originating on the ionized substituent, on the benzene wave functions. For the di- and tri-substituted benzenes, this Coulomb term will depend on the number and on the relative position of the substituents. This fact will produce slight deviations from additivity for the red shift.

An additional reason for deviations from additivity is present if the migration is too large, so that migrations from different substituents react on each other. This effect is apparent in the amines.

(4) Theoretical calculation of the shift in monosubstituted benzenes

For this calculation, the following approximations are made: In the denomina-

TABLE 3

Polysubstituted benzenes

COMPOUND	ν (0–0)	$\Delta\nu$	REFERENCE
(1) Chlorobenzenes			
Chlorobenzene	37,052	−1037	(30)
o-Dichlorobenzene	36,230	−1859	(28)
m-Dichlorobenzene	36,186	−1903 average = 2036	(28)
p-Dichlorobenzene	35,743	−2346 2 × 1037 = 2074	(28)
1,3,5-Trichlorobenzene	35,498	−2591	(28)
1,2,4-Trichlorobenzene	35,108	−2981 3 × 1037 = 3111	(29)
(2) Mixed disubstituted benzenes			
p-Fluorotoluene	36,866	−1223 (CH_3 + F = −876)	(30)
o-Fluorotoluene	37,566	−523	(30)
Chlorotoluene	36,297	−1792 (CH_3 + Cl = −1642)	(30)
Bromotoluene	36,173	−1916 (CH_3 + Br = −1698)	(30)
(3) Methylbenzenes			
Toluene	37,484	−605	(30)
1,3,5-Trimethylbenzene	36,488	−1600 3 × 605 = 1815	(29)
(4) Amines			
Aniline	34,034	−4055	(30)
p-Phenylenediamine ($NH_2C_6H_4NH_2$)	(31,400)	−6690	(23)
	(34,800)	−3290	(12)

tor of Λ (equation 22), namely, $\rho' + \frac{1}{2}S(W + W_j) - S\omega$, W is replaced by ω, i.e., $\int \zeta H_R \zeta \, d\tau$ is neglected, since the ring is neutral; W_j is replaced by its value from equation 13, therefore

$$\Lambda_j = c^j \left\{ \frac{1}{\omega - \omega_j} \left[\rho' - \frac{1}{2}S \int \phi_j H_X \phi_j \, d\tau \right] - S \right\} \qquad (26)$$

In the integral $\int \varphi_j H_X \varphi_j d\tau$, the potential of the substituent is replaced by that of a neutral atom minus a missing π electron, and the former is neglected. Therefore, using the notation of Sklar and Lyddane (26), one has

$$\int \varphi_j H_X \varphi_j \mathrm{d}\tau = -(c^j)^2(aa;\, bb) \tag{27}$$

Furthermore from equation 21′,

$$2\rho' = \int pH_R\zeta \mathrm{d}\tau + \int pH_X\zeta \mathrm{d}\tau = -Q_{12} - (Q_{12} + ab;\, bb) \tag{28}$$

Finally, since these integrals involve p functions belonging to different atomic numbers, Sklar's approximation (24) is introduced. The atomic integral will be designated so that $ab;bb$ (C) means an integral $ab;bb$ calculated for the atomic charge of C. Similarly S (C) will be the overlap calculated by the formula on p. 990 of reference 24, while S without index is calculated by formula 23 of reference 24.

TABLE 4

Data used in calculating red shift

	ω	ω_g	ω_e	$\frac{1}{2}[\ \ ]_g$ FROM EQUATION 29	$\frac{1}{2}[\ \ ]_e$ FROM EQUATION 29	S (C)	S (X)	S
F	15	9.9	7.8	28.5	26.1	0.273	0.058	0.131
OH	12.5	9.7	7.6	20.6	18.2	0.283	0.100	0.201

TABLE 5

Calculated electron migration and red shift

	Λ_g	Λ_e	$(\omega - \omega_g)\Lambda^2_g$	$(\omega - \omega_e)\Lambda^2_e$	$\Delta\nu$ (CALCULATED)	$\Delta\nu$ (EXPERIMENTAL)
F	0.158	0.117	−0.128	−0.099	−230	−271
OH	0.362	0.184	−0.312	−0.167	−1170	−1739

Then

$$\Lambda_j = c^{(j)}\frac{S}{2}\left\{\frac{1}{2}\frac{1}{|\omega - \omega_j|}\left[\frac{ab;\, bb\,(\mathrm{C}) + 2Q_{12}(\mathrm{C})}{S\,(\mathrm{C})} + \frac{ab;\, bb\,(\mathrm{X}) + 2Q_{12}(\mathrm{X})}{S\,(\mathrm{X})} - (c^j)^2 S\left(\frac{aa;\, bb\,(\mathrm{C})}{S\,(\mathrm{C})} + \frac{aa;\, bb\,(\mathrm{X})}{S\,(\mathrm{X})}\right)\right] - 1\right\} \tag{29}$$

The values of the atomic integrals at various distances were kindly supplied by Miss Virginia Griffing. The constants are (6, 25):

$$c_g^2 = \frac{1}{3.6}\,; \qquad c_e^2 = \frac{1}{2.16}$$

The values of ω were taken from reference 24; the values of ω_g and ω_e were kindly supplied by Dr. A. L. Sklar.

Table 4 shows the data used and some of the values calculated for C_6H_5F

and C_6H_5OH. All energies are in electron volts. Table 5 shows the results of the calculations.

The agreement is much better than one could expect, particularly since the change in zero-point energies has been neglected. A decrease in the ionization potential of OH by 0.2 volt increases $|\Delta\nu|$ by 170.

From the data of table 4 an approximate formula seems to be:

$$\begin{aligned} \Lambda_g^2 &= \frac{S^2}{14.4}\left(\frac{27}{|\omega - \omega_g|} - 1\right)^2 \\ \Lambda_e^2 &= \frac{S^2}{8.64}\left(\frac{19}{|\omega - \omega_e|} - 1\right)^2 \end{aligned} \tag{30}$$

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APPENDIX I: MATHEMATICAL APPENDIX

Calculation of the coefficients

The mathematical argument in the general case of n particles is as follows: Consider the deflection of a particle expressed by the normal coördinates, i.e., the inverse equation compared to equation 6″:

$$x_1 = c_1^{(1)}X_1 + c_1^{(2)}X_2 \cdots + c_1^{(s)}X_s \cdots + c_1^{(n)}X_n$$

and for the s^{th} particle

$$x_s = \sum_j c_s^{(j)}X_j \tag{A1}$$

For a particular mode of vibration, e.g., the k^{th}, all X's but X_k are zero.

$$k^{\text{th}}\text{ mode: } x_1 = c_1^{(k)}X_k \qquad x_2 = c_2^{(k)}X_k \qquad x_s = c_s^{(k)}X_k \tag{A2}$$

If a geometrical discussion such as the one in the text shows that in the k^{th} mode

$$x_1{:}x_2{:} \cdots x_s{:} \cdots x_n = a_1^{(k)}{:}a_2^{(k)}{:}a_s^{(k)}{:}a_n^k \tag{A3}$$

then it follows that

$$c_1^{(k)} = a_1^{(k)}b_k \qquad c_2^{(k)} = a_2^{(k)}b_k \qquad c_s^{(k)} = a_s^{(k)}b_k \tag{A4}$$

where b_k is a common arbitrary factor. We decide, for reasons to be given below, to choose b_k so that

$$\sum_s (c_s^{(k)})^2 = 1, \text{ or } b_k^2[(a_1^{(k)})^2 + \cdots (a_s^{(k)})^2 + \cdots] = 1 \tag{A5}$$

Then and only then, the same coefficients can be used for the expressions which are the inverse ones to expression A1:

$$X_k = \sum_s c_s^{(k)}x_s \tag{A6}$$

In other words, it is permissible to read the following scheme either horizontally or vertically:

$$\begin{array}{c|ccc}
 & X_1 & X_2 & X_3 \cdots \\
\hline
x_1 & c_1^{(1)} & c_1^{(2)} & c_1^{(3)} \\
x_2 & c_2^{(1)} & c_2^{(2)} & c_2^{(3)} \\
x_3 & c_3^{(1)} & c_3^{(2)} & c_3^{(3)}
\end{array}$$

Mathematically, one says that the transformation matrix (c) is real orthogonal or, more generally, unitary.

APPENDIX II. OSCILLATION THEOREM

For a continuous string of arbitrary density distribution, one can prove (4) that every number of nodes is represented in one mode of vibration. For a membrane in a case where the variables can be separated, one has two sets of nodal lines, and one can prove that each combination of two numbers, giving the number of nodes in each set, is represented in one and only one mode of vibration.

I am not familiar with any strict mathematical proof that a similar theorem can be applied to the most general system of discrete particles, each tied only to its neighbor, although it seems very plausible. For an open chain of equal particles (and equal springs) or an open chain where all particles but the end particles are equal (3, 7, 8, 14), or for a closed chain of equal particles, or for a square of equal particles, the statement can be found correct by actually writing the solutions of the equations of motion, i.e., the modes of vibration. For regular arrangements as in crystal lattices, the statement can also be proved (1, 2).

APPENDIX III. THE ENERGY AS FUNCTION OF THE NUMBER OF NODES

In the case of a vibrating chord or membrane, it is easy to see that the frequency (and $4\,\pi^2\nu^2$) increases with an increase in the number of nodes (for a membrane, with an increase of the number of nodes of the same kind). If more nodes are inserted in a given length of string, the string is folded more closely and therefore the effective restoring force increases (mathematically $\left|\frac{d^2u}{dx^2}\right|$ increases).

Similarly, for a chain of discrete particles, one can see that the introduction of a new node brings a pair of neighboring particles, which before had been on the same side of the equilibrium position, to opposite sides, and therefore one or more springs are stretched to a greater degree than before, with a resulting increase of frequencies.

In the quantum theory, one can give a similar proof (1, 2). It shall be proved in particular that the electron energy in a molecule increases with the number of nodes in the molecular orbitals, for the case where repulsion between the electrons is included as well as when it is excluded.

We have to assume that there exists, between each pair of electrons as well as between each electron and the positive centers of the molecular skeleton, either a Coulomb potential A/r or no interaction.

Then one proves that the average total kinetic energy (including the motion of the nuclei in respect to the center of gravity) is equal to half the negative average of the potential energy, just as in classical mechanics (27):

$$2 \times \text{average kinetic energy} = -\text{average potential energy}$$

Therefore

$$\text{Total energy} = -\text{average kinetic energy} \tag{A7}$$

or

$$E = +\ \text{average}\ \Sigma \frac{h^2}{8\pi^2 m} \Delta = \int \Psi^* \left\{ \Sigma \frac{h}{8\pi^2 m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y} + \frac{\partial^2}{\partial z^2} \right) \right\} \Psi \, d\tau \tag{A8}$$

summed over all particles, where Ψ is the correct wave function belonging to the assumed potential-energy function. But the Δ operator measures again the absolute value of the curvature, and one sees therefore that the energy increases with an increase in the number of nodes of each kind.

The problem can be considered from a different standpoint. In the hydrogen molecular ion, one can write the energy of the two states originating from atomic 1s states (18):

$$E_g = E_0 + \frac{J+K}{1+S} \quad \text{bonding} \tag{A9}$$

$$E_e = E_0 + \frac{J-K}{1-S} \quad \text{antibonding} \tag{A9$'$}$$

J is the Coulomb integral and K the exchange integral, both negative. Upon subtraction, one finds

$$E_e - E_g = 2\frac{JS - K}{1 - S^2} \tag{A10}$$

Therefore, E_e is higher than E_g only if $|K| > |J|S$. In the hydrogen molecular ion, this is the case; the preceding argument shows that it must always be the case if the correct eigenfunctions are chosen.

The same calculation can be made for a $\pi - \pi$ bond. This is a refinement of the treatment given in Section I,C for such bonds; it shows that in the bonding orbital the attractive effect of the negative charge between the two nuclei (K) is partly compensated by the fact that in the bonding orbital the electrons are less frequently near their nuclei than in free atoms or in the antibonding state (this is expressed by JS in the energy difference). For the correct wave function however, the bonding effect is always predominant.

On the other hand, one finds a difficulty in benzene. Excitation consists in lifting one electron from an orbital with one node (ψ_3 in Section I,D,(2)) to an orbital with two nodes (ψ_5). The molecular excited state turns out (6, 25) to lie higher than the unexcited one if the repulsion between electrons is taken into account. But the energy of orbital ψ_5, without electron repulsion, is lower than that of orbital ψ_3.

In terms such as given for the hydrogen molecular ion, the difference of the energy of the orbitals, which was just called $E_e - E_g$, is written as follows (6, 25):

$$\epsilon_2 - \epsilon_1 = \frac{\sigma_1 - \sigma_2}{\sigma_1 \sigma_2} \{-2Q_z - 2A_1 - 2A_2 - A_3\} + \frac{\sigma_1 + \sigma_2}{\sigma_1 \sigma_2} (R + B) \tag{A11}$$

The σ are normalization factors. $\frac{\sigma_1 - \sigma_2}{\sigma_1 \sigma_2}$ corresponds to (and in case overlap between all but next nearest neighbors is neglected, is exactly equal to) $2\frac{S}{1 - S^2}$; $\frac{\sigma_1 + \sigma_2}{\sigma_1 \sigma_2}$ corresponds to (and if overlap between all but next nearest neighbors is neglected, is exactly equal to) $\frac{2}{1 - S^2}$; $-2Q - 2A_1 - 2A_2 - A_3$ corresponds to J and $R + B$ to $-K$. $\epsilon_2 - \epsilon_1$ turns out negative because $|J|\ S$ is larger than $|K|$, which should not be the case according to the general theorem if the correct eigenfunctions had been used. Therefore the fact that $\epsilon_2 - \epsilon_1$ turns out negative must be due to the choice of eigenfunctions, which are not correct for the potential chosen; in fact, the $2p$ functions used belong to a nuclear charge $3.18e$, while the skeleton potential was chosen with unit nuclear charge.