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# Valence Bond Treatment of Systems involving Orbital Degeneracy

## Part I: Topologically linear Ions

By

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Ground and excited electronic states of the allyl cation and anion, the butadiene radical cation and anion, and of the pentadienyl cation and anion have been calculated by a semiempirical valence bond method. The results of such calculations are in essential agreement with the known properties of such systems. A comparison of the results of the valence bond treatment with those expected on the basis of the qualitative resonance theory yields serious discrepancies which show up the limitations inherent in the latter formalism.

Der Grundzustand und die elektronisch angeregten Zustände der folgenden Systeme wurden mittels einer semiempirischen Valence-Bond-Methode berechnet: Allyl Kation und Anion, Butadien Radikal Kation und Anion, Pentadienyl Kation und Anion. Die Ergebnisse stehen in vernünftiger Übereinstimmung mit den bekannten experimentellen Daten. Ein Vergleich der Resultate, die mittels der Valence-Bond-Methode erhalten werden, mit jenen, die man aufgrund der qualitativen Resonanz-Theorie erwarten würde, ergibt wesentliche Unterschiede, die auf die Grenzen hinweisen, die dem letztgenannten Formalismus eigen sind.

L'état fondamental et les états électroniques excités du cation et de l'anion allyl, du cation radical et de l'anion radical du butadiène et du cation et de l'anion pentadiényl ont été calculés par la méthode semiempirique valence bond. Les résultats de ces calculs correspondent raisonnablement aux données expérimentales connues pour ces systèmes. Une comparaison des résultats théoriques avec les prédictions de la théorie de résonance donne des différences qui démontrent les limites de ce formalisme qualitatif.

## Introduction

Resonance theory, as traditionally used by organic chemists, was originally intended to be a qualitative extrapolation of the valence bond method. It was hoped that certain essential concepts of quantum mechanics could be incorporated in this way into the classical structure theory. To achieve this, a certain number of drastic simplifications had implicitly been made, e. g. 1. that the number of structures to be considered can be reduced to those showing no long bond (Kekulé type structures), 2. that the energy of the most stable of the hybrid states is proportional to the number of such structures, 3. that polar structures have the same weight, irrespective of the amount of charge separation, 4. that the coupling between any pair of structures of the same kind is a constant etc. None of these assumptions and simplifications can be validated on the basis of the VB method.

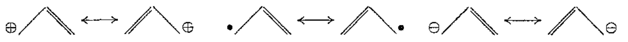
Recent investigations have shown [*10*, *13*, *14*, *16*, *17*, *29*] that those rules of resonance theory that apply to alternant $\pi$-electron systems and that yield valid predictions are grounded in molecular orbital theory in its Hückel approximation. The writing of resonance structures turns out to be a convenient graphical shorthand, (valid only for alternant systems not containing rings of $4n$ carbon atoms) which maps the topology of such systems [*16*, *29*]. As a corrolary, one predicts that resonance theory should fail in the case of non-alternant systems, systems containing hetero-atoms or systems that are heavily substituted. This is indeed the case.

These failures of resonance theory have sometimes been interpreted to mean that the VB method itself fails when applied so such systems. Even though the VB method has been the object of several improvements and extensions in the near past (e. g. inclusion of ionic structures [*3*, *32*, *33*], calculation of matrix elements from molecular integrals [*1*], reformulation in terms of orthogonal atomic orbitals [*22*], extension to triplet states [*21*], population analysis of VB cigenfunctions [*26*]) the pertinent calculations are still missing. In the present series of papers we wish to apply the VB method to systems of chemical interest (ions, radical ions, transition states and intermediates) that involve orbital degeneracy.

In the following discussion we are using the term "*structure*" in two different ways. In the framework of resonance theory it has the usual meaning that the organic chemist intuitively associates with it. In valence bond theory "*structure*" stands for a wave function. It is in this sense that we shall refer to the contribution of a structure to a particular state of the system, or to the energy of a structure.

## Discussion of the Results

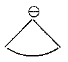
The allyl cation $C_3H_5^+$ (1), the allyl radical $C_3H_5^\bullet$ (2) and the allyl anion $C_3H_5^-$ (3) are represented in resonance theory by the superposition with equal weight of the following pairs of structures:


(1′) (1″) (2′) (2″) (3′) (3″)

The contribution of structures involving a long bond between the terminal centers, namely


(1‴)


(2‴)


(3‴)

is usually neglected, and indeed, for the radical (2), the wave function associated with (2‴) can be shown to be a linear combination of the wave functions corresponding to (2′) and (2″). These two structures are therefore sufficient for the VB description of the allyl radical. However for (1) and (3) the wave functions corresponding to structures (1‴) and (3‴) are not linear combinations of those belonging to the other two structures and have therefore to be included in the canonical set.

If we follow the traditional resonance argument, then we would predict from (1′)⟷(1″) and (3′)⟷(3″) that the charge distribution in (1) and (3) is as follows:

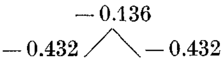
Excess positive charge in (1) according to resonance theory

Excess negative charge in (3) according to resonance theory

The same prediction is obtained according to the simple Hückel treatment of these two odd alternant systems.

If the VB treatment is applied to the set of functions associated with the structures (1′), (1″), (1‴) and (3′), (3″), (3‴), then a quite different charge distribution is calculated if all three centers are assumed to have the same electronegativity.

Excess positive charge in (1)
according to VB theory



Excess negative charge in (3)
according to VB theory

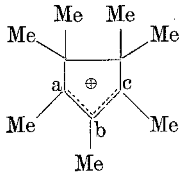
It is seen that the contribution of (1‴) and (3‴) is far from negligible. As a matter of fact, it is of the same magnitude in (1) than the contribution of (1′) and (1″). The contribution of the long bond structure in (3) is somewhat smaller. In (1) as well as in (3) inclusion of the symmetrical structure keeps the electrons further apart. In (3) this effect leads to a somewhat more uneven charge distribution than in (1) with a pronounced accumulation of negative charge on the terminal carbon atoms.

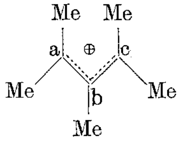
MO-calculations by a complete configuration interaction treatment [*2*] (including multiply excited configurations) of the charge distribution in the allyl cation (1) yield

Excess positive charge in (1) according to a MO-CI treatment

with still rather pronounced charge localisation on the terminal centers.

In the *nmr* spectra of alkyl substituted allyl cations of the following type [*7*]

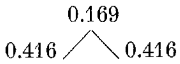




the proton signals of the methyl groups occur at 2.7 ppm (for positions a and c) and at 2.0 ppm (for position b) relative to TMS. Assuming that the proton signal for a methyl group attached to a neutral $sp^2$ center is at 1.6 to 1.7 ppm relative to TMS [*2*] and that the shift to lower field of the methyl proton signals in the substituted allyl cations is due only to the accumulation of positive charge in the $\alpha$-position [*2*, *35*, *37*] then the following mean distribution is obtained from the experimental data:

Experimental charge distribution from *nmr* data

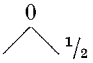
This distribution is that of an allyl cation in which the central carbon atom carries only one alkyl group while the terminal carbon atoms are each connected to two such groups and have, therefore, a lower electron affinity, which favors the accumulation of positive charge on them. If this effect is taken care of in our VB treatment by lowering the energy of structures (1′) and (1″) relative to the energy of structure (1‴) by an amount $k\alpha$, then the following corrected charge distribution is obtained (with $k = 1$ for the particular example).



Excess positive charge in (1) according to VB theory with a correction for the reduced electron affinity of the terminalcenters

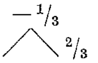
This is in good agreement with observation. From this it is probably safe to conclude that the charge localization in an unsubstituted allyl cation is smaller than that calculated above from the *nmr* data, but probably not as small as indicated by our calculation without the correction for the effect of alkyl substituents on the terminal centers.

It might be mentioned in passing, that in the allyl radical (2), where the long bond structure is not included in the VB calculation and where the resonance approach might be thought to be correct, the spin densities due to the unpaired electron are not



"spin densities" according to resonance theory

This naive interpretation of (2′) ⟷ (2″) is quite misleading and the correct spin distribution obtained according to VB theory from this set is calculated as

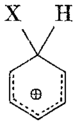


Spin densities according to VB theory

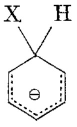
with a negative spin density on the central carbon atom.

In the case of the pentadienyl-cation $C_5H_7^+$, pentadienyl-radical $C_5H_7^\bullet$ and the pentadienyl-anion $C_5H_7^-$ similar relationships are found. Structures which are usually disregarded in the traditional resonance discussion contribute considerably in a VB treatment of these systems. Their slightly higher energy is outweighed by the size of the crossterms which link them to the more stable structures (see matrices given in appendix 2).

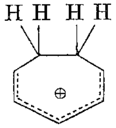
An instructive example is provided by systems of the following type:



(4)

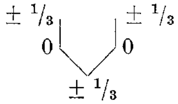


(5)



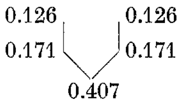
(6)

(4) and (5) are usually assumed to be models for the transition states or the intermediates in electrophilic and nucleophilic substitution reactions. (4), with X = H, is the benzenium cation, alkylated derivatives of which are known [*2*, *18*, *20*, *27*], and (6) is the conjugate acid of cycloheptatriene [*2*, *5*]. Resonance theory and also Hückel MO theory would predict the following charge distribution in the ground state, the + sign referring to the cation, the − sign to the anion:

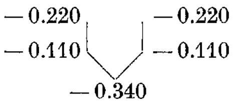


Excess charge according to resonance theory or Hückel MO theory

If we assume for the moment that the CHX grouping in (4) and (5) and the $CH_2CH_2$ link in (6) exert no inductive or other influence on the two terminal AOs, and if we make use of the complete canonical set of structures, we get the following charge distribution in the ground state of our $\pi$-electron system:

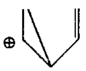


Excess positive charge in (4) or (6) according to VB theory

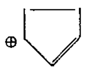


Excess negative charge in (5) according to VB theory

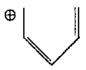
We note first of all that in (4) and (6) more positive charge is found in meta than in ortho positions relative to the saturated center(s). In other words, structures like (7) and (8) provide a larger contribution than structures like (9) and (10).



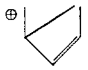
(7)



(8)

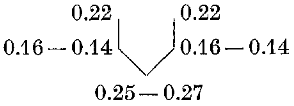


(9)



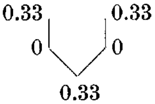
(10)

In (4) with X = H and in (6) we expect as before the electron-releasing effect of the $CH_2$ and $CH_2CH_2$ groupings to increase the contributions of structures (9) and (10) relative to those of (7) and (8). If we include this effect in our VB calculation by assigning lower energies to structures with an empty terminal AO [such as (9) and (10)] relative to those where both these AOs are occupied [such as (7) and (8)] by an amount $k\alpha$, then we obtain an increase in positive charge in ortho and a decrease in para positions. The meta position is very little affected. In diagrams (11) to (16) we compare the results of our VB calculations (with and without inclusion of a perturbation) with the results of MO treatments [*2*] and with the experimental charge distribution obtained from the *nmr* spectra of cation (6) and of the 2, 4, 6-trimethyl derivative of (4) [*2*], that is the conjugate acid of mesitylene. It is seen that the VB treatment yields a prediction for the charge distribution that, in view of the crudeness of the assumptions concerning the relative size of the parameters $\alpha$, $\alpha'$ and $\gamma$ (see appendix 2), is as good as can be expected. Indeed, an MO treatment with complete configuration interaction gives poorer agreement, and only the method of Wheland and Mann [*36*] yields a satisfactory prediction, based, however, on an ad hoc value of the adjustable parameter $\omega$.



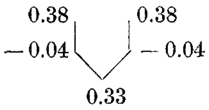
(11)

Experimental charge distribution from *nmr* data [*2*]



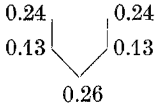
(12)

Distribution according to simple Hückel MO theory and according to resonance theory



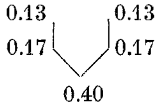
(13)

Distribution according to a SCF MO calculation [2]



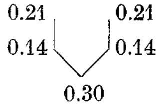
(14)

Distribution calculated according to the method of WHELAND and MANN, with $\omega = 2.8$ [2]



(15)

Distribution calculated by the VB method, without inclusion of a perturbation for the terminal AO*s*. (See Tab. 5 of appendix 2, where the canonical set, the matrix, and the numerical results are listed)



(16)

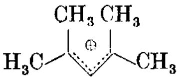
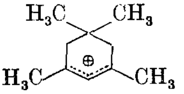
Distribution according to the VB method, including a perturbation for the terminal AO*s*. (Change in the $Q$-values for structures with a positive charge on these AO*s* by one unit of $\alpha$)

The acid-base equilibria between methyl-substituted benzenes and their conjugate acids, that is, the correspondingly substituted cations (4), depend characteristically on the number and positions of the methyl groups [*9*, *12*, *18*, *20*]. This dependence has previously been interpreted on the basis of the charge distribution given by the Hückel approximation, assuming that the methyl groups exert a purely inductive effect [*9*]. Within the limits of error of the experimental data [*20*], however, the distribution predicted in this paper gives just as good agreement when used as a basis for such a perturbation calculation. Dissociation constants are, therefore, a poor test for the charge distribution in such cations, especially in view of the difficulties in choosing a reasonable model for the effect of the alkyl groups [*9*, *12*].

The results listed in Tab. 1 and 5 of appendix 2 show that the two first electronically excited states of the allyl cation have predicted energies of $-1.851\ \alpha$ and $-3.202\ \alpha$, and the first three of the pentadienyl cation of $-1.503\ \alpha$, $-2.320\ \alpha$, and $-2.769\ \alpha$, relative to the ground states of these systems. Assuming $\alpha = -18000\ \mathrm{cm}^{-1}$, the values listed under "VB" in Tab. A are obtained for the position and direction of polarization of the first bands in the electronic spectrum of the cation. These predictions are compared with the experimental results obtained for the 1,3-dimethylcyclopentenyl cation, the 2,4-dimethyl-pentenyl cation and the 1,3,5,5-tetramethylcyclohexenyl cation [*6*] and with those for the 2,4,6-trimethyl derivative of the cation (4) ($X = H$) and for (6) [*2*]. The values in the columns "CCI" are results of those MO calculations including complete configuration interaction, in the columns "LCI" of MO calculations with limited configuration interaction.

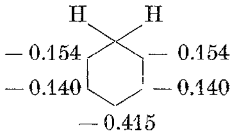
There is a serious discrepancy between predictions obtained from MO theory and from our VB treatment for the sign and magnitude of the shifts in band position, produced by substituents that act only through an inductive effect. Unfortunately, the experimental results [*2*, *4*, *11*, *27*] do not permit a decisive test, although MO predictions from simple Hückel theory seem to agree slightly better with the limited observations [*36*] available. However, the considerable changes in band position that are observed in the spectra of alkyl-substituted allyl cations as a consequence of alkyl substitution on carbon atoms that do not participate in the $\pi$-electron system, [*6*] indicate that other factors, such as changes in solvation may have to be considered before definite conclusions can be drawn.

Table A

| Band | Cation | Band position in cm$^{-1}$ [*6*] | Theoretical predictions | | | |
|---|---|---|---|---|---|---|
| | | | Position | | Polarization | |
| | | | VB | CCI [*2*] | VB | CCI [*2*] |
| I |  | 36400 | 33300 | 52000 | $x$ | $x$ |
| |  | 32800 | | | | |
| |  | 31800 | | | | |
| II | all cations | above 45000 | 57600 | 81000 | $y$ | |

| Band | Proton complex of | Band position in cm$^{-1}$ [*2*] | Theoretical predictions | | | | |
|---|---|---|---|---|---|---|---|
| | | | Position | | | Polarization | |
| | | | VB | CCI [*2*] | LCI [*19*] | VB | CCI [*2*] and LCI [*19*] |
| I | Mesitylene<br>Cycloheptatriene | 28300<br>28400 | 27000 | 28200<br>29500 | 26900 | $x$ | $x$<br>$x$ |
| II | Mesitylene<br>Cycloheptatriene | 39000<br>36400 | 41800 | 36700<br>35100 | 40800 | $y$ | $y$<br>$y$ |
| III | Mesitylene<br>Cycloheptatriene | 49800<br>45400 | 49800 | 52600<br>52000 | 54600 | $y$ | $y$<br>$y$ |

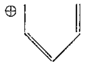
For the anion (5), with X = H, we predict the charge distribution shown below if the inductive effect of the methylene group is taken into consideration. In this particular example, it has been assumed that all structures with a negative charge in positions ortho to the methylene group are destabilized, relative to those structures which have no such charge, by an amount equal to $\alpha$.



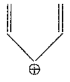
Excess negative charge in (5) according to VB theory, including an inductive effect for the methylene group

The most noteworthy feature of this result is the pronounced accumulation of negative charge in the position para to the methylene group. Such an accumulation, although less pronounced, was predicted even when the inductive effect of the methylene bridge was neglected. We conclude therefore that even in the absence of inductive effects [*36*] and without taking into account changes in bond lengths, there is a tendency for negative charge to accumulate in the para position, because of purely electronic factors. The system (5) (X = H) is assumed to be an intermediate in the Birch reduction. If (5) is attacked by a strongly electrophilic reagent, e. g. by a proton, that yields the reaction product in a strongly exoenergetic reaction step, then the transition state may be assigned a structure very similar to that of the reactants. [*15*] It may be well represented by (5) in association with a loosely bound proton. This leads to the prediction of 1,4 addition in such reductions, rather than 1,2 addition, in agreement with observation. Preferred 1,4 addition is also predicted by MO theory, but only if either bond length alternation, or an inductive effect of the methylene group, or the polarizability of the electron system is taken into account [*36*].

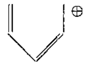
In view of the restriction imposed by resonance theory on the size of the set of structures assumed to be representative of a $\pi$-electron system, it is of interest to examine the contribution of the sets (17), (17′), (17″) and (18), (18′), (18″) to the ground state of the pentadienyl cation [or of (4)] and the pentadienyl anion [or of (5)].



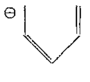
(17)



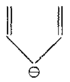
(17′)



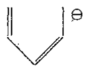
(17″)



(18)

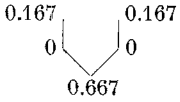


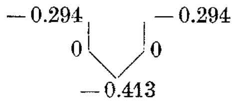
(18′)



(18″)

Such a VB treatment will obviously yield charges in the ortho and para positions only. However, the values in these positions depart from the $^1/_3 : {}^1/_3 : {}^1/_3$ -distribution.





In Fig. 1 and 2 the results of VB treatments based on *a*) the two sets above, *b*) including long bond structures (17‴), (17⁗) and (18‴), (18⁗) and *c*) the complete canonical set are shown. Note that structure (17′) is more stable than (17) and (17″), but (18′) is less stable than (18) and (18″).

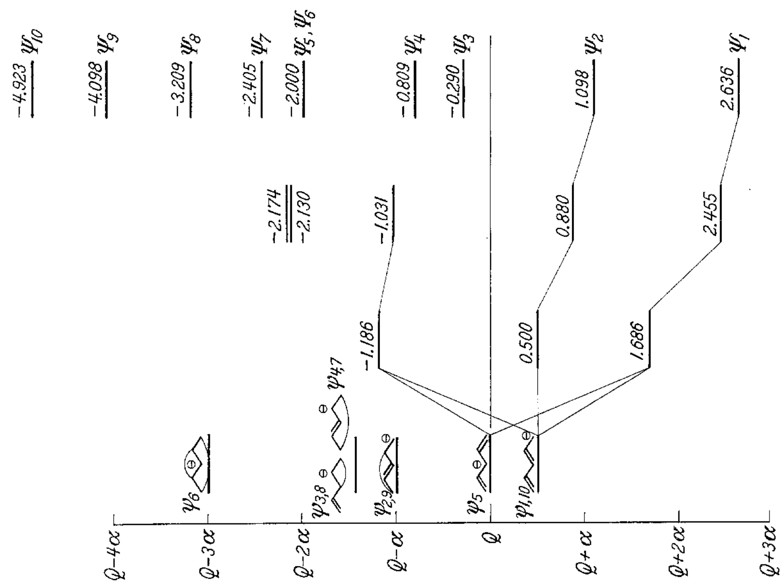


Fig. 2. Energy levels of the pentadienyl anion

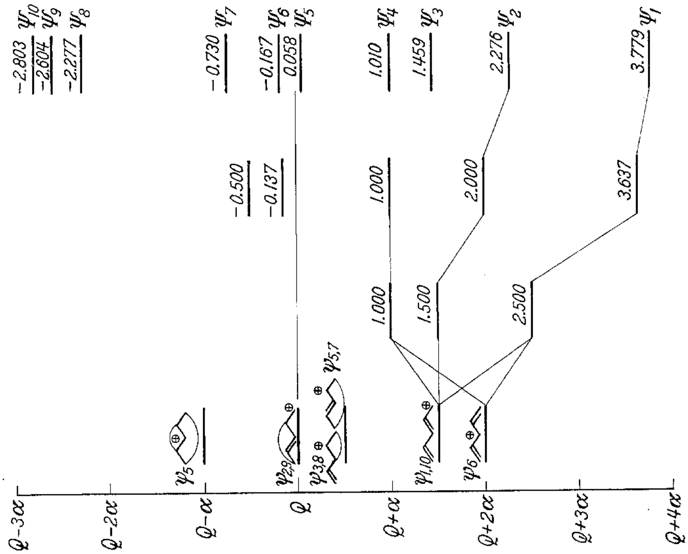
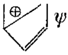
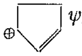


Fig. 1. Energy levels of the pentadienyl cation

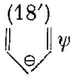
The coefficients of the structures that contribute in the three approximations to the ground state of the two systems are given in Tab. B.

Table B

Pentadienyl-cation

| Appr. | (17) (17'')  $\psi_1$ |  $\psi_2$ | (17''') (17'''')  $\psi_3$ |  $\psi_4$ |  $\psi_5$ | (17')  $\psi_6$ |
|---|---|---|---|---|---|---|
| *a* | 0.408 | | | | | 0.817 |
| *b* | 0.341 | | 0.388 | | | 0.682 |
| *c* | 0.294 | 0.100 | 0.318 | 0.148 | 0.069 | 0.601 |

Pentadienyl-anion

| Appr. | (18) (18'')  $\psi_1$ |  $\psi_2$ | (18''') (18'''')  $\psi_3$ |  $\psi_4$ | (18')  $\psi_5$ |  $\psi_6$ |
|---|---|---|---|---|---|---|
| *a* | 0.542 | | | | 0.643 | |
| *b* | 0.469 | | 0.294 | | 0.622 | |
| *c* | 0.399 | 0.117 | 0.238 | 0.142 | 0.560 | 0.043 |

*Acknowledgement.* We gratefully acknowledge the help of Mr. Hans GRUNDER in checking the numerical results. M. SIMONETTA thanks the Italian Consiglio Nazionale delle Ricerche, E. HEILBRONNER the Schweizerische Nationalfonds (Projekt Nr. 2767) and the CIBA Aktiengesellschaft, Basel, for financial support.

## Appendix 1

### The VB Treatment of Systems involving Orbital Degeneracy

### *A. The Basis Functions*

The first step is to assign wave functions $\psi_j$ to the members of the set of linearly independent structures representing the system under consideration. We assume that for a given system

$M$ = number of electrons
$N$ = number of atomic orbitals
$n$ = number of covalent bonds in the structures.

The original Heitler-London-Slater-Pauling treatment [*24, 30, 34*] applied to cases with $M = N = 2n$, that is to neutral systems with an even number of orbitals (including a phantom orbital [*25*] for radicals) and included only covalent structures. Inclusion of ionic (polar) structures introduces degeneracies, since in such structures, one atomic orbital is doubly occupied and another is vacant so that $M = N \neq 2n$. In the present paper we consider systems with $M = N \pm 1$, the positive sign holds for anions, the negative for cations. Depending on whether $N$ is even or odd we obtain:

| | | | | |
|---|---|---|---|---|
| 1. a) | $N$ = odd | $M = N - 1$ | $n = M/2$ | Cation (singlet) |
| b) | $N$ = odd | $M = N + 1$ | $n = (M-2)/2$ | Anion (singlet) |
| 2. a) | $N$ = even | $M = N - 1$ | $n = (M-1)/2$ | Radical-cation (doublet) |
| b) | $N$ = even | $M = N + 1$ | $n = (M-3)/2$ | Radical-anion (doublet) |

Since the sign of the charge has no influence on the number of independent structures that form the basis, only two cases need be considered: 1. Ions (singlet), 2. Radical-ions (doublet). For both classes Rumer's theorem [*28*] applies.

*1. Ions (singlet, $N$ = odd).* The plus or minus charge (electron hole or electron pair) can occupy any one of the $N$ atomic orbitals of the system. The remaining $N - 1$ atomic orbitals can be arranged on a Rumer circle, so that the total number $Z_I$ of independent structures is

$$Z_I = N \frac{(N-1)\,!}{\left(\frac{N-1}{2}\right)!\left(\frac{N-1}{2}+1\right)!} = \frac{N!}{\left(\frac{N-1}{2}\right)!\left(\frac{N-1}{2}+1\right)!}$$

*2. Radical Ions (doublet, N = even).* The plus or minus charge (electron hole or electron pair) can occupy any one of the $N$ atomic orbitals of the system. A phantom orbital must be added to the odd number of remaining atomic orbitals before they are arranged on the Rumer circle. The number $Z_R$ of independent structures is

$$Z_R = N \frac{N!}{\left(\frac{N}{2}\right)!\left(\frac{N+2}{2}\right)!}$$

With each structure we associate a wave function, which takes one of the following forms, depending on the charge type of the system:

*a) Cations or radical cations.* Assuming that the electron hole (positive charge) occupies atomic orbital $i$, we have:

$$\psi = 2^{-n/2} \sum_R (-1)^R R \left[ (M!)^{-\frac{1}{2}} \sum_P (-1)^P P\, (\bar{a} b \bar{c} \ldots h \bar{k} \ldots s) \right] \tag{3}$$

This function $\psi$ corresponds to a structure in which the atomic orbitals $a$ and $b$, $c$ and $d$ etc. are bonded and in which the orbital $i$ has been omitted. Atomic spin orbitals without dashes above them *(b, d,...s)* are associated with spin functions $\alpha$, those with dashes *($\bar{a}$, $\bar{c}$,...)* with spin functions $\beta$. All other symbols have their usual meaning.

*b) Anions or radical anions.* If the atomic orbital $i$ is doubly occupied we have:

$$\psi = 2^{-\left(\frac{n+1}{2}\right)} \sum_R (-1)^R R \left[ (M!/2)^{-\frac{1}{2}} \sum_P^{(i)} (-1)^P P\, (\bar{a} b \bar{c} \ldots h \bar{i} i \bar{k} \ldots s) \right] \tag{4}$$

The function $\psi$ corresponds again to a structure in which the atomic orbitals $a$ and $b$, $c$ and $d$ etc. are bonded, orbital $i$ being doubly occupied. The index *(i)* above the summation over all permutations indicates that this summation has to be carried out over all permutations of the $M$ electrons over the atomic spin orbitals $\bar{a}$, $b$, $\bar{c}$...$s$, with the exception of those permutations which involve $\bar{i}$ and $i$ only. However the spin-reversal $R$ for electrons occupying the same atomic orbital $i$ has to be included.

An alternative way to write a correct $\psi$-function for structures of anions or radical anions is to allow all permutations of electrons, including those between the atomic spin orbitals $\bar{i}$ and $i$, but excluding spin reversal between electrons occupying the same atomic orbital.

### *B. The Calculation of the Matrix Elements*

The calculation of the matrix elements involves a) the definition of the basic integrals and b) the determination of the coefficients with which each of them is associated in a particular matrix element.

The integrals have been defined previously [*33*] and are included here for the sake of completeness.

**I. The Overlap Integral $S$.** Assuming zero overlap between the atomic orbitals involved, the overlap integral $S_{rs} = \langle \psi_r \mid \psi_s \rangle$ between two structures is different from zero only if the positive or negative charge (electron hole or electron pair) occupies the same atomic orbital in both $\psi_r$ and $\psi_s$. In this case $S_{rs}$ is equal to the coefficient derived from the superposition pattern according to the rules given below for the Coulomb Integral $Q$.

**II. The Coulomb Integral Q.** If $\mathscr{H}$ is the Hamilton operator for the system under consideration, then the Coulomb integral $Q$ is defined as

$$Q = \langle abcd \ldots | \mathscr{H} | abcd \ldots \rangle$$

Such integrals occur in the matrix elements $H_{rs} = \langle \psi_r | \mathscr{H} | \psi_s \rangle$ only if $\psi_r$ and $\psi_s$ contain the same set of atomic orbitals. There is, therefore, no contribution from $Q$ in matrix elements between structures carrying charges on different atomic orbitals.

**III. Exchange Integral $\alpha$.** This exchange integral, the only one occuring in the VB treatment of neutral $\pi$-electron systems with exclusively covalent structures is defined as

$$\alpha = \langle a \ldots ij \ldots | \mathscr{H} | a \ldots ji \ldots \rangle$$

where the product functions before and after $\mathscr{H}$ differ only by the exchange of two atomic orbitals $i$ and $j$ adjacent to one another in the real molecule. Otherwise the integral is set equal to zero.

The integral may be characterized as involving two simultaneous electron jumps between two atomic orbitals adjacent in the molecule.

**IV. Exchange Integral $\alpha'$.** This integral involves two product functions that differ by one or more atomic orbitals in such a way that the two electrons in the exchange occupy three different atomic orbitals in the two functions:

$$\alpha' = \langle a \ldots ij \ldots | \mathscr{H} | a \ldots jk \ldots \rangle \quad i, j \text{ and } j, k \text{ adjacent}$$

For example, such integrals occur in the matrix elements between the $\psi$-functions corresponding to the pair of structures.

 and 

These integrals involve two simultaneous electron jumps between three different atomic orbitals, each electron jumping from one orbital to an adjacent one.

**V. Exchange Integral $\gamma$.** In this integral the two product functions differ only by one atomic orbital. The two atomic orbitals occupied by the same electron in the two product functions must be adjacent:

$$\gamma = \langle a \ldots \ldots i \ldots | \mathscr{H} | a \ldots \ldots j \ldots \rangle$$

This corresponds to a one electron jump between adjacent atomic orbitals.

All other integrals are assumed to be negligibly small and are set equal to zero in our calculations. Furthermore, it is assumed that the exchange integrals $\alpha, \alpha'$ and $\gamma$ are constant for all systems under discussion.

The coefficients with which the different integrals enter the matrix element $H_{rs}$ are obtained with the aid of so-called juxtaposition diagrams, which have been described previously [*33*]. The steps involved in the calculation of the coefficients can be summarized as follows:

1. The diagram for a particular matrix element between two functions $\psi_r$ and $\psi_s$ is obtained by writing above and below a line one of the permutations of the electrons and of the spins among the atomic orbitals. (This will be usually the ground permutation.) Bonded pairs and unshared pairs are connected by arrows, the head and the tail of the arrow signifying spin $\alpha$ and $\beta$ respectively.

For example:

Superposition diagrams for $H_{12}$ of the pentadienyl cation (c. f. Tab. 5), for $H_{13}$ of the allyl anion (c. f. Tab. 2), and for $H_{44}$ of the butadiene radical cation (c. f. Tab. 3). ($z$ = phantom orbital)

$$\begin{tikzcd}[row sep=small, column sep=small] \psi_1: & b \arrow[r] & c & d \arrow[r] & e \\ \psi_2: & b \arrow[rrr, bend right] & c & d \arrow[l] & e \end{tikzcd} \qquad \frac{\psi_1: a \to a \quad b \to c}{\psi_3: a \to b \quad c \to c} \qquad \frac{\psi_4: a \to c \quad d \to z}{\psi_4: a \to c \quad d \to z}$$

2. The electrons of the array below the line are permuted among the spin orbitals in all possible ways, and for each permutation the type of the corresponding integral is identified. Let $P_L$ be the order of the permutation that yields a particular integral.

3. We will now reverse the arrows in both arrays until they match for all the orbitals. Let $R_L$ and $R_U$ be the number of reversals necessary in the lower and in the upper array respectively.

4. If $j$ is the number of islands in the juxtaposition diagram (after permutation of the spin orbitals to yield a particular integral) then the coefficient $K$ of the integral is given by

$$K = 2^{j-n}(-1)^{P_L + R_L + R_U} \text{ for cations and radical cations,}$$
$$K = 2^{j-n-1}(-1)^{P_L + R_L + R_U} \text{ for anions and radical anions.}$$

In the case of the radical cations and radical anions, $n$ includes the bond leading towards the phantom orbital $z$.

For our examples given above we obtain:

| | $P_L$ | $R_U$ | $R_L$ | $j$ | $K$ | Integral |
|---|---|---|---|---|---|---|
| $\psi_1: b \to c \quad d \to e$ | | | | | | |
| $\psi_2: \begin{tikzcd} b \arrow[rrr, bend right] & c & d \arrow[l] & e \end{tikzcd}$ | 0 | 0 | 0 | 1 | $\frac{1}{2}$ | $Q$ |
| $\begin{tikzcd} c & b \arrow[rr, bend right] & d \arrow[ll, bend left] & e \end{tikzcd}$ | 1 | 1 | 0 | 1 | $\frac{1}{2}$ | $\alpha$ |
| $\begin{tikzcd} b \arrow[rrr, bend right] & d \arrow[r] & c & e \end{tikzcd}$ | 1 | 0 | 1 | 1 | $\frac{1}{2}$ | $\alpha$ |
| $\begin{tikzcd} b \arrow[rr, bend right] & c & e & d \arrow[ll, bend left] \end{tikzcd}$ | 1 | 1 | 0 | 1 | $\frac{1}{2}$ | $\alpha$ |

$$H_{12} = \frac{1}{2}(Q + 3\alpha)$$

| | $P_L$ | $R_U$ | $R_L$ | $j$ | $K$ | Integral |
|---|---|---|---|---|---|---|
| $\psi_1: a \to a \quad b \to c$ | | | | | | |
| $\psi_3: a \to b \quad c \to c$ | 0 | 0 | 0 | 2 | 1 | $\alpha'$ |
| $b \leftarrow a \quad c \to c$ | 1 | 0 | 1 | 2 | 1 | $\alpha'$ |

$$H_{13} = 2\alpha'$$

| | $P_L$ | $R_U$ | $R_L$ | $j$ | $K$ | Integral |
|---|---|---|---|---|---|---|
| $\psi_4: a \to c \quad d \to z$ | | | | | | |
| $\psi_4: a \to c \quad d \to z$ | 0 | 0 | 0 | 2 | 1 | $Q$ |
| $\begin{tikzcd} a \arrow[rr, bend right] & d \arrow[rr, bend right] & c & z \end{tikzcd}$ | 1 | 1 | 1 | 1 | $\frac{1}{2}$ | $\alpha$ |

$$H_{44} = Q - \frac{\alpha}{2}$$

### *C. The Eigenvalues and Eigenfunctions*

The matrix elements calculated according to the rules given yield the secular determinant

$$\| H_{rs} - S_{rs} E \| = 0$$

the solution of which gives the eigenvalues $E_J$ and the corresponding linear combinations

$$\Psi_J = \sum_r C_{Jr} \psi_r$$

where the summation includes all structures of the canonical set. The coefficients $C_{Jr}$ satisfy the normalization conditions

$$1 = \sum_r \sum_s C_{Jr} C_{Js} S_{rs} .$$

Because of the orthogonality of the AOs $a, b, c, \ldots, n$, the overlap-Integrals $S_{rs}$ differ from zero only if $\psi_r$ and $\psi_s$ include the same set of AOs.

The charge density on the atom with the AO $k$, when the system is in the state $\Psi_J$, is given by

$$C.D._{Jk} = \pm \sum_t \sum_u {}^{(k)} C_{Jt} C_{Ju} S_{tu}$$

where the summation has to be carried out only over those structures $t$ and $u$ that exhibit a positive (negative) charge on the center $k$. Spin densities can be calculated in different ways, the simplest one being that proposed by SCHUG, BROWN and KARPLUS [*31*]:

$$S.D._{Jk} = \sum_r \sum_s {}^{(k')} C_{Jr} C_{Js} S_{rs} .$$

Here, the summation includes all those structures in which the orbital $k$ is included in the same island of the juxtaposition diagram as the phantom orbital $z$. The remaining terms enter the summation with either the positive or the negative sign depending on the number of bonds separating the orbital under consideration from the phantom orbital in the juxtaposition diagram. An odd number of bonds corresponds to a positive, an even number to a negative sign.

## Appendix 2

The Tab. 1 to 8 contain the results of our calculations. The following conventions have been used:

1. In all the product functions given, the sequence of the spin functions is $\beta\alpha\beta\alpha\beta\alpha\ldots$ beginning with the leftmost AO.

2. As far as possible, the alphabetic sequence of the space orbitals $a$, $b$, $c\ldots$ has been conserved in the product functions. The phantom orbital $z$ of the radical ions is associated with spin $\alpha$ and has to be included to the right of the product functions given in the tables.

3. All matrix elements have been calculated under the conventions 1. and 2. of appendix 1.

4. On the basis of preliminary calculations concerning the relative size of the integrals $\alpha$, $\alpha'$ and $\gamma$, the following simplifying approximation has been used:

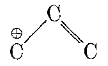
$$\alpha' = \alpha/2, \; \gamma = \alpha$$

5. The eigenvalues are given in terms of the reduced parameter $x_J$

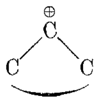
$$E_J = Q + \alpha\, x_J \; .$$

Table 1. *Allyl cation,* $(H_2C \mathrel{\overset{\cdots}{-}} CH \mathrel{\overset{\cdots}{-}} CH_2)^{\oplus}$

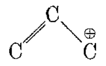
*a) Structures and functions*



$\psi_1 = b - c$



$\psi_2 = a - c$



$\psi_3 = a - b$

*b) Matrix*

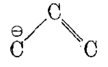
$$\begin{pmatrix} Q+\alpha & \gamma & \alpha' \\ \gamma & Q & \gamma \\ \alpha' & \gamma & Q+\alpha \end{pmatrix}$$

*c) Eigenvalues and linear combinations*

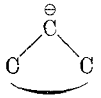
| $\Psi_J$ | $x_J$ | $C_{Jr}$ | | |
|---|---|---|---|---|
| | | $\psi_1$ | $\psi_2$ | $\psi_3$ |
| $\Psi_3$ | –0.851 | 0.365 | –0.857 | 0.365 |
| $\Psi_2$ | 0.500 | 0.707 | 0 | –0.707 |
| $\Psi_1$ | 2.351 | 0.606 | 0.515 | 0.606 |

Table 2. *Allyl anion,* $(H_2C \mathrel{\overset{\cdots}{-}} CH \mathrel{\overset{\cdots}{-}} CH_2)^{\ominus}$

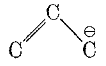
*a) Structures and functions*



$\psi_1 = a - a \quad b - c$



$\psi_2 = \underbrace{a\ b - b\ c}_{}$



$\psi_3 = a - b \quad c - c$

*b) Matrix*

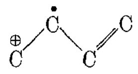
$$\begin{pmatrix} Q & \gamma & 2\alpha' \\ \gamma & Q-2\alpha & \gamma \\ 2\alpha' & \gamma & Q \end{pmatrix}$$

*c) Eigenvalues and linear combinations*

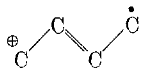
| $\Psi_J$ | $x_J$ | $C_{Jr}$ | | |
|---|---|---|---|---|
| | | $\psi_1$ | $\psi_2$ | $\psi_3$ |
| $\Psi_3$ | –2.562 | 0.261 | –0.929 | 0.261 |
| $\Psi_2$ | –1.000 | 0.707 | 0. | –0.707 |
| $\Psi_1$ | 1.562 | 0.657 | 0.369 | 0.657 |

Table 3. *Butadiene radical cation*, $(H_2C \cdots CH \cdots CH \cdots CH_2)^{\oplus}$

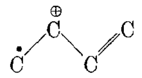
*a) Structures and functions*



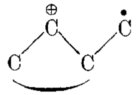
$\psi_1 = b \quad c - b$



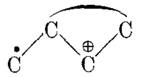
$\psi_2 = b - c \quad d$



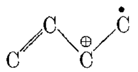
$\psi_3 = a \quad c - d$



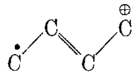
$\psi_4 = a - c \quad d$



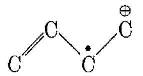
$\psi_5 = a \quad b - d$



$\psi_6 = a - b \quad d$



$\psi_7 = a \quad b - c$



$\psi_8 = a - b \quad c$

*b) Matrix*

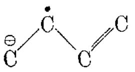
$$\begin{pmatrix}
Q+\frac{\alpha}{2} & \frac{Q}{2}+\alpha & \gamma & \frac{\gamma}{2} & \alpha' & \frac{\alpha'}{2} & 0 & 0 \\
 & Q+\frac{\alpha}{2} & \frac{\gamma}{2} & \gamma & \frac{\alpha'}{2} & \alpha' & 0 & 0 \\
 & & Q+\alpha & \frac{Q+\alpha}{2} & \gamma & \frac{\gamma}{2} & \alpha' & \frac{\alpha'}{2} \\
 & & & Q-\frac{\alpha}{2} & \frac{\gamma}{2} & \gamma & \frac{\alpha'}{2} & \alpha' \\
 & & & & Q-\frac{\alpha}{2} & \frac{Q+\alpha}{2} & \gamma & \frac{\gamma}{2} \\
 & & & & & Q+\alpha & \frac{\gamma}{2} & \gamma \\
 & \text{symmetrical} & & & & & Q+\frac{\alpha}{2} & \frac{Q}{2}+\alpha \\
 & & & & & & & Q+\frac{\alpha}{2}
\end{pmatrix}$$

*c) Eigenvalues and linear combinations*

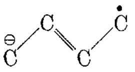
| $\Psi_J$ | $x_J$ | $C_{Jr}$ | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $\psi_1$ | $\psi_2$ | $\psi_3$ | $\psi_4$ | $\psi_5$ | $\psi_6$ | $\psi_7$ | $\psi_8$ |
| $\Psi_8$ | –2.081 | –0.522 | 0.564 | 0.261 | –0.522 | 0.522 | –0.261 | –0.564 | 0.522 |
| $\Psi_7$ | –2.017 | –0.243 | 0.352 | 0.496 | –0.715 | –0.715 | 0.496 | 0.352 | –0.243 |
| $\Psi_6$ | –0.818 | 0.713 | –0.539 | 0.122 | –0.333 | –0.333 | 0.122 | –0.539 | 0.713 |
| $\Psi_5$ | –0.725 | 0.408 | –0.204 | –0.296 | –0.408 | 0.408 | 0.296 | 0.204 | –0.408 |
| $\Psi_4$ | –0.040 | 0.167 | 0.442 | –0.475 | 0.053 | 0.053 | –0.475 | 0.442 | 0.167 |
| $\Psi_3$ | 1.081 | 0.248 | 0.515 | –0.124 | 0.248 | –0.248 | 0.124 | –0.515 | –0.248 |
| $\Psi_2$ | 1.725 | 0.408 | –0.204 | 0.704 | –0.480 | 0.408 | –0.704 | 0.204 | –0.408 |
| $\Psi_1$ | 2.874 | 0.266 | 0.238 | 0.424 | 0.205 | 0.205 | 0.424 | 0.238 | 0.266 |

Table 4. *Butadiene radical anion,* $(\mathrm{H_2C}\overset{\cdots}{-}\mathrm{CH}\overset{\cdots}{-}\mathrm{CH}\overset{\cdots}{-}\mathrm{CH_2})^{\ominus}$

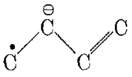
*a) Structures and functions*



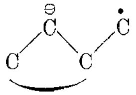
$\psi_1 = a - a\,b\,c - d$



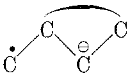
$\psi_2 = a - a\,b - c\,d$



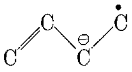
$\psi_3 = a\,b - b\,c - d$



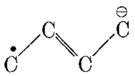
$\psi_4 = a\,b - b\,c\,d$



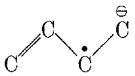
$\psi_5 = a\,b\,c - c\,d$



$\psi_6 = a - b\,c - c\,d$



$\psi_7 = a\,b - c\,d - d$



$\psi_8 = a - b\,c\,d - d$

*b) Matrix*

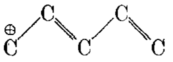
$$\begin{pmatrix}
Q-\frac{\alpha}{2} & \frac{Q+\alpha}{2} & \gamma & \frac{\gamma}{2} & \frac{\alpha'}{2} & \alpha' & 0 & 0 \\
 & Q-\frac{\alpha}{2} & \frac{\gamma}{2} & \gamma & \alpha' & 2\alpha' & 0 & 0 \\
 & & Q-\alpha & \frac{Q-\alpha}{2} & \gamma & \frac{\gamma}{2} & 2\alpha' & \alpha' \\
 & & & Q-\frac{5\alpha}{2} & \frac{\gamma}{2} & \gamma & \alpha' & \frac{\alpha'}{2} \\
 & & & & Q-\frac{5\alpha}{2} & \frac{Q-\alpha}{2} & \gamma & \frac{\gamma}{2} \\
 & \text{symmetrical} & & & & Q-\alpha & \frac{\gamma}{2} & \gamma \\
 & & & & & & Q-\frac{\alpha}{2} & \frac{Q+\alpha}{2} \\
 & & & & & & & Q-\frac{\alpha}{2}
\end{pmatrix}$$

*c) Eigenvalues and linear combinations*

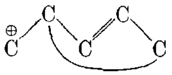
| $\Psi_J$ | $x_J$ | $C_{Jr}$ | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $\psi_1$ | $\psi_2$ | $\psi_3$ | $\psi_4$ | $\psi_5$ | $\psi_6$ | $\psi_7$ | $\psi_8$ |
| $\Psi_8$ | −4.074 | −0.257 | 0.276 | 0.515 | −0.737 | −0.737 | 0.515 | 0.276 | −0.257 |
| $\Psi_7$ | −3.220 | −0.288 | 0.396 | 0.243 | −0.696 | 0.696 | −0.243 | −0.396 | 0.288 |
| $\Psi_6$ | −2.742 | 0.487 | −0.450 | −0.398 | −0.202 | 0.202 | 0.398 | 0.450 | −0.487 |
| $\Psi_5$ | −2.000 | 0 | 0.500 | −0.500 | 0 | 0 | −0.500 | 0.500 | 0 |
| $\Psi_4$ | −1.607 | −0.727 | 0.482 | −0.040 | 0.317 | 0.317 | −0.040 | 0.482 | −0.727 |
| $\Psi_3$ | −0.258 | −0.576 | 0.113 | −0.541 | 0.239 | −0.239 | 0.541 | −0.113 | 0.576 |
| $\Psi_2$ | 0.220 | −0.121 | −0.542 | 0.395 | −0.291 | 0.291 | −0.395 | 0.542 | 0.121 |
| $\Psi_1$ | 1.680 | 0.267 | 0.330 | 0.387 | 0.153 | 0.153 | 0.387 | 0.330 | 0.267 |

Table 5. *Pentadienyl cation,* $(H_2C \cdots CH \cdots CH \cdots CH \cdots CH_2)^{\oplus}$

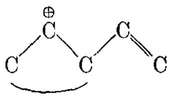
*a) Structures and functions*



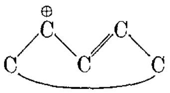
$\psi_1 = b - c\,d - e$



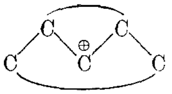
$\psi_2 = \underbrace{b\,c - d\,e}$



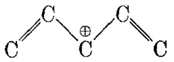
$\psi_3 = a - c\,d - e$



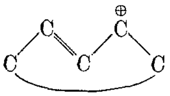
$\psi_4 = \underbrace{a\,c - d\,e}$



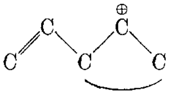
$\psi_5 = \underbrace{a\,b - d\,e}$



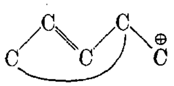
$\psi_6 = a - b\,d - e$



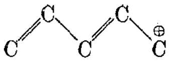
$\psi_7 = \underbrace{a\,b - c\,e}$



$\psi_8 = a - b\,c - e$



$\psi_9 = \underbrace{a\,b - c\,d}$



$\psi_{10} = a - b\,c - d$

*b) Matrix*

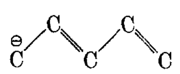
$$\begin{pmatrix}
Q+\frac{3\alpha}{2} & \frac{Q+3\alpha}{2} & \gamma & \frac{\gamma}{2} & \frac{\alpha'}{2} & \alpha' & 0 & 0 & 0 & 0 \\
 & Q & \frac{\gamma}{2} & \gamma & \alpha' & \frac{\alpha'}{2} & 0 & 0 & 0 & 0 \\
 & & Q+\frac{\alpha}{2} & \frac{Q}{2}+\alpha & \frac{\gamma}{2} & \gamma & \frac{\alpha'}{2} & \alpha' & 0 & 0 \\
 & & & Q+\frac{\alpha}{2} & \gamma & \frac{\gamma}{2} & \alpha' & \frac{\alpha'}{2} & 0 & 0 \\
 & & & & Q-\alpha & \frac{Q}{2}+\alpha & \gamma & \frac{\gamma}{2} & \alpha' & \frac{\alpha'}{2} \\
 & & & & & Q+2\alpha & \frac{\gamma}{2} & \gamma & \frac{\alpha'}{2} & \alpha' \\
 & & & & & & Q+\frac{\alpha}{2} & \frac{Q}{2}+\alpha & \gamma & \frac{\gamma}{2} \\
 & & & \text{symmetrical} & & & & Q+\frac{\alpha}{2} & \frac{\gamma}{2} & \gamma \\
 & & & & & & & & Q & \frac{Q+3\alpha}{2} \\
 & & & & & & & & & Q+\frac{3\alpha}{2}
\end{pmatrix}$$

*c) Eigenvalues and linear combinations*

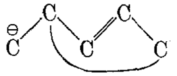
| $\Psi_J$ | $x_J$ | $c_{Jr}$ | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $\psi_1$ | $\psi_2$ | $\psi_3$ | $\psi_4$ | $\psi_5$ | $\psi_6$ | $\psi_7$ | $\psi_8$ | $\psi_9$ | $\psi_{10}$ |
| $\Psi_{10}$ | —2.803 | 0.081 | —0.139 | 0.244 | —0.341 | 1.023 | —0.544 | —0.341 | 0.244 | —0.139 | 0.081 |
| $\Psi_9$ | —2.604 | 0.448 | —0.584 | —0.445 | 0.489 | 0. | 0 | —0.489 | 0.445 | 0.584 | —0.448 |
| $\Psi_8$ | —2.277 | 0.520 | —0.696 | —0.307 | 0.340 | 0.060 | —0.006 | 0.340 | —0.307 | —0.696 | 0.520 |
| $\Psi_7$ | —0.730 | —0.252 | 0.526 | —0.617 | 0.394 | 0 | 0 | —0.394 | 0.617 | —0.526 | 0.252 |
| $\Psi_6$ | —0.167 | 0.052 | —0.251 | 0.608 | —0.125 | —0.273 | —0.333 | —0.125 | 0.608 | —0.251 | 0.052 |
| $\Psi_5$ | 0.058 | 0.397 | —0.096 | —0.182 | —0.498 | 0 | 0 | 0.498 | 0.182 | 0.096 | —0.397 |
| $\Psi_4$ | 1.010 | —0.545 | —0.009 | —0.049 | 0.397 | 0.260 | 0.124 | 0.397 | —0.049 | —0.009 | —0.545 |
| $\Psi_3$ | 1.459 | 0.061 | 0.299 | —0.199 | 0.490 | 0.370 | —0.742 | 0.490 | —0.199 | 0.299 | 0.061 |
| $\Psi_2$ | 2.276 | —0.496 | —0.199 | —0.235 | —0.156 | 0 | 0 | 0.156 | 0.235 | 0.199 | 0.496 |
| $\Psi_1$ | 3.779 | 0.294 | 0.100 | 0.318 | 0.148 | 0.069 | 0.601 | 0.148 | 0.318 | 0.100 | 0.294 |

## Table 6. *Pentadienyl anion,* $(H_2C \cdots CH \cdots CH \cdots CH \cdots CH_2)^{\ominus}$

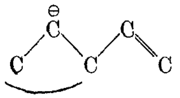
### *a) Structures and functions*



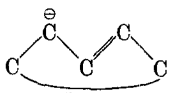
$\psi_1 = a - a\,b - c\,d - e$



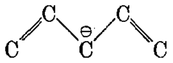
$\psi_2 = a - a\,b\,c - d\,e$



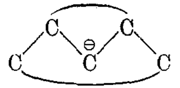
$\psi_3 = a\,b - b\,c\,d - e$



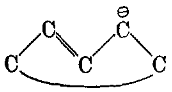
$\psi_4 = a\,b - b\,c - d\,e$



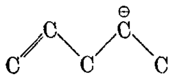
$\psi_5 = a - b\,c - c\,d - e$



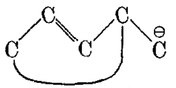
$\psi_6 = a\,b\,c - c\,d\,e$



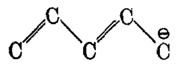
$\psi_7 = a\,b - c\,d - d\,e$



$\psi_8 = a - b\,c\,d - d\,e$



$\psi_9 = a\,b - c\,d\,e - e$



$\psi_{10} = a - b\,c - d\,e - e$

### *b) Matrix*

$$\left(\begin{array}{cccccccccc}
Q+\frac{\alpha}{2} & \frac{Q}{2}+\alpha & \gamma & \frac{\gamma}{2} & 2\alpha' & \alpha' & 0 & 0 & 0 & 0 \\
 & Q-\alpha & \frac{\gamma}{2} & \gamma & \alpha' & \frac{\alpha'}{2} & 0 & 0 & 0 & 0 \\
 & & Q-\frac{3\alpha}{2} & \frac{Q}{2} & \gamma & \frac{\gamma}{2} & \alpha' & \frac{\alpha'}{2} & 0 & 0 \\
 & & & Q-\frac{3\alpha}{2} & \frac{\gamma}{2} & \gamma & 2\alpha' & \alpha' & 0 & 0 \\
 & & & & Q & \frac{Q}{2} & \frac{\gamma}{2} & \gamma & \alpha' & 2\alpha' \\
 & & & & & Q-3\alpha & \gamma & \frac{\gamma}{2} & \frac{\alpha'}{2} & \alpha' \\
 & & & & & & Q-\frac{3\alpha}{2} & \frac{Q}{2} & \gamma & \frac{\gamma}{2} \\
 & & & & \text{symmetrical} & & & Q-\frac{3\alpha}{2} & \frac{\gamma}{2} & \gamma \\
 & & & & & & & & Q-\alpha & \frac{Q}{2}+\alpha \\
 & & & & & & & & & Q+\frac{\alpha}{2}
\end{array}\right)$$

### *c) Eigenvalues and linear combinations*

| $\Psi_J$ | $x_J$ | $C_{Jr}$ | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $\psi_1$ | $\psi_2$ | $\psi_3$ | $\psi_4$ | $\psi_5$ | $\psi_6$ | $\psi_7$ | $\psi_8$ | $\psi_9$ | $\psi_{10}$ |
| $\Psi_{10}$ | —4.923 | —0.144 | 0.193 | 0.364 | —0.421 | —0.500 | 0.913 | —0.421 | 0.364 | 0.193 | —0.144 |
| $\Psi_9$ | —4.098 | 0.341 | —0.466 | —0.466 | 0.636 | 0 | 0 | —0.636 | 0.466 | 0.466 | — 0.341 |
| $\Psi_8$ | —3.209 | —0.450 | 0.565 | 0.361 | —0.234 | 0.247 | —0.590 | —0.234 | 0.361 | 0.565 | —0.450 |
| $\Psi_7$ | —2.405 | 0.316 | —0.411 | 0.540 | —0.150 | —0.385 | —0.188 | —0.150 | 0.540 | —0.411 | 0.316 |
| $\Psi_6$ | —2.000 | —0.334 | 0.605 | —0.542 | 0.334 | 0 | 0 | —0.334 | 0.542 | —0.605 | 0.334 |
| $\Psi_5$ | —2.000 | 0.381 | — 0.210 | —0.341 | —0.381 | 0 | 0 | 0.381 | 0.341 | 0.210 | —0.381 |
| $\Psi_4$ | —0.809 | —0.284 | —0.311 | 0.232 | —0.086 | 0.646 | —0.054 | —0.086 | 0.232 | — 0.311 | —0.284 |
| $\Psi_3$ | —0.290 | —0.321 | 0.175 | —0.046 | 0.620 | —0.378 | 0.334 | 0.620 | —0.046 | 0.175 | —0.321 |
| $\Psi_2$ | 1.098 | —0.542 | —0.198 | —0.198 | —0.073 | 0 | 0 | 0.073 | 0.198 | 0.198 | 0.542 |
| $\Psi_1$ | 2.636 | 0.399 | 0.117 | 0.238 | 0.142 | 0.560 | 0.043 | 0.142 | 0.238 | 0.117 | 0.399 |

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