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PERMUTATIONS IN THE
QUANTUMCHEMICAL DESCRIPTION OF
MOLECULES AND REACTIONS

J. J. C. MULDER

Universiteit Leiden



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STELLINGEN

I

In standaardwerken over combinatorische algebra wordt bij de behandeling van het enumeratie-probleem bij een verdeling van r niet-onderscheidbare objecten over n dozen helaas weinig aandacht geschonken aan die gevallen waarbij de restrictie geldt van p objecten maximaal per doos met $1 < p < r$.

W. A. Whitworth, "Choice and Chance", Hafner, New York (1959) p. 91.

II

Het door Haller afgeleide correlatie-diagram voor de conversie van benzeen naar benzvaleen is onjuist.

I. Haller, J. Chem. Phys. 47, 1117 (1967).

III

Het door Ritchie en King gevonden minimum in het reactiepad van de reactie $H^- + CH_4 \rightleftharpoons CH_5^-$ is een voorbeeld van de soms in ab-initio berekeningen optredende schijnbare minima, veroorzaakt door onvoldoende flexibiliteit in de basis.

C. D. Ritchie, H. F. King, J. Amer. Chem. Soc. 90, 825-843 (1968).

IV

De voorkeur voor de trigonaal bipyramidale structuur boven de tetragonaal pyramidale vorm in moleculen waarin een centraal atoom omringd is door vijf identieke liganden (PF_5), kan niet uitsluitend worden toegeschreven aan kleinere electrostatistische repulsie tussen de liganden.

R. J. Gillespie, J. Chem. Educ. 40, 295 (1963).

H. A. Bent, Fortschr. Chem. Forsch. 14, 1-48 (1970).

V

De opmerking van Bryce-Smith dat Möbius-benzeen in de Hückel benadering niet iso-energetisch zou zijn met de eerste aangeslagen toestand van benzeen is onjuist.

D. Bryce-Smith, Pure and Appl. Chem. 16, 58 (1968).

E. Farenhorst, Tetrahedron Letters (1966) 6465.

VI

De nadruk door Grinter en Heilbronner gelegd op de langstgolvige overgang, doet afbreuk aan hun conclusie dat bij de interpretatie van de electronenspectra van benzeen-derivaten grensstructuren ten enenmale ontoereikend zijn.

R. Grinter, E. Heilbronner, *Helv. Ch. Acta* 45, 2496 (1962).

VII.

Bij de bespreking van de interactie tussen een enzym en een substraat dient naast de studie van de fixatie vooral aandacht gegeven te worden aan de vraag of hiermee een laag-energetische overgangstoestand is gerealiseerd.

VIII

De door de invoering van de Mammoetwet veroorzaakte specialisatie in de twee hoogste klassen van het VWO zal bij het volgen van een universitaire studie meer nadelen dan voordelen opleveren.

IX

De eenzijdige benadering van de motivatie en de capaciteiten van de leden van het wetenschappelijk corps en de studenten, maakt de conclusie van Heyn, dat toenemende ontkoppeling van wetenschappelijk onderzoek en onderwijs naast onvermijdelijk ook gewenst zou zijn, aanvechtbaar.

F. A. Heyn, *Intermediair* 25-1-1970.

X

Democratische besluitvorming en goed functionerend bestuur kunnen in de zin van de quantummechanica opgevat worden als geconjugeerde variabelen.

XI

Bij verwisseling van de kleuren rood en zwart op de nummers 20 en 21 wordt een evenwichtiger structuur van het roulettespel verkregen.

PERMUTATIONS IN THE
QUANTUMCHEMICAL DESCRIPTION OF
MOLECULES AND REACTIONS

PROEFSCHRIFT

VOOR DE ERSTEN GRADE VAN DOCTOR IN
DE WISKUNDE EN NATUURWETENSCHAPPEN AAN
HET RIJKSUNIVERSITEIT TOEGEVOEGD
INSTITUUT VOOR THEORETISCHE BIOLOGIE,
GEPLAATSD IN DE FACULTEIT DER WISKUNDE,
FYSICA EN ASTRONOMIE VAN DE RIJKS
UNIVERSITEIT TE LEIDEN, IN VERBAND
MET HET VERVOLGEN VAN DE WETENSCHAP
TE WISSELINGEN IN 1961.

DOOR

JAN JACOBS CORNELIS MURDER

GEBOREN TE HAARLEM IN 1931

INSTITUUT VOOR THEORETISCHE BIOLOGIE
der Rijksuniversiteit te
LEIDEN

DRUKKERIJ "DE WERK" N.V.
DUTTERDAM

REGULATION IN THE
QUANTUMCHEMICAL DESCRIPTION OF
MOLECULES AND REACTIONS

by

Prof. Dr. G. VON ELFT

Physikalisches Institut der Universität Bonn

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QUANTUMCHEMICAL DESCRIPTION OF
MOLECULES AND REACTIONS

PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN DOCTOR IN
DE WISKUNDE EN NATUURWETENSCHAPPEN AAN
DE RIJKSUNIVERSITEIT TE LEIDEN, OP GEZAG VAN
DE RECTOR MAGNIFICUS DR. J. GOSLINGS,
HOGLERAAR IN DE FACULTEIT DER GENEESKUNDE,
TEN OVERSTAAN VAN EEN COMMISSIE UIT DE SENAAT
TE VERDEDIGEN OP WOENSDAG 17 JUNI 1970
TE KLOKKE 15.15 UUR

DOOR

JAN JACOBS CORNELIS MULDER

GEBOREN TE HAARLEM IN 1934

1970

DRUKKERIJ BRONDER-OFFSET N.V.
ROTTERDAM

PERMUTATIONS IN THE
QUANTUMCHEMICAL DESCRIPTION OF
MOLECULES AND REACTIONS

PROMOTOR: PROF. DR. L. J. OOSTERHOFF

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1977

JAN JACOBS CORNELIS MULDER

LEIDEN, THE NETHERLANDS

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7. A case for the 20-minute method
8. The CH_2 and CH_3 ions

aan mijn ouders

Voor Peggy

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A. GENERAL INTRODUCTION

THE NATURE OF QUANTUM-MECHANICAL METHODS

1. INTRODUCTION

The development of the theory of quantum mechanics would undoubtedly have been impossible without the rigorous treatment of the problems which the physicist has to face in the construction of his models. The development of the theory of quantum mechanics, which was in the stage of the beginning of the 20th century, was characterized by the fact that the methods of calculation were performed in a very simple manner, the so-called "old quantum theory". The development of the theory of quantum mechanics, which was in the stage of the beginning of the 20th century, was characterized by the fact that the methods of calculation were performed in a very simple manner, the so-called "old quantum theory". The development of the theory of quantum mechanics, which was in the stage of the beginning of the 20th century, was characterized by the fact that the methods of calculation were performed in a very simple manner, the so-called "old quantum theory".

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A GENERAL INTRODUCTION

PART I

THE NATURE OF QUANTUMCHEMICAL METHODS

1. Introduction

A flash-back to the birth of quantumchemistry would undoubtedly start from the famous Heitler-London treatment of the hydrogen molecule¹. Looking back at the translucent description of the covalent bond that resulted from this calculation, which was at the same time the beginning of one of the main quantumchemical procedures, the valence bond method, one is led to the question why almost all calculations on molecules are performed nowadays using the molecular orbital method. The origin of this alternative method which makes use of concepts that appear to be completely different from those present in the pioneering contribution to the theory of the chemical bond, can be traced to the orbital theory of the electronic structure of atoms with its consequences for the interpretation of atomic spectra, and the attempts to obtain a comparable characterization of the band spectra of simple molecules. Actually the Hartree-Fock method, developed for the description of atoms^{2, 3}, and subsequently adopted for molecules also, forms the basis of perhaps 90% of present day calculations.

Now for atoms the notion of orbitals is a perfectly natural one, originating from the classical picture of the atom and substantiated by the nature of the exact solutions of the Schrödinger equation for the one-electron atom. The interpretation of the properties of atoms benefits from this picture to such extent that it is pointless to search for another model. In molecules however, we meet a somewhat different situation. It is not surprising that the efforts to formulate an orbital model for molecules by Hund⁴, Mulliken⁵,

Herzberg⁶ and Lennard-Jones⁷ had their source in spectroscopy. The spectra, ionization potentials and electron affinities - all physical properties of the molecule as a whole - would expectedly be much better understood if, as in atoms, the electrons would occupy certain orbitals extending over the whole molecule, which they could leave or enter according to circumstances. Although the physical properties of molecules are an important tool to characterize them and to obtain information about their nature, there are a number of questions that quantumchemistry has to answer, which do not refer to the molecule as a whole, but only to certain atoms or bonds in the molecule. If we may adopt and paraphrase slightly the classification given by Coulson in the first pages of his admirable little book⁸, we have four successive stages of analysis:

- (i) Why do certain atoms combine to form molecules and why do molecules react the way they do?
- (ii) Why do we obtain molecules of definite composition, and does not the bonding process continue until all the atoms in the universe are bound?
- (iii) If we accept the composition of a molecule, why do we have specific valence angles, in short, can we explain stereochemistry?
- (iv) Are we able to explain details of molecular structure like for instance the different bond lengths observed by diffraction methods?

There is one obvious answer to all of these questions: because the balance of energy and entropy wants it that way. Even if we may regard the calculation of the entropy as a separate problem, which need not concern us here, still the calculation of the energy for every relevant molecular situation is clearly a quite impossible project. Therefore it is necessary to snatch from nature the fundamental concepts of chemical binding, to be able to transfer the results of a limited number of quantumchemical calculations to other situations of interest. Such is the essential nature of chemistry that the subject is an impossible one if analogy arguments cannot be made operative. More than often the chemical properties of a molecule - and sometimes even the physical properties, for instance the UV-absorption of the carbonyl group - are to a large extent confined to a part of the molecule. Thus we must judge the merits of our quantumchemical methods as to their performance in furnishing us not only the properties of the molecule as a whole, but especially the behaviour of certain atoms and groups of atoms in a molecule as to their binding characteristics, their structure and reactivity.

We ought to mention here that other factors influence the appreciation for either the molecular orbital or the valence bond method. Performing quantumchemical calculations - or writing programs to let computers do the work - is not an exceptionally difficult mathematical problem, but it certainly keeps man and machine occupied because of its size. A quantumchemical procedure should therefore also be viewed as to its possibilities for implementation. Closely connected is a second factor, namely the question whether one is aiming for highly accurate quantitative results to be obtained by ab-initio methods or by heavily parametrized semi-empirical treatments, or alternatively for qualitative results of wide applicability. It is with these points and those mentioned earlier in mind that we will try to compare some aspects of valence bond and molecular orbital theory.

2. Configurations and structures: the equivalence of the valence bond and molecular orbital methods

The rapid development of molecular orbital theory to the extent that it has superseded the valence bond method almost completely, was brought about by the successive contributions of Hückel⁹, Coulson and Longuet-Higgins¹⁰, Mulliken¹¹ and especially Roothaan¹². The ab-initio calculations as well as the semi-empirical treatments of the last 20 years¹³ can be attributed chiefly to these foundations of the LCAO-MO formalism for polyatomic molecules. Naturally the fact that VB-theory is a many-electron theory from the very beginning and thus has to use properly antisymmetrized wave functions including spin from the outset, whereas the MO-method remains a one-electron theory as far as simple applications are concerned, also tipped the scale in favour of the second approach, especially in the pre-computer era.

In the VB-method every structure wave function is constructed directly from the basis of atomic orbitals donated by the constituent atoms in the molecule. These orbitals can be empty, singly filled or doubly filled. In MO-theory the available atomic orbitals are first combined linearly to LCAO-MO's, the ground configuration is obtained by using the lowest energy molecular orbitals each twice, and in the next stage excited electronic configurations are constructed by means of the occupation of the hitherto empty virtual orbitals with one or two electrons in all possible ways. The demonstration of the equivalence of the two methods was given by Slater¹⁴ and by

Longuet-Higgins¹⁵. They showed that a MO-treatment including full configuration interaction gives identical results to a VB-calculation using all structures, provided that both methods use the same atomic orbital basis set. It is the continuation of Longuet-Higgins' formal analysis of the number of electronic configurations or structures in an N-electron system that forms the contents of the first publication which is included in this thesis. We would like at this point to comment on the results derived in one respect.

It was found possible to obtain closed-form expressions for the number of antisymmetrized product functions (Slater determinants), the number of electronic configurations of a particular multiplicity and the total number of configurations for a general system containing N electrons and N-p basis orbitals. In the derivation a classification was used in terms of doubly occupied orbitals, singly occupied orbitals and empty orbitals. Thus the approach was related to the VB-method where we have covalent structures, corresponding to a maximum number of singly occupied orbitals, singly ionic structures, and so forth. Now in a conventional configuration interaction treatment, starting from a set of molecular orbitals, this type of classification is not used. Instead the configurations are defined as to the degree of excitation (say: i-fold) with respect to a reference configuration, which is either the lowest energy configuration of the particular multiplicity studied, or most commonly the lowest energy configuration of the lowest possible multiplicity. It would be convenient to have simple expressions also, using this division. For instance it was found that the number of configurations of multiplicity $2q+1$ containing r doubly occupied orbitals (r -fold ionic structures) is given by

$$\frac{2q+1}{N-p+1} \binom{N-p+1}{\frac{1}{2}N-q} \binom{\frac{1}{2}N-q}{r} \binom{\frac{1}{2}N-p+q+1}{r-p} \quad (1)$$

A comparable expression is looked for, giving the number of i -fold excited configurations of multiplicity $2q+1$. At the time we had obtained some complicated expressions containing double summations over products of five binominal coefficients, but we expressed our confidence that a further reduction would be possible. Subsequent analysis has shown, however, that this is not the case. Although it is possible of course to get for instance the number of doubly excited singlet configurations as a function of $N(=2n)$ and p :

$$\frac{1}{2} \cdot n(n-p) \{ n(n-p) + 1 \} \quad (2)$$

general closed-form expressions are unattainable.

Having digressed in this way to show the origins of our analysis of the enumeration problem for configurations and structures, we now return to the basis of the molecular orbital and valence bond methods.

3. Some general aspects; the non-orthogonality problem

A valence bond as well as a molecular orbital treatment of a molecule has to start from a choice of basis orbitals pertaining to the constituent atoms. The first question to ask is whether this basis should consist of a set of orthogonal(ized) functions or that the basis functions should preferably be non-orthogonal. In view of semi-empirical developments one may even impose the stronger condition that the basis orbitals should as far as possible have zero differential overlap. The reasons behind such transformations of the basis according to certain criteria are conceptual and mathematical. From a mathematical standpoint the advantages of working with orthogonal basis orbitals are obvious. However, the description of the chemical bond may be less satisfactory when the orbitals on neighbouring atoms are orthogonal. In the first calculations on diatomic molecules with either of the two methods the overlap integrals were retained without difficulty. Only when treating larger molecules the elimination of the overlap integrals becomes desirable. In this respect there is a pronounced difference between MO- and VB-theory.

As we mentioned earlier, in VB-treatments the basis orbitals figure directly in the configurational wave functions. If these basis orbitals are non-orthogonal, in general all the permutations of the electron numbers that are present on account of the antisymmetrization condition, yield non-zero contributions in the evaluation of the matrix elements between the configurational wave functions, which are themselves now non-orthogonal. Nevertheless the overlap integrals are essential to keep the original concept of the chemical bond in this description¹⁶.

On the other hand in the MO-method the LCAO-MO's constructed from non-orthogonal basis functions will still be orthogonal if they are the solutions of an eigenvalue problem or symmetry orbitals for the system. Thus orthogonality of the configurational wave functions obtained from the MO's is ensured and the matrix elements between them are evaluated rather easily. Moreover the description of the bonding situation in MO-terminology is not strongly dependent on the character of the basis orbitals, with the ex-

ception of the more careful population analysis which is necessary in the non-orthogonal case¹⁷.

Next to the non-orthogonality problem of the basis, VB-theory has a second inherent difficulty that complicates the interpretation. If the structure functions are obtained in the standard manner using the Rumer-diagrams¹⁸, the resulting wave functions are in general non-orthogonal even if the basis orbitals were chosen to be orthogonal. This is a consequence of the fact that the scalar products of the spin functions associated with the Rumer-diagrams are unequal to zero. The simplest example is furnished by the two covalent functions in the four-electron problem, for which the overlap is $1/2$. Therefore population analysis using VB-functions is an intricate problem¹⁹.

From the foregoing one would draw the conclusion that the MO-method is preferable in almost every respect. Even though admittedly in the case of diatomic molecules the VB-method gives a better description of the ground state (oxygen is an exception), the advantages seem to disappear when in larger molecules a great number of alternative bonding schemes has to be envisaged. On the other hand, already at an early stage in the development of MO-theory it became apparent that the delocalized molecular orbitals were not altogether suitable for a discussion of specific bonding situations in molecules. It was shown by Lennard-Jones²⁰ that a transformation to localized orbitals was possible, and leads to a more "chemical" representation. In the absence of molecular symmetry the derivation of appropriate localization criteria remains a problem^{21, 22}. Of course if one views the calculation of the properties of each molecule as a separate problem, then the question is completely irrelevant. In that case one should use the MO-method in its ab-initio or semi-empirical version and just go ahead, hoping for the arrival of ever bigger and faster computers.

In addition to what has been said above, one point regarding the MO-method must be mentioned. It can be formulated most clearly for ab-initio calculations of the ground state in systems of closed-shell type. In these cases there is an intermediate goal in the quest for an improved treatment, namely the Hartree-Fock limit. As is well-known, this is the best possible wave function that can be written in the form of one Slater determinant containing the doubly occupied molecular orbitals. In principle sufficient flexibility in the molecular orbitals is obtained only at the expense of using an infinite basis, but in practice satisfactory convergence is reached for restricted basis sets of sufficiently different types of atomic orbitals. The dif-

ference between the energy obtained in this approximation and the true ground state energy is called the correlation energy. The literature regarding the ways and means to transcend this approximation and to describe electron correlation is already extensive²³.

4. The development of the valence bond method

As the molecular orbital method has been treated in all its aspects in many textbooks and reviews^{13, 24, 25, 26}, it is perhaps better to concentrate on the developments in the valence bond method, which in general has not received such attention. Soon after the first applications on simple diatomic molecules, where explicit calculations with full expansion of the Hamiltonian operator, and evaluation of all the matrix elements of the one-, and two-electron operators was practicable, the method became transformed to a semi-empirical scheme in the hands of Heitler²⁷, Hellmann²⁸, Eyring²⁹, Pauling³⁰, Wheland³¹, and Sherman and Van Vleck³². Integrals over the complete Hamiltonian were treated as semi-empirical parameters and overlap integrals were neglected where they appeared explicitly. Most applications have been in the field of resonance energies of conjugated molecules, and covalent structures did suffice to obtain reasonable agreement between theory and experiment. Sklar³³ and Craig³⁴ subsequently applied the method to the interpretation of ultra-violet spectra and found that inclusion of ionic structures was required to obtain states of correct symmetry and intensity for the allowed transitions.

Especially interesting are those cases where the predictions of MO-, and VB-theory are at variance. In this respect we want to mention Craig's treatment of cyclobutadiene³⁵ and pentalene³⁶. Another point that deserves special attention is the often surprisingly good agreement regarding spin densities in simple VB-calculations³⁷. The spin density seems to be a one-electron property that can only be discussed using a proper many-electron theory. Although many useful results were obtained in the early calculations with the VB-method, and organic chemists had - rightly or wrongly - taken a liking to the use of resonance structures, gradually it became apparent that the time had come for a reconsideration of the theory. This became the more urgent as the MO-method had progressed to a more refined formulation with explicit inclusion of electron repulsion, after a period in which most applications had been made using the Hückel method, which likewise is based on matrix elements of a non-explicit Hamiltonian operator.

In 1954-55 McWeeny radically reformulated the valence bond method on a basis of orthogonalized atomic orbitals³⁸. He also remarked that if a symmetrical orthogonalization according to Löwdin³⁹ is used, a procedure that had already been proposed by Wannier⁴⁰ and Landshoff⁴¹ in treatments of solid-state problems, the new basis obtained fulfils to a remarkable degree the condition of zero differential overlap. Naturally this analysis was oriented towards calculations of conjugated molecules where each atom donates one p_z -orbital to the π -electron system. Although McWeeny did show that this version of the VB-method was suitable for semi-empirical development, and obtained some representative results for cyclobutadiene and benzene, the method was not much used until recently. This is understandable because at practically the same moment Pople, Pariser and Parr introduced their now famous simplifications for the MO-SCF-CI treatment of conjugated systems. Nevertheless their parametrization was eminently suited for McWeeny's VB-method. The evaluation of the matrix elements between the structure functions becomes such a simple matter that, as was recently shown by van der Lugt and Oosterhoff⁴² and also by Amos⁴³, if one wants to perform a full configuration interaction treatment, the use of the VB-method is advisable. A drawback of the method in this form is the large number of ionic structures that has to be included, because chemical binding is now dependent on the interaction between structures that differ from each other by a shift of one electron between neighbouring atoms.

The renewed interest in valence bond theory that is manifesting itself in recent years has a number of facets. Molecular orbital treatments in many cases now include quite extensive configuration interaction^{44, 45}, and a multiconfigurational SCF-theory has been developed^{46, 47, 48}. This has lead to a number of contributions regarding the calculation of matrix elements between spinfunctions or in general antisymmetrized product functions^{49, 50, 51, 52, 53, 54}. Furthermore Simonetta and others have treated a number of ions and radicals with either an odd or an even number of electrons^{55, 56, 57}. Finally the attempts to build relations between MO-, and VB-results, either from a formal theoretical standpoint, or directed at practical applications, have been valuable⁵⁸⁻⁶⁶.

Having reviewed some events in the development of the valence bond method, we are now ready to start the discussion of the application of quantumchemical methods to the study of reactions, the subject that will occupy the second part of the introduction.

PART I

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PART II

THE COURSE OF CHEMICAL REACTIONS

1. Introduction

The prediction and explanation of the course of chemical reactions by quantumchemical methods has been a long standing goal in theoretical chemistry¹. The problem has been approached along different lines. One may study the distribution of the electrons in the isolated molecule, and relate the results to its readiness to undergo certain reactions. As the more tightly bound electrons will expectedly be less available, one should also take into account the energies of the molecular orbitals that are occupied by the electrons. Alternatively one may calculate the total energy of the molecule and compare it to the calculated energy of a suitable model of the transition state. In this way an estimate of the energy of activation is obtained.

The majority of quantumchemical treatments of reactivity have been performed in the field of conjugated molecules². As far as ground state reactions are concerned the successive use of resonance structures, charge densities and localization energies to interpret the experimental reactivities of different positions in aromatic systems is rather well documented³. Many other reactivity indices have been suggested, and, at least for alternant hydrocarbons, relations between the different criteria have been obtained⁴.

Recently, however, due to the advent of more powerful computers, it has become possible to calculate the potential energy surfaces of the states of a molecular system during a reaction. Naturally the first attempts in this direction^{5, 6} are well-known. In these early calculations of the preferred pathway in very simple reactions the foundations were laid, which remain valuable in the most sophisticated treatments feasible today.

2. Photochemical reactions

Next to the normal thermal reactions a growing number of photochemical reactions have been studied. We will discuss some theoretical aspects of developments that have taken place in the Organic Chemistry and Theoretical Organic Chemistry departments of this university. It turns out that different theoretical approaches are applicable to these reactions.

In photosubstitution reactions of benzene derivatives, nucleophilic⁷ as well as electrophilic⁸, a pronounced activation of the meta position was found in those cases where this position is inactive in ground state processes. The reactivities could be understood using the calculated charge distribution in the first excited singlet state⁹.

Regarding the photoionization of aromatic hydrocarbons in boric acid glasses it was found that the basicities of the hydrocarbons in the excited singlet states could be correlated with the experimental rates of positive ion formation¹⁰. The observation that in some cases not the first but the second excited state had to be used to obtain the correlation with the calculated excited state localization energy for electrophilic attack, deserves special attention. This surprising fact could be confirmed by experiments with monochromatic light. It may be remarked also that for a series of compounds the order of the basicities in the excited state is often opposite to the order found in the ground state.

A third category, photochemical as well as thermal reactions, are the ring opening and closure reactions in the vitamine D series¹¹. Here it seemed that the symmetries of the highest occupied and the lowest vacant molecular orbital did control the opposite stereochemical course of the reactions.

Many factors influence the total picture of photochemical reactions in such a way, that the outcome is rather unpredictable. Sometimes the wavelength of irradiation is important¹⁰, in other cases it has little influence¹². Singlet or triplet excited states may be involved¹³, and in this respect the lifetime of the excited state. Moreover competing processes that are described as radiative and non-radiative decay¹⁴ may play a role.

A common feature is exhibited by many photochemical reactions, in that a compound or a position which shows little or no reactivity in a ground state process, becomes extremely reactive when the substance is irradiated. A mode of reaction which is clearly excluded thermally, emerges as com-

pletely predominant photochemically. Notwithstanding the complicated nature of photochemical processes one may be able to grasp some fundamental aspects by concentrating on this reversal with respect to ground state properties. The different products obtained in the thermal and photochemical valence isomerizations yield a clear example of this phenomenon. Actually this is a fairly large group of reactions, now called pericyclic reactions¹⁵, for which abundant experimental information is available¹⁶, and the regularities observed are such that theory should provide us with an unequivocal explanation of the course of these reactions. In the second and third publication included in this thesis we have treated this problem using the valence bond method. Because of the rather condensed form in which the material has appeared it may be useful to make some additional comments.

3. Pericyclic reactions

The first interpretations of cycloaddition-, electrocyclic-, and sigmatropic reactions were made employing simple molecular orbital theory¹⁷. The transition from orbital correlation diagrams to state correlation diagrams was introduced almost at the same time by Longuet-Higgins and Abrahamson¹⁸. Although ground state processes are described rather well, little information is obtained regarding photochemical reactions. Moreover the orbital symmetry concept cannot properly be used if the system has no symmetry, and even if symmetry is present, the correlation diagram sometimes fails, because there is no symmetry element of the right type. The butadiene-bicyclobutane and benzene-benzvalene transformations are examples where this difficulty arises. In these cases one is left guessing which orbitals to correlate, and only detailed calculations of the behaviour of the orbital energies during the reaction can solve the problem. Alternative formulations have been put forward by Dewar¹⁹ and Zimmerman²⁰. Their interpretation relies on the aromatic or anti-aromatic properties of the cyclic transition state which can be a normal ring with either none or an even number of negative overlap integrals, or a Möbius ring in which one, or in general an odd number, of the overlap integrals is negative. In a primitive form this model had already been suggested by Evans²¹ to account for the mechanism of Diels-Alder reactions. Valuable contributions to the theory of concerted reactions have also been given by Bader²², Pearson²³, and Salem²⁴. The implications of the symmetries of certain normal modes of vibration,

corresponding to the reaction pathway, for the interaction of the ground state with nearby excited states, has been emphasized.

Van der Lugt and Oosterhoff²⁵ reconsidered the problem using valence bond theory based on orthogonal orbitals. Potential energy surfaces were obtained for the butadiene-cyclobutene interconversion, which was treated as a four electron - four orbital system. The crucial observation which resulted from these calculations was the importance of the potential energy surface of the second excited state, giving the driving force for the photochemical reaction in the disrotatory mode. It could be shown that this state, using MO-language, contains a large contribution from a doubly excited configuration. As to the contributions of the VB-structures there is every indication that the behaviour of the ground state and the second excited state during the reaction is determined by a gradual reversal of the weights of the two covalent structures that resemble the initial substance and the final product. This means then, that a consideration of these two Kekulé-type structures only, but in a valence bond method including overlap integrals, might be sufficient to show in general terms the origins of the course of all pericyclic reactions. The actual analysis confirms these expectations. In agreement with the most recent formulation of the rules for these reactions¹⁵, only the number of electron pairs and the number of negative overlap integrals in the transition state are needed to predict or explain the course of a reaction.

At this point we would like to dwell for a moment on the approximations and restrictions that are present in the derivation. The first approximation is the restriction of the treatment to the relevant electrons and orbitals. The other orbitals and electrons are more or less localized in bonds that are little affected in the reaction pathway. Although changes in hybridization certainly do occur, they will probably be more important in determining the relative energies of the starting point and the final point in the reaction, and will have insignificant influence on the general characteristics of the transition state configuration. The second and third approximation are related. They concern the neglect of non-neighbour overlap integrals and the omission of ionic structures. These approximations are connected intimately to the type of basis orbitals employed. To justify them one has to use a basis of transformed atomic orbitals. One possible way of obtaining these orbitals is a transformation with the matrix $S^{+1/2}$. The new strongly non-orthogonal orbitals might be called anti-Löwdin orbitals. Each of these new orbitals now contains next to the original atomic orbital a heavy contribution

of the orbitals on neighbouring atoms with positive coefficients^{26, 27, 28}. This has three consequences. First the neighbour overlap integrals are larger than between the original atomic orbitals, which is essential to obtain energy differences of the right order of magnitude. Secondly a covalent structure based on these new orbitals contains covalent and ionic structures on the original atomic orbitals. Thirdly, if the non-neighbour terms in the matrix S for the original atomic orbitals are eliminated before constructing $S^{+1/2}$, the non-neighbour overlap integrals between the new orbitals become smaller relative to the neighbour overlap integrals. The whole procedure amounts to confining the binding in a molecule to neighbour interactions by minimizing the non-neighbour binding contributions. Finally the derivation is based on a restriction to cases in which the number of orbitals is the same as the number of electrons, and moreover this last number must be even. Now the experimental evidence regarding the course of radical reactions is flimsy, but a number of ion valence isomerizations have been found to obey the rules¹⁵. The problem in the analysis of these situations is the occurrence of more Kekulé-type structures than the two that resemble the extreme points of the reaction. A preliminary investigation has shown that in this case different types of permutations are leading to terms in the energy and the normalization that are dependent on the occurrence of negative overlap integrals, but that, as was found independently by Murrell²⁹ in a discussion of the aromaticity and anti-aromaticity of odd-membered cyclic polyenes by means of the VB-method, the terms of lowest order in the overlap integral, in this case order one, are of the right sign to accommodate to the observed regularities.

4. Stability of cyclobutadiene and derivatives

In the foregoing we have uncovered the close correspondence between the phenomenon of aromaticity and anti-aromaticity and the course of concerted reactions. In this respect we would like to consider once more the four-electron problem as it is present in cyclobutadiene. On the one hand we want to show how the VB-method accounts for the stability of suitably substituted "push-pull" cyclobutadienes³⁰, and secondly we hope to point out a possible connection between this manifestation of a drastic change in properties by substitution and the eventual occurrence of exceptions to the Woodward-Hoffmann rules, exceptions (more recently: violations) that have

been claimed to be non-existent¹⁵.

When the cyclobutadiene molecule is decorated with donor and acceptor substituents in alternating sequence a stable system is obtained³⁰. This situation has been discussed by Hoffmann³¹, using simple MO arguments. The explanation rests on the removal of the two-fold degeneracy, caused by the D_{4h} symmetry present in the original molecule, in such a way that one orbital is raised in energy and the other one is lowered. Thus, in contrast to the unsubstituted molecule, which, according to this picture, should have a triplet ground state, a singlet ground state is provided for. However, according to complete MO-³² or VB-calculations³³ as well as to the elegant arguments presented by Borden³⁴, cyclobutadiene is expected to have a singlet ground state. The VB-calculations show that this state has the ψ_{A+B} character (symmetry B_{2g}) where A and B are the two Kekulé structures. It is to be expected that a pseudo Jahn-Teller distortion from a square to a rectangular form will stabilize the singlet ground state. Apart from the triplet state (symmetry A_{2g}) there is a nearby singlet excited state with a wave function of ψ_{A-B} type (symmetry A_{1g}). By means of a VB-treatment in which the attractive potentials on the four carbon atoms were lowered and raised alternately by 1,2 eV we have obtained a reversal of the two singlet states in that now the $A_{1g} - \psi_{A-B}$ state is the ground state. Preliminary evidence³⁵ seems to indicate that the substituted cyclobutadiene is square, as could be anticipated on the ground of the aromatic character of the ψ_{A-B} state. Thus the substitution has depressed the "excited state" to such extent that it ends up below the "ground state". A specific influence on the energy of an excited singlet state by the position of donor and acceptor substituents is well-known in benzene derivatives, and has been expressed in empirical rules for bathochromic spectral shifts developed by dye chemists, for instance the partitioning rule for auxochromes (Verteilungssatz der Auxochrome), and Caliezi's rule³⁶.

The interesting point regarding the connection with concerted reactions is the question whether the depression of the energy of the excited state might be large enough to bring it below the Möbius ground state in the cyclobutadiene case. Exploratory calculations have demonstrated that to this end inductive changes are insufficient. The effect of the substituents should be such that the mean number of electrons in the four-membered ring is changed drastically in the direction of two or six. If such substitution is possible, then a thermal disrotatory ring opening could be expected for a cyclobutene

derivative. One piece of experimental evidence seems to point in this direction³⁷. Of course it might very well be that this only happens if steric factors are unfavourable for the normally allowed pathway, so that they cooperate with the electronic effects in diminishing the energy difference between the two modes of reaction. Moreover, in these cases the reaction might not be concerted at all, but proceeding via a, possibly dipolar, intermediate. Additional information regarding these questions is now forthcoming from studies of cycloaddition reactions to the substituted cyclobutadiene³⁵.

With these observations we leave the domain of concerted reactions - although only temporarily - and return for a moment to the meta-activation found in the photosubstitution reactions with benzene derivatives. The reason for this is our inclination to think that a similar situation obtains in these cases as was found for the pericyclic reactions.

5. Photosubstitution reactions: an alternative

To develop a model for these reactions we introduce some gross simplifications. We consider the benzyl anion and the benzyl cation to be suitable in simulating respectively a donor- and an acceptor-substituted benzene molecule. We use ordinary Hückel theory to calculate the energies of the molecular orbitals of the benzyl system in which either the ortho, meta or para carbon atom is taken out of conjugation. In this way we obtain models for the σ -complex in aromatic substitution, which is thought to be close to the transition state. There is a striking difference between the patterns of the orbital energies of the para- and ortho- σ -complexes on the one hand and the meta-system on the other. In the latter we find a two-fold degeneracy at the zero level. Symmetrically below and above there are two times two non-degenerate orbitals. This situation has to be viewed with respect to four different possibilities.

- (i) Donor substituent and electrophilic substitution: six electrons are distributed in the lowest energy orbitals.
- (ii) Donor substituent and nucleophilic substitution: eight electrons in the available orbitals.
- (iii) Acceptor substituent and electrophilic substitution: four electrons present in the conjugated system.
- (iv) Acceptor substituent and nucleophilic substitution: again six electrons have to be distributed.

The two interesting cases are (i) and (iv). Here we have to use the degenerate levels each once, and a cyclobutadiene-like situation results. Thus we have to expect a difficult ground state reaction and an easy photochemical reaction. This is just what is found experimentally³⁸. It can be concluded also that the reversal of reactivity is in general not to be expected for the ortho and para positions.

It must be admitted naturally that the degeneracy is merely accidental and will be absent in any real system. Moreover the simulation of the substituents is rather unrealistic. There will remain, however, a relatively high ground state energy and a low-lying doubly excited configuration with, because of an expectedly small exchange integral between the two molecular orbitals, only slight configuration interaction between them. Viewed as a transition state configuration this implies a barrier in the ground state reaction pathway, and a well in the excited state potential energy surface.

6. A case for the ab-initio method

Although, as follows with some reservations from the previous discussion, qualitative quantumchemical treatments of reactions can be reasonably successful, more elaborate calculations using by preference the ab-initio method, are highly desirable. Even in those cases where the accuracy of the calculations is not what one might call "chemical", one nevertheless has a clear idea about the nature of the remaining approximations and their energy magnitude. The price that has to be paid for this advantage is high indeed. One has to be content with a limited choice in the field of small molecular systems. In this choice one should be guided by the desire to obtain results that are representative for a much larger body of chemical evidence than the data of the particular reaction studied. We have been fortunate in having obtained the opportunity to gain some experience in this type of problems during a stay in the "Centre Européen de Calcul Atomique et Moléculaire" in the Faculté des Sciences, Orsay, a European center for quantumchemistry that has recently been founded through the efforts of Dr. C. Moser. The results of investigations performed in this period in close cooperation with Dr. J.S. Wright, form the contents of the fourth and last paper, included in this thesis.

A search for the full potential energy surface during a chemical reaction is a multidimensional problem. In an ab-initio treatment one has to en-

visage variations in bond angles, bond lengths, exponents of the basis orbitals, and finally of the basis itself. The large number of variables gives rise to two problems. In the first place a large number of calculations is necessary, with its consequences as to computer time. Secondly, even if this proves to be no obstacle to the practical execution of the complete treatment, in the evaluation of the results a number of variables has to be eliminated to make a visualization possible. Therefore one should look for a problem in which it is obvious which geometry changes have to be studied. In addition, the presence of some symmetry elements in the system is a tremendous advantage with respect to the number of variables and the amount of computer time needed.

7. The CH_5^+ and CH_5^- ions

In our case we were motivated by a series of publications regarding the electronic structure of the CH_5^+ ion. Experimental evidence about this system has been obtained from mass spectrometer data³⁹ and from reactions of hydrocarbons in strongly acidic media⁴⁰. The theoretical results as to the preferred geometry have been contradictory and a sound discussion has been lacking. We decided to extend the investigation to CH_5^- , hoping to obtain additional information from the comparison of the two ions. On the one hand it seemed interesting to search for possible differences as to the minimum energy structure, following from the one electron pair difference between the two ions, and in addition the CH_5^- ion is a suitable model for the transition state of a bimolecular nucleophilic substitution reaction, which can be regarded as a stereo-specific non-cyclic concerted reaction, proceeding invariably with inversion of the configuration at the saturated carbon atom. No comparable retention of configuration has been observed in the electrophilic substitution reaction at a saturated center.

In ab-initio calculations, once the problem is defined, the choice of the basis set has to be made. Although other possibilities like atomic Hartree-Fock orbitals, are available, nearly always a Slater orbital- or a Gaussian basis is chosen. The appraisal for either one of these two has fluctuated with the arrival of faster computers and more ingenious programming methods⁴¹. Essentially one is confronted with the following dilemma. Gaussians necessitate a larger basis but integral evaluation times are shorter, whereas Slater orbitals lead to difficult integrations taking up much computer time,

but a small basis may already yield quite good results. In the case of CH_5^+ and CH_5^- it has been an interesting and helpful coincidence that, while we were treating the problem with a minimum basis of Slater orbitals and subsequently with a double- ζ basis, a paper appeared by van der Lugt and Ros⁴², who had independently done the same series of calculations using a Gaussian basis. Although the energies differ - mainly in the cation - the minimum energy geometries obtained by them are very similar to ours.

The pertinent conclusion that can be drawn from the calculations is the pronounced preference for the D_{3h} structure, responsible for inversion in a substitution reaction, that is exhibited by the CH_5^- ion. No such preference for a single structure is present in CH_5^+ . We would like to emphasize that this same characteristic can be noticed in the results of the first exploratory calculations of the two systems in which we varied angles only, and kept all CH bond lengths equal and all hydrogen exponents likewise. Moreover the significant differences in angles between the two ions in the C_{4v} and C_s structures were already present at that stage. Thus the peculiar effect of the larger difference in energy between the C_s - retention - structure and the D_{3h} structure in CH_5^- , compared to the small difference in CH_5^+ , is showing up even when the charge in the ions is distributed more uniformly. This supports, at least in our opinion, the explanation given in the final part of the paper, in that the bonding characteristics together with the number of electron pairs determine the situation, and that electrostatic effects, although certainly important in the magnitude of the final energy differences, are not primarily responsible for the calculated - and observed - phenomenon. In fact a calculation of $\Sigma(r_{\text{HH}})^{-1}$ for equal CH distances at the best angles yields such small differences between the D_{3h} , C_{4v} and C_s structures, when converted to energy units, that a significant preference for one of them must have other reasons. Of course this is just what Ingold and his school have demonstrated in a long and elegant series of experiments⁴³.

PART II

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FINAL REMARKS

The ideas that have been put forward in this introduction and in the papers that follow it, pertain to a number of questions in quantumchemistry. We have tried to express our view that the different nature of the problems in chemistry that should be treated by theoretical methods, necessitates a flexible approach. Whatever type of analysis is used, the nature of the contributions to the energy of a molecular system remains the same; it is the balance of kinetic energy and potential energy of attraction and repulsion. Not always, however, do the magnitudes of these contributions vary from molecule to molecule in an unpredictable way. Many rules operate in the domain of chemical structure and reactions. One of these rules has occupied a central place in our discussion. The gratifying feature in this particular instance has been the fact that this rule is not determined by the magnitude of all the energy contributions, but only by the sign of some of them. The sign-producing capacity exhibited by the permutations could have its influence in other areas as well. Spatial symmetry, which solves so many questions in spectroscopy, is absent in most molecular systems, and mathematics would again render invaluable service to chemistry, if the properties of the permutations would provide us with selection rules for molecular structure and reactions. No rule is without exceptions, and the influence of the permutations in the selection rule for pericyclic reactions might be an exceptional case in itself. Personally we are convinced that other examples will be found, and that they are worth while looking for. With this prospect we conclude our considerations.

The examples that this thesis has dealt with, show that quantumchemical methods have the capability to explain at least some of the rules that govern molecular structure and reactions. But the final vindication of all theoretical treatments lies in the indication and logical insertion of the many exceptions that constitute the challenge of chemistry.

STAINED IN

On the number of configurations in an N -electron system

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Starting from some previously derived results, general closed-form expressions are given for the total number of configurations or structures, the number of configurations of a particular multiplicity, and the total number of antisymmetrized product functions (AP's), in an N -electron system. The number of electrons may be even or odd, and the number of orbitals may assume any value larger than $\frac{1}{2}N-1$ or $\frac{1}{2}(N-1)$ in the N =even and N =odd cases, respectively. Some special cases are mentioned in which the formulae become particularly simple. The results are derived in view of comparing molecular orbital and valence bond calculations on actual molecules when both methods are used in their many-configuration aspect.

1. INTRODUCTION

In the description of many-electron systems, whether one uses the molecular orbital method or the valence bond method, one encounters the problem of deriving the number of structures or configurations of a particular multiplicity. The determination of this number is important for knowing the dimension of the problem in advance; moreover it is interesting, that the total number is composed of the numbers of structures or configurations of a certain type in quite a different way in MO- and VB-descriptions. This point will be reverted to again in the Discussion.

In the VB-method a state of the system is described in terms of a superposition of structures, whereas in the MO-method in general configuration interaction is necessary in describing that same state. In both methods, however, electrons are assigned to orbitals. In the MO-method these orbitals are the molecular orbitals, constructed in some way or another; in the VB-method the basis is formed by the atomic orbitals of the system. Clearly, one has to count the number of ways in which the electrons can be placed in the orbitals, keeping in mind the Pauli principle which allows no more than two electrons, one with α -spin and the other with β -spin, in one orbital. In this way the number of configurations or structures of any multiplicity may be found, given a certain number of electrons and orbitals. The classification which will be used is related to the VB-method. In all cases it has been possible to obtain closed-form expressions.

Part of the analysis of this problem may be found in many places in the literature (Wigner [1], Eckart [2], Kramers [3], Kotani [4]). Up to now the most

complete discussion has been given by Longuet-Higgins [5]. However, there are three reasons for repeating his derivations in a more general way:

(i) Longuet-Higgins did not discuss systems with an odd number of electrons.

(ii) The results for $N = \text{even}$ can be brought in closed form.

(iii) The case where the number of orbitals is larger than the number of electrons was not considered.

The notation of Longuet-Higgins will be used as much as possible, but besides, assuming for the moment a electrons and b orbitals, the following symbols are introduced:

CF (a, b) = the total number of configurations.

CF _{q} (a, b) = the number of configurations of multiplicity $2q + 1$.

AP (a, b) = the total number of antisymmetrized products.

2. SYSTEMS WITH AN EVEN NUMBER OF ELECTRONS

2.1. The total number of configurations

One considers a system of $2n$ electrons ($n = 1, 2, 3, \dots$) and $2n - p$ orbitals ($p < n$). It is evident that if there are no singly occupied orbitals, there will arise as many singlet configurations as there are ways to select n doubly occupied orbitals. The result is:

$$\binom{2n-p}{n}. \quad (1)$$

Only if singly occupied orbitals are present, configurations of higher multiplicity are obtained. Each of these degenerate configurations will have one component with $S_z = 0$. So if one wants to know how many configurations there will be, the possibilities for $S_z = 0$ have to be counted. Out of the $2n - p$ orbitals n orbitals are taken to be filled each with one electron having α -spin; this can be effected in $\binom{2n-p}{n}$ ways. In each of these possibilities one now has to assign the other n electrons with β -spin to n orbitals. Thus one has to repeat the procedure followed for the electrons with α -spin. The resulting total number of configurations is:

$$\text{CF}(2n, 2n-p) = \binom{2n-p}{n}^2. \quad (2)$$

The same result can be obtained by first selecting r orbitals to be doubly occupied ($r < n$). There will be $2n - 2r$ orbitals singly occupied and $r - p$ unoccupied. The number of ways in which this selection can be realized is:

$$\frac{(2n-p)!}{r!(r-p)!(2n-2r)!} \quad \begin{array}{l} p < 0 : r > 0, \\ p > 0 : r > p. \end{array} \quad (3)$$

Out of the $2n - 2r$ electrons in singly occupied orbitals, $n - r$ must have α -spin and the same number β -spin. The number of ways to achieve this is:

$$\binom{2n-2r}{n-r}. \quad (4)$$

Multiplication of (3) into (4) and summation over r (cf. Appendix (A)) also leads to (2).

2.2. The number of configurations of a particular multiplicity

Out of the $\binom{2n-2r}{n-r}$ possible configurations which arise from $2n-2r$ singly occupied orbitals, the number with multiplicity $2q+1$ is (Eckart [2]):

$$\binom{2n-2r}{n-r-q} - \binom{2n-2r}{n-r-q-1} = \frac{(2q+1)(2n-2r)!}{(n-r-q)!(n-r+q+1)!} \quad (5)$$

This number has to be multiplied into (3) and the result summed over r (cf. Appendix (A)):

$$\begin{aligned} \text{CF}_q(2n, 2n-p) &= \sum_{r=p}^{n-q} r!(r-p)!(n-r-q)!(n-r+q+1)! \\ &= \frac{2q+1}{n-p+q+1} \binom{2n-p}{n-q} \sum_{r=p}^{n-q} \binom{n-q}{r} \binom{n-p+q+1}{n-r+q+1} \\ &= \frac{2q+1}{2n-p+1} \binom{2n-p+1}{n-q} \binom{2n-p+1}{n-p-q}. \end{aligned} \quad (6)$$

The upper limit of r is found from (5) as $r = n-q$. The following limitations are imposed on q :

$$\begin{aligned} p &\geq 0 : 0 \leq q \leq n-p, \\ p &\leq 0 : 0 \leq q \leq n. \end{aligned}$$

We adopt the convention that, whenever two alternatives are given for the limit of a summation, as in (6), the lower one holds for $p \geq 0$, the upper one for $p < 0$.

In §4.1 some special cases of (6) will be treated. As verified in the Appendix for the odd case, summation of (6) over all possible q -values leads to (2).

2.3. The total number of antisymmetrized products

In general each configuration contains $2q+1$ components, each of which is a linear combination of antisymmetrized orbital product functions (LCAP). Furthermore, the number of AP's with $S_z=0$ is the same as the total number of configurations. The restriction to an equal number of α - and β -spins must be removed to get all AP's. Assuming k electrons to have α -spin and consequently $2n-k$ to have β -spin, one arrives at:

$$\text{AP}(2n, 2n-p) = \sum_{\substack{k=0 \\ k=p}}^{2n} \binom{2n-p}{k} \binom{2n-p}{2n-k} = \binom{4n-2p}{2n} \quad (7)$$

(cf. Appendix (A)). The result in (7) amounts to the following simple picture. The $2n-p$ orbitals give rise to $4n-2p$ available places for the $2n$ electrons. The number of possible arrangements is given by (7).

As will be shown later on, (7) is equivalent to the expression derived by Longuet-Higgins:

$$\text{AP}(2n, 2n-p) = \sum_{\substack{r=0 \\ r=p}}^n \frac{(2n-p)! 2^{2n-2r}}{r!(r-p)!(2n-2r)!} \quad (8)$$

Finally, using the fact that the total number of AP's must be the same as the total number of components in all configurations of all possible multiplicities, one may proceed from still another direction. Multiplying (6) by $2q+1$ and summing the result over all possible q -values one obtains:

$$AP(2n, 2n-p) = \sum_{q=0}^{n-p} \frac{(2q+1)^2}{2n-p+1} \binom{2n-p+1}{n-q} \binom{2n-p+1}{n-p-q}. \quad (9)$$

This yields an independent check on expression (6), when the equality of (7) and (9) will be proved in the Appendix. Moreover it demonstrates the interrelationship of the different expressions.

3. SYSTEMS WITH AN ODD NUMBER OF ELECTRONS

3.1. The total number of configurations

Let N denote the number of electrons ($N=1, 3, 5 \dots$), and let the number of orbitals be given by $N-p$ ($p < \frac{1}{2}[N-1]$). In this case all configurations are degenerate. One assumes $\frac{1}{2}[N+1]$ electrons to have α -spin and consequently $\frac{1}{2}[N-1]$ to have β -spin, i.e. one considers the component with $S_z = +\frac{1}{2}$ in each configuration. One now places the electrons with α -spin in orbitals, one in each orbital. This leads to $\binom{N-p}{\frac{1}{2}[N+1]}$ possibilities. The electrons with β -spin can be placed in $\binom{N-p}{\frac{1}{2}[N-1]}$ different ways. The total number of configurations thus is:

$$CF(N, N-p) = \binom{N-p}{\frac{1}{2}[N+1]} \binom{N-p}{\frac{1}{2}[N-1]}. \quad (10)$$

As before, this result could have been obtained by first assuming r orbitals to be doubly occupied ($r < \frac{1}{2}[N-1]$), which can be done in

$$\frac{(N-p)!}{r!(r-p)!(N-2r)!} \quad (11)$$

ways. Of the $N-2r$ electrons remaining in singly occupied orbitals, $\frac{1}{2}[N+1]-r$ will have α -spin and $\frac{1}{2}[N-1]-r$, β -spin. The latter arrangement can be made in

$$\frac{(N-2r)!}{(\frac{1}{2}[N+1]-r)!(\frac{1}{2}[N-1]-r)!} \quad (12)$$

ways. Multiplication of (11) into (12) followed by summation over r (cf. Appendix (A)) immediately leads to (10).

3.2. The number of configurations of a particular multiplicity

In the case of $N-2r$ singly occupied orbitals the number of configurations with multiplicity $2q+1$ is (Kramers [3], p. 377):

$$\binom{N-2r}{\frac{1}{2}N-r-q} - \binom{N-2r}{\frac{1}{2}N-r-q-1} = \frac{(2q+1)(N-2r)!}{(\frac{1}{2}N-r-q)!(\frac{1}{2}N-r-q+1)!} \quad (13)$$

Multiplication of (11) into (13) and summation (cf. Appendix (A)) leads to:

$$CF_q(N, N-p) = \frac{2q+1}{N-p+1} \binom{N-p+1}{\frac{1}{2}N-q} \binom{N-p+1}{\frac{1}{2}N-p-q}, \quad (14)$$

which is identical with (6) for the even case. Again the upperbound for r is found from (13): $r < \frac{1}{2}N - q$. As regards q one obtains:

$$\begin{aligned} p > 0 &: \frac{1}{2} < q < \frac{1}{2}N - p, \\ p < 0 &: \frac{1}{2} < q \leq \frac{1}{2}N. \end{aligned}$$

In § 4.2 some special cases will be mentioned. Finally when (14) is summed over q (Appendix), the result is formula (10).

3.3. The total number of antisymmetrized products

By the same kind of argument as used in § 2.3 one is led to the following three formulae:

$$\text{AP}(N, N-p) = \sum_{r=p}^{\frac{1}{2}N-1} \frac{(N-p)! 2^{N-2r}}{r!(r-p)!(N-2r)!} \quad (15)$$

$$\text{AP}(N, N-p) = \sum_{k=p}^{\frac{1}{2}N} \binom{N-p}{k} \binom{N-p}{N-k} = \binom{2N-2p}{N} \quad (16)$$

$$\text{AP}(N, N-p) = \sum_{q=\frac{1}{2}}^{\frac{1}{2}N-p} \frac{(2q+1)^2}{N-p+1} \binom{N-p+1}{\frac{1}{2}N-q} \binom{N-p+1}{\frac{1}{2}N-p-q} \quad (17)$$

The equivalence of (16) and (15) will be shown in the Appendix together with the corresponding even case. The proof that (17) is equal to (16) will also be briefly considered.

4. SPECIAL CASES

4.1. $N = \text{even}$

(i) Substituting $q=0$ in (6), one obtains:

$$\begin{aligned} \text{CF}_0(2n, 2n-p) &= \frac{1}{2n-p+1} \binom{2n-p+1}{n} \binom{2n-p+1}{n-p} \\ &= \frac{2n-p+1}{(n+1)(n-p+1)} \binom{2n-p}{n}. \end{aligned} \quad (18)$$

The right hand side demonstrates the number of *singlet* configurations as a fraction of the total number of configurations.

(ii) When the number of electrons is equal to the number of orbitals ($p=0$) expression (6) yields:

$$\text{CF}_q(2n, 2n) = \frac{2q+1}{2n+1} \binom{2n+1}{n-q}^2 = \frac{2n+1}{2q+1} \left[\frac{(2q+1)(2n)!}{(n-q)!(n+q+1)!} \right]^2 \quad (19)$$

The right hand side is written in this way to show that it contains the number of linearly independent configurations of multiplicity $2q+1$ resulting from $2n$ electrons in $2n$ orbitals, one in each orbital.

(iii) In the latter case the number of singlet configurations is especially interesting:

$$\text{CF}_0(2n, 2n) = (2n+1) \left[\frac{(2n)!}{n!(n+1)!} \right]^2 \quad (20)$$

Here, using VB-language, the expression contains the number of covalent structures, from which the total number of structures may be obtained by squaring and multiplying with $2n+1$.

4.2. $N = \text{odd}$

(i) From expression (14) the total number of doublet configurations is obtained:

$$\begin{aligned} CF_{1/2}(N, N-p) &= \frac{2}{N-p+1} \binom{N-p+1}{\frac{1}{2}[N-1]} \binom{N-p+1}{\frac{1}{2}[N-1]-p} \\ &= \frac{2(N-p+1)}{(\frac{1}{2}[N+1]+1)(\frac{1}{2}[N+1]-p+1)} \binom{N-p}{\frac{1}{2}[N+1]} \binom{N-p}{\frac{1}{2}[N-1]}. \end{aligned} \quad (21)$$

Again the right hand side shows the relation of this number to (10).

(ii) As before the effect of substituting $p=0$ is studied. From (14) one derives:

$$CF_q(N, N) = \frac{2q+1}{N+1} \binom{N+1}{\frac{1}{2}N-q}^2 = \frac{N+1}{2q+1} \left[\frac{(2q+1)N!}{(\frac{1}{2}N-q)!(\frac{1}{2}N+q+1)!} \right]^2. \quad (22)$$

Expression (22) is identical to (19).

(iii) For $p=0$ the number of doublet configurations becomes:

$$CF_{1/2}(N, N) = \frac{1}{2}[N+1] \left[\frac{2 \cdot N!}{(\frac{1}{2}[N-1])!(\frac{1}{2}[N+1]+1)!} \right]^2. \quad (23)$$

Here again one may calculate the total number of doublet structures immediately from the number of covalent doublet structures by squaring and multiplying with $\frac{1}{2}[N+1]$. Expression (23) may also be written as follows:

$$CF_{1/2}(N, N) = \frac{1}{2}[N+1] \left[\frac{(N+1)!}{(\frac{1}{2}[N+1])!(\frac{1}{2}[N+1]+1)!} \right]^2. \quad (24)$$

This way of representing the total number of doublet structures reflects the well-known fact that, as to the covalent structures, one may treat the odd system as the next higher even one, while placing the added electron at infinity.

5. DISCUSSION

In the foregoing analysis a classification of configurations closely related to the VB-method was used. In the MO-method one includes configuration interaction by distinguishing groups of configurations according to the degree of excitation. In general, only singly excited configurations are considered, but in some cases multiple excitations have been taken into account. Thus far a general closed-form expression for the number of i -fold excited configurations of multiplicity $2q+1$ has not been derived. The expressions obtained in the course of our current investigations still contain double summations, but it is expected that this difficulty can be overcome.

The results derived above are needed when comparing the MO- and VB-descriptions of a molecule, if the methods are used to a many-configuration stage. Presently such a comparison is being made by means of a calculation of the overlap between molecular orbital configurations and valence bond structures. In this

way information may be obtained on the character of the ground and excited states for the systems studied. The results will be published in the near future [6].

The author acknowledges with gratitude the privilege of extensive discussions regarding the derivations in the Appendix with Professor P. W. Kasteleyn (Department of Theoretical Physics, Leiden University), who in particular suggested the use of generating functions.

APPENDIX

In the preceding sections some proofs have been omitted, which will now be considered. Altogether six relations ought to be proved but only some of them will be treated in detail. Use will be made of five identities:

$$\sum_{k=0}^c \binom{a}{k} \binom{b}{c-k} = \binom{a+b}{c}, \quad (\text{A})$$

$$\sum_{k=0}^c k \binom{a}{k} \binom{b}{c-k} = a \binom{a+b-1}{c-1}, \quad (\text{B})$$

$$\sum_{k=0}^c k^2 \binom{a}{k} \binom{b}{c-k} = a \binom{a+b-1}{c-1} + a(a-1) \binom{a+b-2}{c-2}, \quad (\text{C})$$

$$\sum_{k=0}^n \binom{a}{k} \binom{a}{2n+1-k} = \frac{1}{2} \binom{2a}{2n+1}, \quad (\text{D})$$

$$\binom{a+1}{b} = \binom{a}{b} + \binom{a}{b-1}. \quad (\text{E})$$

Expression (A) forms a corner-stone in nearly all derivations in which one has to get rid of a summation over binomial coefficients. Formulae (B) and (C) are comparatively simple extensions of (A). Relation (D) follows from a partition of the summation from $k=0$ to $k=2n+1$ into two equal parts, $k=0$ to $k=n$ and $k=n+1$ to $k=2n+1$. In (E) the familiar recurrence relation for binomial coefficients is given. These and many other relations may be found in textbooks on combinatorial mathematics [7-9].

(i) It is to be proved (§3.2) that:

$$\sum_{q=\frac{1}{2}N-p}^{\frac{1}{2}N} \frac{2q+1}{N-p+1} \binom{N-p+1}{\frac{1}{2}N-q} \binom{N-p+1}{\frac{1}{2}N-p-q} = \binom{N-p}{\frac{1}{2}[N+1]} \binom{N-p}{\frac{1}{2}[N-1]}.$$

The following substitutions are made:

$$(1) \quad p < 0 : k = \frac{1}{2}N - q, \quad b = N + 1,$$

$$(2) \quad p > 0 : k = \frac{1}{2}N - p - q, \quad b = N - 2p + 1.$$

In this way one obtains:

$$\text{CF}(N, N-p) = \sum_{k=0}^{\frac{1}{2}(b-2)} \frac{b-2k}{N-p+1} \binom{N-p+1}{k} \binom{N-p+1}{b-k}.$$

The summation is divided into two parts, and (D) is used for the first part, inserting a correction term. The result is:

$$CF(N, N-p) = \frac{b}{2(N-p+1)} \binom{2N-2p+2}{b} - \frac{b}{2(N-p+1)} \binom{N-p+1}{\frac{1}{2}b} - 2 \sum_{k=1}^{\frac{1}{2}(b-2)} \binom{N-p}{k-1} \binom{N-p+1}{b-k}.$$

Substitution of $m=k-1$, followed by application of (E) yields:

$$CF(N, N-p) = \binom{2N-2p+1}{b-1} - \binom{N-p}{\frac{1}{2}[b-2]} \binom{N-p+1}{\frac{1}{2}b} - 2 \sum_{m=0}^{\frac{1}{2}(b-4)} \binom{N-p}{m} \binom{N-p}{b-m-1} - 2 \sum_{m=0}^{\frac{1}{2}(b-4)} \binom{N-p}{m} \binom{N-p}{b-m-2}.$$

Again using (D), corrected for several extra terms, this becomes:

$$CF(N, N-p) = \binom{2N-2p+1}{b-1} - \binom{N-p}{\frac{1}{2}[b-2]} \binom{N-p+1}{\frac{1}{2}b} - \binom{2N-2p}{b-1} + 2 \binom{N-p}{\frac{1}{2}[b-2]} \binom{N-p}{\frac{1}{2}b} - \binom{2N-2p}{b-2} + \binom{N-p}{\frac{1}{2}[b-2]}.$$

Application of (E) now leads to:

$$CF(N, N-p) = \binom{N-p}{\frac{1}{2}[b-2]} \left\{ - \binom{N-p+1}{\frac{1}{2}b} + \binom{N-p}{\frac{1}{2}b} + \binom{N-p}{\frac{1}{2}[b-2]} \right\} + \binom{N-p}{\frac{1}{2}[b-2]} \binom{N-p}{\frac{1}{2}b}.$$

Because of (E) the expression in braces is zero and the result is:

$$CF(N, N-p) = \binom{N-p}{\frac{1}{2}[b-2]} \binom{N-p}{\frac{1}{2}b}.$$

Putting $b=N+1$ or $b=N-2p+1$ this becomes:

$$CF(N, N-p) = \binom{N-p}{\frac{1}{2}[N-1]} \binom{N-p}{\frac{1}{2}[N+1]}.$$

The corresponding even case (§ 2.2) is treated in approximately the same way.

(ii) As regards the equivalence of expression (7) with (8) a proof will be given, which is also valid for the odd case. It may be remarked that $[N/2]$ as an upper-bound in the summations signifies that the summation is to be executed up to and including the largest integral number $< N/2$. ($N=1, 2, 3, \dots$)

$$\sum_{r=p}^{[N/2]} \frac{(N-p)! 2^{N-2r}}{r! (r-p)! (N-2r)!} = \binom{2N-2p}{N}.$$

First a new variable $a=N-p$ is introduced. Instead of deriving the identity thus obtained directly, it is more convenient to consider the corresponding generating functions:

$$\sum_{N=0}^{2a} \sum_{r=N-a}^{[N/2]} \frac{a! 2^{N-2r}}{r! (r+a-N)! (N-2r)!} x^N = \sum_{N=0}^{2a} \binom{2a}{N} x^N = (1+x)^{2a},$$

where the equality on the left is still to be proved. Interchange of the summations

in the first expression gives:

$$\sum_{r=0}^a \sum_{N=2r}^{a+r} \frac{a! 2^{N-2r}}{r! (r+a-N)! (N-2r)!} x^N.$$

Substitution of $m = N - 2r$ yields:

$$\begin{aligned} \sum_{r=0}^a \sum_{m=0}^{a-r} \frac{a! 2^m}{r! (a-m-r)! m!} x^{m+2r} &= \sum_{r=0}^a \binom{a}{r} x^{2r} \sum_{m=0}^{a-r} \binom{a-r}{m} (2x)^m \\ &= \sum_{r=0}^a \binom{a}{r} (x^2)^r \{1+2x\}^{a-r} \\ &= (1+2x)^a \sum_{r=0}^a \binom{a}{r} \{x^2(1+2x)^{-1}\}^r \\ &= (1+2x)^a \{1+x^2(1+2x)^{-1}\}^a \\ &= (1+x)^{2a}, \end{aligned}$$

which is the desired result.

(iii) Finally the following proof was announced (§2.3):

$$\sum_{q=0}^n \frac{(2q+1)^2}{2n-p+1} \binom{2n-p+1}{n-q} \binom{2n-p+1}{n-p-q} = \binom{4n-2p}{2n}.$$

The left-hand side remains unchanged if q is replaced by $-q-1$.

This makes it possible to write:

$$\text{AP}(2n, 2n-p) = \frac{1}{2} \sum_{q=-n+p-1}^{n-p} \frac{(2q+1)^2}{2n-p+1} \binom{2n-p+1}{n-q} \binom{2n-p+1}{n-p-q}.$$

The two cases can be combined into one by the following substitution:

- (1) $p < 0 : k = n + q + 1, \quad b = 2n + 1,$
- (2) $p \geq 0 : k = n - p + q + 1, \quad b = 2n - 2p + 1,$

which yields:

$$\text{AP}(2n, 2n-p) = \frac{1}{2} \sum_{k=0}^b \frac{(b-2k)^2}{2n-p+1} \binom{2n-p+1}{k} \binom{2n-p+1}{b-k}.$$

With the substitution $a = 2n - p$ this becomes:

$$\begin{aligned} \text{AP}(2n, 2n-p) &= \frac{b^2}{2(a+1)} \sum_{k=0}^b \binom{a+1}{k} \binom{a+1}{b-k} - \frac{2b}{a+1} \sum_{k=0}^b k \binom{a+1}{k} \binom{a+1}{b-k} \\ &\quad + \frac{2}{a+1} \sum_{k=0}^b k^2 \binom{a+1}{k} \binom{a+1}{b-k}. \end{aligned}$$

Using the expressions (A), (B) and (C):

$$\begin{aligned} \text{AP}(2n, 2n-p) &= \frac{b^2}{2(a+1)} \binom{2a+2}{b} - \frac{2b}{a+1} (a+1) \binom{2a+1}{b-1} \\ &\quad + \frac{2}{a+1} \left\{ (a+1) \binom{2a+1}{b-1} + a(a+1) \binom{2a}{b-2} \right\} \\ &= \binom{2a+1}{b-1} \left\{ b - 2b + 2 + \frac{2a(b-1)}{2a+1} \right\} \\ &= \binom{2a+1}{b-1} \frac{2a+2-b}{2a+1} = \binom{2a}{b-1}. \end{aligned}$$

Changing a into $2n-p$ and b into $2n+1$ or $2n-2p+1$ one arrives at the required result:

$$AP(2n, 2n-p) = \binom{4n-2p}{2n}.$$

In the corresponding odd case (§3.3) one first substitutes $r=q-\frac{1}{2}$ and then remarks that r may be replaced by $-r-2$. After a further substitution an expression is generated which is the same as its even counterpart, except that it contains N instead of $2n$. The remaining part of the proof is identical.

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...the Woodward-Hoffmann selection rules are obtained from permutation symmetry by means of the Valence Bond method.

CONCERTED organic reactions have found a generally utilized theoretical interpretation in the so-called Woodward-Hoffmann rules.¹ Usually these rules are derived

$$\frac{1}{2} \left(\frac{1}{2} \right)^{2n} = \frac{1}{2^{2n+1}}$$

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Permutation Symmetry Control in Concerted Reactions

By J. J. C. MULDER and L. J. OOSTERHOFF*

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Summary The Woodward-Hoffmann selection rules are obtained from permutation symmetry by means of the Valence Bond method.

CONCERTED organic reactions have found a generally utilized theoretical interpretation in the so-called Woodward-Hoffmann rules.¹ Usually these rules are derived

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from the idea that symmetry of molecular orbitals—and of the electronic configurations obtained from them—is conserved during all stages of a reaction.² A re-investigation from a different viewpoint seemed worthwhile for two reasons.

(i) Recently van der Lugt and Oosterhoff³ introduced a description of electrocyclic processes in terms of Valence

Bond structures. From their results it was concluded that orbital symmetry is irrelevant for processes taking place in the photochemical reactions; the question as to its importance for the interpretation of thermal reactions was left open.

(ii) In two recent symposia and an extensive review,⁴ Woodward and Hoffmann have given a new formulation of the rules. The most significant changes are the abolition of molecular orbitals and symmetry considerations and to a certain extent the restriction to thermal reactions. According to Woodward^{4b,c}: "A thermal pericyclic reaction is symmetry allowed (proceeds smoothly) if the total number of $[4r]_s$ and $[4q + 2]_s$ components is odd."

Using the fact that a suprafacially interacting component is to be identified with an even number of negative overlap integrals, an antarafacially interacting component with an odd number, this rule summarizes in a concise way the joint influence of the number of electron pairs and the number of negative overlap integrals on the course of the reaction.[†] We report how, in a Valence Bond treatment without invoking spatial symmetry, these two factors appear to determine the energy of the transition states for the two modes of a concerted reaction.

If we take the conversion of *cis*-hexatriene into cyclohexa-1,3-diene (Figure 1) and *vice versa* as a typical example,



FIGURE 1

we may say that hexatriene is well represented by its classical formula to which corresponds in quantum chemical terms a structure wave-function ψ_A . Likewise we may associate a structure wave-function ψ_B to cyclohexadiene. A structure wave-function describes an allocation of electron pairs to bonds; we will only take into account the electrons and bonds that are relevant to the reaction, in this case six electrons, the three π -bonds in hexatriene, and the two π -bonds and one σ -bond in cyclohexadiene. In Valence Bond theory the ground-state wave-function for hexatriene should not be represented by ψ_A only, but will contain a small contribution of ψ_B and of other possible structure functions as well.

In the same way the ground-state wave-function of cyclohexadiene will be mainly ψ_B with small amounts of ψ_A and other structure functions mixed in. This may be formulated as follows:

$$\psi_A^{\text{hex}} = \lambda_a \psi_A + \mu_b \psi_B + \dots (\lambda_a^2 \gg \mu_b^2) \quad (1)$$

$$\psi_B^{\text{cd}} = \lambda_c \psi_A + \mu_c \psi_B + \dots (\lambda_c^2 \ll \mu_c^2) \quad (2)$$

In the usual sign convention for structure wave-functions (Pauling⁷) λ and μ will both be positive. In a concerted process the wave-functions (1) and (2) will be interconverted in a continuous way by changing λ and μ monotonically. On the reaction pathway a point will be passed where λ^2 and

μ^2 are equal; presumably this point will be close to the cyclic transition state. Here we will have:

$$\psi^+ = (\psi_A + \psi_B + \dots) / N^+ \quad (3)$$

(N^+ takes care of normalization.)

From general considerations one may infer the existence of an excited state wave function belonging to the transition state configuration of the form:

$$\psi^- = (\psi_A - \psi_B + \dots) / N^- \quad (4)$$

The state corresponding to this wave-function will appear to control the course of photochemical reactions. The selection rules in operation in the reaction will depend on the energies corresponding to the transition-state wave-functions (3) and (4). Evidently, the line of reasoning given for the specific example (Figure 1) is valid for any concerted reaction of this type and the analysis has accordingly been performed for the general case of a $2n$ -electron transition state. The derivation which is described in a separate communication⁸ yields the energies (5) and (6):

$$U^+ = \frac{U_1^+ - (-1)^{n+v} \cdot 2U_c^+}{S_1^+ - (-1)^{n+v} \cdot 2S_c^+} \quad (5)$$

$$U^- = \frac{U_1^- + (-1)^{n+v} \cdot 2U_c^-}{S_1^- + (-1)^{n+v} \cdot 2S_c^-} \quad (6)$$

In these energy expressions the subscripts *i* and *c* refer to *independent* and *cyclic*. The quantities U_1 and S_1 are those parts of the energy and normalization that are *independent* of the number *v* of negative overlap integrals. The number of electron pairs relevant to the transition state is denoted by *n*. Energy quantities *U* are negative, normalization elements *S* are positive. The terms U_c and S_c stand for the contributions to the energy and the normalization resulting from two *cyclic* permutations of the electron numbers of order $2n$, one clockwise the other counterclockwise, in cycle notation: $(1\ 2\ 3\ \dots\ 2n)$ and $(2n\ 2n-1\ 2n-2\ \dots\ 1)$. Because the permutations play an essential role in the argument their influence will be discussed briefly. Any permutation, in a semi-classical picture, can be visualized as a simultaneous jump of electrons from one orbital to another. Precisely this picture caused the introduction of the term exchange integral ("austausch integral") in Heitler and London's treatment of the hydrogen molecule and in the subsequent development of the valence bond theory. Within the Mulliken approximation this exchange integral is proportional to S^2 , the square corresponding to two electrons making the same jump in opposite directions. In the present problem, if the usual approximation of neglect of non-neighbour interactions is made, all the permutations with one exception, give rise to the terms in total energy expression, with signs which are independent of the occurrence of negative overlap integrals. The one exception is formed by the cyclic permutations mentioned before. In the picture used, these cyclic permutations represent the simultaneous jumps of all electrons to their next position in the cycle of atomic orbitals. The energy terms due to these permutations are proportional to the product of all the overlap integrals each occurring to the first power, and now the sign of those terms will be dependent on the number of negative overlap integrals. This gives the factor $(-1)^v$ in equations (5) and (6). The analysis also shows that the two cyclic permutations applied to the spinfunctions forming part of ψ^+ and ψ^- yield the factors $(-1)^n$ and $-(-1)^n$. Finally, the fact that a cyclic permutation of order $2n$ has parity $= -1$ completes the sign fixing procedure.

[†] These two factors have been recognized by others as well. Valuable concepts of normal and Möbius ring; they are also used by states in concerted reactions.

They are present in Zimmerman's⁵ elegant treatment, using the Dewar⁶ in his discussion of aromatic and anti-aromatic transition

Formulae (5) and (6) demonstrate the existence of four energy levels at the transition-state configuration in a concerted reaction. In the very schematic energy diagram (Figure 2) the levels U_i^+ and U_i^- have been drawn at the same height in the left and right of the Figure, and other quantities in (5) and (6) have likewise been taken as equal.

From the scheme given in Figure 2, the rule follows immediately: Thermal reactions require either an odd number of electron pairs and an even number of negative overlap integrals, or an odd number of negative overlap integrals combined with an even number of electron pairs. In addition however, this alternative to Woodward's formulation is of necessity supplemented by its reversal in photochemical processes, provided ψ^- describes the state which determines the course of the photochemical reaction. The relevance of ψ^- in this respect follows from the observation that the present transition states can be regarded as monocyclic polyenes for which it is known from theory as well as experiment that ψ^- corresponds to the lowest excited singlet state. This state may be intrinsically different from the spectroscopic state into which the reacting system was initially excited.³

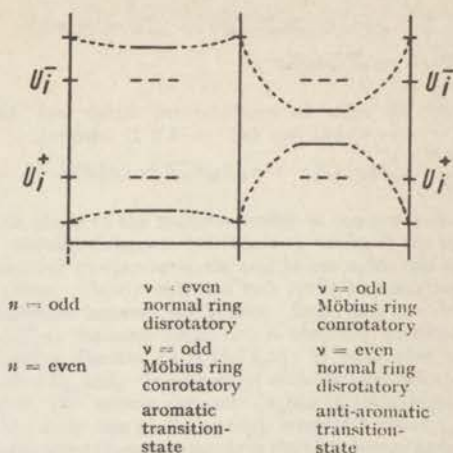


FIGURE 2

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Permutation Symmetry Control: Higher-order Permutations in the Valence Bond Method

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Summary The application of the Valence Bond method to the theoretical description of concerted reactions furnishes an example of the importance of higher-order permutations.

When applying Valence Bond theory to chemical problems, two main approaches may be considered. The first one is to use a basis of orthogonalized atomic orbitals.¹ It has the advantage of yielding simple matrix elements but necessitates the inclusion of a great number of ionic structures because chemical binding is now dependent on the interaction of structures which differ from each other by electron shifts between neighbouring atoms. In the analysis of the mechanism of concerted reactions by this method, van der Lugt and Oosterhoff² found that even the completely ionic structures were needed to obtain the correct selection rules for these processes. The second approach utilizes a basis of non-orthogonal atomic orbitals where one might expect that highly ionic structures are less important and that even a restriction to covalent structures should offer a reasonable description of chemical phenomena.

Now it becomes a difficult problem, however, to estimate the importance of the many higher-order permutations which yield non-zero matrix elements. In the treatment of concerted reactions with this second method, using only covalent structures, we have obtained the surprising result that indeed only the inclusion of the highest-order permutations enables to differentiate between the two modes of reaction.

As has been discussed in the preceding communication,³ one uses the hypothesis that the transition state in a concerted reaction can be described by a wave-function which is a linear combination of two covalent Kekulé-type structure functions ψ_A and ψ_B , that participate equally:

$$\psi^+ = (\psi_A + \psi_B)/N^+ \quad (1)$$

A second function pertains to an excited state belonging to the transition state configuration:

$$\psi^- = (\psi_A - \psi_B)/N^- \quad (2)$$

Using a set of non-orthogonal atomic orbitals a_1, a_2, \dots, a_{2n}

the Valence Bond functions corresponding to the structures A and B (Figure) are constructed in the standard fashion:

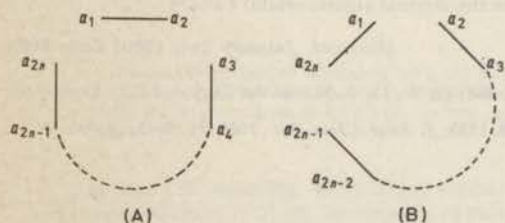
$$\psi_A = \sum_P \epsilon_P P a_1(1) a_2(2) \cdots a_{2n}(2n) \quad (3)$$

[12][34] \cdots [2n-1 2n]

$$\psi_B = \sum_P \epsilon_P P a_1(1) a_2(2) \cdots a_{2n}(2n) \quad (4)$$

[1 2n][2n-1 2n-2] \cdots [32]

The summations include all $2n!$ permutations P each with parity $\epsilon_P = \pm 1$, depending on whether P is even or odd. The spin functions are denoted as products of bond singlets $[ij] = 2^{-1} [\alpha(i)\beta(j) - \beta(i)\alpha(j)]$.



FIGURE

Continuing the analysis we write:

$$\psi^\mp = \sum_P \epsilon_P P u \chi^\mp \quad (5)$$

In this shorthand notation, u stands for the orbital product which is the same for ψ^+ and ψ^- and χ^\mp is an appropriate spin-function—taken to be normalised—which we will consider later. For the moment we suppress the \mp index. The expectation value of the Hamiltonian becomes:

$$U = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{\sum_P \langle P u | H | u \rangle \epsilon_P \langle P \chi | \chi \rangle}{\sum_P \langle P u | u \rangle \epsilon_P \langle P \chi | \chi \rangle} \quad (6)$$

The influence of the permutations in the matrix elements is most conveniently discussed first starting from a consideration of the element $\langle P u | u \rangle$, which can be represented by the following scheme:

$$\begin{pmatrix} P a_1(1) a_2(2) \cdots a_{2n}(2n) \\ a_1(1) a_2(2) \cdots a_{2n}(2n) \end{pmatrix} = \begin{pmatrix} a_1(i) a_2(j) \cdots a_{2n}(r) \\ a_1(1) a_2(2) \cdots a_{2n}(2n) \end{pmatrix} = S_{1i} S_{2j} \cdots S_{2n,r} \quad (7)$$

where S_{pq} = atomic orbital overlap integral and $S_{kk} = 1$. If the usual approximation of neglect of non-neighbour overlap integrals is invoked, systematic inspection of the possible permutations shows that three types of permutations give non-zero matrix elements:

- (i) the identity: $\langle P u | u \rangle = \langle u | u \rangle = 1$
- (ii) permutations that are simple transpositions of electron numbers on neighbouring orbitals or

products of these transpositions having no numbers in common:

$$\langle P u | u \rangle = S_{12}^2 \cdots S_{12n}^2 S_{12}^2 S_{34}^2 \cdots S_{23}^2 S_{45}^2 S_{67}^2 \cdots S_{12n}^2$$

- (iii) two cyclic permutations of order $2n$, in cycle notation $(1 2 3 \cdots 2n)$ and $(2n 2n-1 \cdots 1)$:

$$\langle P u | u \rangle = S_{12} S_{23} S_{34} \cdots S_{2n-1 2n} S_{12n}$$

In the study of the reaction modes in concerted reactions the essential difference between two modes is the number of negative overlap integrals, odd in one mode and even in the other. Clearly only the two cyclic permutations (iii) differentiate between the modes. Regarding the elements $\langle P u | H | u \rangle$ the same distinction is obtained, provided that a positive element $\langle a_p(i) | h_i | a_q(i) \rangle$ is associated with a negative S_{pq} and, in agreement with the Mulliken approximation—the matrix element $\langle a_p(i) a_r(j) | e^2 / r_{ij} | a_q(i) a_s(j) \rangle$ has the same sign as the overlap integral product $S_{pq} S_{rs}$.[†] To implement these arguments in the total energy expression (6) the summation over all the permutations is split up into two parts, the sum Σ' which pertains to the permutations (i) and (ii) and the sum over the two cyclic permutations.

We substitute:

$$U_i = \sum_P \langle P u | H | u \rangle \epsilon_P \langle P \chi | \chi \rangle \quad (8)$$

$$S_i = \sum_P \langle P u | u \rangle \epsilon_P \langle P \chi | \chi \rangle \quad (9)$$

The index i refers to the fact that these expressions are independent of the occurrence of negative overlap integrals. We denote the cyclic permutations by C and we assume that there are ν negative overlap integrals.

$$\langle C u | H | u \rangle = (-1)^\nu U_c \quad (10)$$

$$\langle C u | u \rangle = (-1)^\nu S_c \quad (11)$$

Here $U_c < 0$ and $S_c > 0$ are introduced as the result of the application of either one or the other cyclic permutation. With these substitutions the energy becomes:

$$U = \frac{U_i + (-1)^\nu \cdot 2 U_c \cdot \epsilon_c \langle C \chi | \chi \rangle}{S_i + (-1)^\nu \cdot 2 S_c \cdot \epsilon_c \langle C \chi | \chi \rangle} \quad (12)$$

We now examine the effect of the cyclic permutations on the spin functions.

$$\chi_A = [12][34] \cdots [2n-1 2n] \quad (13)$$

$$\chi_B = [12n][2n-1 2n-2] \cdots [32] \quad (14)$$

Evidently:

$$C \chi_A = (-1)^\nu \chi_B \quad \text{and} \quad C \chi_B = (-1)^\nu \chi_A \quad (15)$$

This yields:

$$\begin{aligned} C \chi^+ &= C \chi_{A+B} = (-1)^\nu \chi^+ \quad \text{and} \\ C \chi^- &= C \chi_{A-B} = -(-1)^\nu \chi^- \end{aligned} \quad (16)$$

[†] A general discussion of matrix elements between antisymmetrized products of non-orthogonal basis orbitals has been given by Prossor and Hagstrom.⁴

For a cyclic permutation of order $2n$ one has $\epsilon_e = -1$ and thus one obtains the final energy expression:

$$U^{\mp} = \frac{U_i^{\mp} \pm (-1)^{n+\nu} \cdot 2U_c^{\mp}}{S_i^{\mp} \pm (-1)^{n+\nu} \cdot 2S_c^{\mp}} \quad (17)$$

It may be of interest to remark that χ_{A+B} and χ_{A-B} are eigenfunctions of the operator C , which commutes with H . Therefore if the spinfunctions χ_A and χ_B would not suffice to describe the transition state but other spin functions should be added—like Dewar structures in benzene—these can only combine if they belong to the same eigenvalue of $C: \pm 1$. The form of (17) would in that case not be changed.

As has been discussed in the preceding communication,³ equation (17) demonstrates the combined influence of the

number n of electron pairs and the number ν of negative overlap integrals on the energy of the transition state in a concerted reaction. From the point of view of the application of the VB method it is most interesting that this result could only be obtained including permutations of the highest order.

Concerning the neglect of ionic structures, their effect can be included to a large extent in the covalent structures by means of a transformation of the atomic orbitals before the construction of the structure wave-functions. The transformation should be such as to cause a heavier non-orthogonality between neighbouring orbitals without increasing the non-orthogonality between non-neighbours. One possibility is a basis \mathbf{a}' obtained by operating with the matrix \mathbf{S}^{\dagger} on the original atomic orbital basis.^{1b}

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³ J. J. C. Mulder and L. J. Oosterhoff, preceding communication.

⁴ F. Prosser and S. Hagstrom, *Internat. J. Quantum Chem.*, 1968, **2**, 89.

THE ELECTRONIC STRUCTURE AND STABILITY OF CH_5^+ AND CH_5^-

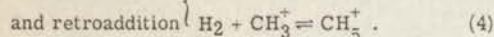
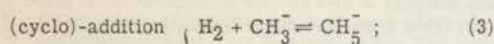
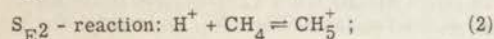
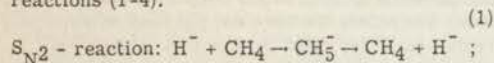
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Geometry-optimized minimum basis set STO calculations are given for the CH_5^+ and CH_5^- ions, together with double ζ -STO results at the computed minima, which give the lowest energies yet reported for the ions. An interpretation in terms of electron pairs is given for the relative stabilities of the various structures.

The ions CH_5^+ and CH_5^- , of which the former has been observed [1,2] can be considered suitable model systems for a number of well-known reactions (1-4).



Both ions have been the subject of previous theoretical studies [3-11], but the results have been contradictory and the interpretation far from complete*. Only in the course of writing the manuscript did we learn that van der Lugt and Ros [14] had independently treated the same problem using a gaussian basis. It appears that their results are very similar to ours (which we feel is encouraging, since the different methods and workers are finally converging on the same result) but there are some differences in interpretation.

Our calculations were performed using a Slater-orbital SCF program written by Dr. R. M. Stevens of Harvard University**. The program

* Two very recent contributions [12,13] have not lead us to reconsider this opinion.

** The authors would like to express their appreciation to Dr. Stevens, who kindly supplied his program to C. E. C. A. M. All calculations were performed at the C.I.R.C.E. computation center, Faculté des Sciences, Orsay.

makes efficient use of molecular symmetry to reduce integral evaluation times, and is discussed in a recent article by Switkes et al. [15]. In the minimal basis calculations a fixed set of carbon exponents was used: $1s = 5.68$, $2s$ and $2p = 1.75$. Hydrogen exponents were allowed to vary. In the search for a minimum energy geometry the variations were taken in the sequence: bond angles, bond distances, hydrogen exponents. In some cases it was necessary to pass through the sequence twice to obtain stable results. Once the optimum single- ζ geometries were found, double- ζ calculations for all exponents were carried out at these minima. To obtain the double- ζ exponents, single- ζ exponents were multiplied by 1.2 and 0.8. This gives a ratio of $\frac{2}{3}$ between the two double- ζ exponents, and corresponds roughly to the best atom double-basis set of Clementi [16]. (See also Rubenstein and Shavitt [17] who suggest this ratio for hydrogen exponents in H_4 .)

In table 1 the SCF energies of some important reactant molecules are given.

Regarding the ions CH_5^+ and CH_5^- we also considered the reversed geometries. With equal bond lengths for the two geometries the following energy differences were found:

$$\text{CH}_5^+ : E_{\text{plan}} - E_{\text{tetr}} = -30.7 \text{ kcal} ;$$

$$\text{CH}_5^- : E_{\text{tetr}} - E_{\text{plan}} = -27.5 \text{ kcal} .$$

We now turn our attention to the calculations of CH_5^+ and CH_5^- . Three main geometries were considered, the same as have been suggested previously. (See van der Lugt and Ros [14] for atom numbering.)

Table 1
Energies and geometries for some reactant molecules. Distances and energies in the tables are expressed in atomic units (0.529 Å and 27.2 eV)

System	Exponent	Geometry	Energy		HF-limit [11]
			single- ζ	double- ζ	
H^-	$1s_{\text{H}} = 0.7$		- 0.4725	- 0.4773 a)	- 0.473
H_2	$1s_{\text{H}} = 1.2$	$R_{\text{HH}} = 1.4$	- 1.1281	- 1.1283 b)	- 1.134
CH_4	$1s_{\text{H}} = 1.2$	tetrahedral $R_{\text{CH}} = 2.066$	-40.127	-40.180	-40.23
CH_3^+	$1s_{\text{H}} = 1.31$	planar $R_{\text{CH}} = 2.066$	-39.178	-39.212	
CH_3^-	$1s_{\text{H}} = 1.03$	tetrahedral $R_{\text{CH}} = 2.236$	-39.264	-39.409	

a) with 0.60 and 0.90 as exponents.

b) with 0.90 and 1.20 as exponents.

Of the three symmetry types C_s , D_{3h} and C_{4v} , the C_s symmetry needs further discussion. C_s symmetry is present only if the H_1CH_2 plane also contains either H_3 , H_4 or H_5 , or is orthogonal to a plane that contains any one of these hydrogen atoms and the vertical axis. But trial calculations showed that for a H_1CH_2 angle of 90° or less, there is free rotation of the CH_2 group relative to the three pyramidal hydrogens. Since the CH_2 angle which gives lowest energy is smaller than 90° , the only restriction we adopt is that H_1 and H_2 are equidistant from the vertical axis through the carbon atom. We also considered briefly a fourth symmetry type, C_{3v} , with a proton or hydride ion approaching methane along a C-H bond axis. This same geometry has been discus-

sed by Ritchie and King [11] for CH_5^- , who found a shallow minimum at a rather large H-H distance. In our calculations we also found this minimum but it disappeared when the hydrogen exponents were optimized for each interatomic distance. Therefore we have not pursued calculations in this symmetry, and believe that conclusions will follow simply from a comparison of the energies of the reactants $\text{CH}_4 + \text{H}^-$, and products $\text{CH}_3^- + \text{H}_2$.

In table 2 we give our results for the optimized geometry, hydrogen exponents, and energies for the CH_5^+ ion, and also the results of van der Lugt and Ros [14] for comparison. (We choose their results for comparison because their gaussian study is the only geometry-optimized ab initio

Table 2
Geometries, hydrogen exponents and energies for CH_5^+

	This work			Ref. [14]		
	C_s	D_{3h}	C_{4v}	C_s	D_{3h}	C_{4v}
Distance CH_1 (au)	2.294	2.104	2.127	2.21	2.13	2.14
Distance CH_3 (au)	2.066	2.084	2.019	2.08	2.11	2.03
Angle H_1CH_2 (degrees)	60.0		80.0	58		82
Angle H_4CH_3 (degrees)	109.5			108		
H_1 exponent	1.29	1.32	1.26			
H_3 exponent	1.26	1.25	1.26			
$E_{\text{tot}}(\text{au})$ single- ζ a)	- 40.310	-40.308	-40.314	- 40.290	-40.284	-40.289
$E_{\text{tot}}(\text{au})$ double- ζ	- 40.356	-40.355	-40.360			
$E_{\text{rel}}(\text{kcal/mole})$	2.5	3.1	0.0	0.0	3.5	0.3

a) For ref. [14], these are GTO results.

search yet reported.) Table 3 presents results for the CH_5^- ion, in a similar format.

Although we do not list orbital energies here, the calculations for CH_5^- show a familiar defect of minimum basis sets—the highest occupied orbital is *positive* in all three symmetries.* Doubling the basis set eliminates this defect, but the highest occupied orbital remains only very weakly bound (e.g. $\epsilon_6 = -0.56$ eV in the D_{3h} structure).

Inspection of tables 2 and 3 shows that our minimum basis set energies correspond closely to the GTO results of van der Lugt and Ros [14]. The geometries are quite similar for CH_5^- , but differ somewhat for CH_5^+ .# The minimum basis set energies lie slightly below the GTO energies, whereas the double- ζ basis set energies are

* See, for example, R. Bonnacorsi et al. [18], who find this result for N_2^- , NCO^- , and NO_2^- in a minimum basis set. Their double- ζ basis set result for NO_2^- , however, shows a negative orbital energy which, using Koopman's theorem, is in good agreement with experiment. Even so, the general question of the usefulness of the Hartree-Fock representation of negative ions is an important one and cannot be ignored. Negatively charged atoms are particularly unsatisfactory in the HF approximation, since the outer electron is almost unbound and can only be properly described by including excited state or even continuum contributions to the wave function [19,20]. The problem is less serious in the case of polyatomic molecules and in exploratory calculations we found no significant CI effect with configurations containing a Rydberg-type 3s orbital on carbon.

Accuracy in the finally obtained geometries: angles $\pm 2^\circ$, distances ± 0.005 au, hydrogen exponents ± 0.05 .

0.06–0.08 au lower, and represent the lowest energies yet reported for these structures. We verify the GTO results insofar as there is very little distinction between structures for CH_5^- , whereas the D_{3h} structure is much preferred for CH_5^+ .

A qualitative explanation for the relative stabilities can be found by considering the following model. The D_{3h} configuration is constructed as a combination of a planar CH_3^+ and a linear arrangement of two $(1s)_\text{H}$ orbitals and the $(2p_z)$ carbon orbital. The C_s configuration is considered as a pyramidal CH_3^+ and a triangular arrangement of two $(1s)_\text{H}$ orbitals and the hybrid carbon orbital (see fig. 1).

We previously found the CH_3^+ structure to be 31.7 kcal/mole more stable in the planar than in the tetrahedral form, which should represent an upper limit for the contribution from this source. Now the inherent differences in stability between a linear and a triangular three orbital system, as a function of the number of electrons present, are well known [11,21]. For the CH_5^+ cation, the D_{3h} structure contains a planar CH_3^+ group (favourable) and a linear 3-center bond containing two

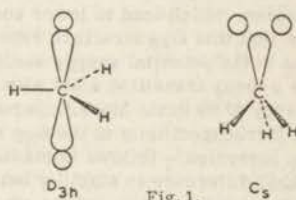


Fig. 1.

Table 3
Geometries, hydrogen exponents and energies for CH_5^-

	This work			Ref. [14]		
	C_s	D_{3h}	C_{4v}	C_s	D_{3h}	C_{4v}
Distance CH_1 (au)	3.388	3.079	2.547	2.92	3.28	2.48
Distance CH_5 (au)	2.100	2.143	2.107	2.10	2.03	2.05
Angle H_1CH_2 (degrees)	83.5		86.0	83		86
Angle H_4CH_5 (degrees)	104.0			102		
H_1 exponent	0.80	0.79	0.92			
H_5 exponent	1.09	1.15	1.09			
E_{tot} (au) single- ζ a)	-40.382	-40.479	-40.363	-40.375	-40.466	-40.379
E_{tot} (au) double- ζ	-40.459	-40.546	-40.459			
E_{rel} (kcal/mole)	54.5	0.0	54.5	56.8	0.0	54.3

a) For ref. [14], these are GTO results.

electrons (unfavourable). The C_s structure contains a pyramidal CH_3^+ group (unfavourable) and a triangular 3-orbital 2-electron bond (favourable). The C_{4v} structure is an intermediate case. Thus there is no clear preference and the structures have similar energies. For CH_5^- , however, the D_{3h} structure has a planar CH_3^+ group (favourable) and a linear 3-orbital 4-electron system (favourable), whereas the C_s structure is unfavourable in both respects. Since the C_{4v} structure is an intermediate case, the D_{3h} structure is seen to be clearly preferred.

We now discuss the reactions (1)-(4) mentioned earlier, neglecting in all comparisons the possible effect of changes in zero-point energy in the transition state or intermediate.

For the S_{N2} reaction (1), the energy of the reactants at infinite distance is calculated from table 1:

$$E(CH_4 + H^-) = -40.657 \text{ au.}$$

This energy is to be compared with the lowest CH_5^- energy found in the double- ζ calculation of the D_{3h} configuration:

$$E(CH_5^-) = -40.546 \text{ au.}$$

By means of calculations with unequal CH_1 and CH_2 distances, which lead to lower energies, we could show that this D_{3h} structure represents a saddle-point in the potential energy surface. Thus we have a clear transition state with an activation energy of 69 kcal. More important, however, the stereospecificity of the S_{N2} reaction - Walden inversion - follows immediately from the 55 kcal difference in stability between the favoured D_{3h} configuration and the other geometries.

For the S_{E2} reaction (2), the small energy differences between the possible CH_5^- geometries demonstrate that in this case no reliable prediction can be made regarding a retention or inversion mechanism. The proton affinity of methane in vacuo is calculated to be:

$$E(CH_5^+) - E(CH_4) = -40.360 + 40.180 = -0.18 \text{ au} = -4.9 \text{ eV.}$$

The experimental value is estimated to lie between -4.95 and -5.53 eV [5].

Using the HF-limit energy for H_2 we calculate:

$$E(CH_3^- + H_2) = -40.543 \text{ au};$$

$$E(CH_3^+ + H_2) = -40.346 \text{ au.}$$

These results show that although CH_5^- would not be expected to be stable with respect to the retroaddition (4), the cation CH_5^+ is about 9 kcal

more stable than the reactants. To our knowledge no experimental information is available to check this result. We mention these reactions because a connection can be established between the stereospecificity of the cycloaddition reactions - explained by Woodward-Hoffmann rules [22,23] - and the unique inversion in the S_{N2} reactions and the expected retention in S_{E2} reactions. The addition of hydrogen to CH_3^- should proceed using a transition state of the type $\sigma[2]_s + \omega[2]_a$ which is a deformed D_{3h} configuration with hydrogens 1 and 2 moved to one side and towards each other. On the other hand the reaction of CH_3^+ and H_2 would use a C_s -structure type transition state with the characteristics $\sigma[2]_s + \omega[0]_s$. In both cases we have an allowed process.

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The first part of the book deals with the early years of the Republic, from the signing of the Constitution in 1787 to the end of the War of 1812. It covers the presidencies of George Washington, John Adams, and James Madison, and the development of the federal government and the states.

The second part of the book covers the period from 1812 to 1845, including the presidencies of James Monroe, James Madison, and James K. Polk. It discusses the War of 1812, the Louisiana Purchase, and the expansion of the United States into the West.

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SAMENVATTING

In dit proefschrift zijn een aantal theoretische onderzoeken beschreven over chemische structuur en reacties. Het eigenlijke onderzoek waarvan de resultaten zijn neergelegd in een viertal publicaties die hier opnieuw zijn afgedrukt, bestaat uit drie duidelijk gescheiden onderdelen. Ten eerste is een studie gemaakt van het enumeratieprobleem dat optreedt wanneer men een aantal electronen verdeelt over een aantal orbitals teneinde electronische configuraties te construeren. Beperkende voorwaarden zijn het Pauli-principe - maximaal twee electronen per orbital - en eventueel de verlangde multipliciteit van de electronische configuratie. In de tweede plaats is met behulp van de valence bond methode een analyse gemaakt van de bindingssituatie die optreedt in de overgangstoestand van pericyclische reacties. Deze reacties zijn gekenmerkt door een synchroon verbreken van aanwezige bindingen en vormen van nieuwe bindingen in de betrokken moleculen, waarbij de overgangstoestand gekarakteriseerd wordt door een cyclus van half gevormde en verbroken bindingen. Tenslotte is getracht door middel van gedetailleerde berekeningen van het ab-initio self consistent field molecular orbital type een inzicht te verkrijgen in de potentiële energie oppervlakken van de grondtoestand bij een aantal eenvoudige model reacties, te weten additie reacties en nucleophile en electrophiele substitutie reacties.

De vier publicaties worden voorafgegaan door een - tamelijk uitvoerige - inleiding, waarin een overzicht wordt gegeven van enige aspecten van de quantumchemische theorie, valence bond tegenover molecular orbital, en ab-initio versus semi-empirisch, vooral in verband met de toepassing voor chemische reacties. Hierbij is in het bijzonder ook aandacht geschonken aan fotochemische reacties die tegenwoordig zowel te Leiden als elders in het centrum van de belangstelling staan. Voorts is in de inleiding een poging gedaan, duidelijk te maken welke relaties er bestaan tussen de op het oog

zeer verschillende onderwerpen hierboven genoemd.

Bij de classificatie van elektronische configuraties bleek het mogelijk tot gesloten uitdrukkingen te komen voor de totale aantallen als functie van het aantal elektronen en orbitals. Zulks was eveneens mogelijk voor sub-totalen van diverse categorieën van elektronische configuraties wanneer als verdelingsmethode het formalisme van de valence bond theorie werd gebruikt. Geen eenvoudige uitdrukkingen konden worden verkregen wanneer gebruik werd gemaakt van het classificatie criterium gangbaar in de molecular orbital methode. Kortweg gezegd komt het er op neer dat men wel een eenvoudige uitdrukking vindt voor het aantal r-voudig ionogene structuren, maar niet voor het aantal i-voudig aangeslagen configuraties.

Wanneer men het experimentele feitenmateriaal over de pericyclische reacties overziet, valt het op dat deze reacties in het algemeen over twee reactiewegen beschikken, waarvan de stereochemische implicaties voor de te vormen producten duidelijk verschillend zijn. Bovendien kunnen de reacties vaak zowel thermisch als fotochemisch gerealiseerd worden, waarbij de gevolgde paden tegengesteld zijn. Het blijkt dat naast deze reactieomstandigheden het aantal elektronenparen dat aan de reactie deelneemt beslissend is voor de te volgen weg. Naast anderen hebben vooral Woodward en Hoffmann met behulp van molecular orbital beschouwingen een theoretische interpretatie van deze verschijnselen gegeven, welke heeft geleid tot een selectieregel die alle thermische reacties van dit type beschrijft. Aanduidingen konden worden gevonden dat de fotochemische reacties tegengesteld moeten verlopen. Richtlijn bij deze processen zou het behoud van de symmetrie van de individuele molecular orbitals zijn, tijdens het verloop van de reactie. Door middel van een valence bond analyse van de energie van de overgangstoestand, waarbij de twee "Kekulé" structuren voor de bindingscyclus werden betrokken, kon nu niet alleen direct de selectieregel voor de thermische reacties worden verkregen, maar volgde bovendien het tegengestelde verloop van de fotochemische reacties automatisch. Opvallend is dat de energiever-schillen in de overgangstoestand resulteren uit de bijdragen van de twee cyclische permutaties van de electronennummers van de hoogste orde; ieder electron schuift naar de volgende beschikbare atomic orbital in de cyclus. De analyse heeft, zoals besproken is in de inleiding, consequenties voor het voorspellen van eventuele uitzonderingen op de selectieregel, maar ook voor de behandeling van het begrip aromaticiteit in cyclische polyenen. In dit verband is ingegaan op de stabiliteit van recent verkregen cyclobutadien deri-

vaten. Tenslotte lijkt het mogelijk om de experimenteel gevonden omkering in reactiviteit van de meta-positie in thermische en fotochemische substitutie reacties van benzeenderivaten op een vergelijkbare wijze te verklaren als dit het geval was bij de pericyclische reacties.

De belangrijkste karaktertrek van de pericyclische reacties is ongetwijfeld hun stereospecificiteit. Deze eigenschap is ook aanwezig in de bimoleculaire nucleophile substitutie reactie aan het verzadigde koolstofatoom, en staat bekend als de Walden inversie. De theoretische behandeling van deze reactie aan de hand van een modelsysteem bestaande uit het molecuule methaan en een hydride-ion neemt een centrale plaats in bij de ab-initio SCF-MO berekeningen. De overgangstoestand voor dit type reactie heeft een trigonale symmetrie en blijkt meer dan 50 kcal/Mol stabiel te zijn dan mogelijke overgangstoestanden met een andere geometrie. Bij de reactie van een proton met methaan is een dergelijke voorkeur voor één bepaalde geometrie niet aanwezig, zodat de gevolgtrekking gemaakt kan worden dat in S_E2 -reacties geen uitgesproken stereospecificiteit te verwachten is. Een ander belangrijk verschil tussen de twee reacties is het optreden van een intermediair CH_5^+ tegenover een CH_5^- transition state. Gezien vanuit het standpunt van de cyclo-additie reacties $H_2 + CH_3^+$ of CH_3^- blijken de gevonden geometrieën te corresponderen met een suprafaciale overgangstoestand voor het twee-electronen probleem en een antarafaciale overgangstoestand voor het vier-electronen probleem. Dit is geheel in overeenstemming met de selectieregel voor deze reacties. De ab-initio berekeningen werden uitgevoerd met een minimum basis van Slater atomic orbitals, en de optimale structuur werd steeds gevonden door variatie van valentiehoeken, bindingsafstanden en exponenten van de waterstof 1s orbitals. De resultaten werden tenslotte verfijnd en gecontroleerd door bij de optimale geometrie "double ζ " berekeningen uit te voeren. Het is echter de interpretatie van de resultaten van de berekeningen in termen van de aantallen elektronen in een lineair respectievelijk driehoekig drie-orbital systeem, waardoor nieuw inzicht wordt gewonnen.

Het theoretisch onderzoek, neergelegd in dit proefschrift, geeft aanleiding de verwachting uit te spreken, dat door een juiste combinatie van analyse van kwalitatieve aspecten en expliciete berekeningen bij aanwezigheid van specifiek lineaire of cyclische bindingssituaties, de quantumchemische theorie in de naaste toekomst ook in het gebied van de chemische reacties belangrijke bijdragen zal kunnen leveren.

Volgens het gebruik in de Faculteit der Wiskunde en Natuurwetenschappen volgt hier een overzicht van mijn academische studie.

Nadat ik in juni 1952 het eindexamen gymnasium B had behaald aan het Tweede Vrijzinnig Christelijk Lyceum te Den Haag, werd in september van dat jaar een aanvang gemaakt met de studie in de scheikunde aan de Rijksuniversiteit te Leiden. Het candidaatsexamen chemie, letter f, werd afgelegd in mei 1956, waarna de studie werd voortgezet onder leiding van de hoogleraren Dr. E. Havinga, Dr. L.J. Oosterhoff en Dr. H. Veldstra. Deze periode werd afgesloten met het doctoraalexamen met hoofdvak organische chemie in juli 1959.

Van september 1959 tot maart 1961 vervulde ik mijn dienstplicht bij de Koninklijke Luchtmacht. Na terugkeer te Leiden werd op de afdeling Theoretische Organische Chemie onder leiding van Prof. Dr. L.J. Oosterhoff begonnen met onderzoekingen in het gebied van de quantumchemie, welke tot dit proefschrift hebben geleid.

Tot november 1961 was ik als doctoraalassistent in dienst van ZWO. Gedurende deze periode werd onderzoek verricht aan molecuulverbindingen van het ladingsoverdrachts-type. Vervolgens kwam ik in dienst van de Universiteit, tot april 1962 als doctoraalassistent, waarna aanstelling als wetenschappelijk ambtenaar volgde. In april 1964 werd ik bevorderd tot wetenschappelijk ambtenaar 1e klasse, welke rang later is omgezet tot wetenschappelijk medewerker 1e klasse, de hoedanigheid waarin ik thans werkzaam ben. Van 1962 tot en met 1964 werkte ik samen met Dr. W.Th.A.M. van der Lugt aan de programmering van quantumchemische problemen voor elektronische rekenmachines waarvan de eerste in april 1962 aan de Universiteit werd geïnstalleerd. Deels om ervaring op te doen bij de parameterkeuze voor semi-empirische berekeningen en de programma's te testen, en voorts als ondersteuning van experimenteel werk op de afdelingen Organische Chemie en Theoretische Organische Chemie werden een groot aantal berekeningen uitgevoerd van het Pariser-Parr-Pople type aan gesubstitueerde aromatische verbindingen. In 1965 werd een aanvang gemaakt met het onderzoek waarvan de resultaten in dit proefschrift zijn neergelegd.

Mijn onderwijstaak gedurende deze jaren heeft bestaan in het voorbereiden en afnemen van de tentamens "Atoomtheorie en Chemische Binding" voor tweede jaars scheikunde studenten. Enkele malen gaf ik voor korte tijd het betreffende college. Sedert enige tijd verzorg ik een college Chemische Binding voor eerste jaars natuurkunde studenten die scheikunde als bijvak

voor hun candidaatsexamen hebben gekozen.

Naast mijn werkzaamheden aan de Universiteit ben ik steeds voor een beperkt aantal uren verbonden geweest als leraar scheikunde aan het Eerste Vrijzinnig Christelijk Lyceum te Den Haag.

De altijd aanwezige bereidheid bij de medewerkers van de afdeling Theoretische Organische Chemie om de resultaten van elkaars werk kritisch te bezien is van grote invloed geweest op de ontwikkeling van dit proefschrift.

Mevrouw G. Gerritsen-de Vries verleende steun bij de programmering en de uitvoering van een aantal berekeningen.

De medewerking die ik heb mogen ondervinden van Rector en collegae van het Eerste Vrijzinnig Christelijk Lyceum bij het verdelen van mijn werkzaamheden heb ik altijd op hoge prijs gesteld.

De directies van de tijdschriften dank ik voor de verleende toestemming om de artikelen hier opnieuw af te drukken.

De heer M. Pison verzorgde de tekeningen.

De mogelijkheden mij door subsidies van de Universiteit en ZWO geboden om enkele malen in het buitenland symposia te bezoeken, cursussen te volgen en in één geval geruime tijd wetenschappelijk werk te verrichten, zijn een sterke stimulans bij mijn onderzoek geweest. Deze mentale injecties hebben de inhoud van dit proefschrift op beslissende wijze beïnvloed.

The first part of the book is devoted to a general introduction to the subject of the history of the English language. The author discusses the various factors which have influenced the development of the language, such as the influence of other languages, the process of borrowing, and the changes in pronunciation and grammar. He also touches upon the role of literature and the spoken language in the evolution of the language.

The second part of the book is a detailed study of the Old English period, from the fifth to the eleventh century. The author examines the Old English language in its various forms, including the Anglo-Saxon dialects and the influence of Old Norse. He discusses the Old English literature, such as the Anglo-Saxon Chronicle and the works of Caedmon and Chaucer, and the changes in the language during this period.

The third part of the book is a study of the Middle English period, from the thirteenth to the fifteenth century. The author discusses the influence of French and Latin on the English language, the development of the Middle English dialects, and the Middle English literature, such as the works of Chaucer and the Pastoral of John Wycliffe.

The fourth part of the book is a study of the Modern English period, from the sixteenth to the present. The author discusses the influence of Latin and French on the English language, the development of the Modern English dialects, and the Modern English literature, such as the works of Shakespeare and the English novel.

The book is written in a clear and concise style, and is suitable for students of English literature and language. It provides a comprehensive overview of the history of the English language, and is a valuable resource for anyone interested in the subject.

