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Extension of Walsh's Rules to More General Systems*

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It is demonstrated that location of hydrogen atoms within bonding distance of a simple triatomic molecule can alter the order of energy levels relative to that of the parent system without significantly changing the behavior of the orbital energies under geometrical variation. As a result the ground state electronic configurations of H_nAB_2 systems often differ from those of triatomics with the same number of electrons and this fact is shown to be directly responsible for the existence of such distinctive geometrical structures as those possessed by cyclopropane, cyclopropyl and allyl cations and cyclopropene. Thus the familiar prescription of Walsh's rules which states that isoelectronic molecules possess identical geometries is seen to be valid only if the systems in question possess the same electronic configuration; in reality it may be an excited state of one system which has the same geometry as the ground state of another and *vice versa*. It is concluded that the methodology of Walsh's rules can be extended to a much larger class of systems than heretofore assumed simply by taking explicit account of the predictable effects of hydrogen addition upon the electronic configuration and hence on the skeletal arrangement of the heavy nuclei.

Es wird gezeigt, daß in Bindungsnähe eines dreiatomigen Moleküls befindliche Wasserstoffatome die Reihenfolge der ursprünglichen Energieniveaus im System ändern können, ohne dabei das Verhalten der Orbitalenergien hinsichtlich geometrischer Veränderungen erheblich zu beeinflussen. Als Folge davon unterscheidet sich die Grundzustands-Elektronenkonfiguration eines H_nAB_2 Systems oft von der entsprechenden der dreiatomigen Moleküle mit gleicher Elektronenzahl, und es läßt sich zeigen, daß diese Tatsache für das Auftreten der besonderen geometrischen Strukturen von Cyclopropan, Cyclopropyl- und Allyl-Kation oder Cyclopropen unmittelbar verantwortlich ist. Die übliche Anwendungsweise der Walshschen Regeln, nach der iso-elektronische Moleküle gleiche Geometrien haben, ist also nur gültig, wenn die entsprechenden Systeme in der gleichen Elektronenkonfiguration auftreten; in Wirklichkeit kann es vorkommen, daß der angeregte Zustand eines Systems die gleiche Geometrie hat wie der Grundzustand eines anderen und umgekehrt. Es zeigt sich dann, daß das Verfahren der Walshschen Regeln auf eine viel größere Klasse von Systemen ausgedehnt werden kann als bisher angenommen wurde, wenn man die vorhersagbaren Wirkungen, welche die Wasserstoffanlagerung auf die Elektronenkonfiguration und damit auf das Kerngerüst der schwereren Atome hat, direkt berücksichtigt.

1. Introduction

The basis for the MO description of molecular geometry is embodied in a series of principles known collectively as Walsh's rules [1, 2]. Although often more complicated to apply in a specific case than the methodology of valence bond theory, these empirical prescriptions have the distinct advantage of being

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* Dedicated to the memory of Prof. K. H. Hansen.

equally applicable to both ground and excited states of molecules. The basic unit in this theory is the correlation diagram, essentially a plot of valence orbital energies as a function of some geometrical variable; the implicit assumption is made that the same diagram is applicable to all systems within a given class, which is to say: a) that the shapes of corresponding orbital energy curves are identical and b) that the stability ordering is also unchanged from one system to another within this class[1]. Originally the details of the various correlation diagrams were worked out by Mulliken [1] and Walsh [2] on the basis of empirical data and certain conclusions relative to the bonding or antibonding character of MO's derivable from symmetry considerations. In the meantime it has been demonstrated that these correlation diagrams can in principle be calculated using self-consistent field theory [3–5].

Irrespective of the method with which the necessary data are obtained, however, the most serious drawback to this general theory, aside from the relatively complicated manner in which it is applied, is the fact that apparently the families of molecules describable in terms of a given correlation diagram are relatively small and at present confined to fairly simple types of systems such as AH_2, AB_2 and HAB species, for example. Obviously enlarging the class of systems to which a given correlation diagram is applicable and thereby extending the scope of the original theory is a quite desirable objective and it is therefore the purpose of the present paper to consider how this possibility can be realized.

2. Possible Extensions of Walsh's Rules

One possible way in which the class of molecules described by a particular correlation diagram could be expanded would be to allow for the addition of an arbitrary number of hydrogen atoms to any member of the original family. For example, one might ask whether all H_nAB_2 systems can be treated on the same footing as AB_2 molecules (where A and B are heavier nuclei than H), whose general correlation diagram is well established. This question can be rephrased in a somewhat different (and not necessarily equivalent) form: do all H_nAB_2 systems which are isoelectronic with a given triatomic species possess the same (or nearly the same) internuclear angle in their respective ground state equilibrium nuclear configuration?

Inspection of a number of typical examples contained in Table 1 shows that there is good reason to look for such a generalization. On the other hand, it is well known, of course, that not every H_nAB_2 system with 22 electrons is linear (as Walsh's rules predict for simple triatomics with a like number of electrons), with cyclopropene (51°), cyclopropyl- ($\approx 80°$) and allyl-cation (120°) obvious counterexamples; nor does every 24-electron species possess a BAB angle in the neighborhood of 120° (for example, cyclopropane, ethylene oxide and ethyleneimine all have much smaller angles of close to 60°). It will therefore clearly be necessary to determine whether the aforementioned counterexamples merely

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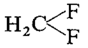
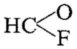
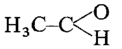
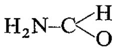
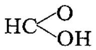
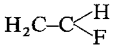
[1] Actually use of the same correlation diagram for two systems implies more than the two relationships given above, namely point for point equality, but it may easily be shown that the results of applying Walsh's rules are unchanged by removing the restriction of equal spacing among the orbital energy curves as long as assumptions a) and b) are valid.

Table 1. Experimental[a] equilibrium angles for various systems with a triatomic skeleton (exclusive of hydrogen atoms); N is the total number of electrons

Molecule		N	Angle	(Degrees)
Dioxyfluoride	F_2O	26	FOF	103.8
Difluoromethane	 $H_2C{<}^{F}_{F}$	26	FCF	108.5
Dimethyl ether	$H_3C{-}O{-}CH_3$	26	COC	111.5
Dimethylamine	$H_3C{-}NH{-}CH_3$	26	CNC	108 ± 4
Ethylamine	$H_3C{-}CH_2{-}NH_2$	26	CCN	110 ± 3
Propane	$H_3C{-}CH_2{-}CH_3$	26	CCC	111.5
Ozone	O_3	24	OOO	116.8
Nitrite ion	NO_2^-	24	ONO	116
Formyl fluoride	 $HC{<}^{O}_{F}$	24	FCO	121.1
Acetaldehyde	 $H_3C{-}C{<}^{O}_{H}$	24	CCO	123.9
Formamide	 $H_2N{-}C{<}^{H}_{O}$	24	NCO	123.6
Formic acid	 $HC{<}^{O}_{OH}$	24	OCO	124.3
Propylene (propene)	$H_3C{-}CH{-}CH_2$	24	CCC	124.8
Vinyl fluoride	 $H_2C{-}C{<}^{H}_{F}$	24	CCF	121
Carbon dioxide	CO_2	22	OCO	180
Nitrous oxide	N_2O	22	NNO	180
Hydrogen azide (ion)	$HN_3(N_3^-)$	22	NNN	180
Cyanamide	$H_2N{-}C{-}N$	22	NCN	180
Diazomethyne	$H_2C{-}N{-}N$	22	CNN	180
Allene	$H_2C{-}C{-}CH_2$	22	CCC	180
Methylacetylene	$HC{-}C{-}CH_3$	22	CCC	180
Ketene	$H_2C{-}C{-}O$	22	CCO	180
Methyl cyanide	$H_3C{-}C{-}N$	22	CCN	180
Methyl isocyanide	$H_3C{-}N{-}C$	22	CNC	180
Borine carbonyl	$H_3B{-}C{-}O$	22	BCO	180
Hydrogen isocyanate	$HN{-}C{-}O$	22	NCO	180

[a] *Tables of interatomic distances and configurations in molecules and ions* (The Chemical Society, London). Spec. Publ. No. 11 (1958) and No. 18 (1965).

represent unusually large numerical discrepancies in the theoretical method or if instead there is a logical extension of the underlying theory which will allow inclusion of these cases in a systematic fashion.

In order to investigate these questions it is necessary to take a closer look at the assumptions, either implicit or explicit, in the application of Walsh's rules in general. In particular it will be helpful to determine how the calculated correlation diagrams of the exceptional systems differ from the more conventional sets of orbital energy curves of apparent general validity for the parent AB_2 molecules.

3. Basis for Walsh's Rules

The underlying basis for Walsh's rules can be summarized in a series of three principles: 1) the valence orbital energies weighted according to occupation are to a good approximation the sole geometry determining factor responsible for the shapes of molecules; 2) altering the nuclear charge of the various atomic centers does not result in any significant changes in the shapes of the valence orbital energy curves in the parent correlation diagram; and 3) such redistribution of the nuclear charge also does not change the order of the various orbital energies. An important corollary of the third point is that the electronic configuration of the molecular ground state is independent of the distribution of nuclear charge.

The first of these principles is generally recognized as the most tenuous even for the simpler systems. The results of non-empirical SCF calculations [3–5] have been used previously to examine the validity of this statement in specific examples and it has been shown that in a few cases other contributions to the total energy such as nuclear and electronic repulsion can significantly influence the shape of the potential surface; this situation arises for triatomic molecules such as Li_2O and LiOH, for example [4], which have strong local centers of positive and negative charge. Nevertheless, none of the H_nAB_2 counterexamples mentioned above would seem to fall into this category any more than do the conventional examples included in Table 1, and thus it seems clear that something more than the effect of other terms in the total energy expression is responsible for the distinctive value of $\sphericalangle$ BAB for these systems.

The question of possible differences between the shapes of corresponding orbital energy curves for AB_2 and H_nAB_2 systems can be answered in a straight-

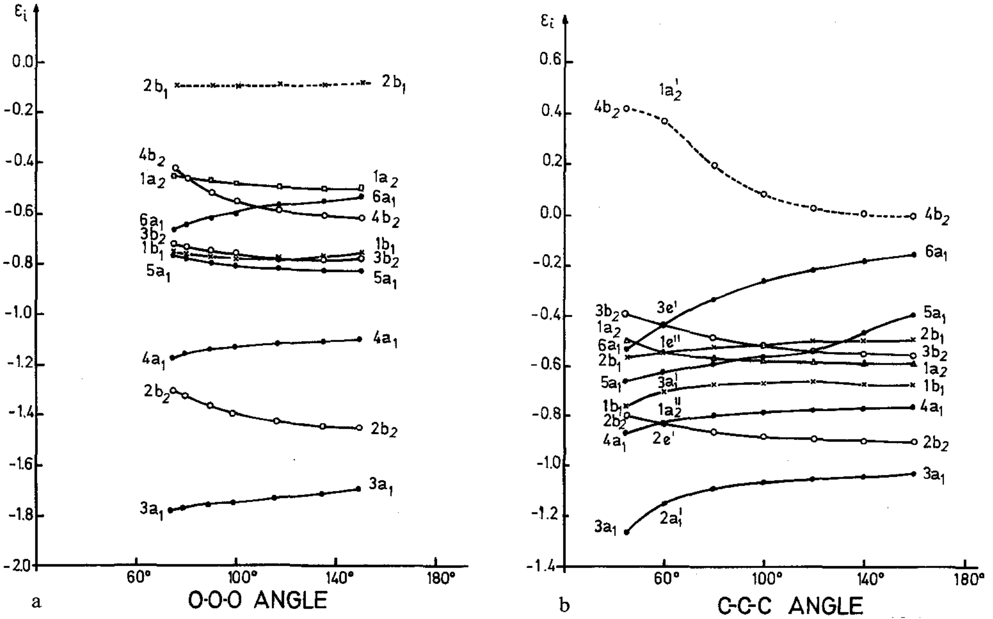


Fig. 1. Correlation diagram for (a) the ground state of ozone and (b) the ground state of cyclopropane. (Energy values are in hartree units)

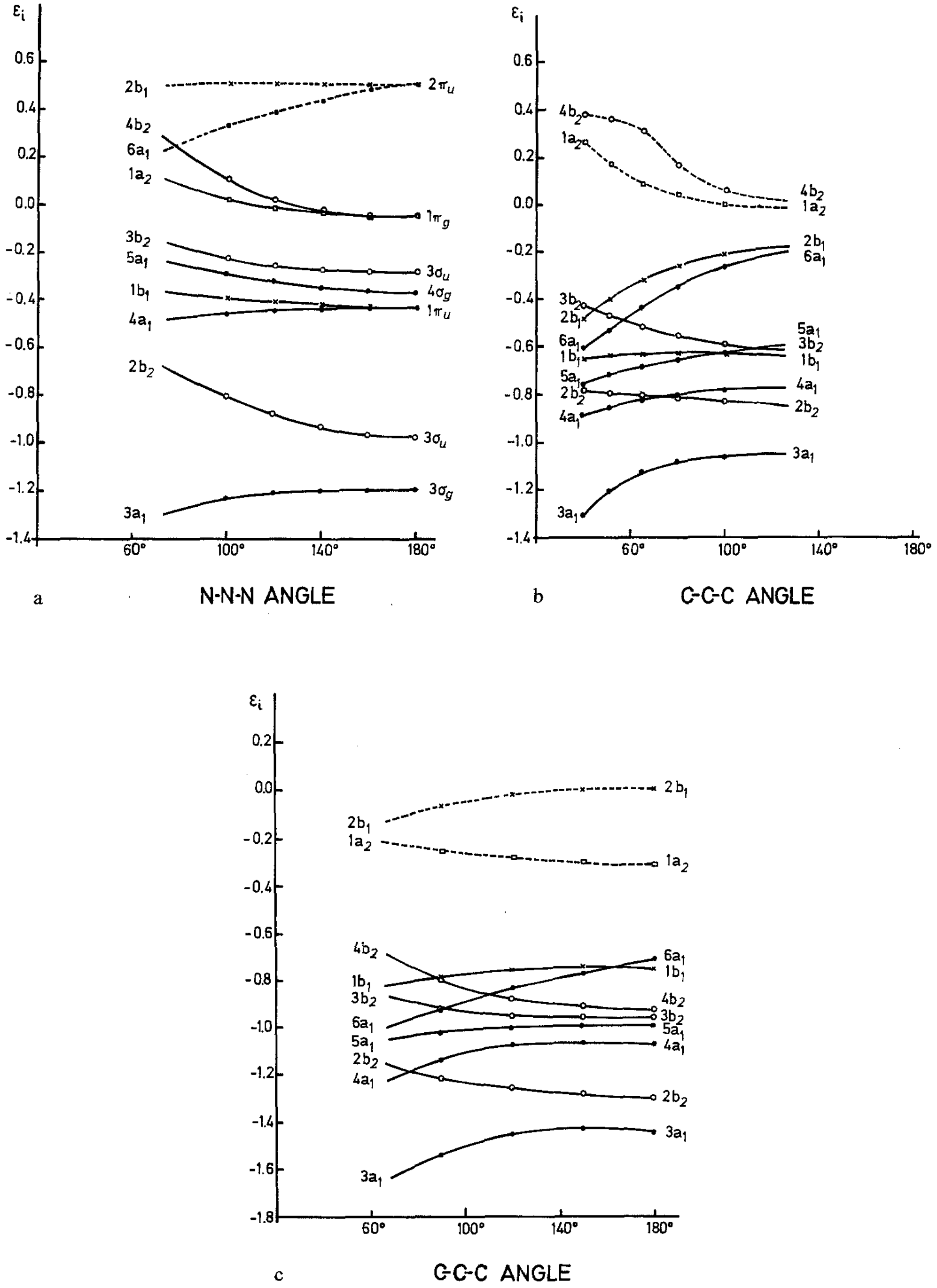


Fig. 2. Correlation diagram for (a) the ground state of N_3^-, (b) the ground state of cyclopropene and (c) the ground state of allyl cation. (Energy values are in hartree units)

forward manner by carrying out SCF calculations for molecules with both typical and unusual geometries from the point of view of Walsh's rules. Comparison of the resulting correlation diagrams for the 24-electron systems ozone [5] and cyclopropane [6] (Figs. 1a, b) shows clearly that with only minor exceptions the variation of orbital energies with $\sphericalangle$ OOO and $\sphericalangle$ CCC respectively follow very much the same pattern; this second principle is seen to be particularly valid for the important upper valence orbital species, $6a_1$, $4b_2$, $1a_2$ and $2b_1$.

Yet the same figures show even more clearly that the third of the aforementioned underlying principles is unquestionably violated in this comparison; in the O_3 ground state configuration the $2b_1$ MO is the least stable of the upper valence orbitals and is thus unoccupied whereas in cyclopropane the highest energy species in this category is the $4b_2$ and is thus left vacant. Similar findings result from SCF calculations for the 22-electron systems azide ion [5] N_3^- (180° equilibrium angle), cyclopropene [7] (51°) and the allyl cation [8] $C_3H_5^+$ (120°), for which only two of the four upper valence species are occupied in their respective ground state electronic configurations. The calculated diagrams for these systems given in Figs. 2a–c show that the two orbitals occupied in each case are: $4b_2$ and $1a_2$ for N_3^-, $6a_1$ and $2b_1$ for cyclopropene, and $6a_1$ and $4b_2$ for

Table 2. Ground state electronic configuration of several hydrocarbons deduced from a group theoretical analysis of their respective valence bond structures

	VB-Description	Occupied MO's			
		a_1	b_2	b_1	a_2
Cyclopropane	3 × 1*s*	2	1		
	3 × CC-bond	2	1		
	2 × CH-bond (central)	1		1	
	4 × CH-bond (terminal)	1	1	1	1
	Total	6	3	2	1
Cyclopropene	3 × 1*s*	2	1		
	3 × CC single bond	2	1		
	π-bond			1	
	2 × CH-bond (central)	1		1	
	2 × CH-bond (terminal)	1	1		
	Total	6	3	2	0
Allyl cation	3 × 1*s*	2	1		
	2 × CC-bond	1	1		
	1 × CN-bond (central)	1			
	4 × CH-bond (terminal)	2	2		
	π-bond			1	
	Total	6	4	1	0
Cyclopropyl cation	3 × 1*s*	2	1		
	3 × CC-bond	2	1		
	1 × CH-bond (central)	1			
	4 × CH-bond (terminal)	1	1	1	1
	Total	6	3	1	1

the allyl cation. In addition one can point to the cyclopropyl cation as a 22-electron system which occupies yet a different pair of upper valence MO's in its ground state, namely the $6a_1$ and $1a_2$ species. Furthermore, an elementary analysis using group theoretical techniques of the VB structures of the various counterexample molecules demonstrates that the calculated MO electronic configurations for these systems are wholly consistent with their valence bond descriptions and in fact easily derivable therefrom without the aid of explicit calculation (Table 2).

The fact remains, however, that the shapes of corresponding orbital energy curves in each of Figs. 1a, b and 2a–c, particularly those of the critical upper valence MO's, are satisfactorily similar, in agreement with the second underlying principle of Walsh's rules. The question thus arises whether the distinctive geometries of systems such as cyclopropane and cyclopropene can be explained consistently in terms of the MO theory simply by modifying the aforementioned third principle to take account of the fact that changes in electronic configuration generally imply alteration of the equilibrium nuclear geometry.

4. Relation between Electronic Configuration and Equilibrium Geometry

If the difference in electronic configuration between an H_nAB_2 molecule possessing an unusual geometry (at least from the standpoint of Walsh's rules) and an isoelectronic member of the parent triatomic family is responsible for the distinction in equilibrium geometry, it should be possible to demonstrate this relationship by carrying out calculations in which one system is forced into the ground state electronic configuration of the *other* and *vice versa.* In order to conveniently discuss the results of these calculations the following notation is introduced: a given electronic configuration is denoted by a quartet (i, j, k, l) where i, j, k and l are the numbers of a_1, b_2, b_1 and a_2 MO's respectively which are *doubly* occupied in this case. If attention is restricted, as will be useful, to those configurations in which only the $6a_1$, $4b_2$, $2b_1$ and $1a_2$ MO's are allowed variable occupation, a total of $\binom{4}{3} = 4$ possible 24-electron configurations and $\binom{4}{2} = 6$

Table 3. Notation for various electronic configurations of 22 and 24 electron molecules, showing respectively the number of doubly occupied a_1, b_2, b_1 and a_2 MO's in each case. The simple integer labels are used to identify these configurations in Figs. 3 and 4

	Label	Electronic configuration
24 electron system	1	(6,4,1,1)
	2	(5,4,2,1)
	3	(6,3,2,1)
	4	(6,4,2,0)
22 electron system	1	(5,4,1,1)
	2	(6,4,1,0)
	3	(5,3,2,1)
	4	(6,3,1,1)
	5	(5,4,2,0)
	6	(6,3,2,0)

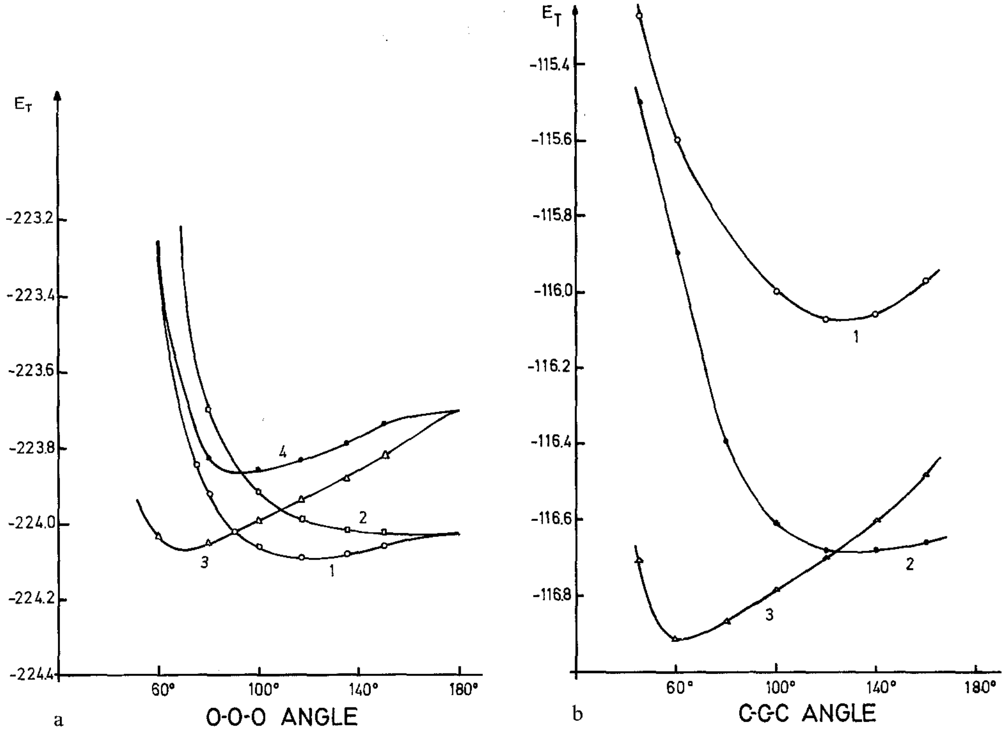


Fig. 3. Angular potential curves for several states of ozone (Fig. a) and cyclopropene (Fig. b). The integer labels for the curves correspond to the electronic configurations given in Table 3. (Energy values are in hartree units)

twentytwo-electron species can be distinguished; the notation used throughout this paper for each of these configurations is given in Table 3.

According to this notation the ground state electronic configuration of ozone is (6,4,1,1) while that of cyclopropane is (6,3,2,1). Potential curves for these and the other two configurations listed in Table 3 are given in Fig. 3a for ozone and from this figure the degree to which electronic configuration determines nuclear geometry is quite apparent; in particular it can be seen that the (6,3,2,1) configuration in ozone is associated with a very small internuclear angle, just as it is in cyclopropane. In other words, what is the ground state electronic configuration of one system corresponds to an excited state of the other; interestingly enough the energy minimum for the "cyclopropane" state of O_3 is calculated to lie only 0.02 hartree (12 kcal/mole) above the absolute potential minimum of its ground state configuration.

Only three of the possible four potential curves of cyclopropane have been obtained (Fig. 3b) but from these results it is clear that the relationship between corresponding states of O_3 and cyclopropane is reciprocal in nature. The ozone ground state configuration (1) corresponds to a very highly excited state of the hydrocarbon, but it still leads to a potential minimum at roughly 120°, the conventional value. The similarity between the potential curves of configuration 2

(Table 3) for each system clearly substantiates the conclusion that the equilibrium geometry of a system is determined to a very large extent by its electronic configuration.

In a completely analogous manner the (6,4,1,0), (6,3,1,1) and (6,3,2,0) excited configurations of N_3^- are seen to correspond to the ground states of the allyl and cyclopropyl cations and cyclopropene respectively; calculated N_3^- potential curves for these SCF states lead to equilibrium angles of 115°, 85° and less than 60° respectively (Fig. 4a), all of which being clearly compatible with the aforementioned ground state equilibrium CCC angles of the hydrocarbons in question. Potential curves for these 22-electron H_nAB_2 molecules (Fig. 4b) further demonstrate the close connection between equilibrium geometry and electronic configuration.

It can therefore be concluded that the conventional AB_2 correlation diagram employed in the application of Walsh's rules can also be used to predict the skeletal geometries of related H_nAB_2 systems as long as it is recognized that the order of orbital energy levels can be altered by the addition of hydrogen atoms; thus it can no longer be simply assumed that isoelectronic molecules possess the same geometries unless they are known to have the same electronic configuration. For simple triatomics it is of course known that the absolute stabilities of the various MO's change upon redistribution of protons among the three centers

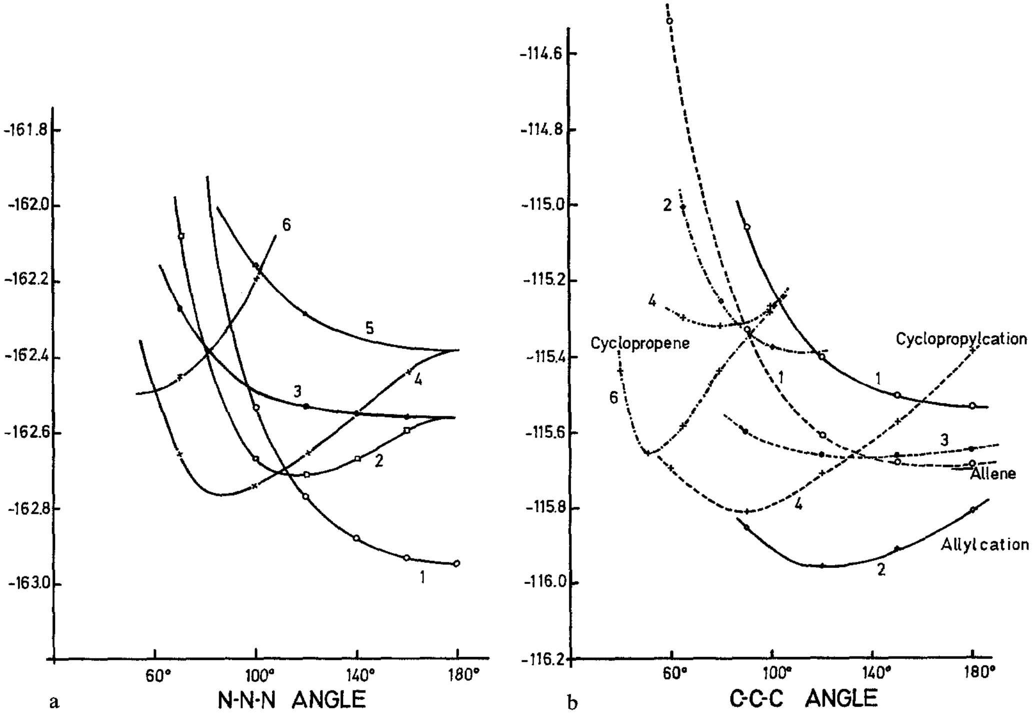


Fig. 4. Angular potential curves for several states of N_3^- (Fig. a) and 22-electron hydrocarbons (Fig. b). The integer labels for the curves correspond to the electronic configurations given in Table 3. (Energy values are in hartree units; dashed lines correspond to cyclopropyl cation states, dotted-dashed lines to cyclopropene and the two solid curves to allyl cation states)

Table 4. Characterization of the uppermost valence orbitals in an AB_2 system

MO		Geometrical trend	Orientation	Charge density maximum[a]
π_u	$6a_1$	Strongly bent	In-plane	Central
	$2b_1$	Bent	Perpendicular	Central
π_g	$1a_2$	Linear	Perpendicular	Terminal
	$4b_2$	Strongly linear	In-plane	Terminal

[a] For typical charge density contour diagrams for these orbitals see for example Ref. [4].

[4, 5, 9] but the subsequent reordering (if any) apparently never leads to a change in the ground state electronic configuration. Nevertheless it is not difficult to understand how such changes in the relative spacing of the energy levels result in substantial differences in the absolute magnitude of corresponding spectral transition energies for isoelectronic species. For example, in ozone the $4b_2$ and $2b_1$ MO's are nearly isoenergetic and this fact leads to the aforementioned proximity of the potential minima for the (6,4,1,1) ground and (6,3,2,1) excited states of this system; increasing the nuclear charge of the end atoms at the expense of the central to give CF_2, however, causes the $4b_2$ to become significantly more stable than the $2b_1$, thereby producing a much larger separation between the corresponding potential minima in this system. This behavior can easily be understood from Table 4, which characterizes the four upper valence MO's according to the location of their respective charge density maxima; increasing the nuclear charge of the terminal atoms obviously adds to the stability of the $4b_2$ while decreasing the charge at the central nucleus has the opposite effect on the $2b_1$.

If the redistribution of protons takes the form of attaching hydrogen atoms to a triatomic skeleton, the changes effected on the various orbital energies can be quite selective. For example, if a pair of hydrogen atoms is situated in the same plane as that containing the three heavy atoms, subsequent mixing of the hydrogen AO's with the orbital of the triatomic parent is understandably more effective for those species whose charge density maxima lie in this plane ($6a_1$ and $4b_2$) than for those which do not (Table 4); similarly the $1a_2$ and $2b_1$ MO's are expected to be selectively stabilized if the hydrogens are located above and below this plane respectively. With these guidelines then it is generally a simple matter to predict the order of the upper valence orbital energies in a given H_nAB_2 molecule, at least to a sufficient degree to ascertain the ground state electronic configuration and thereby, upon subsequent application of Walsh's method, the approximate equilibrium geometry of the system.

5. Application of the Extended Method to C_3H_n Systems

Consideration of various C_3H_n hydrocarbons will be useful in demonstrating the extension of Walsh's rules to general H_nAB_2 systems and should hopefully indicate how the scope of the former theory may be enlarged to deal with molecules formed by the addition of hydrogen atoms to other types of parent species.

a) C_3H_6 *Isomers: Cyclopropane, Trimethylene and Propylene*

If six hydrogens are distributed equally among three carbons two isomers are possible, one with all perpendicular CH_2 groups (cyclopropane) and one with only the central methylene group so oriented (trimethylene). With all the hydrogen atoms out of the CCC plane it is the π type upper valence MO's ($1a_2$ and $2b_1$, see Table 4) which are most susceptible to mixing with the H AO's. The degree of mixing can be judged from the combined charge density contours of these species for 60° cyclopropane shown in Fig. 5; this figure in turn is wholly similar to that representing the contours of the $1b_{3g}$ CH bonding orbital in ethylene [10]. Thus in contrast to the situation for simple triatomic systems the orbital energies of the $1a_2$ and $2b_1$ MO's in cyclopropane lie considerably lower than those of the $6a_1$ and $4b_2$ in-plane species (compare Figs. 1a, b). Consequently it is energetically favorable to occupy the $2b_1$ instead of the $4b_2$ MO in this C_3H_6 isomer; it is of course well known that substitution of the $4b_2$, with its minimum orbital energy occurring for linear geometry, by the $2b_1$ (possessing the opposite geometrical trend) leads to a substantial decrease in internuclear angle, thereby producing in the present case the familiar equilateral triangle arrangement of cyclopropane.

Choosing the other in-plane orbital ($6a_1$), with its strong trend toward bent geometry, for substitution by the $2b_1$ leads to the (5,4,2,1) state, which has a much larger equilibrium CCC angle, but just as in ozone the energy minimum of this configuration (Fig. 3b) is considerably higher than that of the (6,3,2,1) species. In general it can be said that since the ground state electronic configuration of this molecule is associated with the smallest equilibrium angle possible for any of the 24-electron states of triatomics, any type of electronic excitation will lead to at least a partial opening of its CCC ring.

Location of all the terminal hydrogens in the CCC plane naturally has the opposite effect on the upper valence MO's, causing the in-plane $4b_2$ and $6a_1$ species to be considerably more stable than the $1a_2-2b_1$ out-of-plane pair.

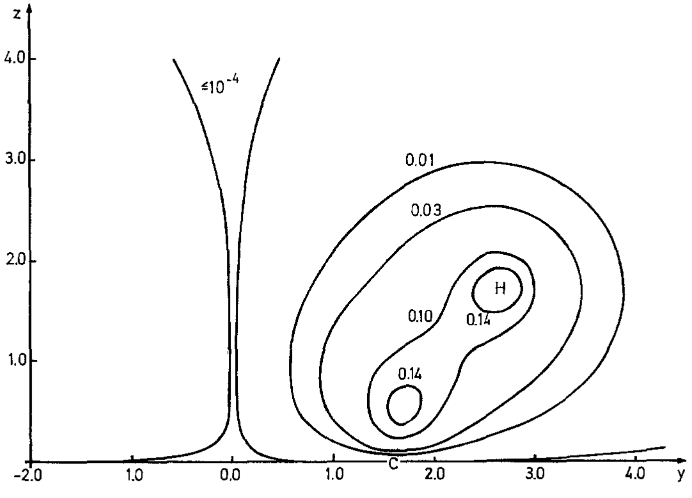


Fig. 5. Charge density contours for the $1e''$ MO of cyclopropane ($\sphericalangle$ CCC = 60°)

A complicating factor for the description of trimethylene, however, is the fact that in the region of 120° ∢ CCC the $1a_2$ and $2b_1$ MO's are nearly isoenergetic, with the $2b_1$ the more stable at smaller angles, the $1a_2$ more stable at larger values. The situation is different from that in a simple triatomic (Fig. 1a) for the reason that the $2b_1$ in trimethylene is much more localized on the termini and therefore much less antibonding[2]. As a result the most stable configuration in this case is open-shell, with partial occupation of both the $2b_1$ and $1a_2$ MO's, and in agreement with Walsh's rules the equilibrium angle possessed by trimethylene [11] is believed to be in the neighborhood of 120°.

The third and most stable C_3H_6 isomer propylene has three hydrogens on one of the terminal carbons, two on the other and one on the central carbon; this system thus does not possess the vertical symmetry plane of all the other AB_2 and H_nAB_2 molecules discussed to this point, so that conclusions drawn for this system are necessarily somewhat less rigorous. Nevertheless with most of the hydrogens in the CCC plane, as is the case at equilibrium, it is once again clear that the in-plane $6a_1$ and $4b_2$ MO's (or their counterparts in the decreased symmetry of propylene) are relatively more stable than the out-of-plane pair. Since all out-of-plane hydrogens are on a terminal carbon, the normal stability ordering (with $1a_2$ below $2b_1$) is expected (Table 4) and therefore the ozone ground state configuration (with $2b_1$ unoccupied) is preferred for propylene and its observed equilibrium CCC angle (Table 1) is thus normal from the standpoint of Walsh's rules[3].

b) Hydrocarbons with 22 Electrons

According to Walsh's rules the normal ground state geometry of triatomics with 22 electrons is linear; the preferred electronic configuration is (5,4,1,1), i.e. the $6a_1$ and $2b_1$ MO's ($2\pi_u$ in linear symmetry) are not occupied. The C_3H_4 isomers allene and methylacetylene have all of their attached hydrogens on the terminal carbons, thus favoring the $4b_2$ and $1a_2$ MO's at the expense of the $6a_1$ and $2b_1$ species (see Table 4). Consequently both of these systems favor a linear arrangement of carbons, in conformity with the general rule.

To obtain a different nuclear arrangement at equilibrium for a 22-electron hydrocarbon it is necessary to attach some hydrogens to the central heavy atom and thereby stabilize either or both of the $6a_1$- and $2b_1$-type MO's. In the first example to be considered, allyl cation $C_3H_5^+$, one hydrogen atom is attached to the central carbon and located in the CCC plane, thereby selectively stabilizing the $6a_1$ species; at the same time rotation of the terminal methylene groups into the plane of the carbons causes an increase in the orbital energy of the out-of-plane $1a_2$-type MO compared to its value in allene. As a result the $6a_1$, with its strong preference for bent geometry, is occupied instead of the $1a_2$, producing the (6,4,1,0) ground state electronic configuration of allyl cation; both the predictions of Walsh's rules and the calculated potential curves of N_3^- (Fig. 4a) are consistent

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[2] Because of CH bonding the $1b_1$ of trimethylene has its charge density maximum at the central heavy atom, also in contrast to the situation in simple triatomics.

[3] That the preferred angle is somewhat larger than that of ozone could indicate a partial mixing of the $2b_1$ and $1a_2$ species (now allowed in the reduced symmetry), although there is really little reason for expecting the theory to be capable of such discrimination under the circumstances.

with the observed equilibrium angle for this system of approximately 120° (Fig. 4b). In addition the theory predicts that the addition of two electrons to this system to give the allyl anion results in the occupation of the $1a_2$ MO and in an accompanying slight increase in CCC angle; the anion, of course, is yet another example of a 24-electron system preferring the normal (6,4,1,1) electronic configuration predicted by the original theory.

Rotating the CH_2 groups of the allyl cation out of the CCC plane to give cyclopropyl cation has the effect of inverting the stability order of the MO's with charge density maxima at the terminal carbons, thereby favoring occupation of the out-of-plane $1a_2$ over the in-plane $4b_2$ species. This change in configuration should be accompanied by a substantial decrease in internuclear angle, as is demonstrated by the calculated potential curves for these systems given in Fig. 4b.

Placing two hydrogens at the central carbon atom further aids those orbitals with substantial central atom character, namely the $6a_1$ and $2b_1$ MO's, so much so that in cyclopropene it becomes energetically favorable to substitute these orbitals for the $4b_2$ and $1a_2$ species occupied in the conventional linear 22-electron systems. The resulting (6,3,2,0) electronic configuration is characterized by the smallest known internuclear angle observed for H_nAB_2 molecules.

c) Other Systems

Just as with simple triatomics the sum of 26 electrons represents the point of complete occupation or saturation of all the possible valence MO's of H_nAB_2 systems. It is not at all surprising then that no particularly novel structures are known for 26-electron members of this family (see Table 1). The well-known tetrahedral angle purported by valence bond theory to characterize all unsaturated bonding situations is thus seen to result according to Walsh's rules from the exhaustion of all available valence MO's; in good analogy with the geometry of F_2O, the corresponding skeletal internuclear angles invariably are found to lie in the neighborhood of 105–110°.

The theory of course is not restricted to systems with an even number of electrons; the allyl radical represents an example of an odd-electron system which is particularly worth noting. Even though this system is isoelectronic with nitrogen dioxide NO_2, its equilibrium CCC angle (120°) is found to be significantly smaller than that of the simple triatomic ($\sphericalangle$ ONO = 135°). This difference is again understandable and indeed predictable from consideration of Walsh's rules because of the fact that the two systems in question differ in ground state electronic configuration. The corresponding anions NO_2^- and $C_3H_5^-$ do possess the same configuration, identical to that of ozone, and approximately the same internuclear angle but ionization of these systems to give the respective free radicals occurs from orbitals of different symmetry, notably the $6a_1$ in NO_2 and (as has already been suggested in the discussion of the allyl cation) the $1a_2$ in C_3H_5. The qualitative theory unambiguously predicts that ionization of a $6a_1$ electron from an ozone configuration will cause a decided increase in internuclear angle but that loss of an electron from the $1a_2$ MO will be followed by a slight decrease in angle in good agreement with what is found.

Thus far the discussion has centered around H_nAB_2 systems with a symmetric BAB skeleton. Inspection of Table 1, however, indicates at least empirically that the present extension of Walsh's rules is equally valid for more general hydride systems with a non-symmetric ABC skeleton. In the case of simple triatomics this similarity between the geometries of symmetric and non-symmetric species has been justified, at least partially, on the basis of non-empirical calculations for NNO [9], from which it can be seen that a definite similarity exists between corresponding MO's of both types of systems (see, for example, Figs. 4–6 of Ref. [9] for a comparison of analogous MO's for symmetric NON and non-symmetric NNO), at least in the range of 180° to 110°. In particular it is found that the correlation diagrams calculated for non-symmetric triatomics are quite similar to those of BAB type in the latter range of internuclear angle.

6. Conclusion

Addition of hydrogen atoms to a triatomic molecule alters the relative stability ordering of the molecular orbitals of the parent system but does not significantly change the behavior of the orbital energies upon bending of the triatomic skeleton. As a result it is possible to predict the equilibrium angles of H_nAB_2 systems on the basis of Walsh's rules simply by allowing for the fact that the ground state electronic configuration of such molecules may differ from that of simple triatomic species with the same number of electrons. Thus the identical arguments used to predict the equilibrium geometries of the excited states of N_3^- and O_3 can be used to ascertain the *ground state* structures of all known H_nAB_2 systems with 22 and 24 electrons respectively, including such distinctive species as cyclopropane and cyclopropene.

The theory is thus seen to be capable of treating large numbers of molecules, inorganic and organic alike, on the basis of a single correlation diagram, albeit one with the added flexibility of allowing the energy levels to be shifted with respect to one another. Although only systems with a triatomic skeleton have been given explicit consideration in the foregoing discussion, the utility of the general theory is by no means restricted to molecules of this type; applications for systems with four heavy atoms, for example, have already been considered in connection with calculations for cyclobutadiene [12] C_4H_4. In addition the theory has the obvious advantage of being equally applicable to ground and excited states, thereby affording the prediction of details of electronic spectra which are otherwise all but inaccessable. It should therefore be possible on the basis of the aforementioned modified H_nAB_2 correlation diagrams to predict the structures of such systems in their excited states in much the same manner as Mulliken and Walsh have been able to do for the parent molecules not containing hydrogens.

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