

Factors Governing Nuclear Geometry and Bond-Orbital Directions in Second Row AH₂ Molecules

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We have obtained valence bond wavefunctions for the neutral, positive ion, and lower excited states of second row AH₂ molecules. A number of simple rules emerge which govern the nuclear geometry and bond-orbital directions. These are explained in terms of valence bond orbital characteristics as well as an analysis of energy components.

I. INTRODUCTION

It is a depressing commentary on our understanding of structural chemistry that a satisfactory explanation of the origin of equilibrium bond angles has still not been presented. There is no doubt that using modern theoretical methods and computational power, one can reproduce experimental geometries accurately at least for small molecules. But the goal of extracting a simple model which successfully connects theory with experiment remains elusive.

A number of models have been proposed. They are comprehensively discussed in the recent review article by Nakatsuji and Koga.¹ Although each of them is successful on some grounds none is completely satisfactory. The valence shell electron pair repulsion (VSEPR) theory,² for example, provides an intuitive rationalization of much experimental data. Yet it turns out, upon quantitative investigation,^{3,4} that the basic assumptions of the model are invalid. Exactly the same statements can be made about the Walsh correlation diagram.^{5,6} In fact, Nakatsuji and Koga¹ summarize evidence indicating that all of the energetic models for molecular shape which have been suggested thus far suffer from a like deficiency.

On the other hand, the Hellman-Feynmann force models developed by Nakatsuji and coworkers¹ and by Deb, *et al.*⁷ are also open to some criticism. It is true that the electrostatic force may be written as a simple classical expression involving the (single particle) electron density. But this expression is valid only for »floating« wavefunctions,⁸ otherwise large errors ensue⁹ due to the terms that are omitted. Moreover, in general the computed electrostatic force (unlike the energy) is extremely sensitive¹⁰ to small errors in the density function. The latter does depend on the non-classical character of the wavefunction and on the precise effect of the two-electron interaction as well. In analyzing the electrostatic force such considerations are ignored. A partitioning of the force expression is made which depends upon a particular choice of basis set, namely atomic orbitals centered on the respective nuclei. This

seems rather arbitrary especially in view of the floating orbital requirement mentioned above. Although some intuition does exist with regard to the separate contributions it is, as yet, not well developed. Finally, the net force is a delicate balance of several competing terms.

We conclude that there is a clear need for a model of molecular geometry based on quantitatively verifiable energetic concepts. This paper represents a step toward that objective.

Since the Hartree-Fock (HF) approximation generally yields good equilibrium geometries, most proposed interpretations rely on the HF wavefunction. In that event molecular orbital properties play a central role. For instance, the well-known Walsh's rules⁵ depend upon the orbital energies which are quantities associated specifically with canonical molecular orbitals. However, the canonical orbitals themselves are delocalized and can not serve as a basis for any analysis based on the chemically appealing concepts of localized bonds, lone pairs, and inner shells. A transformation from canonical to localized molecular orbitals can be made. However, the choice of transformation coefficients is ambiguous; this choice must utilize criteria that lie outside the Hartree-Fock approximation and are not based on the variation principle. Localization is, normally, carried out¹¹ in a way that preserves orthonormality. As a result the orbitals are not as strongly localized as they could be. Furthermore, the original canonical orbitals are obtained without any localization criterion being operative. Thus, even though the Hartree-Fock method constitutes a model that predicts geometries quite accurately, we consider it to be unsatisfactory because it does not provide an »explanation« of its results in terms of the bonds, lone pairs and inner shells and the interactions between them. We suggest that it is more appropriate to use a valence-bond (VB) wavefunction to seek an equally accurate model which does offer the hope of an explanation in terms of the interactions that are intuitively meaningful to chemists.

There are several different forms that have been utilized for the VB wavefunction. We believe it is important both to retain the orbital concept and to determine the best possible orbitals according to the variation condition subject to as few constraints as possible. These criteria lead to a generalization of the Heitler-London-Wang¹² treatment which allows for the atomic orbitals to be modified by scaling, addition of partial ionic character, *etc.* in response to the molecular environment. The best possible VB orbitals¹³ in the sense of the variation principle are the ones that we seek. These orbitals turn out to be localized because that is an effective way to relieve electron repulsion.¹⁴

The first computationally practical procedure for extending the VB orbital treatment to many electrons was formulated by Hunt, Hay, and Goddard.¹⁵ They applied a strong orthogonality constraint between different VB pairs to simplify the calculations. Later Chipman, Kirtman and Palke¹⁶ developed a convenient method which eliminates this constraint and thereby provides optimum localization. Their wavefunction yields the best possible orbitals¹⁷ for the analysis of molecular geometry using localized orbital concepts.

In order to investigate the factors governing molecular geometry we have carried out a series of valence-bond calculations on first row AH₂ molecules. These are the simplest molecules that have variable shape, as measured by the internuclear angle, and it seemed to us that they must be understood before proceeding further. In earlier work¹⁸ on H₂O (as well as NH₃, CH₄, and H₂S)

we discovered an interesting phenomenon called *orbital stasis*, namely that the direction of the bonding orbitals on the central atom remains approximately fixed as the nuclei bend away from equilibrium even for large angle distortion. Thus, our attention was directed toward the problem of the inter-orbital as well as the internuclear angle. There are clearly some factors that affect the former but not the latter. The question also arises as to what is the interplay between the two and whether the difference at equilibrium is »accidentally« small or not.

One way of probing electronic structure is to vary a particular feature so as to see what effect it has on the properties of interest. In the case of AH₂ molecules it is particularly convenient to alter the configuration of the lone pair orbitals. For most species that can be accomplished by considering electronic states of different symmetry. For the closed shell molecules, orbital symmetry may be artificially enforced and the results compared with an unconstrained calculation. Additional information is available by examining the positive ions as well as the neutral species since this causes the remaining orbitals to contract. Finally, the imposition of a partial double occupancy restriction on the σ lone pairs eliminates the in-out splitting which, then, leads to a major change in hybridization that can be revealing. The interpretations offered in this paper are based on computations of the lone pair driven electronic structure variations just described.

From our computations, some simple rules governing the geometry and orbital directions have emerged. For example, the equilibrium internuclear angle turns out to depend solely on the *number* of in-plane (σ) lone pair electrons. The details of the corresponding σ -orbital density are irrelevant although the molecular charge is not. A set of rules for the geometry and orbital directions of AH₂ molecules is given in Sec. III followed by an analysis in terms of orbital characteristics and energy components. The various computational methods that we have used to obtain and to interpret our valence bond wavefunctions are discussed in the following section.

II. COMPUTATIONAL METHODS

As discussed in the Introduction the best orbitals to serve as a basis for interpreting molecular properties should be determined from the most general independent particle wavefunction possible. Nonessential constraints such as the imposition of orthogonality or truncation of the basis should be avoided so as to exclude artificial effects. To this end, we have obtained fully optimized valence-bond wavefunctions by the OTTO¹⁶ method which is summarized below.

Each pair of electrons in the (perfect-pairing) VB wavefunction is described by two orbitals φ_a and φ_b multiplied by a spin function ($\alpha\beta - \beta\alpha$) to give the usual singlet coupling, or ($\alpha\beta + \beta\alpha$) for the triplet coupled pair in the triplet states that were considered. The total wavefunction is an antisymmetrized product of these VB pairs. Inner shell pairs were not doubly occupied, so the only orthogonality amongst the VB orbitals is that due to symmetry, *i. e.* between σ and π orbitals as, for example, in the ³B₁ state of CH₂.

The orbitals were expanded in the double zeta basis sets of Slater functions optimized by Huzinaga and Arnau¹⁹ augmented by a set of 3d functions on the central atom. Exponents were taken from Huzinaga and Arnau's¹⁹ compilations, or from our previous work²⁰, or else they were optimized. Calculations using basis sets of this quality typically give equilibrium geometries

in excellent agreement with experimental results. All angular variations for the neutral species were carried out with the bond distance fixed at the experimental value. For the ions we used the experimental ground state bond length of the corresponding neutral. Equilibrium internuclear angles are not critically sensitive to the bond length.

The expansion coefficients of the VB orbitals were optimized by a two step procedure called OTTO¹⁶. First, the orbitals of a particular pair are optimized in the potential created when all remaining pairs are described by their doubly-occupied primary natural orbital. Then the mixing of the former two orbitals with every other split pair is individually optimized, again in the doubly-occupied sea of the remaining pairs. An iterative cycle consists of one loop through all the pairs using the updated values of the orbital coefficients. In earlier work we have found that the OTTO method yields orbitals that differ insignificantly from the exact VB result in cases where such a comparison is feasible. In a few instances, it was necessary to damp the mixing of different pairs in order to facilitate convergence. Finally, the energy was computed using a perturbation expansion described previously¹⁶.

A quantity of particular interest in these studies is the direction of the bonding hybrid orbitals on the central atom. Each bonding hybrid is composed almost entirely of *s* and *p* AO's on the central atom, so its direction is determined by the relative contributions of the two p_σ (in plane) components. In a double zeta basis set, the orbital direction can be a function of the distance from the central atom nucleus. The direction given by the high exponent bases (ζ_{2p} ranges from 2.2 for B to 3.7 for O) is always within 10° of the diffuse functions, so the variation of direction with radius is small. The contribution of the high exponent $2p$ functions is typically (in the neutral molecules) about one-third that of the more diffuse $2p$ functions, and the region (near $1/\zeta$ a. u.) described by the high exponent functions is close to the nucleus. Since it is the more diffuse $2p$'s that describe the bonding region and since they are the more heavily weighted functions in each of the VB orbitals, we have tabulated their directions, as those of the bonding hybrid. The arguments and conclusions would be the same if we had used a weighted average instead. Hybridization coefficients for the bonding and nonbonding orbitals were obtained by slight modification of a procedure²¹ that has been presented previously.

Some of the arguments that we make are based on an analysis of the electron population of the various atomic orbitals in the basis set. Because these AO's are non-orthogonal, the definition of the population is not unique. We follow here a formulation based on the first-order density matrix devised by Jug²² which is a generalization (with slight modification) of an original treatment due to Chirgwin and Coulson.²³ In this formulation the populations are those of the symmetrically orthogonalized AO's. For sake of comparison, a Mulliken²⁴ type of analysis was also tried using natural orbitals weighted by their occupancies instead of molecular orbitals. The orbital populations obtained were almost exactly the same for the two different procedures.

III. DISCUSSION

For non-linear AH_2 molecules the overall VB wavefunction has either A_1 or B_1 symmetry. In the B_1 states there is one singly occupied pure π orbital, and any remaining nonbonded orbitals are purely σ . The singlet A_1 states

contain two nonbonding σ electrons; the corresponding σ orbitals can and do hybridize with the π 's to form mixtures of the form ($|\sigma\rangle + c|\pi\rangle$ and $|\sigma\rangle - c|\pi\rangle$) where c is a hybridization coefficient. Restricting these nonbonding orbitals to have pure σ symmetry ($c = 0$) raises the molecular energy by only about 10 kcal/mol. The 1A_1 calculations were done with and without such symmetry constraints. In fact, as described below, it turns out to be convenient to use the results obtained for pure σ and π orbitals to generate a zeroth-order model, and then to consider σ - π mixing as an additional factor in cases where it is operative. Since symmetry plays a key role, this model contains an element in common with Walsh's rules⁵. It also contains an element of VSEPR theory² in the sense that lone pair electrons determine the nuclear geometry. On the other hand, our treatment is more quantitative than either of these approaches, and the results are explicable in terms of detailed characteristics and energy components as seen below.

A. Geometry and Orbital Direction Rules

We have discovered a set of geometry and orbital direction rules that govern the nuclear and interorbital bond angles in second row AH₂ molecules. Table I shows that the computed equilibrium internuclear angle depends only on the number of σ nonbonding electrons and on the molecular charge. The characteristic equilibrium internuclear angle for the neutrals that contain two

TABLE I
Calculated Angles

System		Non-bonding orbitals	Equilibrium internuclear angle	Bond-orbital angle
BH ₂		$\sigma^1\pi^0$	126°	125°
CH ₂	triplet	$\sigma^1\pi^1$	128°	139°
NH ₂		$\sigma^1\pi^2$	135°	133°
CH ₂	singlet	$\sigma^2\pi^0$	102°	101°
	hybrid lone pair			
CH ₂	singlet	$\sigma^2\pi^0$	103°	122°
	σ lone pair			
NH ₂		$\sigma^2\pi^1$	102°	121°
H ₂ O	hybrid lone pairs	$\sigma^2\pi^2$	103°	100°
H ₂ O	σ , π lone pairs	$\sigma^2\pi^2$	103°	120°
H ₂ O	σ doubly occupied lone pair	$\sigma^2\pi^2$	102°	88°
CH ₂ ⁺		$\sigma^1\pi^0$	138°	141°
NH ₂ ⁺	triplet	$\sigma^1\pi^1$	138°	141°
H ₂ O ⁺		$\sigma^1\pi^2$	180°	180°
NH ₂ ⁺	singlet	$\sigma^2\pi^0$	107°	103°
	hybrid lone pair			
H ₂ O ⁺		$\sigma^2\pi^1$	110°	125°

σ nonbonding electrons is 102° (the ground states of H_2O and NH_2 and the lowest singlet state of CH_2). Cases with only one σ nonbonding electron have internuclear angles close to 127° . The positive molecular ions display an analogous pattern; σ^2 ions have internuclear angles of 108° as compared to 138° for σ^1 ions. The deviation from constancy in all of the above cases is exceedingly small except for the $\sigma^1\pi^2$ configuration (excited states of NH_2 and H_2O^+) which will be discussed further in the next sub-section.

The ions fall into two series obtained by removing either a π or a σ electron from the appropriate neutral. Regardless of the electronic configuration, the removal of a π nonbonding electron leads to about the same increase in equilibrium internuclear angle. For the four cases contained in the table (including ionization from the $\sigma^1\pi^2$ excited state of NH_2), the angle increase is $6^\circ \pm 2^\circ$. Frozen orbital calculations show that this shift is totally insensitive to relaxation of the σ core. Ionization of a σ nonbonding electron leads to an angle increase of $40^\circ \pm 5^\circ$, and the shift in these cases does depend upon relaxation of the remaining orbitals.

σ - π hybridization causes considerable charge redistribution in the individual VB orbitals, but the electron population of the various symmetrically orthogonalized AO's is only slightly altered. It is not surprising then that the equilibrium internuclear angles are unaffected as well.

The equilibrium bond-orbital angle is also determined by the number of σ nonbonding electrons, but the s - p hybridization of the nonbonding and, hence the bonding orbitals is important as well. For σ^2 configurations the angle is essentially 120° no matter how many π electrons there are.

Usually at equilibrium, the bond-orbital angle will be close to the internuclear angle. This generalization breaks down, however, when either orbital symmetry or double occupancy constraints are applied. Even without such constraints the bonds turn out to be strongly bent in a significant number of instances.

Again we find that the bonding orbitals remain nearly fixed in direction as the internuclear angle is varied. *Orbital stasis* is a much better approximation than complete orbital following.

B. Analysis in Terms of Orbital Characteristics and Energy Components

The fact that, for a given charge, the equilibrium internuclear angle depends only upon the number of nonbonded σ electrons is remarkable considering the concomitant variation in the wavefunction as measured by the electron populations reported in Table II. An explanation for the difference between the σ^1 and σ^2 series can be made in terms of energy components. The total energy is a sum of zero-, one-, and two-electron contributions with the first of these $V(0)$ being the nuclear-nuclear repulsion. $V(0)$ has a minimum at the linear configuration whereas the one-electron component goes through a maximum at a large angle with the result that the sum of the two is nearly linear over a wide angular range near equilibrium. This division points to electron-electron repulsion $V(2)$ as the origin of the energy minimum at a bent geometry. Indeed, the two-electron component does show such a minimum which occurs at angles greater than 134° for the σ^1 series and less than 114° for σ^2 electronic configurations. The position of the $V(2)$ minimum however

TABLE II
 AH₂ Population Analyses

System		Electron population ^a						
		H	2s	2s'	2p _x	2p _x '	2p _z	2p _z '
BH ₂	$\gamma^1\pi^0$	0.82	0.42	0.88	0.78	0.31	0.69	0.23
CH ₂	triplet $\sigma^1\pi^1$	0.76	0.54	0.85	0.82	0.32	0.67	0.25
NH ₂	$\sigma^1\pi^2$	0.75	0.89	0.55	0.82	0.35	0.65	0.25
CH ₂	singlet $\sigma^2\pi^0$ hybrid lone pair	0.79	0.65	0.99	0.83	0.31	1.10	0.40
CH ₂	singlet $\sigma^2\pi^0$ σ lone pair	0.79	0.67	1.01	0.83	0.31	1.13	0.42
NH ₂	$\sigma^2\pi^1$	0.78	0.67	0.97	0.84	0.35	1.12	0.43
H ₂ O	$\sigma^2\pi^2$ hybrid lone pairs	0.65	0.89	0.86	0.90	0.42	1.10	0.51
H ₂ O	$\sigma^2\pi^2$ σ, π lone pairs	0.62	0.88	0.88	0.91	0.44	1.11	0.52
H ₂ O	$\sigma^2\pi^2$ σ doubly occupied lone pair	0.63	0.89	0.86	0.91	0.43	1.11	0.51
CH ₂ ⁺	$\sigma^1\pi^0$	0.67	0.47	0.98	0.82	0.41	0.64	0.31
NH ₂ ⁺	triplet $\sigma^1\pi^1$	0.63	0.52	0.92	0.88	0.45	0.63	0.31
H ₂ O ⁺	$\sigma^1\pi^2$	0.18		0.85	1.18	0.44	0.65	0.35
NH ₂ ⁺	singlet $\sigma^2\pi^0$ hybrid lone pair	0.64	0.59	1.02	0.90	0.45	1.10	0.52
H ₂ O ⁺	$\sigma^2\pi^1$	0.50	0.84	0.93	0.93	0.55	1.10	0.63

^a In each case the prime refers to the tight basis function.

varies considerably within each series. Thus, the constant equilibrium inter-nuclear angle cannot be explained on the basis of electron repulsions alone — a conclusion which is consistent with our previous study of the VSEPR model.

In the course of the energy component analysis just described, we discovered that the ratio of the two-electron energy to the sum of zero- and one-electron energies is astonishingly constant at a value²⁵ close to $-1/3$ (or equivalently $V(2)/E = -1/2$) for the entire set of molecules considered here. As a matter of comparison, we also tested the Politzer-Ruedenberg²⁶ relation $[V(0) - V(2)]/E = 1/3$ which turns out to have a standard deviation nearly an order of magnitude larger. Our ratio depends very slightly ($\sim \pm 0.00001$ per degree) on the internuclear angle, but it is indeed this small variation which causes the minimum in $V(2)$ not to coincide with the minimum in E .

The two $\sigma^1\pi^2$ molecular states (excited states of NH₂ and H₂O⁺ display the worst fit to the geometry rules we have presented. These excited states are exceptional in other ways as well. They are the only ones we've considered that have the same multiplicity as the ground state. If symmetry restrictions are not applied, the wavefunctions jump to the more stable $\sigma^2\pi^1$ configuration. In our calculations, in order to understand this problem and to facilitate con-

vergence, we insisted that each of the orbitals be either pure σ or pure π although the correct A_1 symmetry can be achieved under milder conditions. Indeed one would expect the π^2 pair to hybridize as it does in H_2O , but we were unable to obtain convergence for hybridized orbitals in the $\sigma^1\pi^2$ case. It is possible that the more stringent symmetry restriction has a significant effect on the equilibrium angle. CI calculations²⁷ (as well as experiment²⁸ for NH_2) yield bond angles substantially larger ($\text{NH}_2 = 143^\circ$, $\text{H}_2\text{O}^+ = 180^\circ$) than we've obtained. One should notice, however, that the potential energy curves are rather shallow for both molecules. Hence the exact position of equilibrium may not be very meaningful. At any rate, it is clear that we do not yet understand the factors that determine the equilibrium internuclear angle in the $\sigma^1\pi^2$ excited state.

As far as the ions are concerned, it seems reasonable that the increment in the equilibrium internuclear angle should be less for the π than σ ionization because the bonds are σ . From the population analysis of Table II, we see that π ionization is accompanied by a rearrangement of electronic charge whereby the hydrogen atoms and the more diffuse orbitals on the central atom lose while the tighter orbitals on the central atom gain. But that rearrangement has essentially no effect on the equilibrium internuclear angle. For when we remove the π electron with the σ orbitals frozen, the resulting equilibrium angle is the same as for the reoptimized orbitals. This means that the π electron is responsible for a substantial bending force in the plane of the molecule! In CH_2 , the shift in the angular minimum is due solely to one-electron energy terms, but that is not true for all the molecules.

An analogous treatment of the ions obtained by removing a σ electron reveals that, in this case, the electronic rearrangement is important. Of the two σ -type nonbonding orbitals in the neutral, one is primarily $2s$ while the other has considerable p -character. The orbital that remains in the ion fits the latter description implying that the ionized electron is predominantly $2s$. On the other hand, our population analysis of the entire wavefunction shows that loss of $2p_z$ character (z is the molecular symmetry axis) is the major net effect of σ ionization. Hence, there is a substantial redistribution between $2s$ and $2p_z$ in the bonding orbitals which leads to a large increase in the equilibrium internuclear angle.

The equilibrium interorbital angle, in contrast with the internuclear angle, is sensitive to details of the electron distribution particularly the s - p hybridization. An excellent example is furnished by the set of H_2O calculations where the s - p hybridization is driven by intrapair repulsion between the σ nonbonding electrons. If the nonbonding orbitals are constrained to be σ and π , the equilibrium interorbital angle is 120° which is characteristic of σ^2 configurations. As noted earlier, one of the two σ -type nonbonding orbitals is primarily $2s$ while the other has considerable p -character, resulting in an in/out localization which reduces the intrapair repulsion. If the σ orbital is forced to be doubly occupied, then its hybridization becomes similar to that member of the split pair which is primarily $2s$. Consequently, the central atom bond orbitals are primarily $2p$, which leads to the angle between them being about 90° as we have found.

The above argument implies that 2s orbitals are more advantageous for relieving nonbonded intrapair electron repulsion than 2p_σ. One piece of evidence confirming such an interpretation is the set of hybridizations found for the molecules having one σ nonbonding electron. For that series there is, of course, no intrapair repulsion and the σ nonbonded orbital does turn out to contain considerably more p_σ character than the doubly-occupied orbital of H₂O as would be expected from our model.

In order to analyze the effect of σ—π hybridization in H₂O, consider first the case of CH₂ (¹A₁). An examination of orbital coefficients for the latter molecule reveals that hybridization occurs through transfer of charge from both s and p_z (z is the molecular symmetry axis) to p_π; the magnitude of the hybridization coefficient is |c| ~ 0.3. We speculate that intra-pair electron repulsion is relieved by the up/down localization and, hence, less s character is required. At any rate, σ—π hybridization leaves a partial »hole« in the p_z space which is filled by the bonding orbitals. Consequently, the interorbital angle decreases by about 20°. On the basis of inter-pair repulsion arguments one might come to the opposite conclusion since σ—π hybridization would be expected to reduce lone pair-bond repulsion in the molecular plane. In H₂O the hybridization of the nonbonding π orbitals must also be taken into account. This occurs through charge transfer from p_π to s but not p_z. The above argument, therefore, remains just as valid for H₂O as for CH₂, and we do find about the same increase in interorbital angle.

It should be noted that the charge redistribution between the individual VB orbitals which accompanies σ—π hybridization does not significantly affect the AO populations of the entire wavefunction as seen in Table II (cf. the three calculations for H₂O and the two calculations for CH₂ (¹A₁)). That explains why the equilibrium internuclear angles are unchanged as well. As a result, the latter can be predicted from the simpler symmetry constrained σ—π model.

As observed in the section on geometry rules, several of our molecules, including the ground states of NH₂, H₂O⁺, and CH₂, have strongly bent (> 10°) bonds at equilibrium. This phenomenon is clearly not limited to »strained« systems. It can also be induced by applying symmetry constraints so that σ—π hybridization cannot take place (cf. singlet CH₂ and H₂O). Once the equilibrium interorbital angle is determined, however, it remains insensitive to subsequent changes in the internuclear angle. The bond orbitals followed the nuclei to a greater degree in CH₂⁺ than any other case. As the internuclear angle was varied for this molecule over a range of 30° about equilibrium, the interorbital angle varied by 12°. Most of the other molecules displayed about half as much orbital following. Thus, the *orbital stasis* model gives a reasonable approximation to the true situation.

Although we have made substantial progress towards an understanding of the geometry rules based on energy considerations, a number of lacunae remain. For example, what is the origin of the ratio rule $V(2)/[E-V(2)] = \text{constant}$, and how does one explain the slight, but important, deviation from constancy as a function of internuclear angle? What are the explicit factors responsible for the in-plane bending force due to a π orbital? And so forth. Further investigation is underway to shed light on these questions and, ultimately, to extend the treatment to other molecules.

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SAŽETAK**O faktorima koji određuju geometrijske rasporede jezgri molekula AH_2 i smjerove lokaliziranih veznih orbitala**

Bernard Kirtman i William E. Palke

Izračunane su valne funkcije za troatomske molekule AH_2 s pomoću metode valentne veze, pri čemu centralni atom A pripada drugoj periodi sustava elemenata. Izvedena su jednostavna pravila koja određuju strukturni raspored atoma kao i smjerove lokaliziranih orbitala kemijskih veza. Ta pravila mogu se objasniti karakterističnim svojstvima lokaliziranih orbitala. Rezultati analize potkrijepljeni su razmatranjem komponenata ukupne energije molekula.