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Semiempirical Molecular Orbital Theory and Molecular Geometry. I. Analytic Procedures for Extended Huckel Methods¹

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Abstract: Analytic expressions for orbital electronic energies and charge distributions for the first-row atom dihydrides are developed within the framework of two important variations of extended-Hückel theory. The major purpose of the development is to ascertain in detail the individual effects operative within the different molecular symmetries and how these vary with symmetric changes in geometry. Fairly simple expressions are derived for angular changes both within the original and the kinetic-energy-included methods, and the balancing of energy effects between the a_1 and b_2 symmetry orbitals appear therefrom to be capable in some cases of qualitatively reproducing the correct equilibrium molecular configurations. Correspondences with the Walsh rules are explored. Reasons for agreement with these rules and with empirical structures when found are discussed; why the agreement can be no more than qualitative is also considered. The more complicated expressions for symmetric bond stretching and contraction in these molecules are similarly derived and examined, and some reasons for the general failure of the methods to represent these deformations are detailed.

Optimistic appraisals of the ability of semiempirical molecular orbital theories which explicitly include all (or all valence-shell) electrons to approximate details of equilibrium molecular geometry have been voiced for some time. The apparent success of such theories with molecular shapes, which are mainly angle dependent, may be contrasted with the results they produce regarding molecular sizes. The latter, which are functions principally of equilibrium bond lengths between bound, nearest neighbor atoms, are at best poorly approximated, or, more generally, appear to be beyond the capacity of these methods.

Several questions arise upon consideration of this apparent dichotomy. The first relates to whether the approximate MO representations of angular and stretching displacements from equilibrium are generally of such disparate quality as experience to date implies. If so, what features of the theories in detail are responsible for the difference and how do these features compare with those of more exact theories? Another question of interest concerns the degree of correspondence

between the approximate MO representation for angular displacements and Walsh's rules.² These rules which are qualitatively based upon considerations of hybridization changes and relative amounts of bonding and antibonding character between atom pairs in orbitals of different symmetry provide a useful interface for the connection of the MO results with the behavior of real molecules.

To take advantage of the rules and the considerable amount of information otherwise available,³ the triatomic MH_2 systems have been the principal subjects of this study. With "central atom" M restricted to the first-row elements Be to O, the dihydrides, all with closed-shell configurations, have been examined within the framework of the extended-Hückel (EH),⁴ kinetic-energy included extended-Hückel (KEH),⁵ and, in an accompanying paper, the explicit electron repulsion SCF CNDO2 methods.⁶ Analytic expressions, or

(2) A. D. Walsh, *J. Chem. Soc.*, 2260 (1953).

(3) L. C. Allen and J. D. Russell, *J. Chem. Phys.*, **46**, 1029 (1967); S. D. Peyerimhoff, R. J. Buenker, and L. C. Allen, *ibid.*, **45**, 734 (1966).

(4) R. Hoffmann, *ibid.*, **39**, 1397 (1963), and later papers.

(5) M. D. Newton, F. P. Boer, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **88**, 2353 (1966), and succeeding papers in the same volume.

(6) J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **44**, 3289 (1966).

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good approximations to such expressions, are derived for the energies and charge distributions pertinent to these methods in order that the particular contributions of the various interactions and within the different MO symmetries may be examined term by term. A clearer picture emerges for the effects which must balance to yield an energy-optimized structure. Conversely, where effects which should balance at the correct equilibrium configuration, but do not, are encountered, the failure may be more clearly localized from the analytical than from purely numerical results.

Theory, Parametrization, and Symmetry Considerations

The general secular determinantal equation appropriate to all methods considered

$$|F - S\epsilon| = 0 \quad (1)$$

may be conveniently factored for MH_2 in either the linear $D_{\infty h}$ or bent C_{2v} form *via* symmetry orbital representations. Considering all electrons, the totally symmetric orbital set

$$\psi_{i^+} = C_{i,1s}^+ \varphi_{1sM} + C_{i,2s}^+ \varphi_{2sM} + C_{i,2p_z}^+ \varphi_{2p_zM} + C_{i,H}^+ (\varphi_{H1} + \varphi_{H2}) \quad (2)$$

pertains for the molecule oriented in the XZ plane with the HMH angle ($=2\theta$) bisected by the X axis and corresponds to the e (inner shell), $1a_1$, $2a_1$, and $3a_1$ orbital set arranged in order of increasing energy. In the EH method of Hoffmann and in the CNDO method, only the valence electrons are considered; hence, $C_{i,1s}^+$ is zero and the e orbital is ignored.

Asymmetric orbital sets recognizing the XY and XZ planes of symmetry are, respectively

$$\psi_{i^-} = C_{i,2p_x}^- \varphi_{2p_xM} + C_{i,H}^- (\varphi_{H1} - \varphi_{H2}) \quad (3)$$

which correspond to the $1b_2$ and $2b_2$ orbitals, and

$$\psi_u = \varphi_{2p_yM} \quad (4)$$

which is the $1b_1$ orbital in conventional notation. In linear ($D_{\infty h}$) molecules the $1b_1$ and $2a_1$ MO's become degenerate, both with classification π_u .

The factorization accomplished by use of the symmetry orbital representations leaves at worst one-fourth order (square) matrix (in the KEH method), otherwise one 3×3 , plus one second- and one first-order matrix to be solved, and, in the case of the CNDO calculations, a series of such matrix equations interconnected by the SCF relations. The fourth-order matrices may be reduced in good approximation, as shown in the Appendix, to matrices of third order similar to those encountered in the EH method. The latter, or more precisely, their characteristic equations, are in turn approximated by conveniently soluble quadratic equations which directly yield analytical expressions for the orbital energies.

Depending upon the relative sizes of the diagonal elements in the third-order matrices, one of two methods of reduction to the quadratic form is used. Because of the neglect of differential overlap in the CNDO method, generally one technique for reduction is found to yield the best approximation, where, for the same molecule in the EH and KEH approximation, the other technique is to be preferred. The lower order matrices, of course, present no problems in derivation of the analytical expressions for orbital energies.⁷

Energies and Changes upon Angular Displacement

The EH Approximation. The total energy is generally taken in the EH approximation as the sum over orbital energies weighted by the orbital occupation. For the systems MH_2 with eight or ten electrons in total (six or eight valence electrons), this energy is in the notation used and transformations developed in the Appendix

$$E_{tot} = 2 \sum_i^{\text{occ}} \epsilon_i = 2 \{ (A + D + R - X_{3a_1}) + (\bar{R} + D - X_{2b_2}) + D \} \quad (5)$$

Equivalence of the diagonal elements (VSIP's) for all the $2p_M$ orbitals is recognized. The X 's are the energies of the MO's specified by subscripts. The parenthesized terms are in order for the a_1 and b_2 symmetry orbital blocks; the final term (D) of eq 5 applies in the ten-electron case (b_1). For six total (four valence) electron cases such as BeH_2 and BH_2^+

$$E_{tot} = 2 \{ X_{1a_1} + X_{1b_2} \} \quad (6)$$

From the relations in the Appendix it is apparent that

$$E_{tot} (8 \text{ electrons}) = 2 \{ A + 2D + \delta + \delta' \} \quad (7)$$

$$(10 \text{ electrons}) = 2 \{ A + 3D + \delta + \delta' \}$$

and the energy variation with angle is to the first order in the expansions developed, eq A10 and A15.¹⁵

(7) The energy results for the CNDO calculations may be coupled with compact analytic relations developed some time ago for π -electron calculations⁸ to yield the charge-density and bond-order expressions necessary for the SCF procedure. The matrix reduction method generally required by the CNDO method is presented in the Appendix of this paper for the purpose of continuity of mathematical analysis, and because it is, in some cases, required for the EH and KEH calculations. The charge-density and bond-order relations are detailed, in their proper place, in the accompanying paper.

As implied in the foregoing, the three theoretical methods are examined in their originally proposed forms. Modifications of minor nature which have been made for various purposes are often amenable to the present analysis without substantial change. For example, the geometric mean approximation for off-diagonal matrix element computation in the EH method,⁹ employed mainly in fitting spectral transitions,¹⁰ could easily be incorporated. Changes to square-power dependence on overlap (of the off-diagonal elements in the EH and KEH methods¹¹) are likewise tractable, requiring however, somewhat greater analytical modifications. Variations which prescribe parameter—as opposed to form—modifications under various conditions may be treated to the extent of how explicit the prescriptions are for the conditions encountered. Two types of such modifications are usefully recognized. The first, where structural changes are prejudged and parameters are in consequence initially modified,¹² require no changes in the present analysis. When, on the other hand, the matrix elements are adjusted in the EH or KEH methods on the basis of charge densities or some other property of the solved secular equations, and then iterated to self-consistency,^{13,14} a procedure of the type employed in the CNDO calculations becomes necessary. Further comment on the utility of such variations in treatment of the equilibrium angle and bond length problem follows below; a detailed analysis is presented in the accompanying paper.

(8) C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc. (London)*, **A191**, 39 (1947).

(9) R. S. Mulliken, *J. Chim. Phys.*, **46**, 497, 675 (1949); *J. Phys. Chem.*, **56**, 295 (1952); L. L. Lohr and W. N. Lipscomb, *J. Chem. Phys.*, **38**, 1607 (1963).

(10) C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, **1**, 111 (1962).

(11) (a) D. G. Carroll and S. P. McGlynn, *J. Chem. Phys.*, **45**, 3827 (1966); (b) L. C. Cusachs, *ibid.*, **43**, S157 (1965).

(12) K. Wiberg, *J. Am. Chem. Soc.*, **90**, 59 (1968).

(13) H. Basch, A. Viste, and H. B. Gray, *Theor. Chim. Acta*, **3**, 458 (1965).

(14) D. G. Carroll, A. J. Armstrong, and S. P. McGlynn, *J. Chem. Phys.*, **44**, 1865 (1966).

(15) The A14 expansion truncated after the first term is employed even in cases where $|2Q| \sim |d|$ because of the similarity in form to the generally appropriate eq A10 expansion, and, further, of its similar or in some cases even better representation of $\partial/\partial\theta$ than the multiterm (3 or 4) expansion required under A15.

$$\frac{\partial E_{\text{tot}}}{\partial \theta} = 2 \frac{\partial(\delta + \delta)}{\partial \theta} = 2\partial \left\{ \frac{2(P^2 + Q^2)}{a + d} + \frac{\bar{Q}^2}{\bar{d}} \right\} / \partial \theta \quad (8)$$

At this point it becomes apparent how balancing between the energy changes in the a_1 and b_2 symmetry orbitals upon angular displacement can lead to a minimum energy configuration at some nonextremum internal angle, 2θ . Q and $(a + d)$ for the a_1 orbitals, the latter through R , are strongly dependent upon $\cos \theta$, and \bar{Q} and \bar{d} (through \bar{R}) for the b_2 orbitals are similarly dependent upon $\sin \theta$. Both orbital energy terms are also dependent upon S_{H_1, H_2} , which is a more complicated function of θ . These dependencies become more evident from the rearranged relationship which may be obtained for the δ expansions by taking advantage of the constancy which exists for the sums of various barred and unbarred quantities, *i.e.*, sums of second-order terms in E and F and of first-order terms in G and T .

$$(\delta + \delta) = \frac{\mu_s + \nu\chi}{T\left(\frac{A + D}{2}\right) - G + \chi + k_1} + \frac{\mu_p - \nu\chi}{-(TD - G + \chi + k_2)} \quad (9)$$

Here

$$\mu_j = 2S_{jM, 1SH}^2 \left[\frac{K}{2}(\alpha_{jM} + \alpha_H) - \alpha_{jM} \right]^2 \quad j = 2s \text{ or } 2p\sigma$$

$$\nu = \left\{ \frac{K}{2}(\alpha_{2p\sigma M} + \alpha_H)^2 / [K(\alpha_{2p\sigma M} + \alpha_H) - \alpha_{2p\sigma M}] \right\} - \alpha_{2p\sigma M} \quad (10)$$

$$k_1 = 2S_{2sM, 1SH}^2 [K(\alpha_{2sM} + \alpha_H) - \alpha_{2sM}]$$

$$k_2 = 2\{\alpha_H - \alpha_{2p\sigma M} + \alpha_{2p\sigma M} S_{2sM, 1SH}^2 - S_{2p\sigma M, 1SH}^2 [K(\alpha_{2p\sigma M} + \alpha_H) - 2\alpha_{2p\sigma M}]\}$$

All parameters in eq 10 are independent of θ , and

$$\chi = 2S_{2p\sigma M, 1SH}^2 [K(\alpha_{2p\sigma M} + \alpha_H) - \alpha_{2p\sigma M}] \cos^2 \theta \quad (11)$$

The K which appears above is the proportionality constant relating the off-diagonal to the diagonal matrix elements. G and T contain the explicit S_{H_1, H_2} terms.

It may be verified that for normal bond lengths and parametrization (VSIP's), the μ_j values will generally be large positive quantities, while ν will be much smaller and negative ($\mu_j/\nu \sim -10$). Also, where k_1 will be large and negative, k_2 will be much smaller, since in the latter strong internal cancellation within both the first and second pairs of terms as presented in eq 10 and, further, cancellation between pairs occurs. The strength of the cancellation depends of course upon how close in magnitude α_H and $\alpha_{2p\sigma}$ are, but for the cases under consideration it should always be appreciable. Typical values for these parameters are shown in Table I.

By the same token, there will be cancellation between G and χ as they appear in the denominators of both terms in eq 9, with G the greater in magnitude for comparable α values. Therefore, since T is in the range 0.5–0.75 for normal MH bond lengths and is slowly varying with θ (due to opposite effects on H and F), the numerators of both terms in eq 9 should be positive and the denominators negative at all meaningful values

Table I. Parameters for the Analytic Energy Relations for CH_2 and H_2O (1A_1 States)

| | CH_2 | H_2O |
|---------------------------------|---------------|----------------------|
| $r_{MH}, \text{\AA}^a$ | 1.094 | 0.960 |
| $\alpha_{M2s, 2p}, \text{eV}^b$ | -21.4, -11.4 | -32.3, -14.8 |
| $\mu_{s, p}, \text{eV}^2$ | 45.44, 52.11 | 28.51, 29.71 |
| ν, eV | -3.39 | -2.89 |
| $\chi/\cos^2 \theta, \text{eV}$ | -15.36 | -10.27 |
| $k_{1, 2}, \text{eV}$ | -21.26, -0.54 | -22.15, 1.49 |

^a Bond lengths from experimental sources, tabulated in ref 6. ^b $\alpha_H = -13.6$ eV, all values from ref 17. The orbital exponent for hydrogen is here and elsewhere in this paper taken as 1.2, a better SCF value than unity, and to facilitate comparisons with the KEH and CNDO results. All other exponents are the Slater values.

of θ : for $\theta \geq 45^\circ$, $|k_1 + T(A + D)/2| > (-G + \chi) > |TD + k_2|$. Since χ is negative, the numerator of the first term decreases with increase in θ ; that of the second term increases. Depending upon the relative rates of change of G , T , and χ , the denominators can either decrease or increase. It should be noted that both G and χ decrease in magnitude and T slowly increases with increasing θ .

The numerators of eq 9 are seen therefore to correctly represent the behavior of the orbital energies for the a_1 (in total) and b_2 orbitals upon angular displacement *vis-à-vis* the Walsh rules and general qualitatively based MO expectations. Considered by themselves they are, however, incapable of providing the detail which must exist as regards curvature to produce a preferred configuration; the numerator of the first term decreases as rapidly as that of the second increases with increasing θ . On the other hand, it is certain that while the denominators which contain explicit dependence upon both $\cos \theta$ and S_{HH} must be the means by which the over-all rates of change of energy are determined, their changes must be smaller than (if in the same direction as) those of the numerators so as not to interfere with the correct directional dependence upon angle already noted. That the theory fulfills this latter expectation is verified by recognition of the $-G + \chi$ cancellation noted above. Whether reasonable curvatures are obtained requires examination of specific cases.

For CH_2 (six valence electrons, $r_{CH} = 1.094 \text{\AA}$). $-G + \chi$ is found to monotonically increase over the entire interesting range of increasing θ , sufficiently slowly so as not to interfere with the directions of change dictated by the numerators, but exercising enough influence to bring the rates of change of the two terms to equality in magnitude (opposite in direction) at $\theta = 60 \pm 2^\circ$ where $\delta + \delta$ has its largest negative value. This result agrees excellently with both the exact EH result and observed angle for the 1A_1 state of CH_2 . At small θ , the second term binding increases more rapidly than that of the first decreases, consistent with a smaller and hence more rapidly changing numerator in term two than in term one; see Tables I and II. At larger θ , the numerators rapidly become more nearly equal whereupon the denominators can effect the change, making term two increase in binding energy more slowly than term one decreases, and constituting at the crossover the energy minimum.

Interestingly, if the assumption is made that G , which is entirely angle dependent through S_{HH} , and

Table II. Angular Dependence of Total Energy for CH₂ from Analytic Eq 9^a

| θ , deg | $-\chi$ | S_{HH} | T | $-G + \chi$ | $-\delta$ | $-\bar{\delta}$ | $-(\delta + \bar{\delta})$ |
|-------------------|---------|----------|-------|-------------|-----------|-----------------|----------------------------|
| 45 | 7.68 | 0.258 | 0.486 | 12.05 | 4.158 | 4.360 | 8.518 |
| 50 | 6.35 | 0.215 | 0.484 | 12.37 | 3.974 | 4.847 | 8.821 |
| 54.3 | 5.23 | 0.186 | 0.490 | 12.79 | 3.823 | 5.158 | 8.981 |
| 60 | 3.84 | 0.156 | 0.503 | 13.47 | 3.639 | 5.456 | 9.095 |
| 65 | 2.74 | 0.138 | 0.518 | 14.13 | 3.499 | 5.571 | 9.070 |
| 70 | 1.80 | 0.122 | 0.532 | 14.70 | 3.367 | 5.684 | 9.051 |

^a θ in degrees; S and T unitless; all other quantities in eV.

that part of T which is similarly dependent do not change with angle, which is a pertinent dissection with respect to Walsh's rules, especially for the single b_2 orbital, the rates of change of both δ and $\bar{\delta}$ are substantially decreased. In fact, adopting the value for S_{HH} at $2\theta = 90^\circ$, the energy-*vs.*-angle curve is so severely flattened that five significant figure results obtained in the expansions (which are not this good as approximations) cannot provide a trustworthy estimate for the minimum.

For H₂O (eight valence electrons, two in the symmetry localized b_1 orbital, $r_{OH} = 0.960 \text{ \AA}$), $-G + \chi$ first decreases with increasing θ up to $\sim 55^\circ$, then increases very slowly, again, as in CH₂, not affecting the directions of energy change dictated by the numerators; see Table III. In H₂O, however, the rate of increase in term

Table III. Angular Dependence of Total Energy for H₂O from Analytic Eq 9^a

| θ | $-G + \chi$ | $-\delta$ | $-\bar{\delta}^b$ | $-(\delta + \bar{\delta})^c$ |
|----------|-------------|-----------|-------------------|------------------------------|
| 45 | 16.39 | 1.900 | 2.077, 1.832 | 3.977, 3.732, 3.977 |
| 50 | 16.17 | 1.809 | 2.407, 2.082 | 4.215, 3.891, 4.084 |
| 54.3 | 16.14 | 1.731 | 2.655, 2.269 | 4.386, 4.000, 4.153 |
| 60 | 16.25 | 1.632 | 2.930, 2.477 | 4.562, 4.109, 4.216 |
| 65 | 16.43 | 1.552 | 3.122, 2.625 | 4.674, 4.177, 4.250 |
| 70 | 16.64 | 1.482 | 3.269, 2.742 | 4.751, 4.224, 4.270 |
| 80 | 17.02 | 1.381 | 3.453, 2.893 | 4.834, 4.274, 4.285 |
| 90 | 17.17 | 1.345 | 3.512, 2.942 | 4.856, 4.287, 4.287 |

^a θ in degrees; all other quantities in eV. ^b The first entry from one-term expansion A14 which yield coefficients in Table I. The second entry by exact solution of quadratic for $1b_2$ orbital. ^c The first two entries correspond to sums with the two values given in the $-\bar{\delta}$ columns; the third is obtained from the expansions assuming the value of S_{HH} at 45° (0.3331) does not change with θ .

two (b_2 symmetry) continues greater than the rate of decrease in term one (a_1 symmetry) throughout the entire range of increasing θ , prompting the obviously wrong prediction of linearity for this molecule at this value of r_{OH} . Again, as in the CH₂ case, the variation in S_{HH} , as it contributes to G and T , is found to reinforce the changes as dictated by χ , in agreement with the Walsh analysis, at least as far as the separated b_2 orbital is concerned. This is illustrated in the last column of Table III.¹⁶

(16) The relatively successful prediction of the equilibrium angle in CH₂ has been previously noted;¹⁷ the correct 2θ value for singlet methylene is 103.2° .¹⁸ The failure of H₂O has similarly been noted. The exact numerical EH results indicate a shallow minimum at $\sim 85^\circ$. Claims for improvement by choosing a smaller value of K ,⁹ by contraction of the OH distance,^{11b} and through recognition of the appreciable ionic character of the molecule¹⁴ have been made. The mechanism for improvement under decrease in K may be localized in eq 9. While the largest effect appears to be on μ_s (reducing this value to 2.1 with $K =$

In both the CH₂ and H₂O (¹A₁ states), and presumably as well BH₂⁻, NH₂⁺, and NH₂⁻, the lowest two (most bonding) a_1 and the bonding b_2 orbitals are filled, and the opposed behavior of the symmetry orbitals upon angular change of approximately equal size, with respect to energy, can produce nonextremum values for equilibrium configurations. The analytical details are in agreement with the qualitative precepts of Walsh and indicate, at least for the b_2 orbital which is isolated in the analysis, the mathematical mechanism within the EH framework by which the increase in binding of the $2p_M$ to $1s_{H1}-1s_{H2}$ is coupled to and reinforced by the decrease in antibonding between the $1s_H$'s, with increase in θ , to produce the over-all increase in bonding in this MO. For the six total (four valence) electron cases such as BeH₂ and BH₂⁺, however, only one (the most bonding) a_1 and one b_2 orbital are filled. The effects on both the individual orbitals are easily obtainable; by difference the general nonparameter determined behavior of the second a_1 orbital filled in CH₂, etc., may be inferred.

Straight off, it appears that the energy of the low-lying a_1 level within the EH approximation will increase (become less binding) with increasing angle for any reasonable choice of VSIP's²¹ and equilibrium bond lengths for BeH₂ and BH₂⁺, and for CH₂ as well, albeit weakly contrary to the expectation of Walsh. This may be attributed to the decrease in H-H binding ($1s_{H1} + 1s_{H2}$) being numerically more important than the concomitant increase in $(2s + 2p)_M$, $1s_H$ binding, due not to increased s character of the participating hybrid on M, as claimed by Walsh, but rather to increased participation by hydrogen in the function. This arises because it is through a decrease in p_z rather than an increase in $2s$ that the s character of the hybrid is increased, an observation in agreement with Mulliken²²

1.5), term one is little affected because of a simultaneous decrease in the magnitude of k_1 , which in fact causes a decrease in the rate of fall of term one with increasing angle. Interestingly, $-G + \chi$ changes little. In term two, the decrease in μ appears much less dramatic (μ_p to 12.4 with $K = 1.5$); this is, however, not matched by change in k_2 and, consequently, the rate of change of the whole term is decreased substantially, to the point where a minimum in $\delta + \bar{\delta}$ is found at $75-80^\circ$ (θ). A further and not necessarily great reduction of K might be expected to yield a value close to the observed value for 2θ (104.4⁹).

Effects of reduction of r_{OH} may be submitted to similar analysis. Neither this change nor the entirely empirical reduction of K may be justified within the framework of the EH method, however, as being anymore than attempts to reproduce the correct angular dependence particularly for H₂O. Despite analysis which has shown that a single value of K cannot be expected to hold generally,^{5,19} no recipe for variation of this parameter with constitutional changes is in evidence.

Recognition of charge distribution differences and amendment of the VSIP's based on these distributions, on the other hand, would be entirely compatible with the theory. Weighted averages of the appropriate hybrid and formal ion bounds established for the constituent atoms should allow a more satisfactory representation of the diagonal matrix elements for a molecule whose charges and overlap populations do not appear from the original EH parametrization procedure to be balanced. Such procedures, which are properly recognized as outgrowths and extensions of the ω technique of π -electron theory,²⁰ lead to imposition of cyclical, self-consistent, α -upon-charge distribution adjustments. These procedures are similar in mathematical structure if not entirely in philosophy and content with those imposed in the SCF part of the CNDO calculations, and will therefore be examined in detail along with the analytic CNDO results.

(17) R. Hoffmann, G. D. Zeiss, and G. W. Van Dine, *J. Am. Chem. Soc.*, **90**, 1485 (1968).

(18) G. Herzberg, *Proc. Roy. Soc. (London)*, **A262**, 291 (1961).

(19) Cf. G. Blyholder and C. A. Coulson, *Theoret. Chim. Acta*, **10**, 316 (1968).

(20) G. W. Wheland and D. E. Mann, *J. Chem. Phys.*, **17**, 264 (1949).

(21) G. Pilcher and H. A. Skinner, *J. Inorg. Nucl. Chem.*, **24**, 937 (1962).

(22) R. S. Mulliken, *J. Am. Chem. Soc.*, **77**, 887 (1955).

who noted that substantial s character would be expected even at $\theta = 45^\circ$ in hybrids of first-row atoms. In H_2O , the change in energy of the a_1 level is in agreement with the Walsh rules, here presumably because the second, the OH binding effect, is larger than the first, the HH binding effect. However, more complete calculations suggest the angular effect is in the other direction.^{3, 23, 24}

Equation 6 cast in terms of the expansion (eq A9, A13, and A15) is useful in revealing the origin of some of these variations in the four valence-electron cases.

$$E_{\text{tot}} = 2\{X_{1a_1} + X_{1b_2}\} = 2\{(m - \gamma_-) + D + \delta\} \quad (12)$$

The parameter m , effectively a weighted average of the 2s and 2p VSIP's which is independent of S_{HH} contributions, decreases in magnitude substantially with increased θ .²⁵ This decrease in binding is, however, almost completely offset by an increase in γ_- (positive and becoming more positive) to yield a slow decrease in binding for the $1a_1$ level. The variation in γ_- itself is the result of a partial cancellation of a large increase promoted through MH binding by the S_{HH} -dependent effects, which decrease with increasing θ . Table IV

Table IV. Components for Orbital Energies for BeH_2^a

| | $\theta = 65^\circ$ | $\theta = 75^\circ$ |
|----------------------|-----------------------------|-----------------------------|
| m | -6.62, -6.44 ^b | -6.16, -6.08 ^b |
| γ_- | 9.04 | 9.41 |
| X_{1a_1} | -15.66, -15.83 ^b | -15.57, -15.77 ^b |
| $(\gamma_-)_{s^3}^c$ | 9.04 | 9.68 |
| $(X_{1a_1})_{s^3}^c$ | -15.66 | -15.84 |
| X_{1b_2} | -13.64, -13.64 ^b | -13.78, -13.81 ^b |

^a $r_{\text{BeH}} = 1.343 \text{ \AA}$; $\alpha_{2s} = -9.8$, $\alpha_{2p} = -5.8$, all energies in eV. ^b Values obtained by exact numerical solution. ^c Values obtained by holding S_{HH} at its 65° value (0.0668).

illustrates these effects for the arbitrarily chosen angle values of 65 and 75° for BeH_2 .

Over-all, the binding energy of the $1b_2$ level increases considerably more rapidly over the entire range of 2θ from 90 to 180° than the energy of the $1a_1$ level decreases, and consequently, BeH_2 is predicted to be linear. The same result is obtained for BH_2^+ . On the other hand, the corresponding beryllium and boron dihydride molecules with added electrons which will go into the $2a_1$ level are expected to be bent.

Useful comparisons with the results of more exact calculations and with some numerical EH results on these and other first-row dihydrides may be made.^{3, 24} All composite predictions are found to be in agreement with Walsh as well as with these authors. Particular details are not universally in agreement, interpretation of what the Walsh rules should correspond to theoretically vary, nor, as we have demonstrated is the original EH method trustworthy in a quantitative sense.

The KEH Approximation. By far the most interesting and meaningful result obtained by Newton, Boer, and Lipscomb⁵ from their modification of the EH method concerns the constancy of the scale factor, K . From a number of SCF calculations made with minimal

(23) Cf. F. O. Ellison and H. Shull, *J. Chem. Phys.*, **23**, 2348 (1955).

(24) C. A. Coulson and A. H. Neilson, *Discussions Faraday Soc.*, **35**, 71 (1963).

(25) Note, m is itself the value of the root X_{2a_1} corresponding to an unfilled level here which behaves in accordance with Walsh's rules.

Slater basis sets for simple molecules they were able to demonstrate a remarkable constancy for the K values connecting the potential energy parts of the Hamiltonian matrix elements for orbitals of given n, l, m , independent of the nature of the atoms upon which these orbitals are centered. A fair amount of variation in K was found for variation among $n, l, m:n', l', m'$ pairings, however. The effects of this K variability on the angular dependence of molecular energy may be examined in detail from the relations developed here for this method (eq A4-A7).²⁶

For CH_2 , a pertinent example, with parametrization as suggested in the original references,⁵ the analytical results presented in Table V are obtained. Assuming

Table V. Expansion Parameters for CH_2 in the EH and KEH Approximations^a

| Method | $\mu_{s,p}$ | $-(A + D)/2$ | $-D$ | $-\nu$ | $-k_{1,2}$ |
|------------------|--------------|--------------|-------|------------|-------------|
| EH | 45.44, 52.11 | 16.4 | 11.4 | 3.39 | 21.28, 0.54 |
| KEH ^b | 28.35, 78.36 | 18.55 | 13.06 | 4.26 | 18.79, 0.44 |
| ... ^c | | | | 1.29, 4.26 | |

^a All quantities in eV, except for μ 's which are in (eV)². ^b With $K^{Z^0} = 0$; otherwise parameters as previously given and from ref 5. ^c With $K^{Z^0} = 0.4$; parameters same as in footnote b, but with ν 's for terms one and two as specified. Coefficient 0.844 on χ in denominator of term one applies here as well.

initially for the purpose of comparison with the EH results that the zero overlap ($2s_M, 2p_M$ off-diagonal) term is zero ($K^{Z^0} = 0$, eq A6, A7), the coefficients for the equivalent of eq 9 are given in Table V next to those for the comparable EH calculation. In general, the coefficients of the two methods vary by somewhat larger factors than the variation in the input diagonal matrix elements (A and D), but not always in the same direction. Interestingly, the angle at which the minimum energy is obtained is, however, essentially identical; i.e., $\theta = 60 \pm 2^\circ$, see Table VI. Moreover, the slopes

Table VI. Angular Dependence of Total Energy for CH_2 in the KEH Approximation^a

| θ | $-\chi$ | $-G$ | T | $-\delta$ | $\overbrace{-(\delta + \delta)}_{K^{Z^0} = 0}$ | $\overbrace{-(\delta + \delta)}_{K^{Z^0} = 0.4}$ |
|----------|---------|-------|-------|-----------|--|--|
| 45 | 9.20 | 21.79 | 0.536 | 7.609 | 11.793 | 10.341 |
| 50 | 7.60 | 20.30 | 0.534 | 8.712 | 12.507 | 11.285 |
| 54.3 | 6.19 | 19.25 | 0.539 | 9.329 | 12.806 | 11.787 |
| 60 | 4.60 | 18.13 | 0.552 | 9.999 | 13.091 | 12.316 |
| 65 | 3.29 | 17.40 | 0.567 | 10.274 | 13.060 | 12.492 |
| 70 | 2.15 | 16.83 | 0.582 | 10.416 | 12.934 | 12.553 |
| 80 | 0.56 | 16.00 | 0.602 | 10.640 | 12.756 | 12.655 |
| 90 | 0.0 | 15.93 | 0.615 | 10.496 | 12.484 | 12.484 |

^a θ in degrees, T unitless, all other quantities in eV.

on the opposite sides of the minima are similar, being much sharper on the small- than on the large- θ side, despite the different ways the controlling parameters in terms one and two vary between the methods; compare with Table II. For these results, then, introduc-

(26) Arguments based on apparent cancellation of half the sum of kinetic and nuclear attraction energies in the molecule, relative to the constituent atoms, with the sum of nuclear repulsion energies,⁵ suggests E_{tot} in this method should vary as $1/2(2 \sum \epsilon_i)$ varies with angle. See the accompanying paper for further discussion and implications of this assumed variation.

Table VII. Component Terms of Eq 9 and Changes upon Symmetric Stretching of CH Bonds in CH₂ (EH Approximation)

| Term | Magnitude, sign | Changes as; rate of change; direction |
|--------------|----------------------|--|
| μ_{2s} | Large, + | $S^{2s_{M,1s_H}}$; rapid; smaller |
| $\nu\chi$ | Moderate, + | $S^{2p\sigma_{M,1s_H}}$; moderate; smaller |
| $T(A + D)/2$ | Moderate, - | Complex, $S^{2s_{M,1s_H}}$ most important, reinforced by $S^{2p\sigma_{M,1s_H}}$ opposed by $S_{1s_H1,1s_H2}$; moderate to slow; larger |
| k_1 | Large, - | $S^{2s_{M,1s_H}}$; rapid; smaller |
| $-G$ | Moderate, + | $S_{1s_H1,1s_H2}$; slow; smaller |
| χ | Small, - | $S_{2p\sigma_{M,1s_H}}$; moderate to slow; smaller |
| μ_{2p} | Large, + | $S^{2p\sigma_{M,1s_H}}$; moderate; smaller |
| $T(D)$ | Small, - | See $T(A + D)/2$ |
| k_2 | Small, indeterminate | Rapid change of $S^{2s_{M,1s_H}}$ opposed by $S^{2p\sigma_{M,1s_H}}$ term; moderate to slow; smaller negative than larger positive |

tion of variable K and removal of the kinetic energies appears to have little effect upon the physically meaningful angle-dependent properties of the CH₂ molecule.

If, however, the zero-overlap term, which is always relatively small, is included as the studies in ref 5 indicate it should be to reproduce SCF F -matrix form, very different results are obtained. Because of the $F_{2s,2p_z}$ dependence of P and Q , and v and w , μ_s becomes θ -dependent, and the coefficient of χ in the denominator, unity in the EH approximation and in the KEH approximation where K^{ZO} is zero, becomes smaller than one. Zeroth, second, and fourth power $\cos \theta$ dependence is generated for μ_s ; if the very small $\cos^4 \theta$ term is ignored, the form of eq 9 may be maintained, except for the χ -coefficient difference mentioned, by absorbing the $\cos^2 \theta$ term into the ν coefficient; see Table V.

The effects on the molecular energy of what appear to be small changes in the coefficients determining δ —and compensating changes at that since both the numerator and denominator become less sensitive functions of χ —are nevertheless profound. This is revealed in the last column of Table VI; when K^{ZO} is 0.4, the predicted minimum shifts to beyond 80° (θ), which suggests an almost linear equilibrium configuration. (Precise numerical results obtained by computer solution, in fact, yield only the 90° minimum.)

A somewhat similar situation is found upon examination of H₂O within the KEH framework. With $K^{ZO} = 0$, a minimum is predicted in the region $\theta = 50^\circ$; when $K^{ZO} = 0.4$, the minimum shifts outward by about 10° (20° in HOH angle). The explanation of this effect is illuminating and important to the entire concept of semiempirical predictions of equilibrium bond angles. The major effect of the K^{ZO} term may be localized in the 2a₁ orbital; the orbital energy is always lower (more bonding) where K^{ZO} is zero but by decreasing amounts as the angle opens out to $2\theta = 180^\circ$. For the linear configuration, symmetry precludes any $F_{2s,2p_z}$ contribution. Hence, the energy change for the 2a₁ orbital, and, since it is the orbital most sensitive to the inclusion of the zero-overlap term, the total a₁ orbital energy change with θ must be steeper when K^{ZO} is zero. The effect of including the zero-overlap term (with positive coefficient) is then easily seen to shift outward the internal angle at which the decrease in the a₁ energies matches the increase in the b₂ energies (unaffected by zero-overlap considerations). The effect may likewise be visualized in terms of increased 2p orbital character imposed in the 2a₁ MO by the inclusion of K^{ZO} ; higher 2p_z, 1s_H overlap populations (OP)²⁷

are noted at all angles with this OP vanishing in the linear configuration.

Energies and Changes upon Symmetric Stretching Displacements

The analytic expressions derived in the Appendix and used in dissection of the energy changes accompanying angular displacement may also be used for analysis of symmetric stretching and compression of the MH bonds. For example, eq 9 again separates the effects on the 1a₁ and 2a₁ orbitals from those on the 1b₂ orbital. However, where in the former analysis we had to concern ourselves only with changes in $\cos^2 \theta$ and S_{HH} with change in θ , now all quantities with the exception of ν change with change in r_{MH} . Despite the greater complexity, useful information on the relative importance of contributing effects may be obtained: the components of the two terms of eq 9 and how they may be expected to change upon MH bond stretching are shown in Table VII for the typical case of CH₂.

The first term of eq 9 has a numerator which should decrease in magnitude relatively rapidly as the MH bond is stretched over the entire interesting range (for CH₂ from -0.2 to +0.5 Å about the equilibrium distance 1.094 Å with $2\theta = 103.2^\circ$). At the same time, the denominator should change much less rapidly due to partial cancellation in the changes between $T(A + D)/2$ and k_1 and also between $-G$ and χ . Therefore, the whole term is expected to decrease in magnitude with stretching or become less bonding, which it does as confirmed by computer analysis. Interestingly, from these results one finds it is the energy of the 1a₁ orbital which by rapid loss of bonding determines the direction of change for the term. The 2a₁ orbital becomes more bonding, but considerably more slowly.

In term two, the two components of the numerator, μ_{2p} and $\nu\chi$, both decrease with the same $S^{2p\sigma_{M,1s_H}}$ dependence, but because of the minus sign the rate of change is relatively slow. This and the different behavior of the denominator, due mainly to the difference in behavior of k_2 compared to k_1 , makes predictions of changes in the whole term an uncertain matter. As the exact computer results indicate, the energy of the 1b₂ level becomes more negative (more binding) as the CH bond is stretched over the range 0.894 to near the correct equilibrium distance, but thereafter the energy increases.

(27) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955).

Similar but not identical behavior is found for H₂O. For this molecule, the sum of the a₁ orbital energies increases over the entire interesting range with stretching (same displacements as for CH₂); except at the most distended positions the energies of both the 2a₁ as well as the 1a₁ levels increase. Also, the 1b₂ level exhibits a monotonic increase in energy upon stretching. In BeH₂ where only the 1a₁ and 1b₂ levels are filled, the energy of the 1a₁ level continuously rises; that of the 1b₂ level falls but more slowly. Consequently, the total energy is predicted to increase over the entire range 1.143–1.843 Å.

Accepting these results as typical, it is apparent that the EH method is completely incapable of reproducing the dependence of electronic energy on molecular size. Examination of the results forthcoming from the KEH method leads to the same conclusion. Where in the EH method general monotonic energy increases with MH stretching are noted, in the KEH approximation monotonic decreases (increased binding) are the general result. In the latter method the dependence of the electronic energy upon the two-center kinetic energy and its changes with change in MH distance are sufficiently strong to overcome the dependence upon potential energy assumed to be varying as the two-center overlap integral. Since the kinetic energy integrals are evaluated correctly, at least so far as the use of a single Slater function representation per orbital allows, the initial tendency is to direct the blame for failure of the method on the potential energy and the representation of its variation with geometric change. This would be consistent with results obtained for the EH method. The reasons for poor approximation of molecular sizes (poorer on balance than of shapes) appear, however, to be more complex than this single factor implies.

Conclusions

To the extent the semiempirical methods considered can correctly or to good approximation represent the contributions of the various electronic interactions in a molecule at the correct equilibrium geometry, they may be expected to reproduce angular deformations if the most important of these interactions and their relative weights vary in the same simple geometric way the approximate theories picture them to vary. Interactions represented by one- and two-center one-electron integrals generally do; those represented by more complicated integrals reduced successively by the Mulliken overlap approximation (*i.e.*, $(ij|kk) = \frac{1}{2}S_{ij}[(ii|kk) + (jj|kk)]^8$ will vary as S_{ij} upon angular deformation and also therefore will conform to the simple picture, at least qualitatively.¹⁹ Break-down of the simple methods might then be expected to occur only at the quantitative level, *i.e.*, in reproduction of correct equilibrium angles or, at even more refined a level, in reproduction of correct bending force constants.

The variation in weighting of these interactions is a more difficult problem, being bound up with the SCF procedures employed in exact calculations. A certain amount of this variation may be absorbed within the semiempirical method, provided that it is either moderate, compared to integral change, or proportional to such change. The results obtained for CH₂, where

relatively minor and slowly varying ionic character is predicted for the molecule, and fair judgement of its equilibrium angular properties made, may be contrasted in this light to the results obtained for H₂O. The latter is predicted to be strongly ionic ($q_H \cong \frac{1}{2}$); indications are that unless provisions for this character are properly made, quantitative reproduction of its geometry is out of the question.

Similar problems of weighting should be recognized to exist for both the EH and KEH methods. The simpler method has the virtue of identification of the atom as it exists in the molecule with free atoms in their proper valence states. The improved method removes the unrealistic proportionality constraints between diagonal and off-diagonal Hamiltonian matrix elements, important for the equilibrium configuration, at the cost of obfuscation of the physical origins of the diagonal elements and, therefore, of their variation under demands of the SCF procedure. Additional problems, such as interpretation of the contributions of zero-overlap terms and whether assumption of proportionality of orbital energy with total energy is justified, equally valid in both methods, are revealed concretely in analysis of the KEH method.

Finally, the factors discussed above which contribute to successful reproduction of equilibrium angles in MH₂ and presumably in more complicated systems as well, are much less likely to play dominant roles when nearest neighbor atom separations are considered. Table VIII graphically illustrates one aspect of this difference

Table VIII. Comparative Charge Effects in CH₂ in the EH Method under Angular and Stretching Deformations^{a, b}

| Angle variation at r_{CH} equil | | R_{HH} | Variation of r_{CH} at equil HCH angle | |
|--------------------------------------|--------|---------------|---|--------|
| θ | q_H | | r_{CH} | q_H |
| 45 | +0.120 | 1.56 ± 0.002 | 0.994 | +0.128 |
| 50 | 0.108 | | | |
| 51.6 | 0.106 | | 1.094 | 0.106 |
| 60 | 0.109 | | 1.194 | 0.085 |
| 70 | 0.125 | | 1.294 | 0.062 |
| 80 | 0.143 | | | |
| 90 | 0.150 | 2.186 ± 0.002 | 1.394 | 0.034 |

^a θ in degrees; all distances in Å and charges compared to neutral hydrogen atom. ^b Where entries appear on the same line they represent geometries with equal R_{HH} within the limits shown.

by reproducing the hydrogen atom charge variation in the EH approximation upon stretching as contrasted to angle deformation in CH₂. Three isoradial (equal R_{HH}) situations are shown: in these configurations the differences noted may be ascribed entirely to the MH interaction differences. Where under angular deformation the changes in the ionic character of the molecule are relatively minor, stretching deformations produce a sharp, monotonic, and almost linear decrease in the positive charge on hydrogen which must have an important effect upon the weighting, or, alternatively, the matrix element construction detailed above.

Appendix

Analytic Approximation to the Symmetry-Reduced Eigenvalue Problem. The symmetric 3 × 3 matrices encountered in the EH calculations which include

differential overlap may be orthogonalized by straightforward row and column subtractions.

$$\begin{vmatrix} A-x & 0 & B-Cx \\ & D-x & E-Fx \\ & & G-Hx \end{vmatrix} \rightarrow \begin{vmatrix} A-x & 0 & P \\ & D-x & Q \\ & & R-x \end{vmatrix}$$

With the arithmetic mean approximation for off-diagonal matrix elements and the single subscript notation signifying diagonal elements

$$\begin{aligned} A &= F_{2SM} \\ B &= \sqrt{2}(KS)_{2SM,1SH}(F_{2SM} + F_{1SH})/2 \\ C &= \sqrt{2}S_{2SM,1SH} \\ D &= F_{2pzM} \\ E &= \sqrt{2}(KS)_{2pzM,1SH}(F_{2pzM} + F_{1SH})/2 \\ F &= \sqrt{2}S_{2pzM,1SH} = \sqrt{2}S_{2p\sigma M,1SH} \cos \theta \\ G &= F_{1SH} + (KS)_{1SH1,1SH2}(F_{1SH1} + F_{1SH2})/2 \\ &= F_{1SH}(1 + (KS)_{1SH1,1SH2}) \\ H &= 1 + S_{1SH1,1SH2} \\ P &= (B - AC)T^{-1/2} \\ Q &= (E - DF)T^{-1/2} \\ R &= (G - 2BC + AC^2 \\ &\quad - 2EF + DF^2)T^{-1} \\ T &= (H - C^2 - F^2) \end{aligned} \quad (A1)$$

Recognizing R as positive and large, as it usually is in the EH method, and with A and D both negative, the transformation $x = R - \delta$ may be made which leads to the characteristic equation

$$\delta^3 + \delta^2(a + d) + \delta(ad - (P^2 + Q^2)) - (P^2d + Q^2a) = 0 \quad (A2)$$

with $a = A - R$ and $d = D - R$. Since the general condition exists that one root, δ , will be small and negative consistent with the nature of level interactions, *i.e.*, the isolated level of energy R is raised and $|\delta| \ll |P^2d + Q^2a|$, then to a good approximation

$$\delta_0 = \frac{-v \pm \sqrt{v^2 - 4uw}}{2u} \quad (A3)$$

where $u = a + d$, $v = ad - (P^2 + Q^2)$, and $w = -(P^2d + Q^2a)$. The small value for δ is obviously obtained with the plus root.

In the KEH approximation 4×4 matrices are obtained in the totally symmetric combination by inclusion of the 1s orbital on M. Upon application of the same orthogonalization procedure as above and making the transformation $x = F_{1SM} - \Delta$ it is easily shown that

$$\Delta \cong \frac{V^2}{a'} + \frac{W^2}{r'} \quad (A4)$$

where V and W are, respectively, $(F_{1SM,2SM} - S_{1SM,2SM} \times F_{1SM})t^{-1/2}$ and $\sqrt{2}(F_{1SM,1SH} - S_{1SM,1SH}F_{1SM})t^{-1/2}$ and $t = 1 - S_{1SM,2SM}^2$. The quantities a' and r' are similar to a and d (above) except that they bear the 1s orthogonalization terms and are scaled with respect to F_{1SM} , rather than R . Both are therefore large positive

numbers, generally greater than V and W by two orders of magnitude. Consequently, the root very close to F_{1SM} may be removed from the quartic yielding the following cubic equation

$$\delta^3 + \delta^2(a + d - \Delta) + \delta[ad - (P^2 + Q^2) + (a + d)\Delta] - [P^2d + Q^2a + (P^2 + Q^2)\Delta - \frac{a}{F_{1SM}}(V^2a - W^2d)] = 0 \quad (A5)$$

The cubic is correct to the first order in the perturbation exercised by the 1s orbital terms but ignores for the moment the zero overlap (ZO) term between the 2s and 2p orbitals which is introduced in approximation in the KEH method.

Since F_{1SM} is so large compared to all other terms and Δ so small (*e.g.*, ~ 0.09 eV for CH_2 , with a and d generally in the tens-of-volts region), eq A5 is almost identical with A2, and is taken to be so in light of other more serious approximations used. The a_i energy levels are therefore obtained as in eq A1-A3 with appropriate modification of the relations connecting the diagonal and off-diagonal elements, *i.e.*, proportionality between the potential energy terms.

To correctly reproduce the Hamiltonian matrix in the KEH method as regards the orbital interactions for which the overlap is zero but the F value is not, the empirical relationship

$$F_{a,a'} = K^{ZO} \sum_i S_{ai} S_{a'i} \alpha_i \quad (A6)$$

has been suggested.⁵ This introduces small but often nonnegligible $2s_M, 2p_M$ terms which reduce for the cases under consideration to

$$F_{2s,2p_z} \equiv L = 2K^{ZO} S_{2SM,1SH} S_{2pzM,1SH} \alpha_H = 2K^{ZO} (S_{2SM,1SH} S_{2pzM,1SH}) \alpha_H \cos \theta \quad (A7)$$

and cause the following changes in the terms appearing in eq A3. Now, v and w are, respectively, $ad - (P^2 + Q^2 + L^2)$ and $-(P^2d + Q^2a - 2PQL)$. P , Q , and R are, in order, $(B - AC - LF)T^{-1/2}$, $(E - DF - LC)T^{-1/2}$ and $(G - 2BC + AC^2 - 2EF + DF^2 + 2LCF)T^{-1}$. It is usefully recognized that such ZO terms will appear only in the totally symmetric matrices and have the same angular dependence as the $2p_{z,M}, 1s_H$ interactions.

At this juncture it is useful to note that all cases to be treated within the EH and KEH methods are not satisfactorily approximated by the analytical procedure developed above. For example, BeH_2 in the EH method is characterized by R values which are of similar magnitude and sign as D over much of the interesting θ range. In this and like cases the analysis applied to the CNDO calculations, which is detailed below, is appropriate for the *orthogonalized* EH and KEH matrices. These two principal approximation techniques for the cubics fortunately have contiguous ranges of applicability with some overlapping.

The 3×3 matrices encountered in the application of the CNDO2 method are simpler than those encountered above (since $S_{ij} = 0$ for $i \neq j$ and $S_{ii} = 1$). With the notation carried over from before

$$\begin{vmatrix} A-x & L & B \\ & D-x & E \\ & & G-x \end{vmatrix}$$

A , D , and G are, respectively, F_{2SM} , F_{2pzM} , and $(F_{1SH} + F_{1SH1,1SH2})$. L , B , and E are $F_{2SM,2pzM}$, $\sqrt{2}F_{2SM,1SH}$, and $\sqrt{2}F_{2pzM,1SH}$. The F elements are as derived by Pople and Segal.⁶

Despite the similarity in form to those considered above, these matrices are not amenable to the same reduction method because of general similarity in size of two or more of the diagonal elements. Advantage may be taken of this similarity however by introduction of the transformation, $x = m - y$, which produces the following characteristic equation.

$$y^3 + y^2(a + d + g) + y(ad + ag + dg - B^2 - L^2 - E^2) + 2LBE + adg - (B^2d + L^2g + E^2a) = 0 \quad (A8)$$

Here a , d , and g are respectively $A - m$, $D - m$, and $G - m$.

If m is defined so as to make the constant term in eq A8 zero, the equation yields a root directly ($y = 0$) and consequently reduces to a quadratic which is convenient for present purposes. Precise solution for m would of course require handling a cubic; however, because of the size similarity of two or more of the diagonal elements, plus the fact that the off-diagonal elements B and E are of comparable magnitude to the diagonal elements and L is small, the following very good approximation may be made.

$$m = \frac{-2LBE + B^2D + L^2G + E^2A - adg}{L^2 + B^2 + E^2} \cong \frac{-2LBE + B^2D + L^2G + E^2A}{L^2 + B^2 + E^2} \quad (A9)$$

That the term adg must be small and can thereby be ignored under the conditions outlined may easily be seen from the following analysis. A theorem by Cauchy (1829)²⁸ states that one root of the 3×3 determinant encountered here must lie between the roots for the cofactor obtained by striking the third column and row of the original determinant. The roots of the latter are $(A + D \pm \sqrt{(A - D)^2 + 4L^2})/2$. Further, since the other roots of the third-order determinant must lie one to the high side of the most positive root of the quadratic and the other to the low side of the most negative, the value of m obtained with the smallest value of adg must correspond to the bounded root ($x = m$).²⁹ Therefore, for G bounded by A and D , or G slightly outside these bounds, as the condition of similarity of two diagonal elements implies, it may be shown that the maximum permissible value for $|adg|$ is equal to a small fraction (*i.e.*, $< 1/3$) of the cube of the difference, $A - D$. Consequently neglect of adg can result in an error of only a few per cent in determination of m . As an example of the validity of this approximation, the roots, x , of the zeroth-order CNDO2 matrix for CH_2 ($r_{\text{CH}} = 1.094 \text{ \AA}$, $2\theta = 108.6^\circ$) are -29.80 , -15.21 , and 8.61 eV by exact solution of the cubic and -29.76 , -15.58 , and 8.84 eV employing the approximation for m and the first term of the expansion of the quadratic in y (see eq A13, below). The approximated value of

(28) Cf. T. Muir, "The Theory of Determinants in the Historical Order of Development," Vol. I, Dover Publications, Inc., New York, N. Y., 1960, pp 425-435.

(29) With small L , and ignoring adg , eq A9 states that m is the weighted average (by the squares of the off-diagonal elements) of the diagonal elements, A and D .

m is -15.586 eV compared to the precise value -15.215 eV : the approximated value of the numerator in eq A9 is -5388 (eV)^3 while adg is $\sim -128 \text{ (eV)}^3$. The error introduced by the approximation in m , $\sim 2\%$, is reflected in the average error of the x values derived.

Expansion of the Quadratics. Equation A3 (plus root) may be expanded by conventional means to yield

$$\delta = \frac{2(P^2 + Q^2)}{a + d} \times \left(1 - \frac{4(P^2 + Q^2)}{(a + d)^2 + 12(P^2 + Q^2)} \dots \right) \quad (A10)$$

where $(a - d)^2 \ll 12(P^2 + Q^2) < (a + d)^2$, as is generally the case. For the KEH method the similar expansion, correct to the first explicit order in L

$$\delta = \frac{2(P^2 + Q^2)}{a + d} \times \left(1 - \frac{4(P^2 + Q^2) - 2L(a + d)}{(a + d)^2 + 12(P^2 + Q^2)} \dots \right) \quad (A11)$$

may be derived where the P and Q values are themselves modified by terms in L as previously detailed. The remaining roots of the original cubics may be most expeditiously obtained from the three-component sum and product rules (equal respectively to $-u$ and $-w$) which apply to cubics. Combined with eq A3 or expansions thereof (eq A10), expressions of slightly poorer quality than for the original root δ are obtained which lead to the following expansion.

$$\delta_- \cong -\frac{1}{2} \left((a + d) + \delta_0 - \frac{6(P^2 + Q^2)}{\sqrt{(a + d)^2 + 12(P^2 + Q^2)}} \right) \quad (A12)$$

The quadratic equation obtained from eq A8 upon the setting of m may be conveniently expanded to yield

$$y \equiv m - x = -\tau \pm \sqrt{X} \left(1 + \frac{\tau - (ad + ag + dg)}{2X} \dots \right) \quad (A13)$$

where $\tau = (a + d + g)/2$, $X = L^2 + B^2 + E^2$, and $X \gg \tau - (ad + ag + dg)$. All three roots, the pair in eq A13 and $y = 0$, are obtained together here, in contrast to the two part decompositions necessary for the EH and KEH matrices.

The quadratics which arise for the b_2 symmetry orbitals are most conveniently considered under similar transformations as were applied for the a_1 set. The EH and KEH equations are identical in form in this symmetry and expand to

$$\bar{\delta} = \frac{\bar{Q}^2}{\bar{d}} \left(1 - \left(\frac{\bar{Q}}{\bar{d}} \right)^2 + 2 \left(\frac{\bar{Q}}{\bar{d}} \right)^4 \dots \right) \quad \text{for } |2\bar{Q}| < |\bar{d}| \quad (A14)$$

$$= \bar{Q} \left(1 + \frac{1}{2} \left(\frac{\bar{d}}{\bar{Q}} \right) + \frac{1}{8} \left(\frac{\bar{d}}{\bar{Q}} \right)^2 \dots \right) \quad \text{for } |2\bar{Q}| > |\bar{d}| \quad (A15)$$

Here, $\bar{d} = \bar{D} - \bar{R}$, $\bar{R} = (\bar{G} - 2\bar{E}\bar{F} + \bar{D}\bar{F}^2)\bar{T}^{-1}$, $\bar{T} = (\bar{H} - \bar{F}^2)$, and $\bar{Q} = (\bar{E} - \bar{D}\bar{F})\bar{T}^{-1/2}$. The bar on a

previously defined symbol signifies replacement of $\cos \theta$ by $\sin \theta$ in the $2p\sigma_M, 1s_H$ interaction elements and change in sign in the S_{HH} factors. Note, in the EH method D and \bar{D} are identical, which is not necessarily so in the KEH formulation.

The energies of the b_2 orbitals in the CNDO and special EH cases are obtained in expansion as follows.

$$\bar{y} \equiv -x = -\bar{\tau} \pm \sqrt{\bar{X}} \left(1 + \frac{\bar{\tau}^2 - \bar{d}\bar{g}}{2\bar{X}} \dots \right) \quad (\text{A16})$$

Now $\bar{\tau} = (\bar{d} + \bar{g})/2 = (\bar{D} + \bar{G})/2$, since $\bar{m} = 0$ and $\bar{X} = \bar{E}^2$. The same replacements for bar quantities as before are made; for the CNDO applications exchange of the bond orders $P_{2p_M, 1s_H}$ for $\bar{P}_{2p_M, 1s_H}$ are also made.

Semiempirical Molecular Orbital Theory and Molecular Geometry. II. Analytic Procedures for Charge Redistribution Methods¹

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Abstract: Analysis has been carried out to obtain closed-form energy and electron distribution expressions for the first-row atom dihydrides as represented by extended-Hückel theory modified by self-consistent charge redistribution procedures, and by the similar but theoretically more soundly grounded SCF CNDO2 method. Previous examination of this group of molecules revealed deficiencies in the ability of two important variations of zeroth-order Hückel theory to represent energy upon geometry dependences. From the results obtained here, the specific way in which the charge imbalances established in the zeroth-order results are modified by the variations in electronegativities of the atoms so charged may be followed. Good approximations to the self-consistent energies and charge densities are obtained in both the Hückel and CNDO methods by familiar closed form summation procedures. Exactly how the original and the redistribution parameters interact to change the energy upon geometry dependence are revealed and the reasons why the Hückel redistribution procedure is inherently inferior to the SCF redistribution of the CNDO2 method are examined. The approximate cancellation of hydrogen-hydrogen electron and nuclear repulsions are recognized in the CNDO angle deformation problem and the influence of this cancellation on making the CNDO and extended Hückel procedures appear similar is discussed.

In the preceding paper² analytic expressions were developed for the orbital and total electronic energies of the first-row dihydrides within the framework of two important variations of the extended Hückel method.^{3,4} The major purpose of the development was to ascertain how the various specific interactions recognized by the theory contribute to the computed energies, and how these contributions change with changes in molecular geometry. It seems clear from the results obtained, and those of other investigators,⁵ that such semiempirical theories should be generally better able to approximate the energetics of geometry changes from equilibrium configurations involving displacements of nonnearest neighbor atoms (*i.e.*, bond angle variations) than of neighboring more strongly bound atoms. In neither case, however, would confidence in the energy surfaces generated by these methods as originally formulated seem warranted.

It appears from some recent studies, though, that considerable improvement of these independent electron methods is possible if charge redistribution techniques which alter the atom-type or standard molecule parameters are employed. Such fairly uncomplicated pro-

cedures specifically as applied to the EH method of Hoffmann⁶ have yielded interesting results and appear to be gaining a measure of acceptance in the study of geometrical isomerization of large hydrocarbon molecules and ions (mainly the angular configuration problem).⁷ Parameter adjustment based on charge distributions, which is entirely consistent with the philosophy of the original methods, represents a way, albeit an averaged way, of imposing self-consistent field conditions on the zeroth-order wave functions, and stands the chance of successfully approximating the results of more complete theories if integral variations with geometry change are approximately paralleled. Angular effects are certain on these grounds to be more favorably treated than bond stretches or contractions.

It is not surprising that the CNDO approximations,⁸ which are true SCF methods as applied to wave functions obtained from complete but simplified Hamiltonians, are also capable, without specific modification for the task, of reproducing molecular energy variations with bond angle change quite successfully. Moreover, these methods, originally claimed to not as satisfactorily account for energy changes

(1) Research performed under the auspices of the U. S. Atomic Energy Commission.

(2) S. Ehrenson, *J. Am. Chem. Soc.*, **91**, 3693 (1969).

(3) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963), and later papers.

(4) M. D. Newton, F. P. Boer, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **88**, 2353 (1966), and succeeding papers in the same volume.

(5) Cf. L. C. Allen and J. D. Russell, *J. Chem. Phys.*, **46**, 1029 (1967).

(6) D. G. Carroll, A. T. Armstrong, and S. P. McGlynn, *ibid.*, **44**, 1865 (1966).

(7) Cf. J. E. Baldwin and W. D. Fogelsong, *J. Am. Chem. Soc.*, **90**, 4311 (1968).

(8) J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **44**, 3289 (1966).