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.

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

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 $P_{2p_zM,1sH}$ for $P_{2p_xM,1sH}$ are also made.

Semiempirical Molecular Orbital Theory and Molecular Geometry. II. Analytic Procedures for Charge Redistribution Methods[1]

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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 Huckel procedures appear similar is discussed.

In the preceding paper[2] 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 Huckel 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 procedures specifically as applied to the EH method of Hoffmann[6] 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

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[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).

accompanying nearest neighbor distance variations, may in fact, with certain well-defined exceptions, yield fair energy variation approximations and thereby provide useful insights into this important type of problem. Extensive application of the CNDO2 method in this direction is underway.[9]

As an extension to the work described in ref 2, the first-row closed-shell dihydrides, MH_2, are examined in the framework of the two methods discussed, *i.e.*, the charge redistributed extended Hückel, CREH, and the true SCF CNDO2 methods. The approach is the same as previously adopted in that approximate analytic expressions for the orbital, electronic, and total energies, and where necessary charge distributions, are derived and their changes with angular geometric variation assessed. Where possible, comparisons with Walsh's rules will again be drawn, under the recognition, however, that the electronic and thereby the total energies are not the simple proportional functions of the orbital energies they were accepted to be in the previous treatments discussed.

Theory and Mechanics of Charge Redistribution in the EH Method

The symmetry orbital approach detailed in ref 2 is again used. Employing the same notation, the following exact relationships for the individual symmetry orbital contributions to the total charges for the six and eight-valence electron cases may be obtained either from the orthogonalized matrices[10] or more directly but somewhat more laboriously from the orginal matrices.

$$q_{2s} = 2\left\{1 - \frac{\left(\frac{P}{A-x}\right)^2 + CT^{-1/2}\left(\frac{P}{A-x}\right)}{1 + \left(\frac{P}{A-x}\right)^2 + \left(\frac{Q}{D-x}\right)^2}\right\} \qquad (1)$$

$$q_{2p_x} = 2\left\{1 - \frac{\left(\frac{Q}{D-x}\right)^2 + FT^{-1/2}\left(\frac{Q}{D-x}\right)}{1 + \left(\frac{P}{A-x}\right)^2 + \left(\frac{Q}{D-x}\right)^2}\right\} \qquad (2)$$

$$q_{2s} + q_{2p_x} =$$

$$2\left\{1 + \frac{1 - T^{-1/2}\left[C\left(\frac{P}{A-x}\right) + F\left(\frac{Q}{D-x}\right)\right]}{1 + \left(\frac{P}{A-x}\right)^2 + \left(\frac{Q}{D-x}\right)^2}\right\} \qquad (3)$$

$$q_{2p_z} = 2\left\{\frac{1 - \bar{T}^{-1/2}\bar{F}\left(\frac{\bar{Q}}{\bar{D}-x}\right)}{1 + \left(\frac{\bar{Q}}{\bar{D}-x}\right)^2}\right\} \qquad (4)$$

These equations are generally appropriate for the EH calculations; the density in the out-of-plane orbital, q_{2p_y}, is zero and two respectively in the six- and eight-electron cases. The orbital energies, x, are for the $3a_1$ and $2b_2$ levels, the most antibonding of the particular symmetries in eq 1–4.

Where the quantities $P/(A - x)$, $Q/(A - x)$, and $\bar{Q}/(\bar{D} - x)$ are small compared to unity as they typically are in the cases of interest, the charge densities may be expanded to good approximation about the values obtained from the zeroth-order solutions with the original VSIP's. Recognizing that x_{3a_1}, B, E, and $\bar{E}$ will be quite insensitive to balanced changes in the diagonal elements (*i.e.*, $\Delta\alpha_{2s} \cong \Delta\alpha_{2p} \cong -\Delta\alpha_H$, accompanying charge redistribution, *vide infra*), a remarkably compact expansion may be obtained.

$$\Delta q_M \equiv q_M - q_M{}^0 = \Delta(q_{2s} + q_{2p_x} + q_{2p_z} + q_{2p_y}) =$$

$$\frac{2}{Y}\left\{\left(\frac{C}{T^{1/2}} + \frac{P_0}{A_0 - x}\right)\left(\frac{C}{T^{1/2}} + \frac{2P_0}{A_0 - x}\right)\frac{\Delta A}{A_0 - x} + \right. \qquad (5)$$

$$\left.\left(\frac{F}{T^{1/2}} + \frac{Q_0}{D_0 - x}\right)\left(\frac{F}{T^{1/2}} + \frac{2Q_0}{D_0 - x}\right)\frac{\Delta D}{D_0 - x}\right\} +$$

$$\frac{1}{\bar{Y}}\left(\frac{\bar{F}}{\bar{T}^{1/2}} + \frac{2\bar{Q}_0}{\bar{d}_0}\right)^2\frac{\Delta\bar{D}}{\bar{Q}_0}$$

Here

$$Y = [1 + [P_0/(A_0 - x)]^2 + [Q_0/(D_0 - x)]^2]^2$$

$$\qquad (6)$$

$$\bar{Y} = [1 + (2Q_0/\bar{d}_0)^2]^{3/2}$$

The quantities ΔA, ΔD, and $\Delta\bar{D}$ are, of course, $\Delta\alpha_{2s}$, $\Delta\alpha_{2p_x}$, and $\Delta\alpha_{2p_z}$. The efficacy of this approximation is demonstrated in Table I where sizable and unmatched shifts in diagonal elements about the zeroth-order parametrization for a singlet CH_2-like molecule are tested. It is apparent that the expansion overestimates the charge difference component of the a_1 symmetry somewhat and underestimates that of the b_2 symmetry, for the smaller $\Delta\alpha$'s. At larger $\Delta\alpha$'s both are underestimated but not seriously even though rather large changes are forced.[11] The third line of Table I, it should be recognized, corresponds to ~0.4 electron excess on M if a linear version of α-upon-q dependence, which is somewhat rougher than often used,[7] is invoked and assumes a rather drastic and unrealistic dependence for the hydrogen matrix elements as well.

Table I. Tests of the Charge Density Difference Expansion, Eq 3[a,b]

$\Delta\alpha_M$[c]	$\Delta\alpha_H$	$\Delta(q_{2s} + q_{2p_x})$	$\Delta(q_{2p_z})$	Δq_M
1.2	−1.35	0.127 (0.132)	0.166 (0.148)	0.293 (0.280)
2.4	−2.7	0.298 (0.263)	0.330 (0.296)	0.628 (0.559)
4.8	−5.4	0.606 (0.526)	0.590 (0.591)	1.196 (1.017)

[a] All energies in eV: $A_0 = -21.4$, $D_0 = \bar{D}_0 = -11.4$, and $(\alpha_H)_0 = -13.6$. [b] The first value in each column employing eq 3 and 4, the values in parentheses from eq 5 with the expansion values of δ (ref 2, eq 9) also employed in the equating of $A - x$ and $D - x$ to $a + \delta$ and $d + \delta$, respectively. [c] $\Delta\alpha_M = \Delta A = \Delta D = \Delta\bar{D}$.

It may therefore be concluded that the charge densities, at least in the systems of present interest, will exhibit roughly linear dependence upon the VSIP values employed. If, conversely, the α values are themselves realistically adjustable through equations

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[9] J. A. Pople, private communication.

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

[11] Despite results shown in Table I which appear to be to the contrary, the truncated expansion of eq 3 should generally be of better mathematical quality than that of eq 4. Approximations of the off-diagonal, diagonal quotient terms compensate here to make both estimations appear equally good.

Table II. Charge Redistribution Effects in CH_2 upon Variation of Internal Angle[a]

θ	$(q_{2s} + q_{2p_x})_M^{(1)}$	$q_{2p_z M}^{(1)}$	$q_{\text{tot M}}^{(1)\,b}$	$q_{\text{tot M}}^{(\infty)}$	$-l_{2s}$	$-l_{2p_x}$	$-l_{2p_z}$	$-L$
45	3.143	1.106	4.249 (4.239)	4.063 (4.068)	0.0707	0.0497	0.1291	0.2495
50	3.179	1.046	4.225 (4.216)	4.058 (4.062)	0.0733	0.0430	0.1245	0.2408
54.3	3.212	1.010	4.221	4.058	0.0759	0.0374	0.1228	0.2361
60	3.252	0.976	4.228 (4.217)	4.060 (4.064)	0.0798	0.0298	0.1228	0.2424
70	3.318	0.944	4.262 (4.250)	4.070 (4.076)	0.0871	0.0163	0.1262	0.2296
80			(4.285)	(4.088)				

θ	$\overline{\Delta\alpha}$	$-f_+$	$-f_-$	$\mathfrak{F}$	$(E(\theta) - E(60))^0_{\text{tot}}$	$(E(\theta) - E(60))^\infty_{\text{tot}}$
45	0.746	0.8104	1.0755	2.228	1.154 (0.511)	1.349 (0.710)
50	0.694	0.7744	1.1896	2.072	0.548 (0.216)	0.519 (0.149)
54.3	0.686	0.7488	1.2413	2.020	0.228	0.147
60	0.723	0.7220	1.2635	2.028	0.0 (0.0)	0.0 (0.0)
70	0.836	0.6870	1.2421	2.042	0.088 (0.095)	0.411 (0.575)
80					(0.279)	(1.296)

[a] All energies in eV; l and L values in electrons/eV; q and f values are unitless; θ in degrees. [b] First entries are sums of the first two columns obtained analytically. Values in parentheses are exact computer results for comparison.

which are linear in the orbital densities, then analytic evaluations of the convergence properties accompanying the self-consistent field cycling procedure may be conveniently made. The equation systems are similar to those encountered previously in analysis of ω-technique effects in π-electron theory;[12] similar notation is therefore used. The cycling equations are condensed as follows with inclusion of the damping factor, D, on the adjustment of the α's as it would be imposed in the computational iterative procedure to guarantee convergence.

$$\Delta\alpha_{2s}^{(1)} = \Delta\alpha_{2p_z}^{(1)} = \Delta\alpha_{2p_x}^{(1)} = \Delta\alpha_{2p_y}^{(1)} = \Delta\alpha^{(1)} \tag{7}$$

$$\Delta\alpha^{(1)} = D\omega(q_M^{(1)} - q_M^{(0)}) = D\omega\Delta q_M^{(1)}$$

$$\Delta q_M^{(2)} = l_{2s}\Delta\alpha_{2s}^{(1)} + l_{2p_z}\Delta\alpha_{2p_z}^{(1)} + l_{2p_x}\Delta\alpha_{2p_x}^{(1)} = L\Delta\alpha^{(1)} \tag{8}$$

$$\Delta\alpha^{(2)} = D[A + \omega q_M^{(2)} - (A + \omega q_M^{(0)} + D\omega\Delta q_M^{(1)})] = D\omega[\Delta q_M^{(2)} + (1 - D)\Delta q_M^{(1)}] \tag{9}$$

$$\Delta\alpha^{(n)} = D\omega\sum_{j=0}^{n-1}(1 - D)^j\Delta q_M^{(n-j)} = \Delta q^{(n+1)}L^{-1} \tag{10}$$

It is quickly recognized that the cycling procedure under the conditions outlined is resolvable in terms of geometric series and that consequently, since

$$q^{(n)} - q^{(0)} = \sum_{j=1}^{n}\Delta q^{(j)} \tag{11}$$

$$q^{(\infty)} - q^{(0)} = \Delta q^{(1)} + \frac{LD\omega\Delta q^{(1)}}{1 - [LD\omega + (1 - D)]} = \frac{\Delta q^{(1)}}{1 - L\omega} \tag{12}$$

for $|LD\omega + 1 - D| < 1$. Note, the converged value of the density is properly independent of the damping factor employed to guarantee convergence in the cycling. We are now in a position to analyze the factors contributing to production of the self-consistent densities are how these factors will be affected in detail upon geometric change in the molecular structures.

In CH_2 ($^1A_1$ state, $r_{CH} = 1.094$ Å, $2\theta = 120°$), l_{2s}, l_{2p_y}, and l_{2p_z} are from eq 5, -0.0798, -0.0298, and -0.1228 electron/eV, respectively, and L is therefore -0.2324. With $\omega = 11.9$ eV/electron,[13] the above analysis indicates the largest value of D under which convergence may be obtained is 0.531 and that q_M^∞ will be 4.060. The value of q_M^∞ obtained by complete computer analysis using $D = 0.4$ is 4.064. The limiting value of D for convergence obtained analytically was roughly verified; a computer run with D of 0.6 steadily diverged.

Similarly for H_2O ($r_{OH} = 0.960$ Å, $2\theta = 120°$), l_{2s}, l_{2p_z}, and l_{2p_z} are -0.0474, -0.0200, and -0.1511 electron/eV. Since ω_{2s} and ω_{2p} are not equal (16.9 and 17.4 eV/electron, obtained as the slope for a linear relationship connecting the VSIP's of neutral and uninegative oxygen atoms[6]), a weighted L value of -0.2171 is obtained to be used with $\omega = 17.4$. The largest D value for convergence is therefore predicted to be 0.419 and the analytic q_M^∞ value from eq 12 is 6.190. By computer analysis with $D = 0.4$, q_M^∞ is 6.241. With D at 0.6, the computer cycling diverged, as in the CH_2 runs but much more rapidly, indicating the analytic assessments of maximum D for convergence to be trustworthy. The initial computed densities, $q_M^{(1)}$, are 6.906 and 6.905 by analysis (eq 3 and 4) and full computation; the comparable numbers for CH_2 are 4.228 and 4.217.

Tables II and III present the analytically derived parameters for CH_2 and H_2O which determine the self-consistent densities and, hence, the adjusted diagonal elements and molecular energies. It is easily shown that

$$\alpha_M^{(\infty)} - \alpha_M^{(0)} \equiv \overline{\Delta\alpha} = L^{-1}(q_M^{(\infty)} - q_M^{(1)}) = \frac{\omega\Delta q_M^{(1)}}{1 - L\omega} \tag{13}$$

and

$$2(\delta + \bar{\delta})^\infty = 2(\delta + \bar{\delta})^0 + \Delta E_0^\infty \tag{14}$$

where ΔE_0^∞, which represents the correction to the total electronic energy forthcoming from the establishment of self-consistent charge densities, is obtained

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(12) S. Ehrenson, *J. Phys. Chem.*, 66, 706, 712 (1962).

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

Table III. Charge Redistribution Effects in H_2O upon Variation of Internal Angle[a]

θ	$(q_{2s} + q_{2p_x})_M{}^{(1)}$	$(q_{2p_z})_M{}^{(1)}$	$q_{\mathrm{tot}\ M}{}^{(1)\ b}$	$q_{\mathrm{tot}\ M}{}^{(\infty)}$	$-l_{2s}$	$-l_{2p_x}$	$-l_{2p_z}$	$-L$
45	3.513	1.464	6.977 (6.976)	6.190 (6.256)	0.0441	0.0378	0.1574	0.2380
50	3.543	1.398	6.941 (6.940)	6.187 (6.246)	0.0453	0.0315	0.1560	0.2315
54.3	3.568	1.352	6.920	6.187	0.0462	0.0264	0.1538	0.2251
60	3.600	1.306	6.906 (6.905)	6.190 (6.242)	0.0475	0.0200	0.1511	0.2172
70	3.651	1.253	6.904 (6.903)	6.197 (6.249)	0.0495	0.0100	0.1479	0.2060
80	3.687	1.226	6.913 (6.913)	6.205 (6.260)	0.0510	0.0027	0.1465	0.1987
90			(6.918)	(6.265)				

θ	$\Delta\alpha$	$-f_+$	$-f_-$	$\mathfrak{F}$	$(E(\theta) - E(60))^0{}_{\mathrm{tot}}{}^{c,d}$	$(E(\theta) - E(60))^\infty{}_{\mathrm{tot}}$
45	3.307	0.2116	0.2906	6.938	0.754 (0.583)	1.604 (2.426)
50	3.257	0.1994	0.3520	6.840	0.436 (0.322)	0.619 (0.935)
54.3	3.256	0.1900	0.3960	6.770	0.218	0.169
60	3.296	0.1792	0.4407	6.703	0.0 (0.0)	0.0 (0.0)
70	3.432	0.1640	0.4864	6.642	−0.230 (−0.118)	0.476 (0.698)
80	3.563	0.1544	0.5049	6.624	−0.330 (−0.132)	1.186 (1.880)
90					−0.356 (−0.126)	(2.454)

[a] Footnotes of Table II apply. [b] Includes two electrons from the $b_1(2p_{yM})$ orbital. [c] From column 6, Table III, ref 2. [d] The exact and analytical E_{tot} values are themselves in good agreement. For example, $E(60)^0{}_{\mathrm{tot}}$'s are respectively −161.16 and −161.62; $E(60)^\infty{}_{\mathrm{tot}}$'s are −139.43 and −134.63.

in a straightforward manner by manipulation of the equations for δ and $\bar{\delta}$ given in ref 2.

$$\Delta E_0{}^\infty = 2[\Delta A + \Delta D + (\Delta\delta + \Delta\bar{\delta}) + 0, \Delta D]_0{}^\infty \quad (15)$$

The last bracketed term indicates zero for the six valence-electron, and ΔD ($\Delta\alpha_{2py}$, from the b_1 symmetry orbital) for the eight valence-electron cases.

$$\Delta\delta \cong 2\left\{2\frac{P\Delta P + Q\Delta Q}{a + d} - \delta\frac{(\Delta a + \Delta d)}{a + d}\right\} = f_+\,\overline{\Delta\alpha} \quad (16a)$$

$$\Delta\bar{\delta} \cong \left\{\frac{2\bar{Q}\Delta\bar{Q}}{\bar{d}} - \bar{\delta}\frac{\Delta\bar{d}}{\bar{d}}\right\} = f_-\,\overline{\Delta\alpha} \quad (16b)$$

$$\Delta P/\overline{\Delta\alpha} = -\sqrt{2}S_{2s_M,1s_H}\left\{\frac{K}{4}\,\omega_H + \left(1 - \frac{K}{2}\right)\omega_{2s}\right\}\Big/\omega_{2p}T^{1/2} \quad (17a)$$

$$\Delta Q/\overline{\Delta\alpha} = -\sqrt{2}S_{2p\sigma_M,1s_H} \times \cos\theta\left\{\frac{K}{4}\,\omega_H + \left(1 - \frac{K}{2}\right)\omega_{2p}\right\}\Big/\omega_{2p}T^{1/2} \quad (17b)$$

$$\Delta\bar{Q}/\overline{\Delta\alpha} = -\sqrt{2}S_{2p\sigma_M,1sH} \times \sin\theta\left\{\frac{K}{4}\,\omega_H + \left(1 - \frac{K}{2}\right)\omega_{p2}\right\}\Big/\omega_{2p}\bar{T}^{-1/2} \quad (17c)$$

$$\Delta a/\overline{\Delta\alpha} - (\omega_{2s}/\omega_{2p}) = \Delta d/\overline{\Delta\alpha} - 1 = \left\{\frac{1 + KS_{HH}}{2}\,\omega_H - 2S^2{}_{2s_M,1s_H} \times \left(\frac{K}{2}\,\omega_H + (1 - K)\omega_{2s}\right) - 2S^2{}_{2p\sigma,1s_M} \times \cos^2\theta\left(\frac{K}{2}\,\omega_H + (1 - K)\omega_{2p}\right)\right\}\Big/\omega_{2p}T \quad (18a)$$

$$\Delta\bar{d}/\overline{\Delta\alpha} - 1 = \left\{\frac{1 - KS_{HH}}{2}\,\omega_H - 2S^2{}_{2p\sigma_M,1s_H} \times \sin^2\theta\left(\frac{K}{2}\,\omega_H + (1 - K)\omega_{2p}\right)\right\}\Big/\omega_{2p}T \quad (18b)$$

Therefore

$$\Delta E_0{}^\infty = 2\left\{\frac{\omega_{2s}}{\omega_{2p}} + 1 + (f_+ + f_-) + 0, 1\right\}\overline{\Delta\alpha} \equiv \mathfrak{F}\overline{\Delta\alpha} \quad (19)$$

The particular results of Tables II and III may be summarized as follows and suggest the following factors are important in determining the charge redistribution effects upon electronic energy and differential charge donation.

(1) In both CH_2 and H_2O, the former a case where there is little charge donation predicted by either the zeroth-order or self-consistent results and the latter where appreciable charge donation in the original calculation is substantially moderated by the redistribution procedure, the electron densities are affected only weakly by angular charge. The q_M values vary at most 0.03 electron over the range of the zeroth-order results and by less (~0.01) when the self-consistent results are compared. Still, it should be noted that extrema for charge donation appear in all cases to fairly closely follow the extrema for the electronic energies.

(2) In the case of CH_2, the minimum value for $q_M{}^{(\infty)}$ occurs roughly at the same value of θ as does that for $q_M{}^{(1)}$, a fact attributable to the essential constancy of L over the interesting θ range. L is quite constant, it should be noted, despite variations in the individual l values; the changes cancel rather strongly in the sum. Consequently, since the difference $(q_M{}^{(\infty)} - q_M{}^{(1)})$ remains fairly constant, $\overline{\Delta\alpha}$ is weakly varying with, importantly, a similar functional dependence on θ as characterizes $E^0{}_{\mathrm{tot}}$ and the q values.[14] Coupled with the essentially invariant nature of $\mathfrak{F}$, the characteristics of the $E^\infty{}_{\mathrm{tot}}$ *vs.* θ dependence must be, and are, similar to those evidenced by $E^0{}_{\mathrm{tot}}$. It is interesting that the variations from constancy of L, $\overline{\Delta\alpha}$, and $\mathfrak{F}$ occur only at the extremes of the θ range (45 and 70°), which serve to sharpen the upturn about the minimum in the $E^\infty{}_{\mathrm{tot}}$ *vs.* θ dependence somewhat compared to that for $E^0{}_{\mathrm{tot}}$.

(3) H_2O exhibits rather different behavior compounded of the cumulative effects of several tabulated

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(14) Alternatively, the second relation of eq 13 reveals that $\Delta\alpha$ will vary linearly with $\Delta q_M{}^{(1)}$ for constant L.

factors. Although the analytic zeroth-order electronic energies do not exhibit a distinct minimum over the θ range examined, the q values do, and so do the values of $\overline{\Delta\alpha}$ extracted therefrom. (Where the analytic $E^0{}_{\text{tot}}$ curve flattens out as the linear configuration is approached, a very shallow minimum is observed in the exact computer results at >80°.) The shapes of the $\overline{\Delta\alpha}$ *vs.* θ dependence and its degree of curvature may be attributed in part to the distinct variation in L upon angular variation: where $q_M{}^{(1)}$ has a minimum at ~70°, the minimum is shifted in to ~55° for $\overline{\Delta\alpha}$ with a somewhat sharper rise in the high-θ direction. On the other hand, $\mathfrak{F}$ exhibits a monotonic decrease with increasing θ, flattening out somewhat toward the linear configuration, but sufficiently slowly so that a minimum in the product $\mathfrak{F}\overline{\Delta\alpha}$ is observed in the same vicinity as was the minimum in the $\overline{\Delta\alpha}$ curve itself, and further so that the $\mathfrak{F}\overline{\Delta\alpha}$ curve is quite symmetrical. Imposition of this self-consistency correction produces the $E^\infty{}_{\text{tot}}$ dependence detailed in Table III. A minimum is observed around 60° (experimental value 52.3°), with a somewhat greater slope predicted for a geometry variation toward small values of θ.

The relative sizes of the corrections applied to E^0 to produce E^∞ are usefully compared. In CH_2 these are on the order of 2 eV; in H_2O they are more than 10 times larger (~25 eV). This difference is in part due to the larger $\overline{\Delta\alpha}$ which pertain for the latter, arising from more profound charge donation to M, *i.e.*, greater $\Delta q_M{}^{(1)}$ values, and in part to the larger values of $\mathfrak{F}$. The $\mathfrak{F}$ values for H_2O are larger because of the effect on the $2p_y$ orbital and also because *the effects of redistribution on the δ's as measured by the f values, are much smaller* than in CH_2. The latter effect may in turn be traced to smaller values of P, Q, $\bar{Q}$ and ΔP, ΔQ, $\Delta\bar{Q}$, and χ for H_2O which arise because of the increased differences between the α's and ω's for hydrogen and M.

In contrast, the angular variation in $\Delta E_0{}^\infty$ is only two to three times greater for H_2O than CH_2. This may be attributed to the fact that the $\overline{\Delta\alpha}$ variation with angle is not only relatively, but even absolutely smaller in the H_2O case, but also because $\mathfrak{F}$ contains a larger constant factor for this molecule (arising from the $2p_y$ orbital) which does not vary, insofar as $\mathfrak{F}$ is concerned, with angle. The sizes of these corrections are crucial in producing the minimum at 60°; if they were one-third as large as those shown in Table III, thereby resembling the variation exhibited by CH_2, the minimum would be shifted to higher θ by ~10°, if one-fourth as large an additional shift of ~5° would occur.[15]

Charge Redistribution in the CNDO2 Method

The general SCF relationship among the electronic and orbital energies and charge densities and bond orders

$$E^\infty{}_{\text{elect}} = \frac{1}{2}\sum_i n_i\epsilon_i{}^\infty + \frac{1}{2}\sum_{\mu,\nu} P_{\mu\nu}{}^\infty H_{\mu\nu}{}^\infty \tag{20}$$

may be approximated in the following manner useful for the present purposes of analysis.

$$E^\infty{}_{\text{elect}} = \frac{1}{2}\sum_i n_i(\epsilon_i{}^\infty + \epsilon_i{}^0) - \frac{1}{2}\sum_{\mu(\text{on }A)} P_{\mu\mu}\left\{\left(Z_A - \frac{1}{2}\right)\gamma_{AA} + \sum_{B\neq A} Z_B\gamma_{AB}\right\} \tag{21}$$

The approximation involves the almost complete cancellation within the sums

$$\begin{gathered}\sum_\mu (P_{\mu\mu}{}^\infty - P_{\mu\mu}{}^0)\left(-\frac{1}{2}(I_\mu + A_\mu)\right) \\ \sum_{\mu,\nu\neq\mu} (P_{\mu\nu}{}^\infty - P_{\mu\nu}{}^0)(\beta S)_{\mu\nu}\end{gathered} \tag{22}$$

which arise upon introduction into eq 20 of the equality

$$\sum_i \epsilon_i{}^0 = \frac{1}{2}\sum_{\mu,\nu} P_{\mu\nu}{}^0 H_{\mu\nu}{}^0 \tag{23}$$

The strength of the approximation may be illustrated by consideration of the cases CH_2 (r_{CH} = 1.094 Å, 2θ = 108.6°) and H_2O (r_{OH} = 0.960 Å, 2θ = 100°). For the former the exact and approximate values of the electronic energy are respectively −335.031 and −335.080 eV. For the latter the comparable results are −730.393 and −730.471 eV.[18]

With this relationship it is possible to examine in detail the effects of geometric distortion of the MH_2 species. For these molecules, eq 21 may be made more compact without further approximation upon recognition that $q_M + 2q_H = Z_M + 2$ and some rearranging.

$$\begin{aligned}E^\infty{}_{\text{elect}} = {} & \frac{1}{2}\sum_i n_i(\epsilon_i{}^\infty + \epsilon_i{}^0) - \\ & \left(\frac{Z_M + 2}{2}\right)\left[\left(Z_M - \frac{1}{2}\right)\gamma_{MM} + 2\gamma_{MH}\right] - \\ & q_H\left(\frac{1}{2}\gamma_{HH} - \left(Z_M - \frac{1}{2}\right)\gamma_{MM} + (Z_M - 2)\gamma_{MH} + \gamma_{H1,H2}\right)\end{aligned} \tag{24}$$

and, therefore

$$\frac{\partial E^\infty{}_{\text{elect}}}{\partial\theta} = \frac{\frac{1}{2}\sum_i n_i(\epsilon_i{}^\infty + \epsilon_i{}^0)}{\partial\theta} - \kappa\frac{\partial q_H}{\partial\theta} - q_H\frac{\partial\gamma_{H1,H2}}{\partial\theta} \tag{25}$$

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[15] As a final point concerning these matters, to the extent which the Walsh analysis[16] on the angular configuration of symmetrical triatomic molecules is based upon the filling of MO's with characteristic energy variations and which simply determine the total energy, the present results add little to the conclusions of the previous work.[2] A fact which is noteworthy concerns the balance of effects which determine the a_1 level energies. In both CH_2 and H_2O, the self-consistent energies for these levels appear to have minima close to where the experimental total energy minima lie. This was not observed in the zeroth-order results. It should be recognized, however, that the various hybridization situations (on the different M here, in the symmetric MO's), upon which Walsh constructed the rationale for his rules, have their origins further obscured, beyond that already noted,[2,17] by the mixing of hydrogen effects and among symmetries through the charge redistribution procedure employed. Comparisons of the sort, it will be noted, are even more restricted in the true SCF results following.

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

(17) (a) C. A. Coulson and A. H. Neilson, *Discussions Faraday Soc.*, 35, 71 (1963); (b) S. D. Peyerimhoff, R. J. Buenker, and L. C. Allen, *J. Chem. Phys.*, 45, 734 (1966).

(18) Rather surprisingly, the quality of approximation appears to be insensitive to the magnitudes of the differences ($P_{\mu\nu}{}^\infty - P_{\mu\nu}{}^0$). In CH_2, the P values generated on the first cycle do not change much upon further cycling; in H_2O they do; *viz.*, q_H in CH_2 changes from 0.9872 to 0.9907 at self-consistency, while for H_2O the change is from 0.7718 to 0.8598. The natural cancellation of the P value differences, because of the weaker or stronger normalization conditions appropriate for their components, is apparently sufficient to ensure the goodness of the approximation.

Table IV. CNDO2 Energy and Charge Density Effects in CH_2 with Variation of Internal Angle[a]

θ	$2\Sigma\epsilon_i^0$ +90	$2\Sigma\epsilon_i^\infty$ +129	q_H^0	q_H^∞	γ_{H1H2}	E_{elect} + 335	E_{tot} + 221
45	−0.0481	−0.5166	0.9910	0.9935	9.1209	−0.9432	0.3450
50	−0.2073	−0.6666	0.9911	0.9936	8.4780	−0.4576	−0.5763
52	−0.2313	−0.6574	0.9897	0.9926	8.2578	−0.2610	−0.6193
54	−0.2328	−0.6114	0.9876	0.9910	8.0563	−0.0641	−0.6359
54.3	−0.2311	−0.6009	0.9872	0.9907	8.0276	−0.0310	−0.6362
56	−0.2123	−0.5246	0.9848	0.9888	7.8721	+0.1437	−0.6273
58	−0.1705	−0.3996	0.9814	0.9862	7.7040	0.3542	−0.5949
60	−0.1087	−0.2374	0.9773	0.9830	7.5510	0.5702	−0.5402
70	+0.4415	+1.0702	0.9477	0.9598	6.9777	1.7049	−0.0009

[a] All energies in eV, θ in degrees, charges in units of electrons.

Table V. CNDO2 Energy and Charge Density Effects in H_2O and BeH_2 with Variation of Internal Angle

θ (H_2O)	$2\Sigma\epsilon_i^0$ +140	$2\Sigma\epsilon_i^\infty$ +198	q_H^0	q_H^∞	γ_{H1H2}	E_{elect} + 730	E_{tot} + 540
45	−0.6178	−0.5755	0.7689	0.8612	10.2192	−0.9881	−0.4002
50	−0.6916	−0.3322	0.7718	0.8598	9.5400	−0.3933	−0.6216
52	−0.6906	−0.0956	0.7711	0.8582	9.3048	−0.1568	−0.6580
54	−0.6715	+0.2242	0.7695	0.8559	9.0883	+0.0818	−0.6667
55	−0.6551	0.4173	0.7682	0.8545	8.9868	0.2023	−0.6610
60	−0.5074	1.6367	0.7588	0.8455	8.5410	0.8195	−0.5398
70	+0.0500	5.4967	0.7251	0.8169	7.9124	2.1117	+0.0729
(BeH_2)	+54	+70				+131	+80
45	−0.2327	−0.8843	1.2175	1.1643	7.5341	−0.3742	−0.9082
55	−1.0560	−2.1170	1.2032	1.1629	6.5298	−0.2384	−1.8094
65	−1.5462	−2.8808	1.1892	1.1570	5.9092	−0.1386	−2.3390
75	−1.7998	−3.2956	1.1784	1.1509	5.5468	−0.0480	−2.6135
90	−1.9136	−3.4922	1.1717	1.1466	5.3586	+0.0170	−2.7375

The symbol κ in eq 25 represents the repulsion integral coefficient of q_H in eq 24; the last term in eq 25 it should be noted arises from the derivative of this coefficient in which the only term which is variable with angular displacement is $\gamma_{H1,H2}$.

By application of the Coulson–Longuet-Higgins relationships[10] to the symmetry orbital formalism discussed in the previous paper, the charge density on hydrogen may be obtained. The notation follows the Appendix of ref 2.

$$q_H = \left(\frac{1 \pm 1}{2}\right) \mp \frac{(a + y_\mp)(d + y_\mp) - B^2}{(-y_\mp)(2\tau) + 2X} + \frac{\bar{d} + \bar{y}_+}{2\bar{y}_+ + \bar{\tau}} \quad (26)$$

This expression may be expanded and conveniently truncated for present purposes after the X^{-1} and $\bar{X}^{-1/2}$ terms to yield for the six- and eight-valence-electron cases (upper sign) and four-valence-electron cases (lower sign)

$$q_H = \frac{1}{2}\left\{\left[1 - \frac{g - \tau}{\sqrt{X}} \mp \frac{ad - B^2}{X}\right] + \left[1 - \frac{\bar{g} - \bar{\tau}}{\sqrt{\bar{X}}}\right]\right\} \quad (27)$$

It is easily ascertained from eq 27 that the antisymmetric orbital contribution to q_H, expressed in the second bracketed term, will vary with angle dependent upon whether the change in $\bar{g} - \bar{\tau}$ (equal to $^1/_2(\bar{g} - \bar{d})$) is greater or less than the change in $\sqrt{\bar{X}}$ ($|\bar{E}|$, which varies as sin θ). Assuming with considerable justification that the self-consistent charge density results semiquantitatively parallel the first-order results (see Tables IV and V below), this component would be expected to increase with increasing angle as long as $\bar{g}$ is smaller in magnitude than $\bar{d}$ since $(d\bar{g}/d\theta) < 0$ and would only decrease if $(\bar{g} - \bar{d})d\bar{x}/d\theta$ outweighs $(-2\bar{x})d\bar{g}/d\theta$. The former situation is expected and realized for such cases as CH_2 and H_2O where $(\bar{g} - \bar{d}) \lesssim 0$, and the latter for BeH_2 where the reverse inequality pretains.

The symmetrical orbital components, shown in the first bracketed term, appear somewhat more complicated because of the sign option and the fact that the variable combinations may themselves be of opposite sign. When A and D are both large, or A large, compared to G, $g - \tau$ will be positive. If both A and D are of comparable size to G, as they are in BeH_2, $g - \tau$ will be negative. The product ad will always be negative since M lies intermediate between A and D. In general, then, $g - \tau$ will always increase (become more positive) with increase in angle since $g - \tau$ is equal to $(G + M - A - D)/2$ and both G and M become more positive, and ad will also increase (become more positive) because M becomes more positive. Further, because X is large, the $g - \tau$ term will always be numerically larger than the ad term.

Hence, the symmetric component of q_H must decrease with increasing angle, in the six- and eight-valence-electron cases because larger positive quantities and smaller negative quantities are subtracted from unity, and in the four-electron case because smaller negative quantities, more important than the increasing but small positive quantities to be added, are subtracted from unity. It is clear therefore that q_H must decrease with increasing angle in the BeH_2 case. In CH_2 and H_2O, the components from the two symmetries change in opposite directions. However, because $\bar{X}$ increases proportionally more rapidly than X decreases and because of the additive effects of the two terms constituting the symmetric component, q_H should likewise decrease albeit slowly because of the opposed effects from the two symmetries in these cases with increasing θ.

The behavior of the two symmetry components here, and for the $\Sigma\epsilon_i$ terms as well are seen to closely resemble the behavior noted previously in the analysis of the EH and KEH results obtained for these molecules. Tables IV and V illustrate the angular effects; all numbers are exact computer obtained results with thresholds for convergence, $<5 \times 10^{-4}$ for all $P_{\mu\nu}$. The q_H values displayed are seen to have the angular effects predicted for them. Similar analysis is possible for the zeroth-order and with some additional complications for the self-consistent orbital energy sums as well.[19] Interestingly, but not surprisingly, the $\Sigma\epsilon_i$ values exhibit minima in the cases where minima were observed in the EH and KEH calculations; for CH_2 these minima agree fairly well. In BeH_2, no minima are found. The possible significance of this observation is examined below. It is not, however, necessary to go into these details when the q_H results obtained and corroborated are examined as they apply to eq 25.

Of the last two terms in eq 25, the term $q_H(\partial\gamma_{H1,H2}/\partial\theta)$ is uniformly larger by a considerable amount than the term $\kappa(\partial q_H/\partial\theta)$ even though κ may be much larger than q_H. In the six- and eight-valence-electron cases κ is 10–50 times larger in magnitude than q_H *but the derivatives are in the other direction by 10^2 or greater.* Since κ is negative in these cases, the effect of these two terms together will be to increase E_{elect} (make it a smaller negative number), but at a slower rate than dictated by the last term alone, with increase in θ. In the four-valence-electron case, κ/q_H is smaller in magnitude and generally positive, because κ is small and positive (for BeH_2). Consequently, E_{elect} should again be increased by these terms, but here slightly faster than by the last term alone.

In the six- and eight-electron cases, the first term of eq 25 remains fairly constant over the lower part of the range, principally because each of the orbital energy sums has minima at different values of θ in this region. Even so, the effect of the last two terms (mainly the last one) causes a continual increase in E_{elect}. This increase is continued and accelerated at higher values of θ when the orbital energy sums begin themselves to show substantial increases. In contrast, in the BeH_2 case, the orbital energy sums continually decrease (become larger negative numbers) over the entire range of θ. The larger effect of the final two terms, acting in concert, are still capable of causing E_{elect} to monotonically increase over the entire range. Finally, only when the nuclear repulsion energy (R_{H1H2}^{-1} + *a constant* for the angular distortions considered) is added to the electronic energy to produce the total energy are the over-all effects which truly determine structure all assembled. In the CH_2 and H_2O molecules, the rates of increase of E_{elect} are sufficiently slow in the low θ range, and even thereafter, so as to produce minima in E_{tot}. In BeH_2, the rate of increase in E_{elect} is slow in the low range of θ but decreases at higher θ so that the decreasing rate change in the nuclear repulsion energy is never overcome and no minimum for E_{tot} is found.

Comparisons of the Methods and Conclusions

These results are extremely interesting as regards possible comparisons between the extended Hückel, explicit electron repulsion and even more complete methods. As applied to the energetics of bending in typical MH_2 molecules, the CNDO2 method suggests that the variation in the repulsion between electrons on the two hydrogens is the determining factor in the variation of the electronic energy of the molecule undergoing angular deformation. This effect overcomes the orbital electronic energy effects, *but is itself essentially cancelled out by the nuclear repulsion effect variation, making the total energy vary roughly as the orbital electronic energy.* The forms of the varying repulsion terms, *i.e.*

$$q_H \iint (s_{H1}{}^2(1)s_{H2}(2)/r_{12})\, d\tau_1 d\tau_2$$

$$Z_{H1}Z_{H2}/R_{H1,H2}$$

represent the analogous electron and proton effects on their own kind, cancellation occurring because the derivative of the nuclear repulsion energy is added to $(\partial E_{elect}/\partial\theta)$ to obtain $(\partial E_{tot}/\partial\theta)$ while $q_H(\partial\gamma_{H1,H2}/\partial\theta)$ appears with a negative sign in $\partial E_{elect}/\partial\theta$; see eq 25. It should of course be clearly recognized that only the changes in the repulsions apparently cancel, or that the differences in electron and nuclear repulsions, which may be, and are large in an absolute sense for various MH_2 molecules, are essentially constant functions of the internuclear angle.

This explanation would appear superficially to be in disagreement with the analysis employed in justification of the use of the orbital electronic energies as representative of the total energy in extended Hückel methods. For molecules in or near their equilibrium configuration, it has been demonstrated that to a good approximation

$$\frac{1}{2}\sum_i n_i(E_i{}^m - E_i{}^a) + N = 0 \tag{28}$$

and, hence, that

$$E_{tot} = \frac{1}{2}\sum_i n_i(E_i{}^a + \epsilon_i{}^m) \tag{29}$$

where E_i is the total of one-electron energies, the kinetic and nuclear attraction energies, N is the nuclear repulsion energy, and the superscripts signify whether the atom or molecule is considered.[4,20] Summation is over the appropriate atomic or molecular orbitals which are filled. In the case of present interest, eq 28 implies the angular change in $E_i{}^m$ should oppose the change in nuclear repulsion.

In the CNDO methods, though, E_i arises from the $H_{\mu\mu}$ terms, which in fact contribute the angular variable terms, $V_{H1,H2}$ and $V_{H2,H1}$, the core interaction terms for one hydrogen with an electron on the other hydrogen, besides angularly invariant terms $U_{\mu\mu}$. The former do *not appear in the zeroth-order F matrix* while the latter does. The CNDO2 approximation then sets V_{AB} equal to $Z_B\gamma_{AB}$, which with the MO coefficients necessary for $E_i{}^m$ brings the recipies for cancellation of the nuclear repulsion effects much closer than they originally appeared to be.

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(19) See ref 2 for the analysis of orbital energy contributions in BeH_2 in the EH method where the formalism necessary here is developed and discussed fully.

(20) F. P. Boer, M. D. Newton, and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U. S.*, 52, 890 (1964).

In the broader view it must be recognized, however, that anything like exact correspondence between the extended Hückel and explicit electron repulsion methods such as the CNDO variations should not be expected. It is not reasonable to expect the equality expressed in eq 28 to generally hold, especially in the quest for determination of optimum structures where nearest neighbor bond lengths are continuously varied. In the event that the equality does not hold, the prescriptions adopted to date for charge redistribution in the EH methods, which are entirely dependent upon isolated atom properties, *i.e.*, the valence-state ionization potentials and electron affinities, cannot satisfactorily reproduce the repulsion effects which are explicitly included in such as the CNDO methods. The scope of difficulty in defining meaningful separations of the total energy into orbital energy and repulsion contributions and construction of correlations between the orbital energies and Walsh's rules indicated here are further illustrated in several recent references.[17,21] Allen and coworkers[5,17b] have, however, shown that clean cancellation of the extra-orbital effects are not necessary in order to extract information on equilibrium geometry.

Despite this, since just about the same amount of computational effort is required in application of any charge redistribution corrected EH method as for the CNDO methods, there seems to be little reason to prefer the former over the latter when structural information is sought. Distinction between the EH and KEH methods should be drawn on all previous accounts, however; useful and conceptually important separations of the kinetic and potential energy terms have been obtained in the KEH method. Development of techniques for the introduction of explicit repulsion and Coulomb integral effects[22] which are consistent with this separation and manage to avoid the dilemma implicit in eq 28, and its foundations would still appear to be a desirable goal both practically and for quantum chemical content.

(21) See also, G. Blyholder and C. A. Coulson, *Theor. Chim. Acta*, **10**, 316 (1968); W. A. Bingle, "Molecular Orbitals in Chemistry, Physics and Biology," P. O. Löwdin and B. Pullman, Ed., Academic Press, New York, N. Y., 1964, p 191; C. E. Wulfman, *J. Chem. Phys.*, **31**, 381 (1959).

(22) S. Ehrenson, *Theor. Chim. Acta*, **10**, 209 (1968).

The Anisotropy Factor of Optically Active Ketones

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Abstract: A simple theory for calculating the anisotropy factor $g = 4R_{0i}/D_{0i}$ of optically active ketones is developed. The theory is checked against a set of β-equatorial substituted adamantanones and methyl-substituted cyclohexanones. The dynamic coupling model parameter Θ_{0i}, the ketone transition electric quadrupole moment, is estimated to be 1.5×10^{-25} cgs from data obtained with correction for vibronic coupling. It is determined, independent of the model, that the β-equatorial substituted adamantanones have nonvibronically coupled transition electric dipole moments that have dominant Z polarization (*i.e.*, C=O axis polarization). The same conclusion obtains from the model calculations. The calculations on substituted cyclohexanones for the differential value of their Y-polarized moment relative to their Z moment compare well with experimental values. Consideration of anisotropy factors would seem a means of correcting the inherent bias in ketone rotatory strength calculation to only Z components of the transition electric dipoles.

Early studies of optical activity defined and utilized the wavelength-dependent anisotropy factor $g(\lambda) = \Delta\epsilon(\lambda)/\epsilon(\lambda)$ as a useful comparison of electronic transition circular dichroism to ordinary absorption. Kuhn, Mathieu, and others[2-5] used g *vs.* λ plots to characterize various electronic transitions. The anisotropy factor was often found to be constant throughout a single transition. Its variation was taken to denote a change of transition in that interval.

Later theoretical work has largely abandoned the concept of an anisotropy factor as a detailed function of wavelength. Condon[6] first defined the factor as proportional to the ratio of integrated intensities.

$$g_{0i} = 4R_{0i}/D_{0i} \qquad (1)$$

R_{0i} is the rotatory strength of the $i \leftarrow 0$ transition and is defined by

$$R_{0i} = \mathrm{Im}\{\boldsymbol{\mu}_{0i}\cdot\mathbf{m}_{i0}\} = 0.24 \times 10^{-38}\int\frac{\Delta\epsilon(\lambda)}{\lambda}\mathrm{d}\lambda \quad \text{(cgs)} \qquad (2)$$

where $\boldsymbol{\mu}_{0i}$ and $\mathbf{m}_{i0}$ are the electric and magnetic dipole transition moments, respectively, λ is the wavelength, $\Delta\epsilon(\lambda) = \epsilon_l(\lambda) - \epsilon_r(\lambda)$, $\epsilon_l(\lambda)$ and $\epsilon_r(\lambda)$ are the decadic molecular extinction coefficients for the left and right circularly polarized light, and the universal constants have been evaluated to give cgs units. D_{0i}, the dipole strength of the transition, is defined by

$$D_{0i} = \boldsymbol{\mu}_{0i}\cdot\boldsymbol{\mu}_{i0} = 0.96 \times 10^{-38}\int\frac{\epsilon(\lambda)}{\lambda}\mathrm{d}\lambda \quad \text{(cgs)} \qquad (3)$$

where $\epsilon(\lambda) = [\epsilon_l(\lambda) + \epsilon_r(\lambda)]/2$.

(1) NASA Predoctoral Fellow.

(2) (a) W. Kuhn, *Trans. Faraday Soc.*, **26**, 299 (1930); (b) *Z. Physik. Chem.*, **B8**, 286 (1930).

(3) W. Kuhn and H. L. Lehmann, *ibid.*, **18**, 32 (1932).

(4) J. P. Mathieu, *Ann. Phys.*, **3**, 371 (1935).

(5) T. M. Lowry, "Optical Rotatory Power," Dover Publications, New York, N. Y., 1935, p 393.

(6) E. U. Condon, *Rev. Mod. Phys.*, **9**, 432 (1937).