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Molecular Orbital Calculations of Spin-Spin Coupling Constants for Hydrocarbons

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Abstract: Contact contributions to H-H and ^{13}C -H coupling constants in a selection of hydrocarbons are calculated according to the molecular orbital theory developed by Pople and Santry using one-electron wave functions and energies generated according to the extended Hückel theory. Results are shown to be in semiquantitative agreement with experiment for most types of coupling. Calculated values of directly bonded $J_{^{13}\text{C}\text{H}}$ correlate with the observed values but are uniformly lower by a factor of about 1.5. For coupling through two bonds, both J_{HH} and $J_{^{13}\text{C}\text{H}}$ are calculated to be negative in all the examples studied. This is in agreement with experiments for most saturated hydrocarbons but is in serious error for ethylene and acetylene. Calculated vicinal H-H couplings follow observed values in most of the cases studied.

Most of the recent theoretical studies of spin-spin coupling have utilized the valence-bond (VB) method.¹⁻⁵ A molecular orbital (MO) theory has also been developed, but has, until recently, received less attention. In both the VB and MO methods, use has been made of the "average excitation energy approximation."^{6,7} This leads, in the case of the MO method as developed by McConnell,⁸ to the prediction that all coupling constants between protons are positive. This is in contradiction to experiment. Recently, Pople and Santry⁹ have developed the MO method without invoking the "average excitation energy approximation." In this more general form, couplings of either sign can arise. Pople has applied the theory to evaluate a number of couplings over one bond and found reason-

able agreement with experiment. The theory accounts qualitatively for the variation in geminal couplings with structure,¹⁰ but numerical calculations according to a one-electron MO theory with neglect of overlap give the wrong sign for the coupling in methane,¹¹ as do the earlier VB calculations.^{1,3}

The MO method clearly shows promise and deserves to be tested further. In the present paper, we employ the extended Hückel theory,¹² which includes overlap, to calculate coupling constants in a number of hydrocarbons.

Method

According to Ramsey's general theory,⁵ nuclear spin-spin interactions occur by four distinct mechanisms. The direct dipolar interactions, which lead to a line broadening in solids, average to zero under rapid rotation in liquids.¹³ The nuclear spin-electron spin

(1) M. Karplus, D. H. Anderson, T. C. Farrar, and H. S. Gutowsky, *J. Chem. Phys.*, **27**, 597 (1957).

(2) M. Karplus and D. H. Anderson, *ibid.*, **30**, 6 (1959).

(3) H. S. Gutowsky, M. Karplus, and D. M. Grant, *ibid.*, **31**, 1278 (1959).

(4) M. Karplus, *ibid.*, **30**, 11 (1959).

(5) M. Barfield and D. M. Grant, *ibid.*, **36**, 2054 (1962); *J. Am. Chem. Soc.*, **83**, 4726 (1961); **85**, 1899 (1963).

(6) N. F. Ramsey, *Phys. Rev.*, **91**, 303 (1953).

(7) A. D. McLachlan, *J. Chem. Phys.*, **32**, 1263 (1960); M. Karplus, *ibid.*, **33**, 941 (1960).

(8) H. M. McConnell, *ibid.*, **24**, 460 (1956).

(9) J. A. Pople and D. P. Santry, *Mol. Phys.*, **8**, 1 (1964).

(10) J. A. Pople and A. A. Bothner-By, *J. Chem. Phys.*, **42**, 1339 (1965).

(11) J. A. Pople and C. P. Santry, *Mol. Phys.*, **9**, 301, 311 (1965).

(12) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963), and references therein.

(13) In the liquid crystal nematic phase, direct dipolar interactions often do not average to zero and give rise to large splittings in the observed n.m.r. spectrum. For examples and references see L. C. Snyder and E. W. Anderson, *J. Am. Chem. Soc.*, **86**, 5023 (1964); W. D. Phillips, J. C. Powell, and L. R. Melby, *J. Chem. Phys.*, **41**, 2551 (1964).

(spin dipolar), nuclear spin-electron orbital (spin orbital), and Fermi contact interactions are in general nonzero for liquids. However, the spin-dipolar and spin-orbital contributions are, in the first approximation, negligible if either of the nuclei involved in the coupling is a proton.⁹ We will here restrict our attention to couplings involving protons and need, therefore, consider only the contact contributions to the spin-coupling constant.

In the one-electron MO approximation, the contact contribution, $J^{(3)}_{AB}$, to the coupling of nuclei A and B is given by¹⁴

$$J^{(3)}_{AB} = -(128/9)\pi\hbar^2\beta^2\gamma_A\gamma_B \sum_i^{\text{occ}} \sum_j^{\text{unocc}} (E_j - E_i)^{-1} \times \sum_{\gamma\mu\nu\sigma} c_{i\lambda}c_{j\mu}c_{j\nu}c_{i\sigma}(\phi_\gamma|\delta(r_A)|\phi_\mu)(\phi_\nu|\delta(r_B)|\phi_\sigma) \quad (1)$$

The derivation of eq. 1 is given by Pople and Santry.⁹ They further simplified eq. 1 by retaining only one-center integrals involving valence-shell S orbitals on nuclei A and B. However, not all terms involving the product of a one-center integral with a two-center integral are truly negligible. In the present work we retain the more important terms of this type. Specifically we include all terms for which

$$\begin{aligned} \lambda = \mu = A \text{ and } \nu = \sigma = B \\ \lambda' \neq \mu = A \text{ and } \nu = \sigma = B \\ \mu' \neq \lambda = A \text{ and } \nu = \sigma = B \\ \lambda = \mu = A \text{ and } \nu' \neq \sigma = B \\ \lambda = \mu = A \text{ and } \sigma' \neq \nu = B \end{aligned}$$

where λ and μ are valence-shell S orbitals on A, ν and σ are valence-shell S orbitals on B, λ' and μ' are any valence-shell orbital on an atom located less than 2.0 Å. from A, and ν' and σ' are any valence-shell orbital on an atom located less than 2.0 Å. from B.

One-electron wave functions and energies are computed according to the extended Hückel theory, using the following valence-state ionization potentials (e.v.) for the diagonal matrix elements: $H_{\mu\mu}(\text{H}1\text{S}) = -13.6$, $H_{\mu\mu}(\text{C}2\text{P}) = -11.4$, and $H_{\mu\mu}(\text{C}2\text{S}) = -21.4$. All overlaps are included and the off-diagonal matrix elements are approximated by

$$H_{\mu\nu} = 0.5K(H_{\mu\mu} + H_{\nu\nu})S_{\mu\nu} \quad (2)$$

with $K = 1.75$.¹² Slater atomic orbitals with exponents of 1.2 for hydrogen and 1.625 for carbon are used as the basis set. Slater orbitals cannot be used in the evaluation of the contact integrals $(\phi_\lambda|\delta(r)|\phi_\lambda)$ owing to the improper behavior at the nucleus for 2S orbitals. For this part of the calculation, hydrogen-like orbitals are adopted. The effective nuclear charge, Z_{eff} , is taken as 1.2 for hydrogen. For carbon, Z_{eff} is chosen so that the integral $(2\text{S}|\delta(r_C)|2\text{S})$ has the same value (2.767 a.u.) as that obtained from self-consistent field calculations.¹⁵ This requires a value of 4.11 for carbon.

A version of the extended Hückel theory computer program developed by Hoffman¹² was modified to include the calculation of $J^{(3)}_{AB}$. Input consists of the appropriate $H_{\mu\mu}$, Slater exponent, and atom coordinates for each atomic orbital and the effective nuclear charges for the nuclei whose coupling is to be computed. Pertinent data on the structures assumed for the cal-

culations are as follows: cyclohexane, chair form; cyclopentane, planar, $\angle_{\text{CCC}} = 108^\circ$; cyclobutane, planar, $D_{\text{CH}} = 1.09$ Å., $\angle_{\text{HCH}} = 112^\circ$; cyclopropane, $D_{\text{CC}} = 1.53$ Å., $D_{\text{CH}} = 1.09$ Å., $\angle_{\text{HCH}} = 114^\circ$; ethylene, $D_{\text{CC}} = 1.34$ Å., $D_{\text{CH}} = 1.09$ Å., $\angle_{\text{HCH}} = 120^\circ$; benzene, $D_{\text{CC}} = 1.395$ Å., $D_{\text{CH}} = 1.09$ Å.; acetylene, $D_{\text{CC}} = 1.21$ Å., $D_{\text{CH}} = 1.06$ Å. Unless determined by symmetry or otherwise stated, bond angles are taken as $109^\circ 28'$ and bond distances of 1.10 and 1.54 Å. are used for C-H and C-C bonds, respectively.

Results

The calculated and observed coupling constants are compared in Tables I, II, and III. The signs for these

Table I. Coupling through One Bond, $J_{13\text{CH}}$

Compound	$J^{(3)}_{\text{calcld}}^a$	J_{obsd}^a	Ref.	$J_{\text{obsd}}/J^{(3)}_{\text{calcld}}$
Methane	83	125	c	1.51
Ethane	84	125	d, e	1.50
Cyclohexane	85 ^b	123, 124	c, f	1.45
Cyclopentane	85	128	c, f	1.51
Cyclobutane	93	134	f	1.44
Cyclopropane	107	161	c	1.50
Ethylene	107	156	d, e	1.46
Benzene	100	159	c	1.59
Acetylene	169	249	d, e	1.47

^a Values are given to the nearest c.p.s. ^b Average of the coupling to H_c (86 c.p.s.) and H_a (84 c.p.s.). ^c N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 768 (1950). ^d R. M. Lynden-Bell and N. Sheppard, *Proc. Roy. Soc. (London)*, **A269**, 385 (1962). ^e D. M. Graham and C. E. Holloway, *Can. J. Chem.*, **41**, 2114 (1963). ^f C. S. Foote, *Tetrahedron Letters*, 579 (1963).

Table II. Coupling through Two Bonds

Compound	Coupling	$J^{(3)}_{\text{calcld}}$, c.p.s.	J_{obsd} , c.p.s.	Ref.
Methane	H-H	-16.5	-12.4	f
Ethane	H-H	-16.7		
	¹³ C-H	-4.0	-4.5, -4.8	g, h
Cyclohexane	H-H	-17.0	-12 to -13 ^a	i, j
	¹³ C-H _a	-4.1		
	¹³ C-H _b	-4.2		
Cyclopentane	H-H	-17.5	-8 to -13 ^b	k
	¹³ C-H	-4.2		
Cyclobutane	H-H	-18.1	-4.3 to -9.1 ^c	l
			-13.1, ^a -15.3 ^d	m, n
			-10.9 ^d	
	¹³ C-H	-3.3		
Cyclopropane	H-H	-19.3	-5.6 ^e	o
	¹³ C-H	-2.8		
Ethylene	H-H	-15.2	2.5, 2.3, 2.0	g, h, p
	¹³ C-H	-8.0	-2.4	g, h
Benzene	¹³ C-H	-6.9		
Acetylene	¹³ C-H	-5.9	49.3, 49.7	g, h

^a For derivatives of the parent hydrocarbon. ^b For norbornene and norbornane derivatives. ^c For bicyclo[2.1.1]hexane derivatives. ^d For cyclobutanone derivatives. ^e Predicted for cyclopropane from studies on cyclopropane derivatives: T. Schaefer, F. Hruska, and G. Kotowycz, *Can. J. Chem.*, **43**, 75 (1965). ^f Reference 1. ^g Footnote d, Table I. ^h Footnote e, Table I. ⁱ J. I. Musher, *J. Chem. Phys.*, **34**, 594 (1961). ^j F. A. L. Anet, *J. Am. Chem. Soc.*, **84**, 1053 (1962). ^k P. Lazlo and P. von R. Schleyer, *ibid.*, **86**, 1171 (1964), and references therein. ^l K. B. Wiberg, B. R. Lowry, and B. J. Nist, *ibid.*, **84**, 1594 (1962). ^m M. Takahashi, D. R. Davies, and J. D. Roberts, *ibid.*, **84**, 2935 (1962). ⁿ K. L. Servis and J. D. Roberts, *J. Phys. Chem.*, **67**, 2885 (1963). ^o T. Schaefer, *et al.*, footnote e above. ^p G. S. Reddy and J. H. Goldstein, *J. Mol. Spectry.*, **8**, 475 (1962).

(14) See ref. 9 for the definition of terms used in eq. 1.

(15) J. R. Morton, J. R. Rowlands, and D. H. Whiffen, National Physical Laboratory Report BPR 13, 1962.

Table III. Coupling through Three Bonds

Compound	Coupling	$J^{(s)}$ calcd, c.p.s.	J_{obsd} , c.p.s.	Ref.
Ethane	H-H, $\phi = 0^\circ$	7.8		
	= 30°	5.7		
	= 60°	1.8		
	= 90°	0.2		
	= 120°	3.4		
	= 150°	9.2		
Cyclohexane	H _a -H _a	11.0	9-13 ^a	d, e
	H _a -H _b	1.8	2-6 ^a	d, e, f
	H _c -H _c	1.9	2-4 ^a	f, g
	H-H, <i>cis</i>	7.8	5.8-11.4 ^b	h
Cyclopentane	H-H, <i>trans</i>	3.8	2.1-5.8 ^b	h
	H-H, <i>cis</i>	5.4		
Cyclobutane	H-H, <i>cis</i>	5.1		
	H-H, <i>trans</i>	5.4		
Cyclopropane	H-H, <i>cis</i>	3.7	9.2 ^c	i
	H-H, <i>trans</i>	5.6	6.2 ^c	i
Ethylene	H-H, <i>cis</i>	5.9	11.6, 11.5, 11.4	j, k, l
	H-H, <i>trans</i>	16.8	19.1, 18.8	j, k, l
Acetylene	H-H	8.5	9.6, 9.8, 9.1	j, k, l

^a For cyclohexane derivatives. ^b For norbornane and norbornene derivatives. ^c Predicted for cyclopropane from results on substituted cyclopropanes: Schaefer, *et al.*, footnote e, Table II. ^d Footnote i, Table II. ^e A. C. Huitric, J. B. Carr, W. F. Trager, and B. J. Nist, *Tetrahedron*, **19**, 2145 (1963), and references therein. ^f D. H. Williams and N. S. Bhaca, *J. Am. Chem. Soc.*, **86**, 2742 (1964). ^g Footnote j, Table II. ^h Footnote k, Table II. ⁱ Schaefer, *et al.*, footnote e, Table II. ^j Footnote d, Table I. ^k Footnote e, Table I. ^l Reference 1.

couplings are now established with reasonable certainty, based on the absolute sign of the *ortho* coupling in *p*-nitrotoluene. This coupling has been shown¹⁶ to be positive, and it may be reasonably assumed that all other large H-H couplings through three bonds are also positive. Relative sign determinations, either by spectral analysis¹⁷ or spin-decoupling experiments,¹⁸ allow other couplings to be related to H-H couplings over three bonds and thereby indirectly fix their absolute signs.

The theoretical coupling constants reported here include the contributions from the terms involving products of one- and two-center integrals as described above. In most cases, the calculations have also been carried out with the neglect of these terms so that their effect is easily evaluated. The additional terms contribute from +11 to +27 c.p.s. to the ¹³C-H couplings in Table I, from +1.5 to +8.5 c.p.s. to the H-H couplings in Table II (making the total coupling less negative), from -0.4 to +1.6 c.p.s. to the ¹³C-C-H couplings in Table II, and from 0.5 to +1.0 c.p.s. to the couplings in Table III.

(16) A. D. Buckingham and K. A. McLauchlan, *Proc. Chem. Soc.*, 144 (1963).

(17) For methods see J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959; J. D. Roberts, "An Introduction to the Analysis of Spin-Spin Splitting in High-Resolution Nuclear Magnetic Resonance Spectra," W. A. Benjamin Co., New York, N. Y., 1961. For selected examples see F. Kaplan and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 4666 (1961); R. R. Fraser, R. V. Lemieux, and J. D. Stevens, *ibid.*, **83**, 3901 (1961); C. A. Reilly and J. D. Swalen, *J. Chem. Phys.*, **35**, 1522 (1961); H. Finegold, *Proc. Chem. Soc.*, 213 (1962); H. S. Gutowsky and C. Juan, *J. Chem. Phys.*, **37**, 120 (1962).

(18) R. Freeman and D. H. Whiffen, *Mol. Phys.*, **4**, 321, 386 (1961); J. P. Maher and D. F. Evans, *Proc. Chem. Soc.*, 208 (1961); D. D. Elleman and S. L. Manatt, *J. Chem. Phys.*, **36**, 2346 (1962); R. R. Fraser, *Can. J. Chem.*, **40**, 1483 (1962); R. Freeman, *Mol. Phys.*, **5**, 499 (1962); K. A. McLauchlan and D. H. Whiffen, *Proc. Chem. Soc.*, 144 (1962); B. D. Nageswara Rao, J. D. Baldeschwieler, and J. I. Musher, *J. Chem. Phys.*, **37**, 2480 (1962); P. C. Lauterbur and R. J. Kurland, *J. Am. Chem. Soc.*, **84**, 3405 (1962); F. A. L. Anet, *ibid.*, **84**, 3767 (1962).

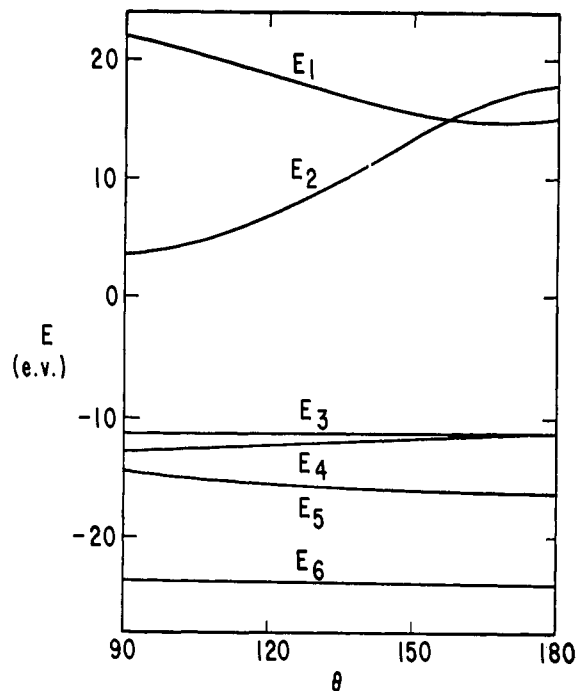


Figure 1. One-electron energy levels for CH₂ as a function of geminal angle.

One disadvantage of the MO method is that the calculated wave functions are delocalized. As a consequence, many different terms enter into eq. 1, and it is difficult to isolate the factors which dominate the coupling. As an aid to the discussion which follows, we include calculations on the CH₂ fragment, where the situation is less complicated. The interatomic angle, θ , is given values of 90° , $109^\circ 28'$, 120° , 150° , and 180° with corresponding C-H bond lengths of 1.1, 1.1, 1.09, 1.08, and 1.06 Å., respectively. The geometric arrangement of the atoms is



with carbon at the origin and the *z* axis perpendicular to the page. The variation in the one-electron energy levels with θ is shown in Figure 1, and wave functions for the extreme angles are given in Table IV. The

Table IV. Wave Functions for Methylene

Orbital no.	c_{H_1}	c_{H_2}	c_{2s}	c_{2p_x}	c_{2p_y}	c_{2p_z}
$\theta = 90^\circ$						
1	0.96	0.96	-1.20	0.61	-0.61	0
2	0.89	-0.89	0	0.74	0.74	0
3	0	0	0	0	0	1.00
4	0.17	0.17	-0.36	-0.60	0.60	0
5	0.43	-0.43	0	-0.43	-0.43	0
6	0.24	0.24	0.71	-0.02	0.02	0
$\theta = 180^\circ$						
1	0.93	0.93	-1.25	0	0	0
2	1.04	-1.04	0	1.41	0	0
3	0	0	0	0	0	1.00
4	0	0	0	0	1.00	0
5	0.42	-0.42	0	-0.51	0	0
6	0.25	0.25	0.70	0	0	0

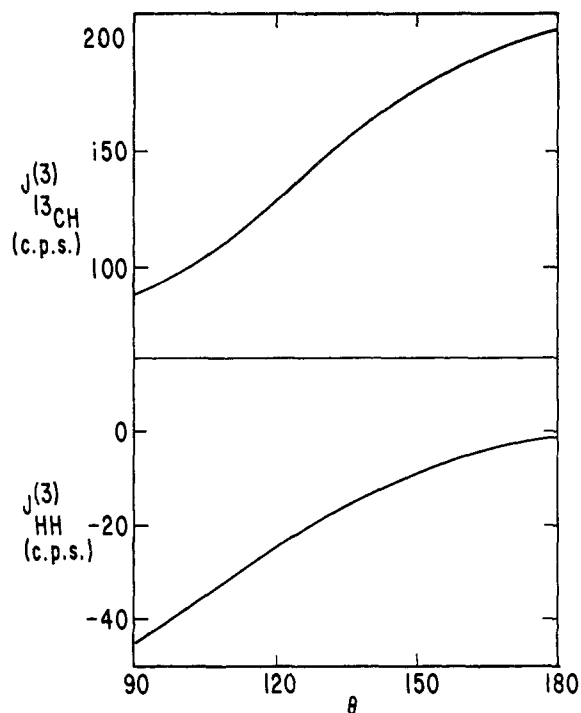


Figure 2. $J^{(3)_{13\text{CH}}}$ and $J^{(3)_{\text{HH}}}$ for CH_2 as a function of geminal angle.

$^{13}\text{C-H}$ and H-H coupling constants are calculated for a six-electron (E_4 , E_5 , and E_6 occupied) singlet ground state and the results are plotted in Figure 2.

Discussion

Before considering the results, it should be pointed out that the present calculations do not include contributions to the coupling from the π electrons in molecules like ethylene, benzene, and acetylene. Owing to the orthogonality of the σ and π orbitals, all terms in eq. 1 involving a π orbital are zero. Nevertheless, it is generally believed that the π electrons do contribute to the coupling, and the failure of the extended Hückel theory to account for this may be traced to the neglect of σ - π interaction. Semiempirical methods for estimating π -electron coupling have been developed by McConnell¹⁹ and by Karplus.²⁰ Where appropriate we shall point out the estimated magnitude for the π contribution to the coupling.

The ^{13}CH couplings (Table I) vary in nearly the same manner as the observed coupling but are consistently low by a factor of about 1.5. The π contribution to the coupling in ethylene has been estimated at -2.6 c.p.s.²¹ A slightly less negative value would be expected for benzene and a somewhat more negative one for acetylene. The terms are a small fraction of the total coupling and do not seriously affect the overall correlation. The calculated couplings through two bonds (Table II) are in fair agreement with experiment for unstrained, saturated hydrocarbons, although the values are consistently too negative. For ethylene and acetylene there is substantial disagreement, and it is unlikely that these failures can be attributed to the neglect of π -electron coupling. The π contribution may be estimated²² at $+1.8$ c.p.s. for ethylene, a value

(19) H. M. McConnell, *J. Mol. Spectry.*, **1**, 11 (1957).

(20) M. Karplus, *J. Chem. Phys.*, **33**, 1842 (1960).

(21) C. Juan and H. S. Gutowsky, *ibid.*, **37**, 2198 (1962).

too small to account for the error. It should be emphasized that the terms in eq. 1 involving a product of a one- and a two-center integral can make a sizable contribution to the coupling, especially through the bonds. Although these contributions do not dominate the total coupling, they generally improve the agreement with experiment.

It will be helpful to a detailed understanding of the couplings through one and two bonds to consider the calculations for the CH_2 fragment. For simplicity we will discuss only the terms in eq. 1 which involve one-center integrals. The $^{13}\text{C-H}$ coupling depends upon contributions from the $6 \rightarrow 1$ and $4 \rightarrow 1$ excitations (see Table IV and Figure 1), these being the only ones involving the carbon 2S atomic orbital in both the occupied and unoccupied molecular orbitals. Although the $6 \rightarrow 1$ and $4 \rightarrow 1$ excitation energies vary with θ , their average, weighted according to the magnitude of the contribution to $J^{(3)_{13\text{CH}}}$, remains nearly constant. The increase in $J^{(3)_{13\text{CH}}}$ with θ (Figure 2) is determined primarily by changes in the orbital coefficients of ψ_4 , the negative contribution from the $4 \rightarrow 1$ excitation going to zero as θ increases to 180° . Since ψ_4 is antibonding in character between hydrogen and the carbon 2S orbital while ψ_6 is bonding, the net result is an increase in the bonding character as θ increases. If the MO's were transformed to localized bond orbitals, this would correspond to increasing carbon 2S character in a C-H bond orbital. Thus, the description is qualitatively consistent with the established correlation of $J_{13\text{CH}}$ with the per cent S character in a localized C-H bond.^{19, 21, 23}

The H-H coupling in the CH_2 fragment is determined by excitations from occupied (bonding) to unoccupied (nonbonding) orbitals in which the coefficients for both H_1 and H_2 are nonzero. From Table IV we see that the excitations are: $4 \rightarrow 1$ and $4 \rightarrow 2$; $5 \rightarrow 1$ and $5 \rightarrow 2$; $6 \rightarrow 1$ and $6 \rightarrow 2$. Level E_3 is not involved, being associated with a localized 2P orbital on carbon. The contributions occur in pairs of nearly equal magnitude but of opposite sign. The net coupling is thus a small difference between rather large numbers. The dominant contribution derives from the difference between the $5 \rightarrow 1$ and $5 \rightarrow 2$ terms in eq. 1, which are positive and negative, respectively. It is seen from Figure 1, that $E_1 - E_5$ decreases and $E_2 - E_5$ increases as θ increases from 90 to 180° . The MO coefficients vary also, but the change in the excitation energies is the major factor in determining the variation of $J^{(3)_{\text{HH}}}$. Thus, the positive contribution increases and the negative contribution decreases as θ increases, and $J^{(3)_{\text{HH}}}$ becomes more positive (Figure 2). This trend and its origin have been discussed previously in terms of a qualitative MO picture,¹⁰ and Pople and Santry have given an interesting analysis of the trend based on a perturbation treatment of the polarizability coefficients.¹¹

Note that, although the general experimental trend is predicted by the CH_2 calculations, the actual values of $J^{(3)_{\text{HH}}}$ are much too negative, while the calculated values for specific molecules (Table II) are closer to the experimentally observed coupling constants. On the

(22) The Karplus equation,²⁰ $J^{\pi_{\text{HH}}} = 2.1 \times 10^{-15} \Sigma(a_{\text{H}}a_{\text{H}}'/\Delta\pi)$ is employed with $a_{\text{H}} = a_{\text{H}}' = -65 \times 10^6$ c.p.s. The excitation energy $\Delta\pi$, calculated here for ethylene is 5 e.v.

(23) J. N. Shoolery, *J. Chem. Phys.*, **31**, 1427 (1959).

other hand, we see that for cyclopentane, cyclobutane, and cyclopropane, where the HCH angle increases in the order given, the calculated coupling constants become slightly more negative with increasing geminal angle. Since the calculated couplings depend on a small difference between large numbers, it is not surprising that these inconsistencies occur. The CH₂ fragment is probably a better model for understanding the variation in J_{HH} with geminal angle. Including the additional atoms for the calculations on molecules seems to introduce additional errors which obscure the basic trend.

The underestimation of J_{CCH} and the generally too negative values for J_{HH} may be related errors. In terms of the CH₂ fragment model, this would result if the theory consistently overestimates E_1 , thus underestimating the positive contribution to $J^{(3)}_{\text{CCH}}$ ($6 \rightarrow 1$ excitation) and to $J^{(3)}_{\text{HH}}$ ($5 \rightarrow 1$ excitation). Since E_1 is determined largely by the value of $H_{\text{C2S,H1S}}$, whereas E_2 is independent of this integral, the use of a smaller value for $H_{\text{C2S,H1S}}$, than that given by eq. 2 would lead to larger values of $J^{(3)}_{\text{CCH}}$ and less negative values of $J^{(3)}_{\text{HH}}$.

It is of interest to compare the present work with that of Pople and Santry where rather more positive geminal H-H couplings (+21 c.p.s. for ethane and +33 c.p.s. for ethylene) were calculated. Their approach differs from ours in the neglect of overlap and in the approximation of the off-diagonal matrix elements by

$$H_{\mu\nu} = 10 \times S_{\mu\nu} \text{ e.v.} \quad (3)$$

In the present work, use of eq. 2 leads to values of $H_{\mu\nu}$ which range from 2 to 3.8 times larger than those given by eq. 3, and, as a result, the excitation energies involved in the present calculations are much larger than those of Pople and Santry. This is partly offset by changes in the orbital coefficients. The main source of the difference in results between the two calculations is probably in the choice of off-diagonal matrix elements. Relative to $H_{\text{C2P,H1S}}$, the value of $H_{\text{C2S,H1S}}$ obtained from eq. 2 is significantly more negative than that obtained using eq. 3. In view of the analysis given in the foregoing paragraph, this should lead to more positive values for $J^{(3)}_{\text{HH}}$.

Turning now to the vicinal H-H couplings given in Table III, we see that the now well-acknowledged variation with dihedral angle, ϕ , is reproduced by the theory. The dependence for ethane resembles that

calculated by Conroy²⁴ more than the earlier Karplus curve.⁴ The agreement between theory and experiment is satisfactory for cyclohexane and cyclopentane. Unfortunately, suitable data with which to compare the calculations for planar cyclobutane are not available.²⁵ Cyclobutane is, of course, actually nonplanar and the vicinal couplings might be rather sensitive to the actual structure. The calculated *cis* coupling in cyclopropane is apparently too low, as is the *cis* coupling in ethylene. Addition of an estimated²⁰ +1.5 c.p.s. π contribution to the couplings in ethylene improves the agreement somewhat. The agreement between calculated and experimental coupling constants in acetylene would appear to be excellent, but when the π contribution of +4.6 c.p.s.²⁰ is included, the total coupling is seen to be too large. The present calculations may be compared with the earlier studies which yielded 6.1 and 11.9 c.p.s., respectively, for the *cis* and *trans* coupling constants in ethylene⁴ and 7 c.p.s. for the coupling in acetylene.¹ Pople and Santry¹¹ calculate values of 6.7 and 10.3 c.p.s. for the *cis* and *trans* couplings in ethylene and 1.9 c.p.s. for acetylene, the π contribution being neglected in all cases.

In evaluating the successes and failures of the method as it is applied here, it should be remembered that the calculations are of an *a priori* nature, carried out with a single set of independently chosen parameters, and based on a theory in which excited triplet and excited singlet states are not distinguished. In view of this, the results seem remarkably good. Further improvement in the results might be obtained if a more reliable method for evaluating off-diagonal matrix elements can be developed. Comparisons of Hartree-Fock and extended Hückel calculations may be helpful in this respect.²⁶

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(24) H. Conroy, *Advan. Org. Chem.*, **2**, 265 (1960).

(25) Values of 11.2 and 7.7 c.p.s. have been found (see footnote *n*, Table II) for the vicinal couplings in 2,2-dibromocyclobutanone, but the analysis does not establish which is the *cis* coupling constant.

(26) F. P. Boer, M. D. Newton, and W. N. Lipscomb, *Proc. Natl. Acad. Sci.*, **52**, 890 (1964); M. D. Newton, F. P. Boer, W. E. Palke, and W. N. Lipscomb, *ibid.*, **53**, 1089 (1965).