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Maximum bond order hybrid orbitals II. Correlativity with C–H and C–C spin-coupling constants*

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Summary. The excellent correlativity between the maximum bond order hybrid orbitals and the nuclear spin-spin coupling constants of directly bonded C–H and C–C is shown in the present paper. The maximum bond order hybrid orbital procedure is performed by use of the first-order density matrices obtained from CNDO/2 calculation to get the bonding hybrid orbitals and the corresponding maximum bond orders for a number of hydrocarbons and hetero-substituted hydrocarbons. The relations between the obtained calculation results and the experimental coupling constants are examined by using the basic relationships proposed by Muller and Pritchard, by Maksic et al. and by Gil, and summarized in the concrete relationships which are the most suitable for the maximum bond order hybrid orbital calculation. The obtained relationships combined with the maximum bond order hybrid orbital calculation is quite successful in predicting substituent effects on the C–H and C–C coupling constants in molecules which contain no substituents of the $-I^-$ type.

Key words: Hybridization – Maximum bond order – Maximum bond order hybrid orbital – NMR – Nuclear spin coupling constant

1 Introduction

Since the use of the second-order perturbation formula for the calculation of nuclear spin-coupling constants by Ramsey [1], various theoretical formulations of the directly spin-coupling constants have been presented [2–32]. These formulas aim mainly at correlating the experimental coupling data with the electronic structures of molecules, especially with the hybrid orbitals [33–35]. Muller and Pritchard [2] proposed for the first time that the C–H coupling constants between directly bonded atoms are proportional to the s-characters of the hybrid orbitals of carbons in the C–H bonds. Muller and Prichard's

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relationship has been used in a quantitative way by Frei and Bernstain [5], by Gunther and Herrig [6], by Newton and Schlman [11], and by Alsenoy et al. [21]. Many researchers [11–21] found that an even better concordance between the experimental and calculated coupling constants is obtained when a constant term is involved. This term which is usually negative is included to correct some of the deficiencies of the method like the average energy approximation and that the coupling is assumed to be only due to the Fermi-contact interaction.

In the early seventies, a modified relationship was derived by Maksic et al. [15] by including the bond overlap in the relationship given by Muller and Pritchard, i.e.:

$$J_{AB} = a(\%s)_A(\%s)_B/(1+S_{AB}^2)+b \tag{1}$$

where S_{AB} is the bond overlap integral of the A–B bond. This relationship has been largely used in the maximum overlap hybrid orbital calculation [15–19]. Based on this relationship and the hybrid orbitals constructed by using the maximum overlap method, many quantitative predictions of the nuclear spin coupling constants for a large number of hydrocarbons and hydrosilanes have been made successfully. In addition, based on the early theoretical studies on the C–H coupling constants, an improved relationship [28] has been presented.

All these pioneering works described above show that the hybrid orbitals constructed by the maximum overlap method and by localization of the molecular orbitals are all fairly useful in calculation of the nuclear spin coupling constants, which inspire us to investigate the relations between the constants and hybrid orbitals constructed by other methods. In the preceding paper of this series [38], based on the simplified calculation scheme [36] of the maximum bond order [37] and the basic idea of the maximum overlap symmetry orbital method, a simple and systematic procedure has been presented for obtaining simultaneously the bonding hybrid orbitals called the maximum bond order hybrid orbitals (MBOHO's) [38] and Jug's maximum bond orders [37]. By use of this procedure, one can obtain the all bonding hybrid orbitals and the bond orders of single and multiple bonds in a molecule from the first-order density matrix calculated by use of a molecular orbital calculation. The main purpose of the present paper is to show the excellent correlativity between the MBOHO calculation results and the nuclear spin coupling constants. First of all, the CNDO/2 method and MBOHO procedure are employed to get the MBOHO's and the corresponding maximum bond orders for a number of hydrocarbons and heterosubstituted hydrocarbons. Then the basic relationships proposed by Muller and Pritchard, by Maksic et al. and by Gil will be used to examine the relations between the obtained MBOHO calculation results and the coupling constants, J_{CH} and J_{CC}, and to give the concrete relationships which are the most suitable for the MBOHO calculation.

2. Results and discussion

The maximum bond order hybrid orbital procedure presented in the preceding paper [38] has been used to calculate the bonding hybrid orbitals and the maximum bond orders for a number of hydrocarbons and heterosubstituted hydrocarbons. The obtained results are listed in Tables 1 to 4. For all calculations the CNDO/2 approximation [39] has been exployed to obtain the density matrices. The all bond lengths and angles of the molecules described by Sutton

[40] have been adopted, and the standard geometries of the others listed in Tables 1 to 4 have been used [39]. The order numbers of molecules in the tables correspond to those in Fig. 3.

The MBOHO calculation results will be employed to examine the relationships derived by the scholars mentioned above. Of the employed relationships, only the one derived by Maksic et al. will be changed slightly. Comparing the bond orders obtained by us with the bond overlaps obtained by Maksic et al. [15] for hydrocarbons, one can find that the bond order is almost about one and one-third times the bond overlap of the same bond. Thus the bond overlap S_{AB} can be changed into three-quarter times bond order P_{AB} in order to generalize the relationship derived by Maksic et al.

2.1 C–H *coupling constants*

By applying the least-squares procedure for hydrocarbons listed in Table 1 we get the following concrete form of the relationship derived by Muller and Pritchard:

$$J_{CH} = 6.16(\%s)_C - 23.95 \qquad (SD = 3.64\ \text{Hz}) \tag{2}$$

If the bond order is included we can obtain the following relationship from that derived by Maksic et al.:

$$J_{CH} = 17.063(\%s)_C/((4/3)^2 + P_{CH}^2) - 25.01 \quad (SD = 3.41\ \text{Hz}) \tag{3}$$

However, when heterosubstituted molecules are included (Tables 1 and 2) Eqs. (2) and (3) become:

$$J_{CH} = 6.25(\%s)_C - 24.25 \qquad (SD = 4.60\ \text{Hz}) \tag{4}$$

$$J_{CH} = 17.207(\%s)_C/((4/3)^2 + P_{CH}^2) - 24.45 \quad (SD = 4.39\ \text{Hz}) \tag{5}$$

The molecules marked by the notation # have been used to obtain Eqs. (2)–(5). The calculated results are listed in Tables 1 and 2, respectively.

Comparing Eq. (2) with Eq. (4) one can find that a better agreement with the experimental J_{CH} constants is produced for hydrocarbons. It is in agreement with the results obtained by Alsenoy [21] in the modified INDO approximate treatment. Comparing Eq. (2) with Eq. (3) and Eq. (4) with Eq. (5) one can find that little better results are obtained by including the bond order. This confirms the works including the bond overlap reported by Maksic et al. [15]. However, in contrast to the conclusion based on the maximum overlap hybrid orbital calculation [15], the MBOHO calculation results for all the molecules investigated here show that Eqs. (2) and (4) in which the bond overlap or bond order are not included can also be employed to give good results, though Eqs. (3) and (5) are slightly better than them. As the maximum bond order hybrid orbital method can be employed conveniently to treat molecules included heteroatoms, a generalized application based on the hybrid orbitals becomes possible.

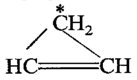
Based on the MBOHO calculation, we have also investigated the relationship proposed recently by Gil [28], and get the following relationship:

$$J_{CH} = 0.705(\%s)_C^{3/2} + 44.91 \qquad (SD = 5.27\ \text{Hz}) \tag{6}$$

It follows that a positive constant is involved as pointed out by Gil [28]. The MBOHO calculation gives a large constant and the poor results are presented in Eq. (6), which is contrary to Gil's conclusion for other calculation results.

Some trends in the J_{CH} values [44–48] are evident from Tables 1 and 2. For instance, the increase of the J_{CH} with the decreasing of CCC angle along the series:

Table 1. Comparison of the experimental and calculated vlaues of J_{CH} (in Hz) for hydrocarbons

No.	Molecule	$(\%s)_C$	Bond order P_{CH}	J_{CH} Calc.			Experiment	
				Eq. (3)	Eq. (5)	INDO	J_{CH}	Ref.
1#	CH_4	25.00	0.9995	128.61	130.47	122.91[a]	125.0	15
2#	$CH_3{-}CH_3$	24.26	0.9892	125.17	127.00	122.12[a]	124.9	15
3#	$CH_2{=}CH_2$	29.95	0.9823	161.32	163.45	156.70[a]	156.2	21
4#	$CH{\equiv}CH$	44.46	0.9921	249.65	252.53	232.65[a]	248.7	21
5#	$\overset{*}{C}H_3{-}C{\equiv}CH$ (6)	24.49	0.9866	126.88	128.72	122.01[a]	131.0	21
6#	$CH_3{-}C{\equiv}\overset{*}{C}H$	44.61	0.9923	250.54	253.54	232.53[a]	247.6	21
7#	$CH_2{=}C{=}CH_2$	31.10	0.9743	169.58	171.78	155.50[a]	168.2	23
8#	Cyclopropane	29.24	0.9849	156.56	158.65	155.20[b]	160.5	21
9#	Cyclopropene	39.60	0.9850	220.88	223.51	228.57[c]	226.0	21
10#	Cyclobutane	25.91	0.9850	135.87	137.79	128.30[b]	136.0	21
11#	$C_6H_5{-}C{\equiv}\overset{*}{C}H$	44.53	0.9922	250.06	252.94	231.41[a]	251.1	5
12#	$C_6H_5{-}C{\equiv}C{-}\overset{*}{C}H_3$ (6)	24.49	0.9861	126.93	128.78		131.3	5
13#	$\overset{*}{C}H_3CH_2C_6H_5$ (1)	24.92	0.9865	129.56	131.42		127.0	5
14	$\overset{*}{C}H_3CH_2C_6H_5$ (1′)	23.81	0.9903	122.27	124.07			
15#	$\overset{*}{C}H_3C(CH_3)CH_2$ (2′)	24.66	0.9866	127.93	129.79		126.0	2
16	$\overset{*}{C}H_3C(CH_3)CH_2$ (2)	24.89	0.9918	128.79	130.64		126.0	2
17	$\overset{*}{C}H_3CH{=}CH_2$ (3)	24.94	0.9911	129.17	131.03	122.44[a]		
18	$\overset{*}{C}H_3CH{=}CH_2$ (3′)	24.00	0.9858	123.93	125.74			
19	$CH_3\overset{*}{C}H{=}CH_2$ (3)	29.05	0.9775	156.34	158.43	151.15[a]		
20	$CH_3CH{=}\overset{*}{C}H_2$ (4)	30.84	0.9841	166.61	168.78			
21	$CH_3CH{=}\overset{*}{C}H_2$ (4′)	29.91	0.9839	160.85	162.98			
22	$(CH_3)_2C{=}\overset{*}{C}H_2$	30.93	0.9849	167.06	169.24	156.34[a]		
23	$\overset{*}{C}H_2CH_2CH_3$ (1)	24.75	0.9911	128.00	129.85			
24	$\overset{*}{C}H_3CH_2CH_3$ (1′)	23.97	0.9901	123.28	125.09			
25	$CH_3\overset{*}{C}H_2CH_3$	23.33	0.9809	120.28	122.06	119.37[a]		
26	$CH_3C{\equiv}CCH_3$ (6)	23.97	0.9820	124.15	125.96			
27	$HC{\equiv}C{-}C{\equiv}CH$	44.45	0.9924	249.53	252.41			
28	$CH_2CH{-}CH{=}\overset{*}{C}H_2$ (4)	31.20	0.9853	168.68	170.87	166.36[a]		
29	$CH_2CH{-}CH{=}\overset{*}{C}H_2$ (4′)	29.99	0.9853	161.17	163.30	149.24[a]		
30	$CH_2CH{-}\overset{*}{C}H{=}CH_2$	29.41	0.9782	158.50	160.60	155.22[a]		
31	$\overset{*}{C}H_3{-}C_6H_5$ (3)	24.05	0.9861	124.20	126.02			
32	$CH_3{-}C_6H_6$ (3′)	24.18	0.9918	124.40	126.22			
33	$C_6H_5\overset{*}{C}H_2CH_3$	23.23	0.9777	119.99	121.77			
34	$C_6H_6CH{=}\overset{*}{C}H_2$ (4)	30.80	0.9828	166.54	168.71			
35	$C_6H_5CH{=}\overset{*}{C}H_2$ (4′)	29.74	0.9890	159.79	161.90			
36	$C_6H_5{-}\overset{*}{C}H{=}CH_2$	28.99	0.9790	155.77	157.86			
37		30.68	0.9811	166.02	168.19			
38	Cyclohexane	21.97	0.9799	111.91	113.62	118.10[b]		

[a] Ref. [23] [b] Ref. [25] [c] Ref. [21]

Table 2. Comparison of the experimental and calculated vlaues of J_{CH} (in Hz) for heterosubstituted hydrocarbons

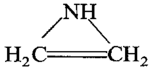
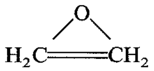
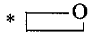
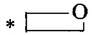
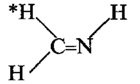
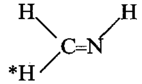
No.	Molecule	$(\%s)_C$	Bond order P_{CH}	J_{CH} Calc.			Experiment	
				Eq. (3)	Eq. (5)	INDO	J_{CH}	Ref.
39#	CH_3F	26.99	0.9919	144.44	143.72	140.08^{a}	149	2
40#	H–CN	48.27	0.9850	277.44	277.80	232.68^{a}	275	46
41#	H–C(O) NH_2	32.72	0.9678	180.25	182.97	188.29^{a}	187	21
42#	CH_3OH (3)	26.00	0.9917	138.25	137.57	135.27^{a}	141	47
43#	CH_3OH (3′)	26.88	0.9903	143.75	143.22		144	47
44#	CH_3–CN (6)	24.03	0.9813	125.94	126.42	122.44^{a}	136	47
45#	CH_3NH_2 (3′)	25.66	0.9905	136.13	135.59	129.92^{a}	133	47
46	CH_3NH_2 (3)	25.03	0.9893	132.19	131.80			
47#	CH_3OCH_3 (2)	26.20	0.9908	139.50	138.92	135.50^{a}	140	23
48	CH_3OCH_3 (2′)	25.99	0.9896	138.19	137.75			
49#	$\overset{*}{C}H_3CH_2F$ (1)	24.38	0.9902	128.13	127.64	127.47^{c}	126.4	21
50	$\overset{*}{C}H_3CH_2F$ (1′)	24.33	0.9895	127.81	127.40			
51	CH_3–$\overset{*}{C}H_2F$	25.75	0.9825	136.69	137.05	137.13^{a}		
52#	$\overset{*}{C}H_3NHCH_3$ (2′)	25.65	0.9891	136.06	135.69	136.75^{c}	132	47
53	$\overset{*}{C}H_3NHCH_3$ (2)	24.88	0.9910	131.25	130.67	136.75^{c}	132	47
54#	$\overset{*}{C}H_3CHO$ (3)	24.47	0.9897	128.69	128.27	121.36^{a}	127	47
55	$\overset{*}{C}H_3CHO$ (3′)	23.87	0.9818	124.94	125.38			
56#	CH_3–$\overset{*}{C}HO$	31.39	0.9702	171.94	174.19	164.51^{a}	172.4	23
57#	$\overset{*}{C}H_3C(O)CH_3$ (2)	24.37	0.9918	128.06	127.40	127.25^{c}	126	47
58	$CH_3C(O)CH_3$ (2′)	24.25	0.9854	127.31	127.35			
59#	$\overset{*}{C}H_3$–COOH (3)	25.13	0.9918	132.81	132.14	120.61^{a}	130	2
60	CH_3–COOH (3′)	24.05	0.9851	126.06	126.13			
61#		29.78	0.9841	161.88	162.14	163.40^{b}	168	21
62#		30.74	0.9834	167.88	168.25	166.10^{b}	175.8	21
63#		25.11	0.9842	132.69	132.87	140.50^{c}	137.3	21
64#		27.67	0.9842	148.69	148.91	142.80^{b}	148	21
65#	$\overset{*}{C}H_3C(O)C_6H_6$ (3)	24.21	0.9918	127.06	126.41	120.29^{a}	125.7	23
66	$\overset{*}{C}H_3C(O)C_6H_6$ (3′)	24.27	0.9854	127.44	127.48	120.29^{a}	125.7	23
67#	C_6H_5–$\overset{*}{C}HO$	31.90	0.9724	175.13	177.11	159.08^{a}	173.7	23
68#	H–C=CF	46.69	0.9898	267.56	266.90	251.54^{a}	277.5	21
69	CH_3–CF_3 (6)	24.52	0.9895	129.00	128.59			
70	FCH=$\overset{*}{C}H_2$ (4)	30.84	0.9834	168.50	168.88	162.36^{a}		
71	FCH=$\overset{*}{C}H_2$ (4′)	30.61	0.9833	167.06	167.45	153.26^{a}		
72	F$\overset{*}{C}$H=CH_2	32.78	0.9802	180.63	181.51	183.11^{a}		
73	$\overset{*}{C}H_3CHF_2$ (3)	24.70	0.9895	130.13	129.17			
74	$\overset{*}{C}H_3CHF_2$ (3′)	24.82	0.9899	130.88	130.42			
75	CH_3–CHF_2	27.32	0.9771	146.50	147.59	156.98^{a}		
76	$\overset{*}{C}H_3CH_2OH$ (1)	24.05	0.9903	126.06	125.57			
77	$\overset{*}{C}H_3CH_3OH$ (1′)	24.41	0.9894	128.31	127.91			
78	CH_3–$\overset{*}{C}H_2OH$	26.36	0.9817	140.50	141.00			
79	$\overset{*}{C}H_3CH(CH_3)F$ (5)	23.97	0.9901	125.66	125.09			

Table 2. (continued)

No.	Molecule	$(\%s)_C$	Bond order P_{CH}	J_{CH} Calc.			Experiment	
				Eq. (3)	Eq. (5)	INDO	J_{CH}	Ref.
80#	$\overset{*}{C}H_3CH(CH_3)F$ (5′)	24.02	0.9907	125.88	125.34			
81	$\overset{*}{C}H_3(CH(CH_3)F$ (5″)	24.85	0.9914	131.06	130.44			
82	$(CH_3)_2\overset{*}{C}HF$	24.34	0.9756	127.88	128.99	129.80^a		
83	$\overset{*}{C}H_3CH(OH)CH_3$ (5)	23.99	0.9904	125.69	125.19			
84	$\overset{*}{C}H_3CH(OH)CH_3$ (5′)	23.90	0.9905	125.13	124.61			
85	$\overset{*}{C}H_3CH(OH)CH_3$ (5″)	24.78	0.9915	130.63	129.99			
86	$(CH_3)_2\overset{*}{C}HOH$	23.51	0.9753	122.69	123.79	123.03^a		
87	$\overset{*}{C}H_3CH_2CN$ (1)	24.03	0.9898	125.94	125.50			
88	$\overset{*}{C}H_3CH_2CN$ (1′)	24.51	0.9899	128.94	128.48			
89	$CH_3\text{–}\overset{*}{C}H_2CN$	23.06	0.9722	119.88	121.27	119.84^a		
90	$(CN)CH{=}\overset{*}{C}H_2$ (4)	30.97	0.9843	169.31	169.57			
91	$(CN)CH{=}\overset{*}{C}H_2$ (4′)	30.11	0.9841	163.94	164.21			
92	$(CN)\overset{*}{C}H{=}CH_2$	28.94	0.9710	156.63	158.59			
93	$CH_2{=}CF_2$	30.74	0.9817	167.88	168.49	160.11^a		
94	$\overset{*}{C}H_3CH_2NH_2$ (1)	23.94	0.9908	125.38	124.83			
95	$\overset{*}{C}H_3CH_2NH_2$ (1′)	24.38	0.9897	128.13	127.69			
96	$CH_3\text{–}\overset{*}{C}H_2NH_2$	23.66	0.9787	123.63	124.37	126.3^a		
97	$CH_3\text{–}NC$ (6)	25.50	0.9874	135.13	134.95			
98	$C_6H_6\text{–}\overset{*}{C}H_2OH$	25.29	0.9825	133.81	134.19			
99	$\overset{*}{C}H_3O\text{–}N{=}O$ (3)	26.54	0.9871	141.63	141.48			
100	$\overset{*}{C}H_3O\text{–}N{=}O$ (3′)	26.37	0.9913	140.56	139.92			
101		32.76	0.9860	180.50	180.53	167.04^a		
102		34.87	0.9863	193.69	193.69	181.93^a		
103	$\overset{*}{C}H_3COOCH_3$(3)	25.08	0.9916	132.50	131.85		147	2
104	$CH_3\text{–}NO_2$	25.74	0.9912	136.63	136.01	129.78^a	146.7	23
105	CH_2F_2	29.52	0.9837	160.25	160.57	166.79^a	184.5	21
106	CHF_3	31.17	0.9750	170.56	172.13	212.19^a	239.1	21
107	$H\text{–}C(O)F$	37.37	0.9723	209.13	211.68	244.77^a	267.0	23
108	$H\text{–}\overset{*}{C}OOCH_3$	35.94	0.9713	200.38	202.81	214.20^a	226.2	23

^{a} Ref. [23] ^{b} Ref. [25] ^{c} Ref. [21]

cyclohexane (38), cyclobutane (10) and cyclopropane (8), discussed by Foote [44] and Maksic et al. [15], is very well reproduced. We also note an increase of the J_{CH} constants of the C–H bonds α to the heteroatom in small saturated heterocyclic compounds along the series: cyclopropane (8), aziridine (61) and ethylene oxide (62). The calculated J_{CH} values for the systems in which CH fragments occur in *cis*/*trans* pairs with some substituted ethylene (20, 21; 28, 29; 34, 35; 70, 71; 90, 91) are collected in Tables 1 and 2. One can see from the tables that the calculated J_{CH} values for the hydrogen *cis* with respect to the substituent are larger than those for the corresponding *trans*. In addition, we also find ourselves in an excellent position to check Bent's rule [41], "Atomic *s*-character concentrates in orbitals directed towards electropositive substituents".

Moreover, one can get different J_{CH} values for the C–H bonds existing in different chemical environments (20, 21; 42, 43; 49, 50 etc.). This is coincident with the chemical intuition. For instance, Eq. (4) applied to methanol (42 and 43) gives 138.25 Hz and 143.75 Hz, closing to the experimental values 141 Hz and 144 Hz [47]. For vinyl fluoride (70, 71 and 72), our calculations do place the three distinct J_{CH} values in the correct experimental order [23]. The similar results are also obtained for CH_2=NH (101 and 102).

The experimental J_{CH} values collected in Tables 1 and 2 against *s*-characters of the carbon hybrids involved in the different C–H bonds also give one single straight line as discussed by Alsenoy et al. [21]. The overall relationship between the experimental coupling constants and those calculated by use of Eq. (5) is demonstrated in Fig. 1. From the near-unity value of the slope of the least-squares-adjusted line in Fig. 1 one can see that the calculated results from MBOHO calculation have nearly the same sensitivity to structural effects as the experimental ones.

Inspection of Tables 1 and 2 also reveals some defects in the quantitative prediction of substituent effects for a few molecules (44, 103, 104), in which the substituents belong to the type $-I^-$ defined by Pople and Gordon [12]. The similar troubles also existed in the INDO treatment [23]. Other unsuccessful examples are difluoromethane (105), fluoroform (106), formyl fluoride (107) and methyl formate (108). All these molecules contain more ionic characters. It seems

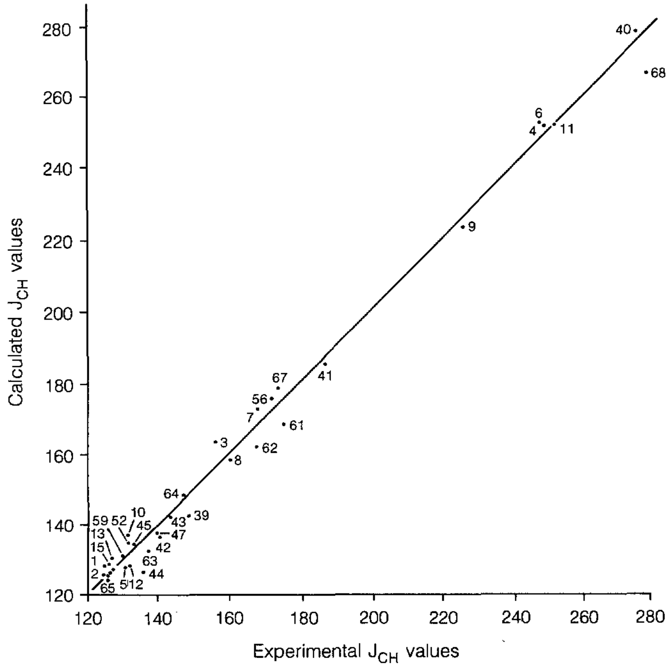


Fig. 1. Comparison of the calculated J_{CH} values with the experimental J_{CH} values

that the defects for these molecules are caused by using the approximate density function obtained from the CNDO/2 calculation and neglecting other factors, such as the molecular polarity, in Eqs. (4) and (5).

2.2 C–C coupling constants

A similar investigation has also been carried out for the nuclear spin coupling constants for various C–C bonds listed in Tables 3 and 4. Assuming a linear dependence, for twenty-one C–C bonds (marked by #) listed in Tables 3 and 4, one can get:

$$J_{CC} = 0.0586(\%s)_{C_1}(\%s)_{C_2} - 13.4 \quad (SD = 6.43\ \text{Hz}) \tag{7}$$

$$J_{CC} = 0.1620(\%s)_{C_1}(\%s)_{C_1}/((4/3)^2 + P^2_{CC(\sigma)}) + 0.71 \quad (SD = 4.07\ \text{Hz}) \tag{8}$$

where $P_{CC(\sigma)}$ is the σ-bond order of the C–C bond. For the multiple C–C bonds $P_{CC(\sigma)}$ can be evaluated by depleting the total bond order of the π-bond order. The standard deviation of Eq. (8) can be reduced if we do not represent all the points in a single line. For the calculation of the coupling constants of the single C–C bonds (Table 3) we get:

$$J_{CC} = 0.1592(\%s)_{C_1}(\%s)_{C_2}/((4/3)^2 + P^2_{CC(\sigma)}) + 2.20 \quad (SD = 2.82\ \text{Hz}) \tag{9}$$

while for the calculation of J_{CC} of the multiple C–C bonds (Table 4) we get:

$$J_{CC} = 0.1692(\%s)_{C_1}(\%s)_{C_2}/((4/3)^2 + P^2_{CC(\sigma)}) - 5.05 \quad (SD = 5.42\ \text{Hz}) \tag{10}$$

Comparing Eq. (7) with Eq. (8), one can also obtain a better result by including the bond order. Equations (8), (9) and (10) are demonstrated in Fig. 2.

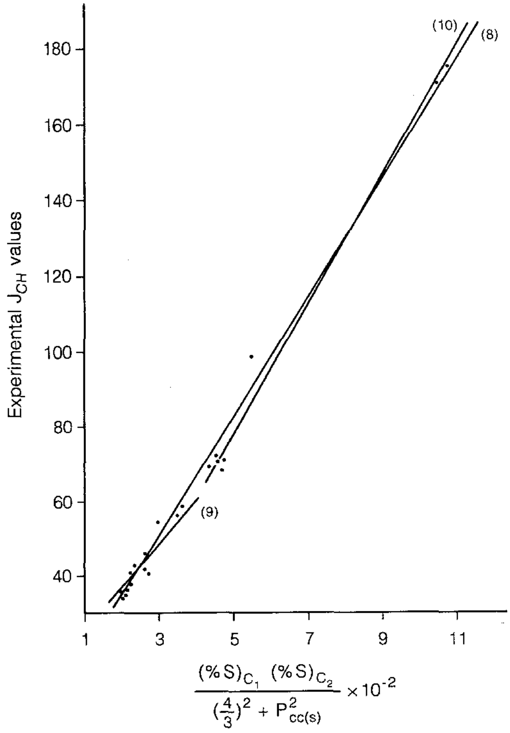
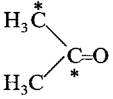
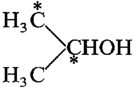
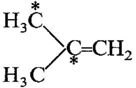
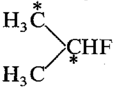
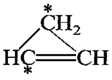
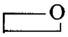
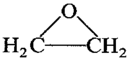
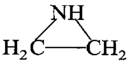


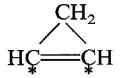
Fig. 2. Correlativity of the experimental J_{CC} values with the MBOHO calculation results

Table 3. Comparison of the experimental and calculated vlaues of J_{CC} (in Hz) for single C–C bonds

No.	Molecule	$(\%s)_{C_1}$	$(\%s)_{C_2}$	$P_{CC(\sigma)}$	J_{CC} Calc.		Experiment		
					Eq. (8)	Eq. (9)	INDO	J_{CC}	Ref.
1#	CH_3–CH_3	27.25	27.25	1.3694	33.64	34.56	41.5[a]	34.6	11
2#	$\overset{*}{C}H_3$–$\overset{*}{C}H$=CH_2	27.07	32.10	1.3750	39.08	39.91	55.4[a]	41.9	21
3#	$CH_2\overset{*}{C}H$–$\overset{*}{C}HCH_2$	33.54	33.54	1.4688	47.02	47.71	71.1[a]	53.7	21
4#	C_6H_5–$\overset{*}{C}H_2$–$\overset{*}{C}H$	27.44	26.55	1.3376	33.80	34.72	42.6[a]	34.0	5
5#		27.14	34.21	1.3620	42.11	42.89	65.3[a]	40.6	21
6#	CH_3–CHO	27.77	36.78	1.4169	44.42	45.16	64.0[a]	39.4	21
7#	CH_3–CN	27.93	48.53	1.4782	56.12	56.65	76.7[a]	57.3	21
8#	$\overset{*}{C}H_3$–$\overset{*}{C}H_2CN$	26.44	26.95	1.3250	33.38	34.30	40.7[a]	33.0	21
9#	CH_3–$\overset{*}{C}H_2$–$\overset{*}{C}N$	48.57	27.44	1.4562	56.10	56.63	76.2[a]	55.2	21
10#	CH_3–CH_2NH_2	27.30	27.88	1.3384	35.26	36.15	47.0[a]	35.8	48
11#	$C_6H_5\overset{*}{C}(O)$–$\overset{*}{C}H_3$	27.27	34.01	1.3584	42.18	42.95	66.0[a]	43.3	5
12#	CH_3–CH_2OH	27.14	28.47	1.3499	35.48	36.37	49.6[a]	37.7	24
13#		28.07	27.28	1.3205	35.94	36.82	49.6[a]	38.4	24
14		27.18	31.03	1.3545	38.53	39.37			
15	$\overset{*}{C}H_3$–$\overset{*}{C}$≡CCH_3	28.08	45.52	1.4745	53.11	53.69			
16	$\overset{*}{C}H_3$–$\overset{*}{C}H_2$–CH_3	26.67	27.31	1.3334	33.89	34.81			
17	$\overset{*}{C}H_3$–$\overset{*}{C}$≡CH	26.53	44.44	1.4109	51.39	52.01	77.5[a]		
18	C_6H_5C≡$\overset{*}{C}$–$\overset{*}{C}H_3$	44.50	26.52	1.4173	51.20	51.82			
19	CH_3–CH_2F	26.94	29.31	1.3528	36.17	37.04	49.6[a]		
20	CH_3–CHF_2	26.65	31.91	1.3407	39.24	40.07	62.2[a]		
21	CH_3–CF_3	26.42	34.85	1.3300	42.77	43.53	80.8[a]		
22		27.17	28.44	1.3218	36.22	37.10	50.1[a]		
23	Cyclopropane	20.77	20.77	1.3731	19.79	20.95	11.58[b]	(10.0)	12
24	Cyclobutane	24.09	24.09	1.2544	28.76	29.77	25.6[b]		
25		22.25	19.32	1.3291	20.36	21.51			
26		25.43	24.90	1.2718	30.92	31.89			
27		22.01	22.01	1.4877	20.37	21.52			
28		21.96	21.96	1.4469	20.89	22.03			

[a] Ref. [24] [b] Ref. [21]

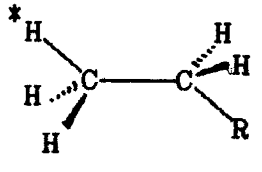
Table 4. Comparison of the experimental and calculated values of J_{CC} (in Hz) for multiple C–C bonds

No.	Molecule	$(\%s)_{C_1}$	$(\%s)_{C_2}$	$P_{CC(\sigma)}$	J_{CC} Calc.		Experiment		
					Eq. (8)	Eq. (10)	INDO	J_{CC}	Ref.
29#	$CH_2{=}CH_2$	40.11	40.11	1.2950	76.15	73.74	82.8[a]	67.6	48
30#	$CH{\equiv}CH$	55.54	55.54	1.0825	170.13	171.09	163.6[a]	171.5	15
31#	$CH_2{=}C{=}CH_2$	37.79	50.00	1.2919	89.52	87.70	108.5[a]	98.7	21
32#	$CH_3{-}\overset{*}{C}H{=}\overset{*}{C}H_2$	39.25	38.85	1.2439	75.00	72.54	81.5[a]	70.0	21
33#	$\overset{*}{C}H_3{=}\overset{*}{C}H{-}CH{=}CH_2$	38.81	37.05	1.2547	70.20	67.53	79.0[a]	68.8	48
34#	$C_6H_5{-}\overset{*}{C}{\equiv}\overset{*}{C}H$	55.47	55.10	1.0319	174.89	176.88	156.3[a]	175.9	15
35#	$C_6H_5{-}\overset{*}{C}H{=}\overset{*}{C}H_2$	39.45	38.43	1.2314	75.27	72.82	81.6[a]	70.0	15
36#	$\overset{*}{C}H_2{=}\overset{*}{C}HCN$	38.93	38.03	1.2528	72.36	69.79	81.1[a]	70.6	24
37	$CH_3{-}\overset{*}{C}{\equiv}\overset{*}{C}H$	55.56	55.39	1.0351	175.69	177.71	161.3[a]		
38	$(CH_3)_2{-}\overset{*}{C}{=}\overset{*}{C}H_2$	37.94	38.14	1.2486	70.96	68.33			
39	$CH_3\overset{*}{C}{\equiv}\overset{*}{C}CH_3$	55.48	55.48	1.0652	171.92	173.77			
40	$C_6H_6\overset{*}{C}{\equiv}\overset{*}{C}{-}CH_3$	55.50	54.97	1.0700	169.81	171.57			
41	$HC{\equiv}CF$	53.30	64.35	1.0309	196.32	199.25	199.8[a]		
42	$CH_2{=}CF_2$	51.39	38.53	1.2273	98.39	96.97	118.9[a]		
43	$CH_2{=}CHF$	38.55	44.66	1.2560	83.83	81.77	95.4[a]		
44		38.14	31.84	1.3556	55.12	51.78	51.2[b]		

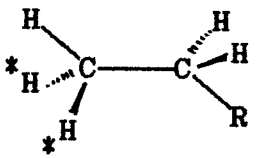
[a] Ref. [24] [b] Ref. [21]

Some trends in the J_{CC} values are also evident from Tables 3 and 4. For instance, the relative increase of J_{CC} values in going from cyclopropane (23) to ethylene oxide (27) and oxetane (26), and from cyclopropane (23) to cyclobutane (24) are produced. The J_{CC} values in cyclopropene (44) are lower than that of ethylene (29), similar to the J_{CC} value of ethane (1) and exceeds that of cyclopropane (23).

The calculated J_{CC} values in going from ethyl fluoride (19) to 1,1-difluoroethane (20) and 1,1,1-trifluoroethane (21), and from vinyl fluoride (43) to

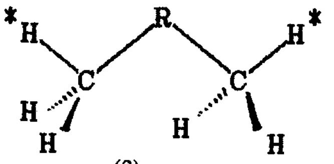


(1)

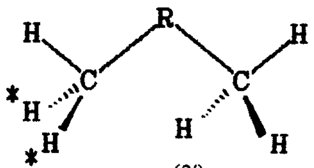


(1′)

R = H, CH_3, C_6H_5, F, OH, CN, NH_2.



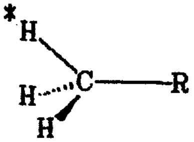
(2)



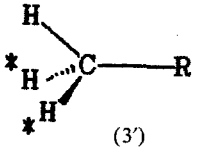
(2′)

R = O, NH, $C{=}CH_2$, CO.

Fig. 3.

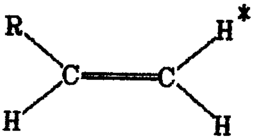


(3)

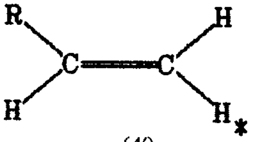


(3′)

$R = C_6H_5, OH, NH_2, CH{=}CH_2, CHF_2, CHO, C(O)C_6H_5, COOH, COOCH_3, O{-}N{=}O.$

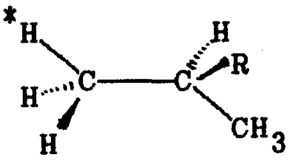


(4)



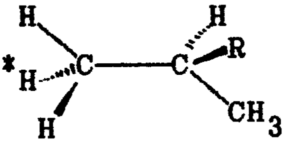
(4′)

$R = H, CH_3, C_6H_5, F, CN, CH{=}CH_2.$

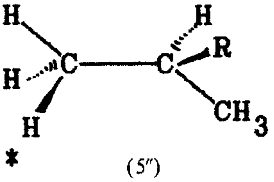


(5)

$R = F, OH.$

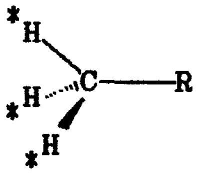


(5′)



(5″)

$R = F, OH.$



(6)

$R = C{\equiv}CH, C{\equiv}N, CF_3, NO_2, N{\equiv}C,$

$C{\equiv}C{-}CH_3, \quad C{\equiv}C{-}C_6H_5.$

Fig. 3. Molecular geometries

1,1-difluoroethylene (42) are increased. These relevant increasing trends compare well with the INDO calculation results obtained by Maciel et al. [24]. Also, the calculated J_{CC} values of ethyl alcohol (12) and *iso*propyl alcohol (13), and ethyl fluoride (19) and *iso*propyl fluoride (22) are very close to each other and in better agreement with the experimental fact. The calculated results for some twenty-eight singly bonded C–C bonds and sixteen multiple bonded C–C bonds are listed in Tables 3 and 4, respectively.

3 Summary and conclusion

Calculation of the nuclear spin-spin coupling constants is one of the most thoroughly investigated problems. The calculation methods are largely based upon valence-bond or molecular orbital developments from Ramsey's second-order perturbation formula for the Fermi-contact term. Application of the maximum bond order hybrid orbital method employing the CNDO/2 approximation is successful in accounting for the available experimental results on the directly bonded C–H and C–C coupling constants in terms of the Fermi-contact interaction, and in predicting substituent effects on J_{CH} and J_{CC} in molecules which contain no substituents of $-I^-$ type. This confirms that the hybridization is a dominant factor in determining and influencing the variations of the direct spin-spin coupling constants, and the Fermi-contact interaction is responsible for the magnitude of the coupling of the bonded nuclei as pointed out by others before.

The relationships based on the MBOHO calculation obtained in the present paper seem to be well enough tested to be safely used for qualitative, or even quantitative purposes, not only suitable for the hydrocarbons, but also for the heterosubstituted hydrocarbons. The numerical comparison shows that Eq. (5) based on the MBOHO calculation is the best one of the relationships which are suitable for the calculation of J_{CH} in the heterosubstituted hydrocarbons. All the standard deviations in the present paper compare very well with those obtained by others. The calculated results are in good agreement with the experimental ones. Some predicted results are also presented.

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