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Approximate Self-Consistent Molecular Orbital Theory of Nuclear Spin Coupling. I. Directly Bonded Carbon–Hydrogen Coupling Constants[1a]

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Abstract: With the employment of finite perturbation methods, a self-consistent perturbation theory is applied in the INDO molecular orbital approximation to the calculation of isotropic nuclear spin coupling between directly bonded carbon and hydrogen for a series of molecules. Including perturbations associated only with the Fermi contact mechanism, J_{CH} values are calculated for a wide variety of compounds. Regarding hydrogen 1s and carbon 2s atomic orbital densities at the nuclei as fixed parameters, good agreement with experimental trends is obtained for hydrocarbons and for molecules with $-\mathrm{I}^+$ substituents (–F, –OR, $-NR_2$, =O, etc.), but not for molecules with $-\mathrm{I}^-$ substituents ($-CF_3$, –C(O)X, $-NO_2$, –CN, etc.). The correspondence between calculated and experimental results is improved qualitatively when these densities are varied in accordance with a simple correction based on Slater's rules. For those molecules for which the experimental trends are qualitatively reproduced, a sensitivity to substituent effects is predicted which is closer to the experimental results than what would be predicted by simple arguments based on carbon s character.

One of the most frequently studied classes of nuclear spin–spin coupling constants, and one which has appeared quite frequently in qualitative theoretical arguments, is the directly bonded C–H constant. Relatively straightforward experimental access *via* satellite experiments and intriguing early interpretations in terms of carbon hybridization generated a great deal of experimental activity directed toward this nmr parameter.[2–20] The early hybridization arguments were based largely upon valence-bond[21,22] or molecular orbital (MO)[2b,23] developments from Ramsey's[24] second-order perturbation formula for the Fermi contact term,

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using the average ΔE approximation. One of the several largely equivalent forms which result from such developments is given in eq 1, which results from a MO treatment in which the average ΔE is invoked.[23,25] In

$$J_{\mathrm{CH}} = (4/3)^2 h\beta\gamma_{\mathrm{C}}\gamma_{\mathrm{H}}(\Delta E)^{-1}s_{\mathrm{C}}{}^2(0)s_{\mathrm{H}}{}^2(0)P_{s_{\mathrm{C}}s_{\mathrm{H}}}{}^2 \quad (1)$$

this expression β is the Bohr magneton, $s_{\mathrm{C}}{}^2(0)$ is the carbon 2s orbital density at the carbon nucleus, and $P_{s_{\mathrm{C}}s_{\mathrm{H}}}$ is the carbon 2s–hydrogen 1s element of the first-order density matrix (sometimes referred to as the charge-density, bond-order matrix).

Interpretations of J_{CH} in terms of only hybridization, or "carbon s character," arguments largely pivot on the factor $P_{s_{\mathrm{C}}s_{\mathrm{H}}}{}^2$, and effectively assume the factor $(\Delta E)^{-1}s_{\mathrm{C}}{}^2(0)s_{\mathrm{H}}{}^2(0)$ to be constant. Such assumptions have been criticized.[2a,26–29] Indeed, alternative views based on assuming a dominant importance of variations in ΔE or in $s_{\mathrm{C}}{}^2(0)$ have been presented for substituted methanes.[28,29]

The more general MO approach which does not make the average ΔE approximation[25] is difficult to apply satisfactorily because of problems associated with constructing good excited-state wave functions, and because of serious cancellation difficulties. The analogous valence-bond treatment, also avoiding the average ΔE approximation, appears to share the cancellation difficulty.[30]

Recently a conceptually simple theoretical method for calculating second-order properties, utilizing finite perturbation techniques, has been under development in this laboratory. In its initial applications it has employed INDO (intermediate neglect of differential overlap) molecular orbital wave functions[31] in an approximate SCF framework.[32,33] Details of this general approach to perturbation calculations and its application to the Fermi contact spin-coupling interaction[32,33] have been discussed previously. Briefly, it involves the computation of an unrestricted, single determinant, INDO[31] molecular orbital wave function in the presence of a contact perturbation of the form given by

$$h_{\mathrm{B}} = (8\pi/3)\beta\mu_{\mathrm{B}}s_{\mathrm{B}}{}^2(0) \quad (2)$$

due to presence of the nuclear moment μ_{B}. Then, using the Hellmen–Feynmann theorem, it is shown that the reduced coupling constant K_{AB} can be expressed as

$$K_{\mathrm{AB}} = (8\pi/3)\beta^2 s_{\mathrm{A}}{}^2(0)s_{\mathrm{B}}{}^2(0)\left(\frac{\partial}{\partial h_{\mathrm{B}}}\rho_{s_{\mathrm{A}}s_{\mathrm{A}}}(h_{\mathrm{B}})\right)_{h_{\mathrm{B}}=0} \quad (3)$$

where $\rho_{s_{\mathrm{A}}s_{\mathrm{A}}}$ is the diagonal spin density matrix element corresponding to the valence s orbital of atom A, and K_{AB} is defined as $(2\pi/\hbar\gamma_{\mathrm{A}}\gamma_{\mathrm{B}})J_{\mathrm{AB}}$. Thus, within the framework of the approximations employed, it is the sensitivity of the spin density in the orbital s_{A} to the presence of the nuclear spin perturbation μ_{B} which determines the coupling constant. This basic approach is equivalent in principle to a complete, self-consistent perturbation calculation involving the sum over all appropriate excited states; however, it is computationally easier than the alternative, which has not yet been employed for molecules of typical chemical interest.

In a preliminary survey, the trends in coupling constants calculated by this method were in good general agreement with established trends in experimental values.[32,33] The present paper, devoted to directly bonded C–H couplings, is the first in a series concerned with applying this method systematically to a variety of spin–spin systems.

Results

All calculations were based on eq 3, the numerical evaluation being carried out as described previously.[33] The computations, performed on the CDC 1604A computer, required run times typified by the 32 min involved in one pyridine calculation. Except for a few explicitly noted cases, all calculations were based on the standard geometrical model used previously in this laboratory.[33,34]

The computed coupling constants are presented in Tables I–IV. Table I contains results for compounds of the type CHXYZ, *i.e.*, substituted methanes. Calculations on molecules not possessing sufficient symmetry generally give computed J_{CH} values which are different for different C–H bonds. In such cases the values given in Table I are the weighted averages. Table II presents analogous results for XHC=Y compounds, *i.e.*, substituted ethylenes, formaldehydes, and formaldimines. Table III give results for compounds with triple bonds, HC≡X, and Table IV, the results for some aromatic compounds. In addition to the computed J_{CH} values, Tables I–IV also give the computed values of $P_{s_{\mathrm{C}}s_{\mathrm{H}}}$. These were obtained from the calculations on the perturbed molecules. However, they are nearly equivalent to values obtained in the absence of the perturbation. The computed bond orders for α and β spins usually differ by less than 0.1%, and resultant $P_{s_{\mathrm{C}}s_{\mathrm{H}}}$ values are nearly independent of the position or presence of the perturbation. For a few clearly specified cases, C–H coupling constants calculated at the CNDO level of approximation are given in Tables I–IV. Also included in Tables I–IV are the available experimental results relevant to the computed J_{CH} values.

Discussion

Overall Trends. In agreement with experimental experience, a general tendency toward increasing J_{CH} values is noted in progressing from Table I to Table II (or IV) to Table III. This corresponds to the well-known crude relationship between J_{CH} and carbon coordination or hybridization. It is particularly evident if closely analogous compounds are considered, *i.e.*, the hydrocarbons ethane (16), ethylene (60), and acetylene (95), the fluoro compounds ethyl fluoride (41) and vinyl fluoride (69), or the nitrogen compounds methylamine (27), formaldimine (75–76), and hydrogen cyanide (96). The MO parameter $P_{s_{\mathrm{C}}s_{\mathrm{H}}}$, which conveys information on the "hybridization or carbon s character" from these MO calculations, is given in Tables I–III; in these

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Table I. J_{CH} in HCXYZ Compounds

	Calculated			Experimental		
Compound[b]	J_{CH}	$P_{s_{C}s_{H}}$	ΔJ_{CH}[a]	J_{CH}	ΔJ_{CH}[a]	Ref
1. HCH_3 (CNDO)	93.19	0.4992	−29.72	125.0	0.0	2b
2. HCH_2CH_3 (CNDO)	93.31	0.4918	−29.60	124.9	−0.1	16
3.* $HCH(CO_2H)_2$	111.12	0.4726	−11.79	132.0	7.0	7
4. $HC(CH_3)_3$	114.17	0.4679	−8.74			
5.* $HC(CN)_3$	114.44	0.4604	−8.47			
6.* $HC(CH_3)_2CN$	114.69	0.4656	−8.22	135.5	10.5	20a
7.* $HC(CN)_2CH_3$	114.79	0.4631	−8.12			
8. $HCH(CH_3)_2$	119.37	0.4809	−3.54			
9.* $HCH(CN)_2$	119.67	0.4756	−3.24	145.2	20.2	12
10.* $HCH(CN)CH_3$	119.84	0.4784	−3.07	135.5	10.5	20a
11.* $HCH_2CO_2C_2H_5$	120.15	0.4890	−2.86	130.3	5.3	20a
12.* $HCH_2COC_6H_5$	120.29	0.4870	−2.62	125.7	0.7	17
13.* HCH_2CO_2H	120.61	0.4895	−2.30	130.0	5.0	2b
14.* HCH_2CHO	121.36	0.4891	−1.55	127.0	2.0	2b
15.* $HCH_2C{\equiv}CH$	122.01	0.4878	−0.90	132.0	7.0	2b
16. HCH_2CH_3	122.12	0.4910	−0.79	124.9	−0.1	16
17. $HCH_2CH{=}CH_2$	122.44	0.4896	−0.47			
18.* HCH_2CN	122.47	0.4884	−0.44	136.1	11.1	20a
19. HCH_3	122.91	0.4985	0	125.0	0	2b
20. $HC(CH_3)_2OH$	123.03	0.4844	0.12			
21.* $HC(OH)(CH_3)C_6H_5$	123.69	0.4831	0.78	142.5	17.5	17
22. $HC(OH)[CH(CH_3)_2]_2$	125.35	0.4850	2.44	136.0	11.0	8
23. $HCH(CH_3)NH_2$	126.30	0.4920	3.39			
24. $HCH(OH)CH(CH_3)_2$	128.22	0.4974	5.41	140.0	15.0	8
25.* HCH_2NO_2	129.78	0.5042	6.78	146.7	21.7	11
26. $HCF(CH_3)_2$	129.80	0.4926	6.89			
27. HCH_2NH_2	129.92	0.5032	7.01	133.0	8.0	2b
28. $HCH(OH)C(CH_3)_3$	130.18	0.4985	7.27	132.0	7.0	8
29. $HCH_2N{=}CH_2$	131.95	0.5020	9.04			
30. $HCH_2N(CH_3)CHO$	132.04	0.5050	9.13	138.0	13.0	4
31. $HCH_2N^+H_3$	132.13	0.5053	9.22	145.0	20.0	
32. $HCH(CH_3)OCH_2CH_3$	133.25	0.5000	10.34			
33.* $HCH(OH)CF_3$	133.11	0.5035	10.20	147.5	22.5	12
34. HCH_2OH	135.27	0.5125	12.36	141.0	16.0	2b
35.* $HCH(NO_2)_2$	135.33	0.5076	12.42	169.4	44.0	11
36. HCH_2OCH_3	135.50	0.5114	12.59	140.0	15.0	7
37.* $HCHFC_6H_5$	136.33	0.5064	13.42	151.0	26.0	7
38. $HCH[N(CH_3)_2]_2$	136.44	0.5044	13.52	136.6	11.6	11
39. HCH_2OCHO	136.89	0.5125	13.98	147.0	22.0	2b
40. $HC(OH)_2CH_3$	137.07	0.5073	14.16			
41. $HCHFCH_3$	137.13	0.5082	14.22			
42. $HCH_2OC_6H_5$	138.21	0.5105	15.30	143.0	18.0	2b
43.* $HCHFCN$	138.63	0.5050	15.72	166.0	41.0	12
44. HCH_2F	140.08	0.5191	17.17	149.1	24.1	11
44a. $HCH(OH)_2$	150.05	0.5251	27.14			
45. $HCH(OCH_3)_2$	151.67	0.5270	28.76	161.8	36.8	11
46. HCF_2CH_3	156.98	0.5283	34.07			
47.* HCF_2CN	159.98	0.5246	37.07	205.5	80.5	12
48. $HCHF_2$	166.79	0.5466	43.88	184.5	59.5	11
49. $HC(OH)_3$	169.48	0.5463	46.57			
50. $HC(OCH_3)_3$	170.75	0.5443	47.84	186.0	61.0	7
51. $HCF(OCH_3)_2$	180.95	0.5527	58.04			
52. HCF_3	212.29	0.5828	89.38	239.1	114.1	11

[a] Difference between J_{CH} for a given compound and that of methane. [b] Compounds in which the most electronegative substituent atom is not connected directly to the C–H carbon are marked with an asterisk.

terms the relationship between calculated values of J_{CH} and carbon s character is demonstrated in Figure 1, which shows a trend of increasing J_{CH} with increasing $P_{s_{C}s_{H}}{}^2$. This trend is in rough qualitative agreement with the popular view which interprets changes of J_{CH} with changes of carbon s character. However, some aspects of this apparent trend require further information, especially for molecules which are not hydrocarbons.

The apparent tendency of the present method to yield increased J_{CH} values for substituent changes which correspond to substantial increases in computed $P_{s_{C}s_{H}}$ values holds even in those cases for which this method predicts the incorrect sign of the increment in J_{CH}. Thus, an incorrect prediction that a given substituent effect should lead to a decrease in J_{CH} is generally paralleled by a decrease in $P_{s_{C}s_{H}}$, so that the direct application of eq 1 using the INDO values of $P_{s_{C}s_{H}}{}^2$ would also give the qualitatively incorrect prediction of J_{CH}. Possible reasons for such failures are discussed in a later section. Another relevant aspect of the trend shown in Figure 1 concerns the relative sensitivities of the computed J_{CH} and $P_{s_{C}s_{H}}{}^2$ values to structural changes. If only the hydrocarbons are considered, a nearly linear plot is obtained, as shown in Figure 2, which shows that both $J_{CH,calcd}$ and $P_{s_{C}s_{H}}{}^2$ vary with about the same sensitivities to structural changes. Hence, in the special case of *hydrocarbons*, the simple "s-character view" is in close agreement with the results obtained by eq 3. However, viewing the HCXYZ, HXC=Y, HC≡X compounds of

Table II. J_{CH} in $\overset{H}{X}\!\!>\!C{=}Y$ Compounds

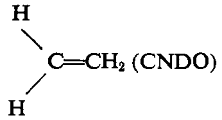
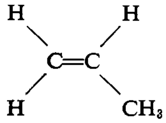
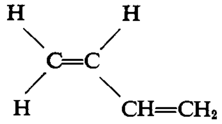
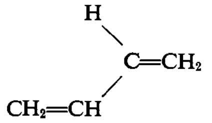
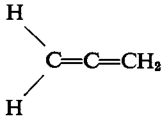
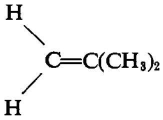
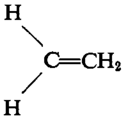
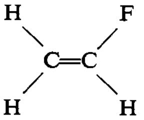
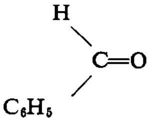
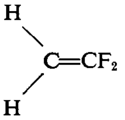
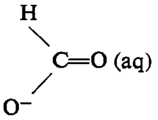
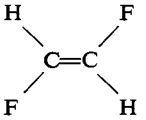
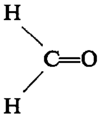
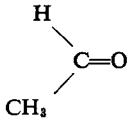
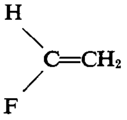
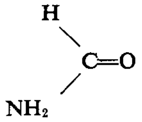
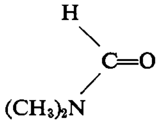
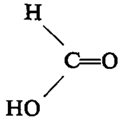
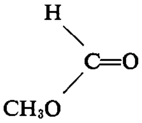
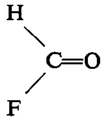
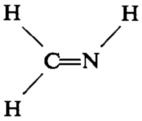
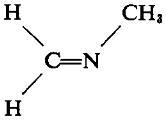
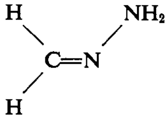
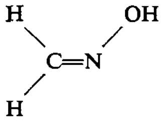
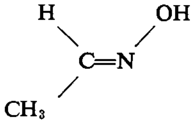
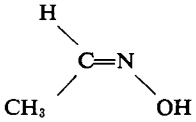
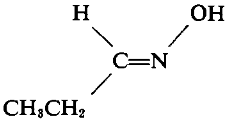
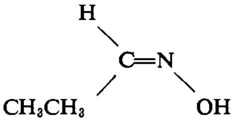
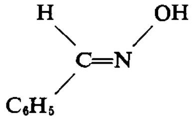
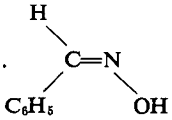
Compound		Calculated			Experimental		
		J_{CH}	$P_{s_Cs_H}$	ΔJ_{CH}[a]	J_{CH}	ΔJ_{CH}[a]	Ref
53.	 (CNDO)	127.63	0.5484	−29.07	156.2	0.0	16
54.		151.15	0.5417	−5.55			
55.[b]		149.24	0.5392	−7.46			
56.[b]		163.36	0.5513	6.66			
57.		155.22	0.5338	−1.48			
58.		155.50	0.5490	−1.20	168.2	12.0	5
59.		156.34	0.5454	−0.36			
60.		156.70	0.5471	0.0	156.2	0.0	16
61.[b]		153.26	0.5444	−3.44	159.18	2.98	18[a]
62.[b]		162.36	0.5536	5.66	162.16	5.96	18[a]
63.		159.08	0.5493	2.38	173.7	17.5	10
64.		160.11	0.5523	3.41			
65.	 (aq)	178.83	0.5881	22.13	194.8	38.6	13
66.		179.51	0.5704	22.81			
67.		180.51	0.5794	23.81	172.0	15.8	10
68.		164.51	0.5571	7.81	172.4	16.2	10
69.		183.11	0.5731	26.41	200.2	44.0	18

Table II (*Continued*)

Compound	Calculated			Experimental		
	J_{CH}	$P^{s}_{\mathrm{C}^{s}\mathrm{H}}$	$\Delta J_{\mathrm{CH}}{}^{a}$	J_{CH}	$\Delta J_{\mathrm{CH}}{}^{a}$	Ref
70. 	188.29	0.5738	31.59			
71. 	189.78	0.5736	33.08	191.2	35.0	10
72. 	214.05	0.6078	57.35	222.0	65.8	4
73. 	214.20	0.5996	57.50	226.2	70.0	10
74. 	244.77	0.6273	78.07	267.0	90.8	4
75. 	167.04	0.5637	10.34			
76.[b]	181.93	0.5746	25.23			
77. 	175.54	0.5657	18.84			
78.[b]	176.28	0.5696	19.58			
79. 	176.02	0.5654	19.32			
80.[b]	185.79	0.5748	29.09			
81. 	168.65	0.5618	11.95			
82.[b]	188.25	0.5775	31.55			
83. 	160.06	0.5467	3.36	163.0	6.8	18b
84. 	182.37	0.5642	25.67	177.0	20.8	18b
85. 	157.14	0.5445	0.44			
86. 	178.70	0.5619	22.00			
87. 	165.29	0.5434	8.59			
88. 	175.41	0.5552	18.71			

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[a] Difference between J_{CH} for a given compound and that of ethylene. [b] C—H coupling corresponding to H^{b} in a $\begin{matrix}{}^{a}\mathrm{H}\\{}^{b}\mathrm{H}\end{matrix}\!>\!\mathrm{C}$ group (for which H^{a} fits the convention indicated in the table heading).

Table III. J_{CH} in $HC\equiv X$ Compounds

	Compound	Calculated			Experimental		
		J_{CH}	$P_{s_Cs_H}$	ΔJ_{CH}[a]	J_{CH}	ΔJ_{CH}[a]	Ref
89.	$HC\equiv CH$ (CNDO)	205.50	0.6600	−27.15	249.0	0.0	16
90.	$HC\equiv CC_6H_5$	231.41	0.6579	−1.24	251.0	2	2b
91.	$HC\equiv CC(CH_3)_2OH$	231.66	0.6584	−0.99	253.0	4	14
92.	$HC\equiv CCH_2OH$	231.69	0.6582	−0.96	248.0	−1	14
93.	$HC\equiv CCN$	231.80	0.6576	−0.85			
94.	$HC\equiv CCH_3$	232.53	0.6587	−0.12	248.0	−1	2b
95.	$HC\equiv CH$	232.65	0.6593		249.0		16
96.	$HC\equiv N$	232.68	0.6755	0.03	269.0	20	20b
97.	$HC\equiv CN(CH_3)_2$	242.36	0.6671	9.71			
98.	$HC\equiv COCH_3$	246.54	0.6715	13.89			
99.	$HC\equiv CF$	251.54	0.6763	18.89			
99a.	$HC\equiv \overset{+}{N}H$	278.43	0.7115	45.78	320.0	71	20b

[a] Difference between J_{CH} for a given compound and that of acetylene.

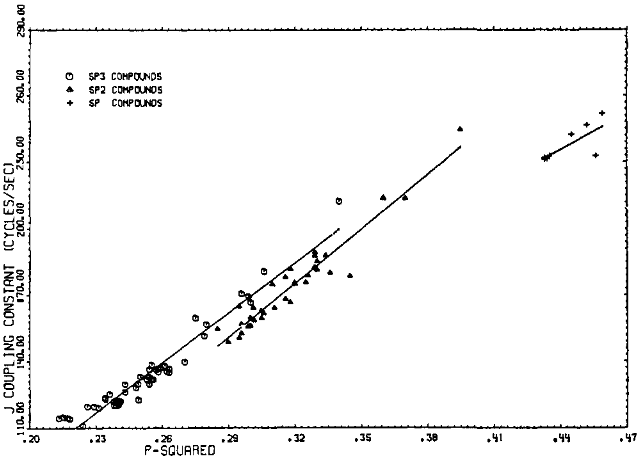

Figure 1. Plot of calculated values of J_{CH} *vs.* calculated values of $P_{s_Cs_H}{}^2$ for compounds in Tables I–III.

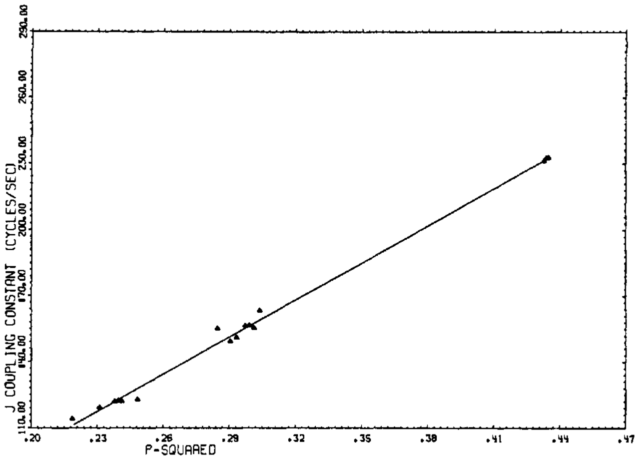

Figure 2. Plot of calculated values of J_{CH} *vs.* calculated values of $P_{s_Cs_H}{}^2$ for hydrocarbons in Tables I–III.

Figure 1 as distinct sets yields a different view for *substituent effects:* the least-squares correlation lines imposed upon the results of Tables I–III separately indicate that the computed J_{CH} values within each set are substantially more sensitive to substituent variation than the corresponding $P_{s_Cs_H}{}^2$ values. These correlations indicate that the present method is capable of predicting large substituent effects on J_{CH} without giving such large variations in carbon s character.

Another interesting aspect of Tables I–IV emerges from a comparison of the results obtained at the CNDO level of approximation (results 1, 2, 53, 89, 100) with those obtained on the same compounds using the INDO method (results 19, 16, 60 95, 105, respectively). Invariably the CNDO calculations gave J_{CH} values smaller than the analogous INDO calculations by about 29 ± 2 Hz. These differences are not associated with corresponding differences in the computed $P_{s_Cs_H}{}^2$ values. Earlier discussions[33,35] have focused upon the necessity of including the one-center exchange integrals, which distinguish the CNDO and INDO methods, in calculations of geminal H–H coupling constants. The present results indicate the importance of the carbon 2s, carbon 2p exchange integral in making positive contributions in calculations of J_{CH}. This relationship is demonstrated in Table V, where results of calculations with selective neglect of such integrals for some hydrocarbons are collected. It is clear from these results that the most important exchange integral in this regard is the one between the carbon 2s orbital and the carbon 2p orbital which points in the direction of the C–H bond axis (or with the largest projection along that direction). This is consistent with a simple valence-bond picture of the transmission of spin density from carbon 2s to hydrogen 1s along the C–H σ bond.[36] Small positive contributions are also associated with the exchange integrals between 2s and 2p orbitals normal to the C–H bond axis. From the results on ethylene and benzene it appears that the neglect of such integrals associated with π systems leads to more substantial reductions in calculated coupling constants than the neglect of those associated with σ bonds to other atoms.

HCXYZ Compounds. Inspection of Table I reveals a mixture of successes and failures in the qualitative prediction of substituent effects, *i.e.*, the change in J_{CH} accompanying the replacement of hydrogen with some other group in methane or a substituted methane. Qualitatively successful predictions are generally obtained for methanes substituted only with alkyl groups, NR_2 groups (other than nitro) (27, 30, 38), OR groups (22, 24, 28, 34, 36, 39, 42, 45, 50), or F atoms (44, 48, 52). Substantially unsuccessful predictions are obtained with molecules in which substituents of the types carbonyl (3, 11–14), nitrile (6, 9, 10, 18, 43, 47), nitro

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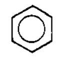
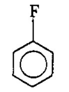
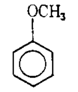
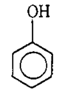
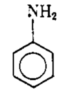
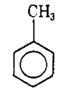
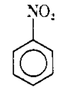
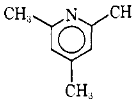
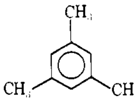
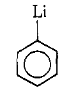
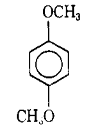
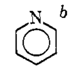
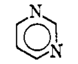
(35) L. Salem and P. Loeve, *J. Chem. Phys.*, 43, 3402 (1965).

(36) M. Barfield and D. M. Grant, *Advan. Magnetic Resonance*, 1, 168 (1965).

Table IV. J_{CH} in Some Aromatic Compounds

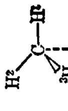
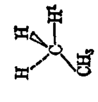
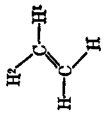
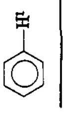
		Calculated						Experimental			
		J_{CH^1} ΔJ_{CH^1}[a]	J_{CH^2} ΔJ_{CH^2}	J_{CH^3} ΔJ_{CH^3}	P_{sCsH^1}	P_{sCsH^2}	P_{sCsH^3}	J_{CH^1} ΔJ_{CH^1}	J_{CH^2} ΔJ_{CH^2}	J_{CH^3} ΔJ_{CH^3}	Ref
100.		115.99 −24.31			0.5247			158.5 0.0			15
101.		135.90 −4.40	143.85 3.55	141.58 1.28	0.5181	0.5247	0.5225	155.0 −3.5	163.0 4.5	161.0 2.5	19
102.		142.38 2.08	141.30 1.00	141.01 0.71	0.5194	0.5227	0.5220				
103.		137.53 −2.77	141.26 0.96	141.34 1.04	0.5191	0.5288	0.5222				
104.		140.15 −0.15	139.35 −9.95	141.26 0.96	0.5215	0.5205	0.5221				
105.		140.30 −0.00			0.5213			158.5 0.0			15
106.		143.55 3.20	138.80 −1.50	140.65 0.35	0.5235	0.5199	0.5215				
107.		144.94 4.64	144.97 4.67	142.00 1.70	0.5254	0.5256	0.5227				
108.		148.34 8.04				0.5274			158.5 0.0		15
109.		148.61 8.31			0.5272			154.0 −4.5			
110.		149.45 9.15	130.21 −9.09	138.05 −1.23	0.5136	0.5129	0.5193				
111.		149.78 9.48			0.5216			161.0 2.5			15
112.	 [b]	154.6 14.30	143.91 3.61	139.75 −0.55	0.5327	0.5260	0.5229	170.0 11.5	163.0 4.5	152.0 −6.5	10
113.		208.44 68.14			0.5954			206.0 47.5			5b

[a] Difference between J_{CH} for a given compound and that of benzene. [b] Geometry taken from B. Bak, L. Hansen-Nygaard, and J. Rastrup-Anderson, *J. Mol. Spectry.*, **2**, 361 (1958).

(25, 35), and trifluoromethyl (33) are attached to the CH fragment of interest. These predictions are especially unsuccessful in that they lead to changes in J_{CH}, which are either much too small or of the wrong sign, in the replacement of a hydrogen with one of these groups. A particular deficiency of the method in its present form is its apparent insensitivity to experimentally obvious differences between the CN and CH_3 groups, as demonstrated by the close similarity between the computed J_{CH} values for compounds 4–7, for compounds 8–10, for compounds 46 and 47, or for compounds 41 and 43.

It is of interest to inquire whether the conspicuous failures mentioned above for certain HCXYZ compounds are due to deficiencies in the basic approach, *i.e.*, eq 3, or to limitations of the INDO molecular orbital formulation in its present form. In this regard it is observed that the substituents which lead to the more conspicuously incorrect predictions are those for which the most electronegative atom is not attached directly to the CH fragment, but is separated from it by one additional atom, usually carbon. This is essentially the type of substituent classified as $-I^-$ by Pople and Gordon,[34] where this designation is applied to substituents which withdraw electron density from an attached hydrocarbon fragment as a whole and polarize the electron distribution within the fragment so that electrons are drawn to the site of substitution. Compounds containing such substituents are marked in Table I by an

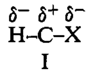
Table V. The Effect of Neglecting One-Center Exchange Integrals[a] on Computed J_{CH} Values

Compound	INDO	$(sp_x\|sp_x) = 0$			$(sp_y\|sp_y) = 0$			$(sp_z\|sp_z) = 0$			$(sp_x\|sp_x) = 0$, $(sp_y\|sp_y) = 0$			$(sp_y\|sp_y) = 0$, $(sp_x\|sp_x) = 0$, $(sp_z\|sp_z) = 0$	
		C—H¹	C—H²	CH³—CH⁴	CH¹	CH²	CH³—CH⁴	CH¹	CH²	CH³—CH⁴	CH¹	CH²	CH³—CH⁴	CH¹	CNDO
	122.9	121.2	101.8	116.1	121.2	121.2	106.4	99.5	118.6	118.6	119.2	99.8	99.8	95.5	93.2
	122.1	120.1			119.7			98.7			117.5			93.9	93.3
	156.7	154.4	139.2		151.5	151.5		135.3	150.0		149.2	133.3		127.2	127.6
$H—C\equiv C—H^1$	232.7	228.5			228.5			215.2			224.4			204.8	205.5
	140.2	138.7			135.4			118.0			133.8				116.1

[a] Except for the CNDO entries, the indicated exchange integrals are centered on the carbon atom in the CH nuclear spin system.

asterisk. On the other hand, the type of substituent for which eq 3 yields J_{CH} values which are at least qualitatively satisfactory are those classified as $-I^+$ by Pople and Gordon,[34] a designation referring to electron-withdrawing substituents which polarize the electron distribution within the hydrocarbon fragment in a manner drawing electrons from the site of substitution. This division of substituent types in the present calculations might suggest the possibility that the present INDO method is capable of representing electron distributions in molecules containing only $-I^+$ substituents, but is limited when $-I^-$ substituents are present, at least with regard to spin density in open-shell calculations. However, there is an alternative view which is considered below.

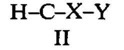
Focusing attention on compounds with only $-I^+$ substituents in Table I (unmarked by asterisk) reveals a reasonably good qualitative accounting of substituents effects on J_{CH} in substituted methanes. This is displayed in Figure 3, which includes the line resulting from a least-squares straight-line fit. It is important to note that this result is obtained on the basis of calculations which include *only* the Fermi contact mechanism, and which use a *fixed* set of atomic parameters, *i.e.*, maintain $s_C^2(0)$ and $s_H^2(0)$ as *constants*. This demonstrates that the *main* features of C–H coupling constants in these substituted methanes can be accounted for without invoking additional coupling mechanisms or changes in the atomic s-orbital densities. Similar results have been obtained for fluoromethanes,[37a] using an independent-electron MO approach. Thus, while variations in s-orbital densities may constitute appreciable contributions or corrections, such contributions clearly do not dominate the variation of J_{CH} in these systems as has been suggested previously.[29] These contributions are usually viewed as being dependent on the local charge distributions, either qualitatively in the language of the expansion or contraction of s orbitals,[2a] or semiquantitatively *via* the application of Slater's rules[38] for effective nuclear charges. In the present case there may be a significant parallel between the distinctly different patterns of charge distribution in the hydrocarbon fragments attached to $-I^+$ and $-I^-$ substituents and the significantly different levels of agreement found in Table I for the corresponding classes of compounds. The alternation of charge which typically results from CNDO and INDO calculations can be represented for the former case by the formula I (where X



$$\overset{\delta^-}{H}\text{–}\overset{\delta^+}{C}\text{–}\overset{\delta^-}{X}$$

I

stands for the $-I^+$ substituent) and the latter case can be represented by the formula II (where X–Y stands for



$$\overset{\delta^+}{H}\text{–}\overset{\delta^-}{C}\text{–}\overset{\delta^+}{X}\text{–}\overset{\delta^-}{Y}$$

II

the $-I^-$ substituent). In I and II the δ^+ and δ^- refer to net positive and negative local charges, but do not imply equal magnitudes. Because of the great fractional variation between typical electron populations of hydrogen atoms compared to carbon atoms, a given devi-

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(37) (a) J. N. Murrell, P. E. Stevenson, and G. T. Jones, *Mol. Phys.*, 12, 265 (1967); (b) R. Ditchfield, M. A. Jensen, and J. N. Murrell, *J. Chem. Soc., A*, 1674 (1967).

(38) J. C. Slater, *Phys. Rev.*, 36, 57 (1930).

Table VI. Typical Results of Applying Eq 5 to the J_{CH} Values of Table I

Compound	Calculated[a] f_C	f_H	$[\Delta J_{CH}]_{f=1}$[b]	$[\Delta J_{CH}]_f$[c]	Exptl ΔJ_{CH}[b]
HCH_3	1.012	0.9917	0	0	0
HCH_2CHO	0.9934	1.011	−1.6	−1.5	2.0
HCH_2CO_2H	0.9865	1.019	−2.3	−2.1	5.0
$HCH_2CO_2C_2H_5$	0.9854	1.017	−2.8	−2.9	5.3
HCH_2NH_2	1.058	0.9855	7.0	9.3	8.0
HCH_2CN	1.014	1.008	−0.4	1.8	11.1
HCH_2OCH_3	1.083	0.9649	12.6	18.2	15.0
$HCH(CN)_2$	1.020	1.019	−3.2	1.0	20.2
HCH_2NO_2	1.010	1.034	6.9	12.3	21.7
HCH_2F	1.108	0.9724	17.2	27.6	24.1
$HCH(OCH_3)_2$	1.144	0.9415	28.8	40.0	36.8
$HCHFCN$	1.107	0.9844	15.7	27.7	41.0
$HCH(NO_2)_2$	1.012	1.063	12.4	22.1	44.0
$HCHF_2$	1.196	0.9592	43.9	67.9	59.5
$HC(OCH_3)_3$	1.195	0.9278	47.8	66.0	61.0
HCF_2CN	1.193	0.9661	37.1	61.0	80.5
HCF_3	1.275	0.9545	89.4	134.9	114.1

[a] For molecules having nonequivalent hydrogens, the reported values are the appropriate averages. [b] Difference between J_{CH} for a given compound and that of methane (values taken directly from Table I). [c] Difference between J_{CH} for a given compound and that of methane (values calculated from results of Table I, using eq 5).

ation from electroneutrality (zero atomic charge density) would be expected to alter the electron shielding characteristics of H considerably more than those of carbon. Then, if the δ^- and δ^+ net charges in the H–C fragments of I or II were of roughly comparable magnitudes, the values of $s^2(0)$ for the hydrogen 1s orbital should exhibit generally greater variation than those of the carbon 2s orbital. The same qualitative conclusion might be drawn even if the variation in δ values for hydrogen were appreciably smaller than that for carbon. In these terms $s_H^2(0)$ and $s_C^2(0)$ for case I (the $-I^+$ case) should be generally smaller and larger, respectively, than for a neutral and nonpolar H–C fragment. For the $-I^-$ case, the pattern of charges in formula II would qualitatively predict an increase in $s_H^2(0)$ and a decrease in $s_C^2(0)$ with respect to the neutral, nonpolar case. The resulting values of $s_C^2(0)s_H^2(0)$ will then be larger or smaller than the corresponding value for neutral atoms by amounts which depend upon the deviations from local atomic charge neutrality and the relative sensitivities of $s_C^2(0)$ and $s_H^2(0)$ to such deviations.

In order to draw crude, qualitative guidelines for these effects, we have used a formula analogous to that employed by Grant and Litchman.[29] This employs a carbon 2s orbital of the form

$$(Z/a_0)^{3/2}\{A + B(Z/a_0)r\} \exp(-Zr/2a_0) \quad (4)$$

and uses Slater's screening rules for the effective nuclear charge Z on the assumption that they apply to partial electron populations. In this way we obtain a correction factor $f = f_C f_H$ (viewed as the product of a factor due to carbon and a factor due to hydrogen) given by eq 5, where the denominator $\{s_C^2(0)s_H^2(0)\}_0$ corresponds to

$$f_C f_H = s_C^2(0)s_H^2(0)/\{s_C^2(0)s_H^2(0)\}_0 = (1.0 - 0.30q_H)^3([3.25 - 0.35q_C]/3.25)^3 \quad (5)$$

the nonpolar, neutral case and where q_H and q_C refer to the net electron densities on hydrogen and carbon, respectively. Results obtained by this formula for a sample of compounds chosen from Table I are presented in Table VI. There it is demonstrated that this sort of adjustment leads to improved general agreement with experimental results. Focusing attention on the factors f_C and f_H leads one to the conclusion that the correction could be improved if a modified approach were employed in which the hydrogen 1s shielding constant (0.30) was increased relative to the carbon 2s shielding constant (0.35), *i.e.*, if the effective nuclear charge and $s^2(0)$ values for hydrogen 1s were even more sensitive to local atomic charge density, relative to the sensitivities of the carbon 2s values, than predicted by eq 5. However, justification for any such modification would involve considerations beyond the scope of the present application. Nevertheless, these *qualitative* results suggest that the major source of disagreement for the starred compounds in Table I may be due to the fact that constant values were chosen for $s_C^2(0)$ and $s_H^2(0)$. Furthermore, in making this type of correction, the variation of $s_H^2(0)$ may be at least as important as the changes in $s_C^2(0)$. Litchman and Grant[39] have recently questioned their earlier neglect of $s_H^2(0)$ variation in substituted methanes.[29]

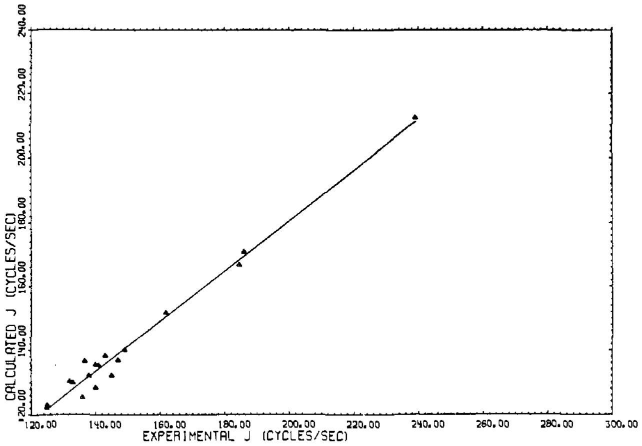

Figure 3. Plot of calculated J_{CH} values *vs.* experimental J_{CH} values for compounds of Table I with no $-I^-$ substituents (entries in Table I without asterisk).

HXC=Y Compounds. The comparisons between experimental and computed J_{CH} values for the HXC=Y

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(39) W. M. Litchman and D. M. Grant, *J. Am. Chem. Soc.*, **89**, 6775 (1967).

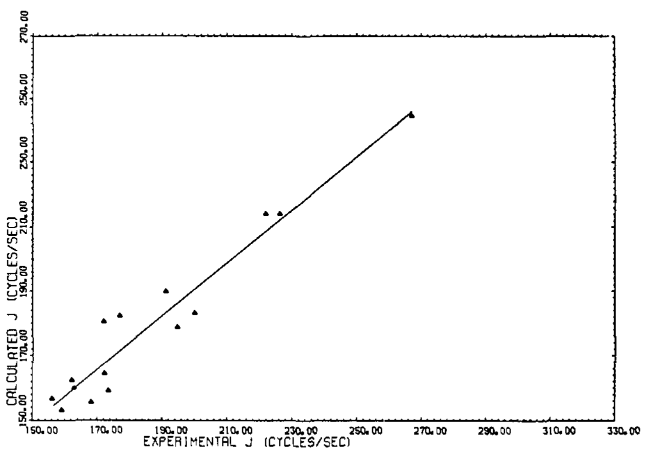
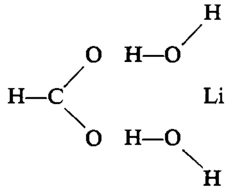


Figure 4. Plot of calculated J_{CH} values *vs.* experimental J_{CH} values for compounds in Table II.

system available in Table II reveal a considerably better qualitative agreement than that experienced with the substituted methanes of Table I. These comparisons are shown graphically in Figure 4, which displays an approximate correspondence with the experimental trend. While the agreement is not as close as that represented for HCXYZ compounds in Figure 3, it must be emphasized that the results plotted in Figure 4 have not been selected from Table II in an arbitrary way. All available comparisons were included in Figure 4, and it seems likely that fair qualitative agreement is possible only because experimental data are not available for compounds containing the more troublesome $-I^-$ substituents of Table I, except for entries 61 and 62. For entry 61, the experimental order with respect to ethylene is not reproduced by the theory. However, these calculations do place the three distinct J_{CH} values of vinyl fluoride (61, 62, and 69) in the correct experimental order.

It is interesting to note that the computed J_{CH} values listed in Table II for formic acid (72) and the formate ion (65) were obtained from calculations on structures with rather arbitrary but hopefully representative intermolecular interactions included. Thus, in the formic acid case, a dimer geometry was adopted which is consistent with the available electron diffraction data.[40] A calculation for a formic acid monomer using "standard geometry" yields the value 219.2 Hz, clearly out of line with respect to the ester value. For the formate ion, a geometry of the type III, including two interacting



III

water molecules and a lithium cation, was employed.[41] This configuration gave a J_{CH} value of 178.8 Hz. A calculation on an *isolated* formate ion with "standard geometry" yielded the value 106.5 Hz. Thus, the inclusion of the types of interactions represented in structure I, hydrogen bonding and the field of a cation, bring the calculated result from a value corresponding to serious disagreement into the correct range. This does not imply that such a structure is representative of the "average" configuration, but suggests that such interactions may be important in the calculations of properties of solutes. The general significance and potential usefulness of such calculations which include solvent molecules along with the solutes of primary interest are under investigation. The inclusion of hydrogen-bonding configurations for formaldehyde, with water reflecting the presence of the aqueous solvent used in the experiment, are incapable of improving the agreement significantly for that species; only small reductions in the coupling constant are obtained. However, it is of interest that the J_{CH} value computed for the hydrate, with which formaldehyde might be in rapid equilibrium in aqueous solution, is only 150.0 Hz.

In the last section of Table II is a collection of calculated J_{CH} values for systems in which CH fragments occur in *cis*/*trans* pairs with respect to some substituent. Substantial *cis*/*trans* differences are noted for most cases. Of particular interest because of possible practical value in structure determinations are the geometrical effects in oximes (81–88). The predicted J_{CH} values for the hydrogen *cis* with respect to the OH group are between 10 and 20 Hz smaller than those for the hydrogen in the corresponding *trans* relationship. Recently there has appeared one example of relevant experimental data,[18b] and this case supports the predicted trend.

H—C≡X Compounds. It is difficult to evaluate the relative success of the present method in accounting for substituent effects on J_{CH} in the HC≡X systems reported in Table III. Thus, for those compounds for which both calculated and experimental values are available, the ranges of each cover only a few hertz. Furthermore, some of the experimental values were obtained by the early rapid-passage, dispersion-mode technique for which uncertainties of this magnitude can be expected.[14]

Aromatic Compounds. Relatively few accurate experimental data are available for comparison with the calculated results on six-membered-ring aromatic compounds given in Table IV. Some values have been reported on the basis of rapid-passage, dispersion-mode experiments but these have been excluded from the table because of the relatively large uncertainties frequently associated with them. Both promising trends and incorrect predictions are apparent in the comparisons which are available in Table IV. The calculated J_{CH} values for fluorobenzene are in the experimentally correct order with respect to each other and the value for benzene. The same is true of the $J_{CH}{}^1$ values of compounds 111–113. In addition, the calculated J_{CH} values for pyridine (113) are in good experimental correspondence with respect to both their internal order and their relationships to the benzene value. The reasonable qualitative agreement for the widely different $J_{CH}{}^1$ values in the series benzene, pyridine, pyrimidine may again be associated with the fact that the most electronegative atoms in the latter two compounds are attached directly to the CH fragment of interest. More experimental data are required before a more meaning-

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[40] J. Karle and L. O. Brockway, *J. Am. Chem. Soc.*, **66**, 574 (1944). The O···H—O distance and the O—H distance employed in the calculation are 2.70 and 1.08 Å, respectively.

[41] Distances (Å) employed in the calculation: $R_{CH} = 1.08$, $R_{CO} = 1.31$, $R_{O\cdots H} = 1.30$, $R_{O\cdots H\text{-}O} = 2.40$, $R_{OH} = 1.08$, $R_{OLi} = 2.01$.

ful evaluation of the present method can be made for aromatic systems.

Summary and Conclusion

Application of approximate self-consistent molecular orbital theory with the INDO and finite perturbation approximations is moderately successful in accounting for the available experimental results on directly bonded C–H coupling constants in terms of a Fermi contact mechanism. The method is quite successful in predicting substituent effects on J_{CH} in methanes which contain no substituents of the $-I^-$ type, and in accounting for gross structural (hybridization) changes. Improved results appear likely, especially for compounds containing such substituents, if corrections can be made for variation of atomic s-orbital densities at both nuclei. The present results indicate that it is unnecessary to invoke such large changes in carbon s character as would be necessary in the popular hybridization view of J_{CH}. It should be kept in mind that some errors are likely to result from the use of "standard geometries" rather than actual geometries in the calculations.

Approximate Self-Consistent Molecular Orbital Theory of Nuclear Spin Coupling. II. Fermi Contact Contributions to Coupling between Carbon and Directly Bonded Atoms[1a]

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Abstract: The SCF finite perturbation method is applied to the Fermi contact contributions to spin–spin coupling between directly bonded CC, CN, and CF in a wide variety of molecules. The INDO molecular orbital approximation is used. Computed values of J_{CC} are in qualitatively good agreement with experimental values for noncyclic systems, especially if intermolecular interactions are included in appropriate cases. The method is far less successful in accounting for J_{CN} and J_{CF}; possible reasons for these difficulties are discussed.

A great deal of interest has been focused upon the measurement and interpretation of spin–spin coupling constants between directly bonded atoms.[2] Much of this interest has centered upon couplings between carbon and another atom, most frequently hydrogen,[3] and the suggested relationships between the coupling constants and bond hybridization parameters. On the assumption of the dominance of the Fermi contact mechanism, such relationships were predicted from the early valence-bond[4,5] and molecular orbital (MO)[6,7] approximations of Ramsey's formulation, using the average excitation energy (ΔE) approximation. A molecular orbital form of this approximate approach yields a proportionality between the coupling constant J_{AB} and the parameter $P_{s\ s_B}{}^2$, where $P_{s_As_B}$ is the element of the first-order density matrix[8] between the valence-shell s orbitals of the atoms A and B involved in the coupling.

In part I of this series[3] detailed consideration was given to directly bonded C–H coupling constants. There it was shown that the $P_{s_As_B}$ parameters, as computed by the INDO[9] molecular orbital method, do not manifest sufficient sensitivity to substituent effects to account well for experimental trends in J_{CH}. However, promising results were obtained by application of the approximate SCF finite perturbation method reported recently by Pople, McIver, and Ostlund.[10–12] This method is based on a general framework for the calculation of second-order properties which has been described in detail elsewhere.[11,12] In its application to the Fermi contact spin-coupling interaction,[12] it involves the calculation of an open-shell molecular orbital wave function under the influence of the perturbation

$$h_B = (8\pi/3)\beta\mu_B s_B{}^2(0)$$

due to the presence of a nuclear moment μ_B. It has been shown[12] that in the INDO approximation this leads to an expression for the reduced coupling K_{AB} given by

$$K_{AB} = (8\pi/3)\beta^2 s_A{}^2(0) s_B{}^2(0)\left(\frac{\partial}{\partial h_B}\rho_{s_As_B}(h_B)\right)_{h_B=0} \qquad (1)$$

where β is the Bohr magneton, $s_A{}^2(0)$ is the valence-shell s-orbital density of atom A at its nucleus, $\rho_{s_As_A}$ is the

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[1] (a) Research supported in part by Grant GP6458 from the National Science Foundation; (b) Special National Institutes of Health Fellow, on leave from the University of California, Davis; (c) Postgraduate Scholar of the National Research Council of Canada.

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