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 $-\mathrm{I}^-$ 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 $P_{\mathrm{s}\ \mathrm{s_B}}{}^2$, where $P_{\mathrm{s_As_B}}$ 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 $P_{\mathrm{s_As_B}}$ 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

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

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

$$K_{\mathrm{AB}} = (8\pi/3)\beta^2 s_{\mathrm{A}}{}^2(0)s_{\mathrm{B}}{}^2(0)\left(\frac{\partial}{\partial h_{\mathrm{B}}}\rho_{\mathrm{s_As_B}}(h_{\mathrm{B}})\right)_{h_{\mathrm{B}}=0} \qquad (1)$$

where β is the Bohr magneton, $s_{\mathrm{A}}{}^2(0)$ is the valence-shell s-orbital density of atom A at its nucleus, $\rho_{\mathrm{s_As_A}}$ 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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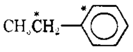
Table I. Calculated and Experimental Values of J_{CC}

Compound	Et	*i*-Pr	*t*-Bu	Calculated			Experimental		
				J_{CC}	$P_{s_As_B}$	ΔJ_{CC}^a	J_{CC}	ΔJ_{CC}^b	Ref
a. sp³–sp³									
$C^*H_3C^*(CH_3)_2CN$			×	39.9	0.2322	−1.6	33.6	−1.0	17
$C^*H_3C^*H_2CN$	*			40.7	0.2425	−0.8	33.0	−1.6	27
$C^*H_3C^*H_2CH_2OH$	*			40.7	0.2440	−0.8	34.2	−0.4	18
$C^*H_3C^*H_2CO_2H$	*			41.0	0.2450	−0.5			
$C^*H_3C^*(CH_3)_3$			×	41.0	0.2345	−0.5	36.9	2.3	17
$C^*H_3C^*H_3$	*			41.5	0.2490	0	34.6	0	19, 20
$C^*H_3C^*(CH_3)_2H$		√	×	42.0	0.2405	0.5			
$C^*H_3C^*H_2C_6H_5$				42.6^c	0.2454	1.1	34 ± 1	−0.6 ± 1	7
$C^*H_3C^*H_2CH_3$	*	√		42.1	0.2453	0.6			
$C^*H_3C^*(CH_3)_2NH_2$			×	45.6	0.2420	4.1	37.1	2.5	17
$C^*H_3C^*H(CH_3)NH_2$		√		46.8	0.2482	5.3			
$C^*H_3C^*H_2NH_2$	*			47.0	0.2538	5.5			
$C^*H_3C^*(CH_3)_2OH$			×	47.6	0.2465	6.1	39.5	4.9	17
$C^*H_3C^*H_2OCH_2CH_3$	*			47.6^d	0.2571	6.1			
$C^*H_3C^*H_2OH$	*			49.6	0.2592	8.1	37.7	3.1	18
$C^*H_3C^*H(OH)C_6H_5$				49.6	0.2542	8.1	38.1	3.5	7
$C^*H_3C^*H(CH_3)OH$		√		49.6	0.2542	8.1	38.4	3.8	18
$C^*H_3C^*H_2F$	*			49.6	0.2606	8.1			
$CH_3C^*H_2C^*H_2OH$				49.8	0.2535	8.3	37.8	3.2	18
$C^*H_3C^*H(CH_3)F$		√		50.1	0.2560	8.6			17
CH_3CHF_2				62.2	0.2753	20.7			
CH_3CF_3				80.8	0.2927	39.3			
b. sp³–sp²									
				50.0^c	0.2588	−15.3			
$C^*H_3C^*H{=}CH_2$				55.4	0.2734	−9.9			
$C^*H_3C^*OC_2H_5$				63.4	0.2817	−1.9	38.4	−1.7	18
$C^*H_3C^*OH$				64.0^d	0.2885	−1.3	39.4	−0.7	21
$C^*H_3C^*OCH_3$				65.3	0.2833	0	40.1	0	21
$C^*H_3C^*OC_6H_5$				66.0^e	0.2820	0.7	43.3	3.2	7
$C^*H_3C^*OO^-(aq)$				71.1^f	0.3006	5.8	51.6	11.5	21
$C^*H_3C^*ON(CH_3)_2$				78.7^g	0.2951	13.4	52.2	12.1	21
$C^*H_3C^*OOH$				80.7^h	0.3046	15.4	56.7	16.6	21
$C^*H_3C^*OOC_2H_5$				82.4^i	0.3040	17.1	58.8	18.7	21
$C^*H_3C^*OF$				91.6	0.3125	26.3			
c. sp³–sp									
$C^*H_3C^*{\equiv}\overset{+}{O}$				64.4^j	0.3551	−12.3	46.5	−10.0	22
$(CH_3)_3C^*C^*N$				71.3	0.3228	−5.4	52.0	−4.5	22
$(CH_3)_2C^*HC^*N$				74.5	0.3298	−2.2	54.8	−1.7	22
$CH_3C^*H_2C^*N$				76.2	0.3352	−0.5	55.2	−1.3	22
$C^*H_3C^*N$				76.7	0.3393	0	56.5	0	22
$C^*H_3C^*{\equiv}CH$				77.5	0.3314	0.8	67.4	10.9	18

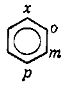
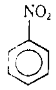
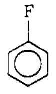
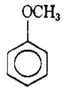
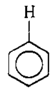
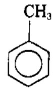
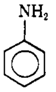
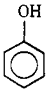
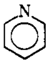
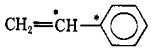
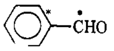
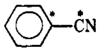
	Calculated									
	J_{CC}			$P_{s_As_B}$			Experimental			
Compound	(*x*,*o*)	(*o*,*m*)	(*m*,*p*)	(*x*,*o*)	(*o*,*m*)	(*m*,*p*)	(*x*,*o*)	(*o*,*m*)	(*m*,*p*)	Ref
d. aromatic, sp²–sp², 										
	78.9	75.2	75.0	0.3342	0.3318	0.3315	55.4	56.3	55.8	18
	88.6	76.8	75.7	0.3468	0.3336	0.3319				
	87.4	74.7	76.1	0.3414	0.3313	0.3322		58.2	56.0	18
	76.1	76.1	76.1	0.3326	0.3326	0.3326	57.0	57.0	57.0	18
	73.5	74.3	76.3	0.3257	0.3306	0.3327				

Table I (*Continued*)

	Calculated						Experimental			
	J_{CC}			$P_{s_As_B}$						
Compound	(x,o)	(o,m)	(m,p)	(x,o)	(o,m)	(m,p)	(x,o)	(o,m)	(m,p)	Ref
	80.6	76.2	76.6	0.3354	0.3324	0.3328	61.3	58.1	56.2	18
	85.2[k]	76.1	76.2	0.3414	0.3326	0.3324				
 [l]		83.7	72.7		0.3465	0.3295		53.8	53.8	18

	Calculated		Experimental	
Compound	J_{CC}	$P_{s_As_B}$	J_{CC}	Ref
	e. sp^2–sp^2			
	62.7	0.2968		
$CH_2{=}C^*HC^*H{=}CH_2$ (*trans*)	71.1	0.3074		
$C^*H_2{=}C^*H_2CH{=}CH_2$ (*trans*)	79.0	0.3480		
$C^*H_2{=}C^*HCO_2H$	74.8	0.3443	70.4	18
$C^*H_2{=}C^*HCN$	81.1	0.3512	70.6	18
$C^*H_2{=}C^*HCH_3$	81.5	0.3531		
$C^*H_2{=}C^*HC_6H_5$	81.6	0.3517	70 ± 3	7
$CH_2{=}CH_2$	82.2	0.3573	67.6	19, 20
	82.3	0.3173		
$C^*H_2{=}C^*HF$	95.4	0.3760		
$C^*HF{=}C^*HF$ (*cis*)	108.3	0.3918		
$C^*H_2{=}C^*F_2$	118.9	0.4004		
$C^*HF{=}C^*HF$(*trans*)	119.8	0.4023		
	f. sp^2–sp			
	90.6	0.3570	80.3	7
$CH_2{=}C^*H{=}C^*{\equiv}CH$	102.2	0.3626		
$C^*H_2{=}C^*{=}CH_2$	108.5	0.4067		
$C^*H_2{=}C^*{=}O$	113.3	0.4274		
$C^*H_2{=}C^*{=}C{=}CH_2$	120.7	0.4121		
	g. sp–sp			
$HC{\equiv}C^*{-}C^*{\equiv}CH$	147.5	0.4375		
$C_6H_5C{\equiv}C^*{-}C^*N$	148.7	0.4481	155.8	7
$HC^*{\equiv}C^*C_6H_5$	156.3	0.5025	175.9	7
$H_2C{=}C^*{=}C^*{=}CH_2$	156.6	0.4588		
$C_6H_5C^*{\equiv}C^*CN$	156.8	0.4997		
$HC^*{\equiv}C^*CH_3$	161.3	0.5056		
$HC^*{\equiv}C^*H$	163.6	0.5084	171.5	19, 20
$HC^*{\equiv}C^*CN$	164.9	0.5059		
$HC^*{\equiv}C^*{-}C{\equiv}CH$	165.2	0.5063		
$HC^*{\equiv}C^*N(CH_3)_2$	178.5	0.5240		
$HC^*{\equiv}C^*OCH_3$	188.2	0.5360		
$HC^*{\equiv}C^*F$	199.8	0.5474		
$FC^*{\equiv}C^*F$	273.6	0.6046		

[a] Calculated value of J_{CC} minus the calculated value of J_{CC} for reference compound (ethane, acetone, or acetonitrile for sections a, b, or c, respectively). [b] Experimental difference between J_{CC} for a given compound and that of the reference compound. [c] Average of results calculated for conformations with the ethyl carbons in the plane of the aromatic ring and perpendicular to it. [d] Calculations based on structure III. [e] Result obtained with oxygen and all carbons one plane. [f] Calculations based on structure I. [g] Result obtained with oxygen, nitrogen, and all carbons in one plane. [h] Calculations based on structure II. [i] Average of results calculated for conformations with the ethyl carbons in the plane of the acetoxy group and perpendicular to it. [j] Calculations based on structure with R_{CO} = 1.16 Å, with linear CCO configuration. [k] Average of results calculated for the two conformations with oxygen and all carbons in the same plane. [l] Geometry taken from B. Bak, L. Hansen-Nygaard, and J. Rastrup-Anderson, *J. Mol. Spectry.*, **2**, 361 (1958).

diagonal spin density matrix element corresponding to that orbital, and K_{AB} is defined as $(2\pi\hbar\gamma_A\gamma_B)J_{AB}$. This approach avoids the difficult cancellation problems associated with the MO[13] and valence bond[14] developments on Ramsey's second-order perturbation formula without the average ΔE approximation.

The present paper is the second in a series devoted to exploring the consequences of applying this new method to the calculation of spin–spin coupling constants. The main concern here is the calculation of directly bonded CC, CN, and CF coupling constants.

Results

All the calculations reported here are implementations of eq 1, the numerical computations being carried

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(13) J. A. Pople and D. P. Santry, *Mol. Phys.*, **8**, 1 (1963).
(14) M. Barfield, *J. Chem. Phys.*, **48**, 4458, 4463 (1968).

Table II. Calculated and Experimental Values of $J_{^{13}C^{15}N}$

Molecule	Calculated[a] J_{CN}[a]	$P_{s_C s_N}$	Experimental J_{CN}[b]	Ref
$(CH_3)CC^*N^*$	8.6	0.3411	(−)15.0	22
$(CH_3)_2CHC^*N^*$	7.8	0.3427	(−)15.4	22
$CH_3CH_2C^*N^*$	7.0	0.3444	(−)16.4	22
$CH_3C^*N^*$	6.2	0.3461	−17.5	22, 30
$C^*H_3N^*{=}CHC_6H_5$ (*trans*)	3.1	0.1888	$-3 \leq J_{CN} \leq 3$	31
CN^-(aq)	−1.3	0.3011	±5.9	22
$C^*H_3N^*H_2$	−4.6	0.2124	±(7 ± 1)	31
$C^*H_3N^*H_3Cl^-$(aq)	−8.4	0.2192	$-8 \leq J_{CN} \leq 8$	31
$CH_3N^*{=}C^*HC_6H_5$ (*trans*)	−16.0	0.2493	±(7.1)	31
$CH_3C^*(O)N^*H_2$	−24.8	0.3061	$-15 \leq J_{CN} \leq 15$	31
$CH_3C^*(O)N^*HC_6H_5$	−31.8	0.3045	±(13.0 ± 1.5)	31

[a] Calculations were for $J_{^{13}C^{14}N}$, converted to $J_{^{13}C^{15}N}$ by multiplication by the factor $(\gamma_{^{15}N}/\gamma_{^{14}N})$. [b] Signs in parentheses are assumed on the basis of the acetonitrile data.

Table III. Calculated and Experimental Values of J_{CF}

	Calculated		Experimental	
Molecule	$-J_{CF}$	$P_{s_C s_F}$	$(-)J_{CF}$	Ref
FCH_3	237.3	0.1677	157.5	34
$FCH_2C_6H_5$	213.7	0.1663	165.0	35
$FC(CH_3)_3$	206.7	0.1634	167.0	35
FCH_2CH_2OH	235.4	0.1660	167.0	36
FCH_2CO_2H	264.9	0.1663	181.0	36
$FCFH_2$	231.2	0.1760	234.8	35
p-$FC_6H_4OCH_3$	216.0	0.1868	237.0	35
$FCFHCH_2OH$	228.7	0.1739	240.5	36
p-$FC_6H_4CH_3$	212.6	0.1869	241.0	35
$FCFHCN$	219.7	0.1740	243.5	36
FC_6H_5	212.9	0.1868	244.0	35
p-$FC_6H_4CF_3$	218.5	0.1867	252.0	35
p-$FC_6H_4C(O)CH_3$	214.9	0.1867	253.0	35
$FCF_2C{\equiv}CF_3$	182.9	0.1844	256.0	35
p-$FC_6H_4NO_2$	222.0	0.1865	257.0	35
FCF_3	150.3	0.2031	259.2	34
FCF_2CN	186.4	0.1841	264.0	36
FCF_2OCF_3	167.4	0.1990	265.0	35
$FCF_2N(CF_3)_2$	181.3	0.1940	269.0	35
$FCF_2(p$-$C_6H_4F)$	194.4	0.1845	271.0	35
FCF_2CH_3	192.0	0.1849	271.0	35
$FCF_2N(CF_3)NO_2$	188.2	0.1940	273.6	37
FCF_2H	214.4	0.1874	274.3	34
FCF_2CH_2OH	211.9	0.1838	278.0	35
FCF_2CO_2H	237.0	0.1824	283.2	34
$FCF{=}CH_2$	219.4	0.2017	287.0	35
$FCF_2C(O)CH_3$	231.3	0.1824	289.0	35
$FC(O)F$	190.5	0.2191	308.4	34
$F(CO)CH_3$	268.3	0.1985	353.0	35
$F(CO)H$	275.9	0.2017	369.0	35

out on the CDC 1604A computer according to the scheme described previously.[12] Molecular geometries used in the calculation were based on the standard geometrical model,[15] with a few exceptions noted in the tables. For some species questions of conformation arise. Such calculations were performed on what was considered the preferred conformation if previous experience from other calculations on analogous geometrical arrangements[3,16] indicated that such conformational effects were not likely to be critical. In cases where important conformational influences were anticipated, results were obtained for more than one conformation, as specifically noted in the tables.

The result of these calculations on J_{CC}, J_{CN}, and J_{CF} are collected in Tables I, II, and III, respectively, with available experimental comparisons. The J_{CN} values were computed for ^{14}N and then converted to $J_{^{13}C^{15}N}$, for comparison with experimental values. These conversions were made by multiplying $J_{^{13}C^{14}N}$ by the ratio $\gamma_{^{15}N}/\gamma_{^{14}N}$, on the assumption that the nitrogen isotope effect can be neglected. Tables I–III also give the $P_{s_A s_B}$ values computed in the spin coupling calculations. These are essentially the same as those obtained from closed-shell INDO calculations, without the perturbation.

Discussion

Carbon–Carbon Coupling Constants. The calculated J_{CC} values given in Table I cover a wide range, as do the experimental results available for comparison.[7,17–22] All the calculated values were positive, and all of the experimental data are assumed to have the positive sign. This is based upon Grant's[23] determination that the signs of J_{CH} and J_{CC} for the directly bonded atoms in acetic acid are the same, the earlier determination of a positive J_{CH} for the methyl group by Buckingham and McLauchlan,[24] and the assumption that all directly bonded carbon–carbon couplings have the same sign.

The table is arranged in sections, according to the basic types of carbon coordination or hybridization: section a covers compounds with relevant carbon–carbon bonds which could approximately be described as sp^3–sp^3, section b as sp^3–sp^2, section c as sp^3–sp, section d as aromatic C–C, section e as sp^2–sp^2, section f as sp^2–sp, and section g as sp–sp.

Within each section the results are arranged in increasing order of calculated J_{CC} values. A rough trend of increasing calculated and experimental J_{CC} values is observed as one progresses from section a to section g, in qualitative agreement with the simple hybridization, or "s-character," view. A more critical examination of this view can be made in terms of the values of $P_{s_A s_B}$ obtained from the density matrices in these calculations.

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(16) J. A. Pople, G. E. Maciel, J. W. McIver, Jr., and N. S. Ostlund, unpublished results.

(17) W. M. Litchman and D. M. Grant, *J. Am. Chem. Soc.*, **89**, 6776 (1967).

(18) F. J. Weigert and J. D. Roberts, private communication.

(19) R. M. Lynden-Bell and N. Sheppard, *Proc. Roy. Soc.*, **A269**, 385 (1962).

(20) D. M. Graham and C. E. Holloway, *Can. J. Chem.*, **41**, 2114 (1963).

(21) G. A. Gray, P. D. Ellis, D. D. Traficante, and G. E. Maciel, *J. Magnetic Resonance*, in press.

(22) G. A. Gray, Ph.D. Dissertation, University of Calif., Davis, Sept 1967.

(23) D. M. Grant, *J. Am. Chem. Soc.*, **89**, 2228 (1967).

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

Figure 1 demonstrates the trend of increasing computed J_{CC} with increasing $P_{s_As_B}{}^2$. The line obtained from a linear least-squares fit indicates that these two calculated parameters have approximately the same overall sensitivities to changes in structure. However, both parameters vary somewhat less rapidly overall than the experimental numbers. Thus, the calculated values of either J_{CC} or $P_{s_As_B}{}^2$ are about equally successful in accounting in a qualitative manner for the experimentally observed overall trend for the cases considered in Table I. However, this overall trend is largely dictated by gross changes in carbon hybridization or coordination, and the limitations of the simple view based on $P_{s_As_B}{}^2$ values become more apparent when one considers substituent effects in separate classes of closely related compounds.

Section a of Table I shows that calculated J_{CC} and $P_{s_As_B}{}^2$ values tend to increase with measured J_{CC} values, with some reversals. Some of the compounds included in this section can be grouped together as ethyl, isopropyl, or *t*-butyl compounds, for purposes of examining trends within a series of closely related species; these are indicated in the table by an asterisk, a check, and an ×, respectively. When comparisons of calculated J_{CC} and $P_{s_As_B}{}^2$ and J_{CC}(exptl) are made separately for the first and last of these series (there are insufficient experimental data for consideration of isopropyl compounds), no reversals appear. It should be noted that $-\mathrm{I}^-$ as well as $-\mathrm{I}^+$ substituents are represented in these series. This is in contrast to the case of previously reported J_{CH} calculations,[3] where $-\mathrm{I}^-$ substituent effects were not handled satisfactorily by the type of computation described above. The J_{CH} work indicated that the computed substituent effects could be improved, especially for $-\mathrm{I}^-$ substituents, if a correction was included to account for variation in $s_C{}^2(0)$ and $s_H{}^2(0)$. Qualitative guidelines for this correction were discussed, including one based on the use of Slater screening rules,[25] and it may be of interest to see how such guidelines would alter the pattern of values given in Table I. For this purpose we use eq 2, which is

$$s_C{}^2(0)s_C{}^2(0)/\{s_C{}^2(0)s_C{}^2(0)\}_0 = \{(3.25 - 0.35q_A)(3.25 - 0.35q_B)/(3.25)^2\}^3 \quad (2)$$

based on the same assumptions as described previously,[3] where $\{s_C{}^2(0)s_C{}^2(0)\}_0$ stands for the value appropriate to a neutral, nonpolar C-C fragment, and where q_A and q_B represent the net charge densities on carbon atoms A and B, respectively. The result of applying this correction to some entries of Table I is given in Table IV, where it is seen that this correction does not alter the quality of agreement substantially. This is because screening of the carbon 2s orbital is not highly sensitive to small changes in q.

In any case, it can be concluded that changes in computed J_{CC} and $P_{s_As_B}{}^2$ are roughly equally successful in accounting for the variation in J_{CC}(exptl) for section a.

The compounds in section b for which J_{CC}(exptl) values are available for comparison can all be classified as acetyl compounds or derivatives. Within this series the calculated and experimental J_{CC} values yield a monotonic relationship, with no reversals. This relationship is clearly not linear; however, in placing the species in the correct experimental order, it represents a definite improvement on the trend of $P_{s_As_B}{}^2$ values, for which some reversals are noted. Furthermore, the increase in calculated J_{CC} values of about 30% in progressing from methyl ethyl ketone to ethyl acetate is in closer correspondence with the corresponding experimental value (about 53%) than is the corresponding increase of $P_{s_As_B}{}^2$ (about 15%).

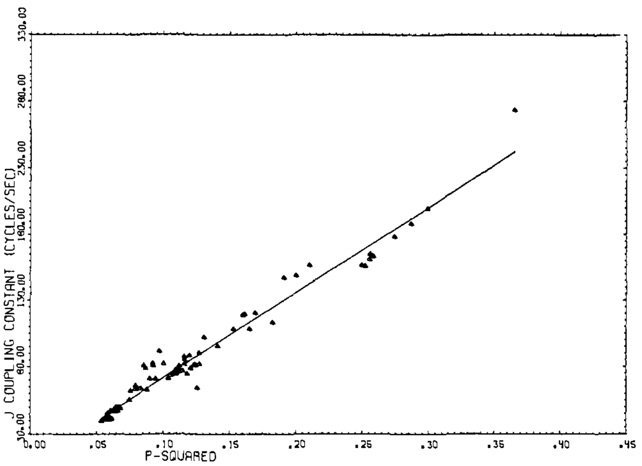

Figure 1. Plot of calculated J_{CC} values *vs.* calculated $P_{s_Cs_C}{}^2$ values from Table I.

The only remaining section of Table I which contains a number of precise J_{CC}(exptl) values for comparison is section c. For this selection of species the calculated values of J_{CC} again yield a monotonic correlation with measured values, while severe reversals occur with $P_{s_As_B}{}^2$. The highest calculated value of $P_{s_As_B}$ corresponds to the lowest observed coupling constant in the series, whereas the highest measured J_{CC} value corresponds to a calculated $P_{s_As_B}$ which is lower than three others in the series.

A few experimental values of J_{CC} are available for the ring carbons in aromatic compounds, as indicated in section d. This section of the table displays a rather close relationship between computed J_{CC} and $P_{s_As_B}$ values. The correspondence between calculated and experimental J_{CC} values appears rather poor, and was not improved by the application of eq 2. However, the range of available experimental values is rather small and additional data will be required before a clear evaluation of the method can be given for aromatic compounds.

The few vinyl compounds with experimental J_{CC} values represented in section e appear to constitute another case for which agreement with calculated J_{CC} (or $P_{s_As_B}{}^2$) values may be poor. Again, the application of eq 2 leads to no apparent improvement. However, there are insufficient experimental data to test the predictions satisfactorily. A paucity of experimental results likewise preclude conclusive judgements on the calculated results summarized in sections f and g.

An additional point of interest is the geometrical configurations chosen in the calculations which lead to three of the numbers in section b. For the calculation on acetate ion in aqueous solution, the hydrogen-bonding configuration shown as structure I was employed.[26] A calculation on the isolated acetate ion using the same

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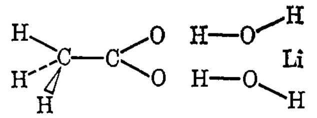
[25] J. C. Slater, *Phys. Rev.*, 36, 57 (1930).

[26] Interatomic distances (Å) used: $R_{CH} = 1.08$, $R_{CO} = 1.31$, $R_{O\cdots H} = 1.20$, $R_{O\cdots H-O} = 2.30$, $R_{OH} = 1.08$, $R_{OLi} = 1.84$.

Table IV. Results of Applying Eq 2 to Calculated J_{CC} Values

Compound	Et	*i*-Pr	*t*-Bu	Calculated				Exptl
				$[\Delta J_{CC}]_{f=1}$[a]	f_A	f_B	$[\Delta J_{CC}]_f$[b]	ΔJ_{CC}[c]
				a. sp^3–sp^3				
$C^AH_3C^B(CH_3)_2CN$			×	−1.6	1.020	1.021	−1.4	−1.0
$C^AH_3C^BH_2CN$	*			−0.8	1.020	1.020	−0.6	−1.2
$C^AH_3C^BH_2CH_2OH$	*			−0.8	1.019	1.007	−1.2	−0.4
$C^AH_3C^B(CH_3)_3$			×	−0.5	1.018	1.018	−0.4	2.3
$C^AH_3C^BH_3$	*			0	1.018	1.018	0	0
$C^AH_3C^BH_2C_6H_5$	*			1.1	1.018	1.018	1.2	0.6 ± 1
$C^AH_3C^B(CH_3)_2NH_2$			×	4.1	1.011	1.052	5.5	2.5
$C^AH_3C^B(CH_3)_2OH$			×	6.4	1.008	1.074	8.9	4.9
$C^AH_3C^BH_2OH$	*			8.1	1.007	1.083	11.1	3.1
$C^AH_3C^BH(OH)C_6H_5$				8.1	1.008	1.078	11.0	3.5
$C^AH_3C^BH(CH_3)OH$		√		8.1	1.006	1.079	11.0	3.8
$CH_3C^AH_2C^BH_2OH$				8.4	1.007	1.080	11.2	3.2
				b. sp^3–sp^2				
$C^AH_3C^BOC_2H_5$				−1.9	0.9923	1.103	−2.0	−1.7
$C^AH_3C^BOH$				−1.3	0.9933	1.102	−0.8	−0.7
$C^AH_3C^BOCH_3$				0	0.9941	1.100	0	0
$C^AH_3C^BOC_6H_5$				0.7	0.9925	1.102	0.7	3.2
$C^AH_3C^BOO^-(aq)$				5.8	0.9822	1.176	10.7	11.5
$C^AH_3C^BON(CH_3)_2$				13.4	0.9868	1.142	17.3	12.1
$C^AH_3C^BOOH$				15.4	0.9851	1.173	23.4	16.6
$C^AH_3C^BOOC_2H_5$				17.1	0.9854	1.165	23.5	18.7
				c. sp^3–sp				
$C^AH_3C^B{\equiv}O^+$				−12.3	0.9770	1.209	−5.1	−10.0
$(CH_3)_3C^A{-}C^B{\equiv}N$				−5.4	1.021	1.039	−5.3	−4.5
$(CH_3)_2C^AH{-}C^B{\equiv}N$				−2.2	1.022	1.039	−2.0	−1.7
$CH_3C^AH_2{-}C^B{\equiv}N$				−0.5	1.020	1.040	−0.2	−1.3
$C^AH_3{-}C^B{\equiv}N$				0	1.014	1.041	0	0
$C^AH_3{-}C^B{\equiv}CH$				0.8	1.023	1.000	−1.7	10.9

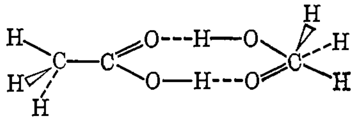
[a] Difference, taken directly from Table I, between the calculated value of J_{CC} for a given compound and that of a reference (ethane for section a, acetone for section b, and acetonitrile for section c). [b] Difference between the calculated value of J_{CC}, corrected by the factor $f = f_A/f_B$ given in eq 2, for a given compound and that of the reference. [c] Difference between the experimental value of J_{CC} for a given compound and that of the reference.



I

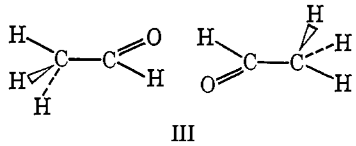
configuration as that of the acetate fragment in I gave the J_{CC} value 46.0, far below what would be expected from the trend of J_{CC} in that section. Calculations in which the Li^+ ion was not included, and with two water fragments in a variety of configurations including that of structure I, gave results approximately midway between the values obtained with the isolated acetate ion and with structure I. Thus, it appears that inclusion of the cation field in some way is a prerequisite to representing properly the saturated aqueous solution employed in the experiment.[21] Lithium ion was included in the calculation rather than the sodium ion of the experiment, as the latter is not presently included in the INDO method.

The acetic acid number given in section b was obtained from a calculation on the hydrogen-bonded dimer structure shown as structure II. Interatomic distances

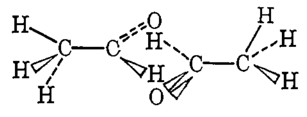


II

used were essentially those given by Karle and Brockway from electron diffraction measurements.[27] A calculation on a monomer fragment of II gave the value 83.2 Hz, out of line with the experimental trend. The calculated J_{CC} for acetaldehyde was 70.3, considerably higher than was expected for this compound in view of the experimental results for the aldehyde-ketone set in section b and the calculated values for the ketones. In investigating this discrepancy, we explored the consequences of employing hydrogen-bonded dimer configurations analogous to structure II. Indeed, it was found that the types of intermolecular interactions implied by such a dimer structure bring the calculated value into a range agreeing with the experimental trend. The value quoted in section b was obtained from a calculation based on structure III.[28] It is interesting that an alternative configuration with one formyl group in a plane 1.70 Å above the other (IV) gives nearly the same calculated J_{CC} as a monomer configuration. Thus, it



III



IV

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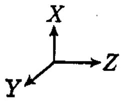
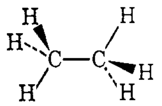
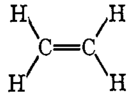
(27) J. Karle and L. O. Brockway, *J. Am. Chem. Soc.*, **66**, 574 (1944).

(28) The geometry employed for each monomer fragment was standard. Each intermolecular $R_{O\cdots H(formyl)}$ was 1.83 Å.

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



Compound	INDO[b]	$(sp_x\|sp_x) = 0$	$(sp_y\|sp_y) = 0$	$(sp_z\|sp_z) = 0$	$(sp_y\|sp_y) = 0$ $(sp_x\|sp_x) = 0$	$(sp_z\|sp_z) = 0$ $(sp_y\|sp_y) = 0$ $(sp_z\|sp_z) = 0$
	41.5	41.8	41.8	33.2	42.1	34.1
	82.2	82.9	73.4	74.6	74.1	67.5
H—C≡C—H	163.6	161.5	161.5	157.9	159.2	154.0

[a] The neglected one-center exchange integrals, which are indicated in the heading, are centered only on one carbon atom. [b] Result of INDO calculations (no one-center exchange integrals neglected).

appears that the hydrogen-bonding type interaction implied by structure III is directionally selective.

If isolated species rather than structures I–III are used in the calculations, then the deviations from a monotonic relationship between $P_{s_As_B}{}^2$ and $J_{CC(exptl)}$ are even more serious than those demonstrated in section b. Thus, the net result of employing polymolecular structures is to *minimize* the deviations from a monotonic $P_{s_As_B}{}^2$ *vs.* J_{CC}(exptl) trend, and to *remove* the deviations from a J_{CC}(calcd) *vs.* J_{CC}(exptl) relationship. The intent here is not to attach special significance to the geometrical arrangements represented by structures I and III, but merely to point out that the types of intermolecular interactions which they manifest need to be considered in quantum chemical calculations on such liquid substances. The importance of solute–solvent interactions in the calculation of nmr parameters is under further investigation.

Table V shows the influence of one-center exchange integrals on the calculation of J_{CC} for ethane, ethylene, and acetylene. The exchange integrals between the 2s and one or more selected 2p orbitals of one of the carbons (that bearing the perturbation in the calculation) were set to zero. For ethane it is seen that inclusion of only the exchange integral involving the 2p orbital directed along the C–C axis is critical to the calculation, implying that only this one is directly associated with an important coupling mechanism. Similarly, for acetylene it is seen that omitting the $(sp_\sigma|sp_\sigma)$ exchange integral results in a reduction in the computed J_{CC} value which is nearly three times the reduction obtained by omitting either of the $(sp_\pi|sp_\pi)$ integrals. However, with ethylene, it appears that the neglect of the exchange integrals involving the 2p orbital directed along the C–C axis or the 2p orbital involved in the π bond leads to similar reductions in the computed J_{CC} values. Thus, each appears to be associated with a coupling mechanism contributing significantly to the observed result. Such contributions are consistent with a valence-bond view of spin-density transmission associated with exchange terms.[29]

Carbon–Nitrogen Coupling Constants. The calculated J_{CN} values in Table II range from 8.6 to −31.8 Hz, exhibiting a sign change which is characteristic of neither the J_{CC} nor $J_{CH}{}^3$ values obtained by the same method. Since reliable sign information is available only for one entry, acetonitrile,[30] it is difficult to draw definitive conclusions concerning relative success in accounting for most of the experimental data[22,31] by this theory. Nevertheless, some pertinent comments can be made.

First, it should be noted that the theory exhibits no simple relationship between $P_{s_Cs_N}{}^2$ and J_{CN}. This is in contrast with our results on J_{CC} and J_{CH}, where a loose monotonic relationship prevailed. In the latter case this was true even for calculated substituent effects of the wrong sign.[3] Indeed, the simple view in which $P_{s_Cs_N}{}^2$ plays a role of dominant importance is capable of yielding only positive values of the reduced carbon–nitrogen coupling, *i.e.*, negative signs for $J_{^{13}C^{15}N}$, considering the negative sign of $\gamma_{^{15}N}$. Thus, the present results lend no support to interpretations which attempt to relate J_{CN} to carbon and nitrogen "s characters."[31]

For acetonitrile, the experimentally established negative sign of $J_{^{13}C^{15}N}$ is not in agreement with the value calculated here. This indicates that this theoretical method in its present form is incapable of predicting consistently the correct sign for J_{CN}, or possibly that another coupling mechanism makes substantial contributions. The former alternative cannot be ruled out on the grounds that correct signs have been obtained by this method for other couplings between directly bonded atoms (*e.g.*, C–H, C–C, and C–F); a transition from positive to negative reduced couplings along the series C–C to C–F has been predicted,[13,16] and C–N may consitiue a case where there is a variation in sign for different molecules. Such a situation would appear to magnify deficiencies in the method in comparison to a case such as C–H where all reduced couplings are positive and rather large. In any case, if one assumes the

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

(30) W. McFarlane, *Mol. Phys.*, 10, 603 (1966).

(31) G. Binsch, J. B. Lambert, B. W. Roberts, and J. D. Roberts, *J. Am. Chem. Soc.*, 86, 5564 (1964).

same sign for J_{CN} in all of the alkyl nitriles of Table III, then it is seen that the theory gives the correct experimental order of algebraically increasing $J_{^{13}C^{15}N}$ values with increasing methyl substitution. The sign of J_{CN} for methylamine and its hydrochloride, with σ bonds between saturated carbon and nitrogen, is in agreement with the sign frequently deduced for J_{NH} in species with hydrogen bonded to saturated nitrogen,[13,32,33] and also obtained by the present method.[12]

Corrections based on a formula for J_{CN} analogous to eq 2 give some appreciable alterations, but, of course, do not remove the problem of sign disagreement for acetonitrile.

Carbon–Fluorine Coupling Constants. Calculated values of J_{CF}, listed in Table III according to increasing values of the corresponding experimental results,[34–37] are all negative. This is consistent with the determination of Tiers[38] that CH and CF coupling constants in fluorodichloromethane have opposite signs, and the well-known positive sign of directly bonded CH coupling constants.[24] As negative signs for reduced coupling constants between directly bonded atoms are not readily accommodated by the simple views which pivot upon "s characters," it is not surprising that monotonic relationships are not exhibited between the calculated J_{CF}(calcd) and $P_{s_Cs_F}$ values, or between $P_{s_Cs_F}$ and experimental J_{CF} values. Only for certain sets of structurally similar compounds does the former relation appear; only a very crude overall correlation of the latter type is obtained. What is more serious is the absence of a promising correspondence between calculated and experimental values of J_{CF}. This might be due in part to a need for including contributions from the spin dipolar or orbital coupling mechanisms in calculations for directly bonded CF. Previous theoretical estimates of such J_{CF} contributions have been appreciable, but not of dominant magnitude.[13,39] A second possibility is that the Fermi contact term is indeed dominant, but not handled properly by the SCF finite perturbation method in its present INDO form; this would imply a deficiency of the INDO wave functions in representing the transmission of induced spin density within the directly bonded CF fragment. However, it may be noted that this same method was successful in accounting for the J_{CH} trends for fluoromethanes and fluoroethylenes.

Another possible source of error in the application of eq 1 is the fact that $s_A^2(0)$ and $s_B^2(0)$ are assumed to be fixed constants. In the CF fragment, the contraction or expansion of s orbitals, discussed above for J_{CC}, may be more important than in the usually less polarized CC fragments. In that case, variation in $s_A^2(0)$ or $s_B^2(0)$ might become appreciable in J_{CF} calculations, whereas in J_{CC} calculations, its neglect may not preclude on a formula analogous to eq 2 was carried out for the results in Table III, the considerable alterations in calculated J_{CH} values led to no pattern of general improvement.

Summary and Conclusions

The application of SCF finite perturbation theory, in the INDO approximation, to Fermi contact spin coupling gives J_{CC} values which are in generally good qualitative agreement with experimental data, reproducing the known trends. The method appears promising for its predictive value in this case, and is considerably more reliable than the simple "s character" approach. The inclusion of intermolecular interactions in the calculations can lead to dramatic effects for some species. The application of this method to the calculation of J_{CN} and J_{CF} is far less successful, indicating a need to improve upon the INDO wave functions or possibly to include other spin–spin coupling mechanisms.

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(32) Y. Kato, M. Miura, and A. Saika, *Mol. Phys.*, **13**, 491 (1967).
(33) A. J. R. Bourn, D. G. Gilles, and E. W. Randall, *Nucl. Magnetic Resonance Chem., Proc. Symp., Cagliari, Italy, 1964*, 277 (1965).
(34) S. G. Frankiss, *J. Phys. Chem.*, **67**, 752 (1963).
(35) N. Muller and D. T. Carr, *ibid.*, **67**, 112 (1963).
(36) G. P. VanDerKelen and Z. Eeckhaut, *J. Mol. Spectry.*, **10**, 141 (1963).
(37) R. K. Harris, *J. Phys. Chem.*, **66**, 768 (1962).
(38) G. V. D. Tiers, *J. Am. Chem. Soc.*, **84**, 3972 (1962).
(39) J. N. Murrell, P. E. Stevenson, and G. T. Jones, *Mol. Phys.*, **12**, 265 (1967).