A Localized Spin Orbital View of Fermi Contact Coupling of Geminal Nuclear Spins

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Abstract: Energy-localized spin orbitals from the INDO treatment of the representative molecules CH_4, C_2H_6, C_2H_4, C_2H_2, H_2CO, H_4C_2O, and H_2C_2O are examined to identify the origin of the differences in signs of the $^2J_{HH}$. The sign appears to be determined by a balance between one-center exchange energies and chemical valency effects (isovalent hybridization) related to the % s character of carbon hybrids. The results as analyzed thus far suggest an important, but as yet not perfectly clear, effect of hyperconjugation for ketene on the CH-localized spin orbitals.

The model of molecular electronic structure consisting of hybrid atomic oribitals combined with the idea of propagation of electron spin density imbalance *via* spin polarization through the bonds of a molecule has played an important role in understanding the Fermi contact mechanism for nuclear spin coupling. For example, the concept adequately accounts for the negative values of $^2J_{HH}$ in C_2H_6, CH_4, and ethylenic CH_2 in C_2H_2O and for the positive values of $^3J_{HH}$ in C_2H_6, C_2H_4, and C_2H_2. The concept fails, however, when applied to $^2J_{HH}$ of C_2H_4O and for ethylenic CH_2 in compounds such as C_2H_4, H_2CO, and H_2CNH. The concept is also impotent in rationalizing the order $^3J_{syn} < {}^3J_{anti}$ for C_2H_6 and C_2H_4.

Past investigations of the Fermi mechanism for nuclear spin coupling of geminal hydrogens fall into one of four groups: those which apply non-SCF, infinitesimal perturbation theory to either the complete set of symmetry-based (canonical) molecular orbitals or to arbitrarily chosen localized molecular orbitals;[1] those which apply the finite perturbation technique[2] within the framework of self-consistent canonical molecular orbitals; those which apply double, infinitesimal perturbation theory to localized SCF orbitals to include electron correlation effects;[3] and those which adopt a predisposed model for atomic hybrids, which are then subjected to valence bond perturbation arguments.[4]

The purpose of these studies has been to determine the appropriateness of a self-consistent localized spin orbital view of the J_{HH} for molecules such as mentioned in the opening paragraph. The treatment presented here is to be distinguished from the others in that we start with the self-consistent α and β spin canonical MO's, obtained from the INDO finite difference method[2a,5] of calculating the Fermi contribution to J_{HH}, and individually "energy minimize"[6a] these to yield SCF-localized spin orbitals for each molecule. The reported success[2] of the finite difference method in giving the correct signs and magnitudes of geminal and vicinal J_{HH}, combined with the reasonableness of the INDO localized orbitals,[7] made the studies worthwhile.

Two questions to be answered by a localization study are of special interest: is spin polarization of localized electron pairs propagated in the expected fashion and is the spin polarization of each C–H pair alone sufficient to account for the sign and magnitude of the proton spin density? A more general question, which can only partially be answered by localization studies, relates to the signs of the various $^2J_{HH}$.

Calculational Methods. The theoretical methods used here have been treated in other places so only a brief overview should be required. The basic MO method is the INDO approximation unaltered from the original prescription.[8] Our initial studies with CH_4 and H_2CO used literature values of the structural parameters, but as the scope of our studies broadened we utilized the "standard" geometries suggested by Pople, *et al.*[5] This is the source of the discrepancies between our values for $^2J_{HH}$ in CH_4 and H_2CO and those of Pople, *et al.* (−6.1 and 31.9 Hz, respectively).

The nuclear spin–spin coupling constant calculations were performed by the method of finite differences suggested by Pople's group.[2] In the interests of economy our programming uses a nuclear spin perturbation, $h = 10^{-2}$, with a density convergence criterion of 10^{-6} to yield estimated errors in coupling constant ≤ 1 Hz. Under these constraints we obtain values for the various J_{HF} of C_2H_3F which are less than 0.8 Hz different from those reported[2] using a three orders tighter convergence demand.

Results and Discussion

Orbital Hybridization. Figure 1 presents in a qualitative way the localized orbital results regarding spin

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(1) J. A. Pople and D. P. Santry, *Mol. Phys.*, **9**, 311 (1965), and references cited therein.

(2) (a) J. A. Pople, J. W. McIver, and N. S. Ostlund, *J. Chem. Phys.*, **49**, 2960, 2965 (1968); (b) G. E. Maciel, J. W. McIver, Jr., N. S. Ostlund, and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 4151 (1970); (c) N. S. Ostlund, M. D. Newton, J. W. McIver, and J. A. Pople, *J. Magn. Resonance*, **1**, 298 (1969).

(3) C. Barbier, B. Levy, and P. Mille, *Chem. Phys. Lett.*, **17**, 122 (1972).

(4) M. Karplus, *J. Amer. Chem. Soc.*, **85**, 2870 (1963).

(5) The geometries used in our calculations were those of J. A. Pople and M. Gordon, *ibid.*, **89**, 4253 (1967). The finite difference programing of the INDO method in our calculations utilizes a somewhat relaxed convergence requirement compared to that advocated in ref 2. Our calculations used $h = 10^{-2}$ and a density convergence test of 10^{-6} which produces J's with errors of 1 Hz or less.

(6) (a) C. Edminston and K. Ruedenberg, *Rev. Mod. Phys.*, **35**, 456 (1963); (b) C. Edminston and K. Ruedenberg, *J. Chem. Phys.*, **43**, 597 (1965); the curvature test for convergence of E. Switkes, W. N. Lipscomb, and M. D. Newton, *J. Amer. Chem. Soc.*, **92**, 3847 (1970), and M. D. Newton, E. Switkes, and W. N. Lipscomb, *J. Chem. Phys.*, **53**, 2645 (1970), has been incorporated into the earlier version of our localization program (T. G. M. Dolph, M. J. Shultz, and K. F. Purcell, No. 198, Quantum Chemistry Program Exchange, University of Indiana, Bloomington) so that we routinely test the localized orbitals for convergence.

(7) W. England and M. S. Gordon, *J. Amer. Chem. Soc.*, **91**, 6864 (1969).

(8) D. A. Dobash, Quantum Chemistry Program Exchange, University of Indiana, Bloomington, Ind., No. 141.

propagation throughout the molecules. The location[9] of the nuclear spin perturbation is identified with an asterisk (the H at this position was given an α nuclear spin). On localization, the occupied orbitals arise as combinations of hydrogen 1s orbitals, normalized hybrids on each heavy atom, and "tails" due to intrinsic delocalization.[6] Each heavy atom possesses two sets (for α and β spin) of four normalized hybrid atomic orbitals (the four in each set are not *exactly* orthogonal to each other), and it is the difference in the α and β hybrid orbital populations of each pair which is pictured for each molecule in Figure 1. Spin propagation is generally seen to alternate from atom to atom, and hybrids about a common atom all tend to have the same spin polarization, with some important exceptions. The oxygen lone pair polarizations of H_2CO and H_2CCO are *not* controlled by the one-center exchange integrals nor, necessarily, are the polarizations of CH hybrids geminal to the perturbed CH* hybrids. These findings are important in that they make very clear the necessity of considering one-center exchange integrals to be important but not necessarily dominant influences on the nature of e^-,e^- interactions and the spin distribution in molecules. Interestingly, reference to Table I shows that the sign of the spin density and greater than 95% of its magnitude at each hydrogen atom arise from within the spin-polarized electron pair defining the CH bond. This is important for the localized orbital model since it means that spin-polarized "tails" of the *several* other localized orbitals do not, *in sum*, contribute significantly to the spin densities (and therefore the coupling constant) between geminal and vicinal H atoms. This result is all the more important in considering the order syn < anti in vicinal couplings. The answer to the question "is the spin polarization of each CH pair alone sufficient to account for the sign and magnitude of the hydrogen spin density?" is definitely yes. At the same time, it is obvious that one-center exchange integrals are not sufficient to account, in all cases, for the observed spin densities. As this INDO method makes no provision for the inclusion of two-center exchange integrals, it is necessary that other influences on the spin distribution of the geminal CH hybrids must be sought among more conventional concepts of bonding in molecules.

Table I. LMO Partitioning of Spin Densities

Molecule	Bond[a]	% delocalization[b]	ρ_H[c]	$\rho_{H(total)}$[c]	$J_{H_3H_x}$, Hz Calcd	Obsd
CH_4	H_3C_1	0.03	−233.4			
	H_4C_1	0.03	−4.9	−5.0	−5.3	−12.4
C_2H_4O	H_4C_2	0.48	−251.9			
	H_5C_2	0.48	7.7	8.0	8.4	5.5
	H_6C_3	0.48	3.9	3.7	3.9	
	H_7C_3	0.48	6.2	5.9	6.2	
CH_2O	H_3C_2	0.23	−255.5			
	H_4C_2	0.23	23.8	25.5	26.8	∼41
C_2H_2O	H_4C_3	2.83	−237.2			
	H_5C_3	2.83	−11.5	−11.2	−11.8	−15.8
C_2H_6	H_3C_1	0.55	−247			
	H_4C_1	0.55	−4.0	−3.9	−5.2	
	H_5C_1	0.55	−4.0	−3.9	−5.2	
	H_6C_2	0.55	+2.5	+2.6	+3.3	
	H_7C_2	0.55	+2.6	+2.6	+3.3	+8.0[d]
	H_8C_2	0.55	+16.1	+16.1	+18.6	
C_2H_4	H_3C_1	0.86	−241.5			
	H_4C_1	0.86	+3.4	+3.7	+3.2	+2.5
	H_5C_2	0.86	+7.7	+7.9	+9.3	+11.7
	H_6C_2	0.86	+21.8	+22.0	+25.2	+19.1
C_2H_2	H_3C_1	0.55	−208.1			
	H_4C_2	0.55	+9.4	+9.3	+11.0	+9.5

[a] Numbering as in Figure 1. [b] The sum of α and β densities, as a per cent of two electrons, not contained in orbitals on the two atoms defining the bond. [c] The difference in α and β densities for the designated hydrogen atom 1s orbital from the bond identified in column 2. The fourth column gives the difference from the appropriate bond orbital, while the fifth column gives the total from all orbitals. Units are 10^{-4} electron. [d] Average of J_{vic}.

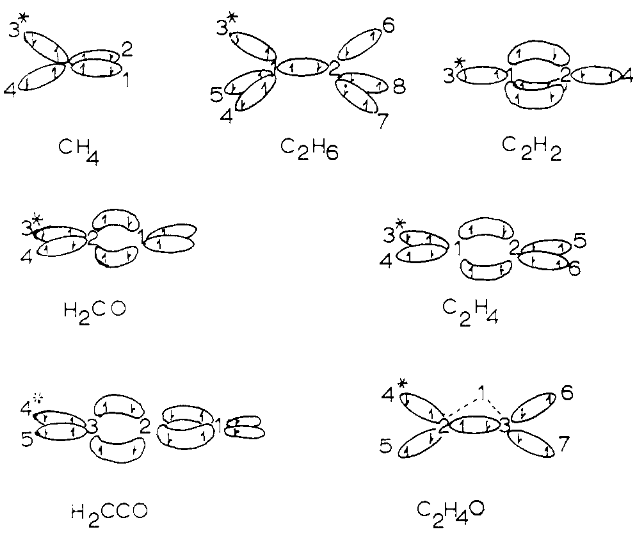

Figure 1. Qualitative molecular orbital spin polarizations for an α nuclear spin at the starred hydrogen.

Before exploring the role of spin-independent effects on the spin distribution among hybrids about a given atom, we need to understand the behavior of the exchange integral between equivalent hybrids at an atom ($K_{h,\bar{h}}$) as a function of the fractional valence s character[6b] (f_s) of the equivalent hybrids h and $\bar{h}$. The results show (Figure 2 is plotted for the specific case of a carbon atom)[10] that the one-center exchange integral between electrons in different hybrids is greatest for sp^3 hybrids and falls off rapidly as the s character increases. Thus we expect one-center exchange integrals to exhibit their greatest influence on the geminal coupling of protons bound by "sp^3" hybrids to the same carbon. It would appear the $^2J_{HH}$ of CH_4 and C_2H_6 (Figure 1) reflect the importance of $K_{h,\bar{h}}$ for sp^3 hybrids. Ethylene oxide might be considered to be another example of the "sp^3" case but the carbon hybrids to hydrogen in this molecule are best thought of as "sp^2" type (*vide infra*). On the other hand, C_2H_4 and H_2CO (and C_2H_4O) are of the "sp^2" type and one-center exchange integrals should be of less importance in these cases.

One approach[1] to identification of spin-independent influences on charge distribution in geminal bonds is based on Pople's model for bond delocalization in

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[9] A referee has noted that the location of the perturbed nucleus in a molecule with nonequivalent geminal hydrogens such as CH_2CHF, while not affecting the computed $^2J_{HH}$, will yield an ambiguity for the localized orbital model used here. Whether this ambiguity is of practical concern remains to be investigated.

[10] The appropriate Slater–Condon parameters for carbon were taken from J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967).

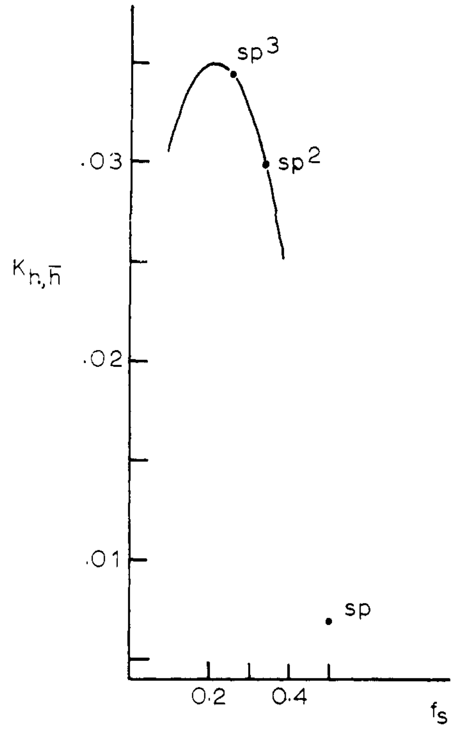


Figure 2. Variation with fractional s character of the exchange integral between two equivalent, orthogonal s/p hybrid atomic orbitals for carbon.

paraffins.[11] This non-SCF, one-electron model begins by assuming a basis set of hydrogen 1s orbitals and orthogonal sp, sp^2, or sp^3 atomic hybrids (fixed s/p ratios) as dictated by the idealized molecular structures. Completely localized molecular orbitals are then developed under the assumption of zero-valued matrix elements between other than directly overlapping basis functions. Then by introducing one- and two-center matrix elements as perturbation terms, and turning to infinitesimal perturbation theory, one charts the development of long-range bond orders between basis orbitals as a result of orbital delocalization (alternately, mixing of original (occupied and virtual) localized orbitals) to form the more customary canonical molecular orbitals.

Now to the geminal coupling problem. Presuming one needs only account for the Fermi contact contribution to the reduced coupling constant for the A,B nuclear pair, the expression for K_{AB} reduces to (using infinitesimal perturbation theory)

$$K_{AB} \propto S_A{}^2(0)S_B{}^2(0)\pi_{S_AS_B}$$

where S_A and S_B are the valence atomic orbitals for nuclei A and B. The quantity $\pi_{S_AS_B}$ is Coulson's atom–atom mutual polarizability.

$$\pi_{m,n} = 4\sum_i^{\text{occ}}\sum_j^{\text{vir}}(\epsilon_i - \epsilon_j)^{-1}C_{im}C_{in}C_{jm}C_{jn}$$

In the zeroth-order localized orbital model, $\pi_{m,n} = 0$ for orbitals on nonbonded atoms; consequently, long-range nuclear couplings are not accounted for at this level. To account for geminal and vicinal couplings, delocalization of electrons, *via* mixing of occupied and unoccupied orbitals, is unavoidable. Taking the approach summarized in the preceding paragraph, infinitesimal perturbation theory is applied to the non-SCF, zero-order localized molecular orbitals to determine the effects of one- and two-center basis orbital interactions on the $\pi_{m,n}$. The results for geminal hydrogen atoms are summarized in the expression

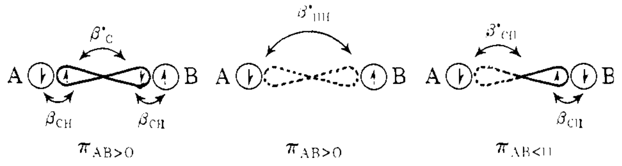
$$\pi_{S_A,S_B} = [4\beta_{CH}'^2 - 4\beta_C'^2 - (\beta_{HH}' - \beta_C')^2]/16\beta_{CH}^3$$

In this expression, all β's are negatively valued ($\beta_{m,n} = \langle\phi_m|H|\phi_n\rangle$) with β_{HH}' representing the direct interaction of geminal hydrogen 1s orbitals, β_C' representing the interaction between hydrids at the same heavy atom, β_{CH} representing the interaction between a heavy atom hybrid and the directly bound hydrogen, and β_{CH}' representing the interaction of one heavy atom hybrid and the other hydrogen. The interpretation of this formula tells us that the one-center interaction β_C' forces $^2K_{HH}$ to positive values, as does the direct interaction β_{HH}'. β_{CH}' is the only interaction tending to make K_{HH} negative.

Now the atom–atom polarizability has the chemical interpretation,[12] stemming from the relation

$$\pi_{i,j} = \partial P_{ii}/\partial\epsilon_j$$

of the change in electron density for orbital *i* brought on by a change in the energy of orbital *j*. This establishes a direct link between the sign of K_{AB} and more readily appreciated electron distribution concepts, as both exhibit the same dependence on β_{HH}', β_C', and β_{CH}'. The chemical interpretation of the introduction of an α nuclear spin at the hydrogen labeled A is that the hydrogen 1s orbital becomes more electron attracting for β spin and less attracting for α spin electrons; the following sketches illustrate, in terms of electron distribution, how nonzero β_C' provides for propagation of these electronegativity effects *via* the second and third orbitals of a four-orbital four-electron system (*cf.* butadiene), how β_{HH}' provides for transmission in the simple two-orbital two-electron system, and how nonzero β_{CH}' provides for the propagation in a three-orbital three-electron system (*cf.* allyl). Thus, while the independent electron formalism lies at the foundation of this model (no electron exchange integrals included), a propagation of spin density is developed after a distinction is made between α and β spin spatial functions, and a proper application of the atom–atom polarizability concept to the nuclear spin coupling problem is made.



The approach just discussed implicitly introduces different orbitals for different spin concurrently with delocalization brought on by a nonmagnetic perturbation of the initial orbitals. The inclusion of one-center exchange integrals, as in an SCF procedure, will augment the effect of β_{CH}' but oppose the effects of β_{HH}' and β_C'. Thus, it is conceivable that the positive value computed by the independent electron model of $^2K_{HH}$ for a tetrahedral carbon (β_C' is estimated to dominate $\pi_{S_AS_B}$ for sp^3 carbon hybrids) could be turned about by

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[11] J. A. Pople and D. R. Santry, *Mol. Phys.*, 7, 269 (1963).

[12] M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969, pp 197, 198.

sufficiently large one-center electron exchange integrals for carbon. Presumably this is the reason for the opposite signs of ${}^2K_{HH}$ which result from finite perturbation theory applied to the (SCF) CNDO and INDO formalisms.

The linear variation of β_C' with fractional s, f_s, character of the geminal hybrids is easy to derive: $\beta_C' = f_s(\epsilon_s - \epsilon_p)$, where ϵ_s and ϵ_p are the valence AO energies under the independent electron model. β_C' is thus negative with a smaller value for sp^3 hybrids ($f_s = 0.25$) than for sp^2 hybrids ($f_s = 0.33$). Consequently, as the electron exchange integral for geminal hybrids decreases sharply with hybrid s character the quantity $\beta_C'^2$ becomes (linearly) larger and the ${}^2K_{HH}$ should become less negative or more positive.

The delocalization of the localized orbitals model of geminal couplings is, by virtue of its simplicity, certainly instructive but, as developed and presented, does not reveal some aspects of the problem of use to the chemist. In addition, it is not an SCF model (among other points, it uses identical s/p ratio hybrids for occupied and virtual orbitals), its derivation is formally limited by the properties of even alternate systems (*cf.* the theory of alternate hydrocarbons) and is not applicable without modification to H_2CO, H_2C_2O, etc., and there has been no provision for including one-center exchange integrals (although such an effect could be introduced).

The finite perturbation technique is nicely suited for application, as originally introduced, to SCF procedures which may (INDO) or may not (CNDO) incorporate one-center energies. As applied with the CNDO or INDO techniques an analysis of the geminal coupling problem would normally proceed in terms of delocalized (canonical) molecular orbitals. Given an interest in the chemical usefulness of localized orbital concepts, it is of some interest to analyze the geminal coupling in terms of SCF-localized spin orbitals. In comparing the one-electron localized orbital model to the SCF-localized orbital model it is important to distinguish that the former localized orbitals are created without reference to geminal interactions (β_C', β_{HH}', β_{CH}'), and these zeroth-order orbitals are subsequently mixed to effect delocalization whereas the INDO-SCF-localized spin orbitals are defined only *after* these interactions and the one-center exchange integrals have had their effects on spin distribution.

The application of perturbation theory (to first order in the nuclear spin perturbation) to an initially localized set of molecular orbitals indicates no change is to be expected in the total ($\alpha + \beta$) electron density in any basis orbitals because of equal but oppositely directed changes in α and β electron probabilities (equal but oppositely signed perturbations for the α and β spin systems). For the spin density, however, a change is required. Application of the mutual polarization concept to the unperturbed zero-order localized molecular orbitals shows that heavy atom s/p hybridization ratios in *individual* α and β spin spatial functions can change on introduction of the nuclear spin, particularly *if* the constraint of identical s/p ratios in occupied and virtual orbitals is relaxed. This is an aspect of the spin density propagation not brought out in the preceding discussion and can be fully realized only in an SCF approach where the s/p ratios of hybrid spin orbitals are not constrained. The occurrence of the interaction represented by β_C' and the presence of tails in the SCF-localized orbitals are important to this point. Relaxation of this constraint leads to the expectation that changing the s/p ratio of one hybrid will induce changes in the s/p ratios of neighboring hybrids (Bent's isovalent hybridization concept). It is perhaps important to make clear at this point that the s/p ratios of the various atomic hybrids which result from the SCF procedure are ultimately affected to some degree by our criterion for generating the localized orbitals, *i.e.*, the minimization of interorbital electron repulsion which, interestingly, leads to localized orbitals of minimum exchange energies. This property is unique to the localized orbitals discussed here.

Table II. Electronegativity Perturbation Results

Compd	f_s[a]	Δf_s^*	Δf_s
CH_4	0.271	−0.091	+0.070
C_2H_4O	0.346	−0.119	+0.133
C_2H_4	0.327	−0.109	+0.115
H_2CO	0.395	−0.135	+0.208
H_2C_2O	0.329	−0.079	+0.079

[a] f_s is the fractional s character of the carbon hybrid to the geminal hydrogen atom; Δf_s^* and Δf_s are the changes in f_s for the directly perturbed and geminal hybrids, respectively.

Qualitatively, the consequences of variable s/p ratios are as follows. The introduction of an α nuclear spin at one hydrogen causes that hydrogen to act as an electron withdrawing substituent toward β- spin electrons but electron releasing toward α spin electrons. Thus, the polarization of the carbon hybrid directed to the spin-bearing proton should be such as to increase in p character for β spin and decrease in p character for α spin. With even qualitative applicability of the isovalent hybridization concept,[13] the geminal carbon hybrids should increase in s character for β spin and decrease in s character for α spin. This then leads to α spin density at the geminal proton. In summary, dominance by the one-center exchange integral effect leads to the same spin on both geminal protons (both β spin for an α nuclear spin at one of them), while the electronegativity hybridization concept leads to opposite electron spin at the two protons. It must be demonstrated now that the above view of propagation of spin density among hybrids is visible in SCF terms and that an "sp^3" set of hybrids is less polarizable or responsive to the electronegativity effect of the hydrogen nuclear spin than an "sp^2" set of hybrids. To accomplish this in a manner consistent with the nuclear spin perturbation, we performed closed shell calculations (same sign perturbation for both α and β electron spins) on CH_4, C_2H_4, H_2CO, and C_2H_4O using the same perturbation of the hydrogen 1s Fock element as was used for β spin electrons in the open shell calculations for the coupling constants. The results are shown in Table II, where it is seen that this electronegativity perturbation on CH_4 is of much less importance (both to the perturbed hybrid and the one geminal to it) than for the "sp^2" cases of C_2H_4, H_2CO, and C_2H_4O. The relationship between the change in s character of a CH hybrid and the s character of the geminal CH hybrid is dramatically illustrated in Figure 3.

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(13) For a partial discussion see K. F. Purcell and W. C. Danen, *J. Amer. Chem. Soc.*, **94**, 7613 (1972).

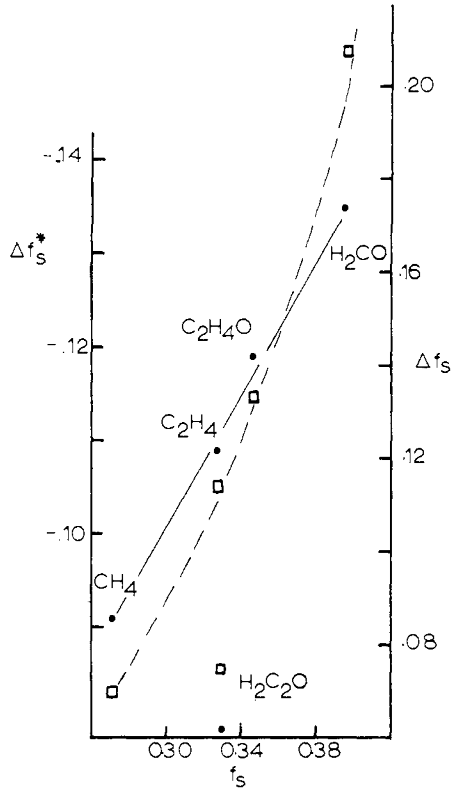

Figure 3. (——) Computed change in fractional s character of the carbon hybrid directed toward the spin-bearing hydrogen nucleus (Δf_s*) and (---) that for the geminal hybrid (Δf_s) as a function of fractional s character of the unperturbed hybrids.

It is impossible at present to put the relationships $K_{\text{h},\bar{\text{h}}} = F(f_s)$ and $\Delta f_s = F'(f_s)$ on the same scale so that both may be directly tied to the $^2J_{HH}$. Thus, the argument that the $^2J_{HH}$ in CH_4 and C_2H_6 are dominated by exchange forces while the $^2J_{HH}$ of C_2H_4 and C_2H_4O are dominated by spin-independent factors cannot be cleanly proven at this point. (Similarly, it has not been formally shown that inclusion of the e^-,e^- exchange energy correction to β_C' in the fixed s/p ratio model is sufficient to alter the signs of $^2K_{HH}$ of CH_4 and C_2H_6.) There is, of course, the indirect support of these ideas that one-center exchange energy is dominant in the cases of CH_4 and C_2H_6 while valency factors predominate for C_2H_4 that comes from the (SCF) CNDO/2 calculations of Pople, McIver, and Ostlund.[2a] There it was shown that omitting the one-center exchange term leads to the wrong sign for $^2J_{HH}$ of CH_4 and C_2H_6 (the INDO calculations predict the correct sign), while the CNDO/2 calculations on C_2H_4 give the correct sign with $^2J_{HH}$ too large in magnitude (INDO simply reduces the magnitude). As an aside, it is worthwhile to note that subjugation of H_2O and NH_3 to CNDO/2 and INDO shows their hybrids to behave like CH_4.[2a] For the series CH_4, C_2H_4, C_2H_4O, and H_2CO it is interesting to note that as the s character of the CH carbon hybrids increases the $^2J_{HH}$ also increases, in keeping with the idea of increasing imbalance between one-center exchange and spin-independent effects on $^2J_{HH}$. The large increase in $^2J_{HH}$ on replacing $=CH_2$ of ethylene by the more electronegative $=O$ to form formaldehyde is consistent with our expectation from application of Bent's model.

The molecule ketene was included for study as it is an example of an "sp^2" case for which the sign of $^2J_{HH}$ is opposite to that of other ethylenic CH_2 fragments. It was initially supposed, probably unrealistically, that the carbon hybrids to the hydrogens would reveal "sp^3" character and fall completely in line with the above arguments. Unfortunately such is not the case (see column 2, Table II), and it would appear that where hyperconjugation is important (refer to the per cent delocalization column in Table I) we find it necessary to pursue studies of the effect of hyperconjugation on the localized spin-orbital model of $^2J_{HH}$.[14] At this point we might surmise that hyperconjugation would translate into a dampened ability of a CH hybrid to respond to the electronegativity perturbation at H*; consistent with this idea is the finding (Table II and Figure 3) that the "sp^2" hybrids of H_2C_2O respond to the electronegativity perturbation to the reduced degree found for CH_4. There is, however, more to this situation than simply a dampening of the normal electronegativity effect since our CNDO/2 calculation for ketene predicts $^2J_{HH}$ to be negative unlike all the other molecules considered here; this would seem to imply the operation of hyperconjugation, when examined from a hybrid s character view, results in an anti-Bent effect not apparent in Table II. (It is true that the CNDO/2 $^2J_{HH}$ (−4.6 Hz) is much smaller than that of INDO (−11.8 Hz), so that the valency effects can be inferred to act in the same direction as, and are subordinate to, the exchange energy!) In short, it is apparent that the hyperconjugation has a dramatic effect on the Fermi contact mechanism for $^2J_{HH}$ in ketene; an item for future study then is how, within the framework of the SCF-localized spin-orbital scheme, does the operation of hyperconjugation alter the ability of the CH_2 carbon hybrids to respond to the electronegativity perturbation at one of the H atoms?

Orbital Mixing. In the preceding section we commented that the distribution of spin density among the various atomic orbitals can be viewed as a consequence of mixing, *via* the introduction of the perturbing nuclear spin, of occurpied and virtual orbitals of the unperturbed molecule;[15] the mixing is different, of course, for α and β spin orbitals. In particular, we are interested in the effect of the perturbation in generating nonzero spin density for a basis orbital (here, at the geminal nucleus).

The formalism for projecting the α and β spin molecular orbitals of the perturbed calculation onto the parent molecular orbitals is straightforward and yields a result for the spin density at the geminal valence s orbital of

$$\rho_s(\text{gem}) = \sum_k^N c_{sk}\left\{\sum_l^N c_{sl}\Delta_{kl}\right\}$$

where c_{sk} and c_{sl} are the geminal 1s LCAO coefficients

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[14] Analysis of hyperconjugative effects in terms of infinitesimal perturbation theory using *canonical orbitals* has been given by J. A. Pople and A. A. Bothner-By, *J. Chem. Phys.*, **52**, 1339 (1965).

[15] Each localized virtual orbital of C_2H_4 is similarly directed as the corresponding occupied orbital and possesses a node between overlapping atomic hybrids. A similar comment applies to the localized orbitals of ketene with one exception. The two occupied orbitals defining the C–C bond are of the bent variety while the virtual counterparts appear as σ* and π* orbitals (not bent as are the CO virtual orbitals). The curvature analysis reveals these orbitals to correspond to a true maximum in intraorbital repulsions, albeit a fairly flat maximum in the direction of mixing of these orbitals, and several randomized starts at localization yielded the same final localized orbitals.

Table III. ρ_{sk}(gem) ($\times 10^4$) for Each Molecular Orbital

	Molecule									
	C_2H_2O		C_2H_4		C_2H_6		C_2H_4		C_2H_6	
Basis	Localized		Localized		Localized		Canonical		Canonical	
Orbital	CH_4 (gem)	-10.16	CH_4 (gem)	2.03	CH_4 (gem)	-4.43	a_g	-1.63	a_{1g}	-1.16
	CH_3	0.09	CH_3	1.08	CH_3	0.26	b_{1u}	-6.03	a_{2u}	-2.52
	$CC_1 + CC_2$	0.03	$CC_1 + CC_2$	0.02	CC	0.00	b_{3u}	5.35	e_u	0.21
	$CO_1 + CO_2$	-1.22	$CH_5 + CH_6$	0.49	$CH_6 + CH_7 + CH_8$	0.05	a_g	-6.01	a_{1g}	-1.59
	$O_1 + O_2$	0.00			CH_5	-0.05	b_{2g}	11.94	e_g	0.90
							π	0.0		

in parent molecular orbitals k and l, and this is the SCF analog of the mutual polarizability equation given earlier. In fact it may be shown that the summations over k and l may be restricted to occupied and virtual orbitals only.

Thus the general spin density (ρ) arises from unequal mixing of α and β spin parent molecular orbitals (k,l) as measured by Δ_{kl} and, specifically, the spin density at the geminal 1s orbital (ρ_s(gem)) reflects this unequal mixing, but weighted by the "differential overlap" between molecular orbitals k,l, at the geminal 1s orbital ($c_{sk}c_{sl}$).[16] The form of the last equation suggests a possible interpretation of the mixing phenomenon.

$$\rho_s(\text{gem}) = \sum_{k}^{\text{occ}} \rho_{ks}(\text{gem})$$

That is, ρ_s(gem) is factored into one contribution from each occupied parent molecular orbital being mixed with *all* parent virtual molecular orbitals.

Table III shows the results of this kind of analysis of the geminal spin density for C_2H_6 and C_2H_4. The simplicity of the localized orbital scheme is quite apparent and ketene is seen to be very much like C_2H_6 but quite different from C_2H_4, again reflecting that the ketene and C_2H_6 geminal couplings are of the same sign.

Examination of the terms $c_{sk}c_{sl}\Delta_{kl}$ for different pairs k,l shows only three types of (occupied $\leftrightarrow$ virtual) orbital mixing to be important. Mixing of the σ and σ^* orbitals of the same (geminal) bond produces spin densities of opposite signs for C_2H_4 ($+7.41 \times 10^{-5}$) and H_2C_2O (-86.14×10^{-5}) and alone is sufficient to determine the sign and approximate magnitude of ρ_s(gem) for ketene but not so completely for ethylene. Second, there is the cross mixing of the σ and σ^* orbitals of one CH bond with the σ^* and σ, respectively, of the other. These are of the same sign ($+12.43 \times 10^{-5}$ and $+3.94 \times 10^{-5}$) in both molecules but the cross interaction for ethylene is three times larger than in ketene and of the same importance as the same bond σ,σ^* mixing. Finally, there are orbital mixings involving the vicinal orbitals (4CH's in C_2H_4 and 4CO's in H_2C_2O) which contribute negatively in both molecules (-0.54×10^{-5} and -13.59×10^{-5}) but by a factor 25 times larger in ketene. The difference in vicinal bond contributions for C_2H_4 and H_2C_2O can be attributed *directly* to hyperconjugation in ketene while the differences in in-bond and cross-bond CH orbital contributions are only *indirectly* attributed to hyperconjugation. The most important effects, however, arise from the σ,σ^* orbitals of the CH_2 bonds and how these differ for α and β spin orbitals. It is this aspect of hyperconjugative control of ${}^2J_{HH}$ and the greater localization of ${}^2J_{HH}$ in the CH_2 group of ketene which will be the basis for further study, in the context of SCF-localized spin orbitals.

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[16] This is one way ($c_{sk}c_{sl} \neq 0$) that localized orbital tails (due to intrinsic delocalization) can enter into the coupling constant problem. In Table III, small but nonnegligible contributions to ρ_s(gem) arise primarily when k or l selects either the geminal CH σ or σ^* orbital. The high degree of localization of the orbitals renders the $c_{sk}c_{sl}$ product very small for the other k,l pairs.

Localized Magnetic Susceptibility Anisotropies

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Abstract: A theoretical framework is given for partitioning the individual elements in the total magnetic susceptibility tensor (χ_{aa}, χ_{bb}, and χ_{cc}) into local contributions. Molecular data are analyzed to give local values of χ_{aa}, χ_{bb}, and χ_{cc} for either atoms or bonds. These values can be added to give the total molecular magnetic tensor elements for a wide range of nonstrained, nonaromatic compounds. The method is used to estimate relative aromaticities, interpret data from Cotton–Mouton experiments, and to gain information about molecular structure. The values given here are also of use in determining neighbor group effects in proton magnetic shielding.

The magnetic susceptibility tensor describes the quadratic response of a molecule to an external magnetic field. The evaluation of this quantity has been a problem of theoretical and experimental interest for many years. Although the measurement of the average value of the magnetic susceptibility is relatively

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