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The Relative Importance of Delocalization Terms in Proton Spin-Spin Coupling Constants

By

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An expression for the atom-atom polarizability between the 1*s* orbitals of geminal or vicinal protons has been derived by perturbation theory using the POPLE-SANTRY Theory of σ electron systems. The coupling constants calculated on this basis agree well with these obtained from full molecular orbital calculations. Expressions have been obtained for the variation of vicinal coupling constants with dihedral angle in ethane and the HCC bond angle and C-C bond length in ethylene, and these agree well with corresponding expressions obtained using the VB method.

Es wurde ein Ausdruck für die Atom-Atom-Polarisierbarkeit zwischen den 1*s* Orbitalen geminaler bzw. vicinaler Protonen abgeleitet mittels Störungsrechnung unter Benutzung der POPLE-SANTRY-Theorie für σ-Elektronensysteme. Die auf dieser Basis berechneten Koppelungskonstanten stimmen gut mit denen aus einer vollständigen MO Rechnung überein. Es wurden Ausdrücke erhalten für die Änderung der vicinalen Koppelungskonstanten mit dem Diederwinkel in Äthan sowie dem HCC Bindungswinkel und der C-C Bindungslänge in Äthylen, die gut mit den entsprechenden Ausdrücken aus der VB Methode übereinstimmen.

A l'aide de la théorie de POPLE et SANTRY sur les systèmes d'électrons σ, nous dérivons de la théorie des perturbations une expression pour la polarisabilité atome-atome entre les orbitales 1*s* des protons géminaux ou vicinaux. Les constantes de couplage ici calculées s'accordent bien à celles obtenues des calculs OM complets. Les expressions obtenues pour la variation du couplage vicinal avec l'angle dihédrique dans l'éthane, et l'angle HCC et la distance C-C dans l'éthylène, s'accordent bien aux formules correspondantes de la méthode de la mésomérie.

Introduction

POPLE and SANTRY have derived a molecular orbital expression in which the contact contribution to proton spin-spin coupling constants is related to the mutual atom-atom polarizabilities of the hydrogen 1*s* orbitals. $J_{ab} = C\,\pi_{ab}$, where C is a constant [*9*]***. The polarizabilities π_{ab} are calculated from LCAO σ-molecular orbitals obtained with the inclusion of small delocalization terms. However, whilst making calculations based on this formula we have found that the results are very sensitive both to the nature and the magnitude of the weak delocalization terms that are taken into account. For example, if one only includes intra-atomic perturbation terms between orbitals on the same carbon atom (as in SANDORFY's C method for σ-electron delocalization) [*12*], one obtains negligible coupling between vicinal protons.

A straightforward calculation suffers from the deficiency that it is not easy to identify the important delocalization terms. This not only makes it difficult to

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[***] $C = 6.27 \times 10^3$ c. p. s. ev^{-1} if the hydrogen 1*s* orbitals have an exponential constant $\zeta = \frac{1}{2}$.

decide on the best set of empirical parameters to be used in a calculation, but also one obtains no picture of the routes along which nuclear spin coupling occurs.

Because atom-atom polarizabilities are derived by considering the effect of a small perturbation on the molecular orbitals of the system, and also the delocalization terms can be considered as a perturbation on a set of localized molecular orbitals, it should be possible to carry through a calculation in which both these perturbations are applied to a set of localized molecular orbitals, and thus obtain an algebraic expression for the polarizabilities in terms of the delocalization parameters. In this paper we will derive such an expression for the atom-atom polarizabilities which are important for the interpretation of geminal and vicinal proton coupling constants in hydrocarbons. With such an expression available one can draw a comparison between the theory of coupling constants and the valence bond approach which introduces small deviations from perfect pairing through exchange interactions between "non-bonded" orbitals.

Theory

If the σ-molecular orbitals of a hydrocarbon are built up from hydrogen $1s$ orbitals and hybridized carbon orbitals and all the off diagonal elements in the Hamiltonian matrix between orbitals formally associated with different electron pair bonds are put equal to zero, then one obtains localized orbitals and the mutual polarizabilities for different hydrogen orbitals are all zero. We will use such a set of orbitals as the basis for a perturbation expansion of the delocalized orbitals of the system.

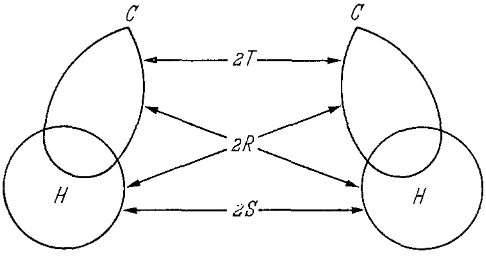


Fig. 1. The delocalization resonance integrals between two CH bonds

To illustrate the approach we consider first the effect of introducing interaction terms between two sets of localized CH orbitals, a bonding and an anti-bonding orbital of each. We can identify three types of interactions (resonance integrals) leading to delocalization and these are labelled 2 R, 2 S and 2 T, as shown in Fig. 1 for the case of two equivalent CH bonds (t represents a hybrid carbon orbital, h a hydrogen $1s$ orbital).

We will assume for the moment that the hydrogen and carbon orbitals have the same energy ($\alpha_H = \alpha_C = \alpha$). The localized molecular orbitals of the system (appropriate to a Hückel calculation with neglect of overlap) will then be as follows:

$$\begin{array}{ll} & \textit{Energy} \\ \left.\begin{array}{l}\psi_2' = (h_2 - t_2)/\sqrt{2} \\ \psi_1' = (h_1 - t_1)/\sqrt{2}\end{array}\right\} & \alpha - \beta \\ \left.\begin{array}{l}\psi_2 = (h_2 + t_2)/\sqrt{2} \\ \psi_1 = (h_1 + t_1)/\sqrt{2}\end{array}\right\} & \alpha + \beta \end{array}$$

with $\beta = \beta_{h_1 t_1} = \beta_{h_2 t_2}$. One then constructs an interaction matrix in which the parameters R, S and T appear. In addition we include a perturbation to evaluate the mutual polarizability of the two hydrogen orbitals, $\pi_{h_1 h_2}$. The simplest way to do this is to make use of the relationship [2]

$$\pi_{\mu\nu} = \frac{\partial^2 E}{\partial \alpha_\mu \, \partial \alpha_\nu} \tag{1}$$

that is, one introduces perturbations to the coulomb integrals of the two hydrogen atoms and evaluates the second derivative of the energy in terms of these perturbations. We define $2\,D_1$ and $2\,D_2$ as the perturbations to the coulomb integrals for h_1 and h_2 respectively. The complete energy matrix then has the following form:

$$\begin{array}{cc} \begin{matrix} \psi_1 \\ \psi_2 \\ \psi_1' \\ \psi_2' \end{matrix} & \begin{bmatrix} \alpha+\beta+D_1 & 2\,R+S+T & D_1 & S-T \\ 2\,R+S+T & \alpha+\beta+D_2 & S-T & D_2 \\ D_1 & S-T & \alpha-\beta+D_1 & -2\,R+S+T \\ S-T & D_2 & -2\,R+S+T & \alpha-\beta+D_2 \end{bmatrix} \end{array} \tag{2}$$

$\pi_{h_1 h_2}$ is then given as $\frac{1}{4}$ of those terms in the expression for the total energy (twice the sum of the two lowest eigenvalues) which are proportional to $D_1 D_2$.

The simplest method of solving this problem is to first diagonalize the matrix with $D_1 = D_2 = 0$ (by constructing symmetry MO's and diagonalizing the resulting 2×2 matrices exactly), and then use the second-order perturbation theory to obtain the eigenvalues of the transformed matrix (with D_1 and D_2) in which R, S and T do not appear off the diagonal. In this way the following result is obtained for the leading terms in the perturbation expansion of $\pi_{h_1 h_2}$.

$$\pi^{(1)}_{h_1 h_2} = [4\,R^2 - S^2 - 5\,T^2 + 2\,ST]/4\,\beta^3 \,. \tag{3}$$

It is important to note that there are no first-order contributions from R, S or T. This is in accord with the fact that the bond order between two hydrogen 1*s* orbitals is linear in R, S and T and within the average energy approximation $\pi_{h_1 h_2} = P^2_{h_1 h_2}/\Delta E$ [8].

Because β is a negative quantity the term in R^2 contributes to negative coupling, those in S^2 and T^2 to positive coupling, and the ST term either positive or negative depending on the signs of S and T. It is interesting that the coefficient of S^2 (which gives a direct coupling between the two hydrogen orbitals) is much smaller than the coefficients of R^2 and T^2.

Expression (2) applies also to an unsymmetrical situation when there are two different R-type interactions, say R and R', if R is replaced by $\frac{1}{2}(R + R')$.

Expression (2) is valid in the approximation of the coulomb integrals of the hydrogen and carbon hybrid orbital being equal. To examine the effect of relaxing this restriction we have derived the leading term in the expansion of $\pi_{h_1 h_2}$ which is of order $(\alpha_H - \alpha_C)/\beta$ — the algebra in this case is rather unwieldy and the coefficients were obtained by a computer diagonalization of the relevant matrices for chosen small values of the parameters R, S, T and $\alpha_H - \alpha_C$. The following addition to expression (3) results.

$$\pi^{(2)}_{h_1 h_2} = \frac{(\alpha_H - \alpha_C)}{\beta^4}\, R\,(1.5\,S - 2.5\,T) \,. \tag{4}$$

The only first-order contributions to the bond order between two hydrogen orbitals arise from the R, S and T parameters [10]. It is therefore expected that interactions involving orbitals other than those in the two CH bonds will contribute higher order terms to $\pi_{h_1 h_2}$. This can easily be confirmed by considering the eigenfunctions and eigenvalues of matrix (2) for the case $R = S = T = 0$. These eigenfunctions still represent localized CH bonding orbitals and there are no contributions to the eigenvalues of order $D_1 D_2$. Let the two bonding orbitals which result from this case be χ_1 and χ_2, and let there be an interaction between these and some antibonding orbital ψ_r' associated with a CC bond or another CH bond (interactions with other bonding orbitals will not change the total energy). The interaction matrix will have the following form.

$$\begin{array}{c} \chi_1 \\ \chi_2 \\ \psi_r' \end{array} \begin{bmatrix} \alpha + \beta + f(D_1) & 0 & A \\ 0 & \alpha + \beta + f(D_2) & B \\ A & B & E_r' \end{bmatrix} \tag{5}$$

Clearly the effect of ψ_r' on the total energy of χ_1 and χ_2 will be correctly given to order A^2 and B^2 by second-order perturbation theory, and this energy will still contain no terms in $D_1 D_2$.

We shall now show that $\pi^{(1)}_{h_1 h_2}$, given by expression (3), can account for the main features of geminal and vicinal coupling constants, and for these cases it gives a good approximation to values of $\pi_{h_1 h_2}$ calculated by an exact evaluation of the delocalized molecular orbitals.

Discussion

We will consider first the case of vicinal coupling, taking ethylene and ethane as examples, but allowing for all possible dihedral angles φ between the two CCH planes.

Following POPLE and SANTRY [9] we assume that the resonance integrals are proportional to the corresponding overlap integrals $\beta_{ab} = kS_{ab}$. The delocalization terms R, S and T are then given by the following expressions.

Ethane ($R_{\mathrm{CC}} = 1.53$ Å, $R_{\mathrm{CH}} = 1.09$ Å, all angles 109°28′)

$$2\,R = k\,[0.5\,S_{hs} + (0.391\cos\varphi - 0.253)\,S_{h\sigma}]$$

$$2\,S = kS_{hh};\ R_{\mathrm{HH}} = (7.185 - 2.122\cos\varphi)^{\frac{1}{2}}$$

$$2\,T = k\,[0.25\,S_{ss} - 0.289\,S_{s\sigma} + 0.083\,S_{\sigma\sigma} + 0.667\cos\varphi\,S_{\pi\pi}]$$

Ethylene ($R_{\mathrm{CC}} = 1.35$ Å, all angles 120°)

$$2\,R = k\,[0.577\,S_{hs} + (0.315\cos\varphi - 0.365)\,S_{h\sigma}]$$

$$2\,S = kS_{hh};\ R_{\mathrm{HH}} = (7.672 - 1.767\cos\varphi)^{\frac{1}{2}}$$

$$2\,T = k\,[0.333\,S_{ss} - 0.471\,S_{s\sigma} + 0.167\,S_{\sigma\sigma} + 0.5\cos\varphi\,S_{\pi\pi}]\,.$$

The overlap integrals involving p orbitals have been defined in terms of σ and π components relative to the appropriate internuclear axis (which is the $C_1 - C_2$ or $H_1 - C_2$ axis), with the positive lobe of a $p\sigma$ orbital pointing towards the other nucleus.

Fig. 2 and 3 show the relative contributions to $\pi^{(1)}_{h_1 h_2}$ from each term in expression (3) as a function of the dihedral angle. The overlap integrals have been calculated using Slater orbitals, but with $\zeta_{\mathrm{H}} = 1.2$. In both cases the term in T^2

makes the greatest contribution, although the others, particularly ST and R^2 have an important influence on the ratio $J_{\varphi=0}/J_{\varphi=180°}$.

Shown also in the figures are the values of $\pi_{h_1h_2}$ obtained by a complete solution of the molecular orbital problem with the following parameters: $k = -10$ ev $\alpha_s = -16.0$, $\alpha_p = -13.0$, $\alpha_h = -13.6$ ev. (Reasons for this choice will be given later.) With such parameters the contribution from $\pi^{(2)}_{h_1h_2}$ (expression 4) is never

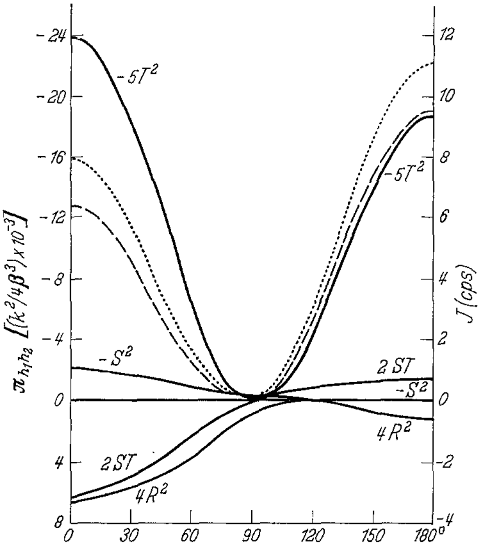


Fig. 2

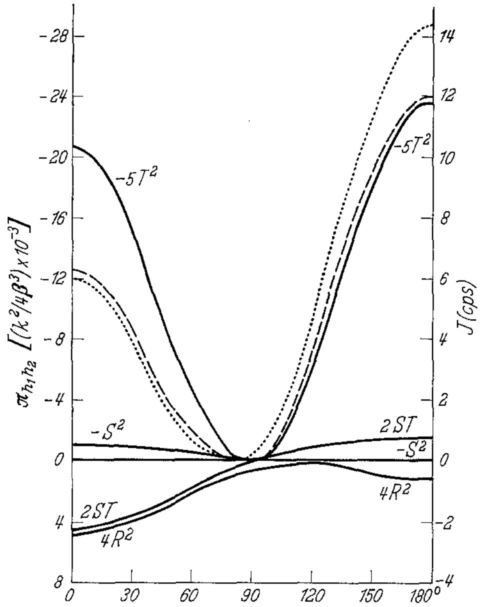


Fig. 3

Fig. 2. Dependence of $\pi_{h_1h_2}$ and J for ethane on the dihedral angle. Full lines give relative contributions from the terms in expression (3). Dashed line is $\pi^{(1)}_{h_1h_2}$ and dotted line is $\pi_{h_1h_2}$ obtained by a full MO calculation

Fig. 3. Dependence of $\pi_{h_1h_2}$ and J for ethylene on the dihedral angle. Convention as in Fig. 2

more than 10% of $\pi^{(1)}_{h_1h_2}$. The difference between $\pi_{h_1h_2}$ and the perturbation values we have derived must therefore come from the interactions occurring through other CC or CH bonds. The absolute values obtained with the above parameters are in reasonable agreement with the experimental values which are given in the table.

We turn now to geminal coupling constants. These are large and negative for sp^3 carbon atoms and small but positive for sp^2 atoms (see the table).

For geminal coupling the parameter T does not depend on resonance integrals but on the difference between α_s and α_p. For two carbon hybrids making an angle ϑ with one another $T = -\cos\vartheta\,(\alpha_s - \alpha_p)/2\,(1 - \cos\vartheta)$. Thus T is negative and its modulus increases as ϑ increases. The parameter R is given by the following expression.

$$R = \frac{1}{2}\sqrt{\frac{-\cos\vartheta}{1-\cos\vartheta}}\cdot\left(\beta_{hs} - \sqrt{-\cos\vartheta}\,\beta_{h\sigma}\right),$$

where β_{hs} and $\beta_{h\sigma}$ are now resonance integrals between atoms bonded together. The modulus of R decreases as the angle increases.

The contribution from the S^2 and ST terms are difficult to estimate reliably because S depends sensitively on ζ_H. It is certain however that the modulus of S will decrease as ϑ increases, and the values shown in Fig. 4 have been calculated on the basis of $\zeta_H = 1.2$.

The geminal coupling constant has a positive contribution from the S^2 and T^2 terms and a negative contribution from the R^2 and ST terms. In order to get agreement in an absolute sense with the experimental results it is necessary that the T^2 term shall not be too large. If one takes α_s and α_p from observed ionization potentials as proposed by POPLE and SANTRY [9] ($\alpha_s = -16.0$ ev, $\alpha_p = -11.2$ ev) one finds that J_{gem} is positive for both sp^3 and sp^2 atoms although the difference between the two (~ 8 c. p. s.) is qualitatively in agreement with experiment. If the separation of the s and p levels, is reduced then the T^2 term becomes less important and the coupling constant is reduced. Fig. 4 shows calculations carried out for $\alpha_s - \alpha_p = -3$ ev, which we have found to give the best overall fit with experiment when one considers both geminal and vicinal coupling constants. A similar improvement was found earlier for directly bonded ^{13}C-H coupling constants when α_p was taken as -13.0 ev instead of -11.2 ev [3].

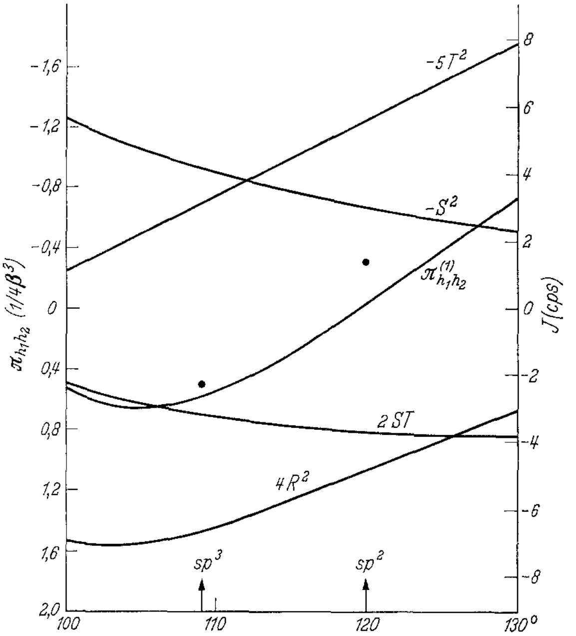


Fig. 4. Dependence of $\pi_{h_1h_2}$ and J for geminal coupling on the HCH angle. The results of the full MO calculation for ethane and ethylene are shown by the dots

The results of full calculations on the hydrocarbons for both values of α_p are summarized in the table.

Using valence bond methods KARPLUS [4] has obtained expressions for the variation of coupling constants with certain molecular dimensions. For comparison we have derived similar expressions using the perturbation formula (3).

Table

Comparison of experimental coupling constants with values obtained from an exact calculation of $\pi_{h_1 h_2}$

		$\alpha_p = -13.0$ ev	$\alpha_p = -11.2$ ev	Exp. [7]
CH_4	J_{gem}	−2.1	+1.2	−12.4
C_2H_6	J_{gem}	−2.3	+2.1	
	J_{trans}	13.1	19.5	$\frac{1}{3} J_t + \frac{2}{3} J_g = 8.0$
	J_{gauche}	2.2	2.8	
C_2H_4	J_{gem}	1.5	10.3	2.5
	J_{trans}	16.4	23.8	19.1
	J_{cis}	8.7	8.5	11.6
C_2H_2	J_{HH}	4.3	9.3	9.6

I. Variation of J_{vic} for ethane-like fragments with dihedral angle.

KARPLUS $J = 4.2 - 0.5 \cos\varphi + 4.5 \cos 2\varphi$

This work $J = 3.96 - 1.49 \cos\varphi + 3.96 \cos 2\varphi$.

II. Variation of J_{cis} for ethylene-like fragments with the CC bond length (r in Å).

KARPLUS $J = 6.1\,[1 - 2.9\,(r - 1.35)]$

This work $J = 5.7\,[1 - 2.6\,(r - 1.35)]$.

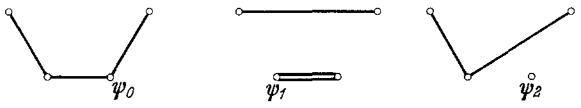
III. Variation of J_{cis} for ethylene-like fragments as a function of the HCC bond angle (ϑ).

	110^0	120^0	130^0
KARPLUS	16.0	6.1	2.1
This work	10.1	5.7	2.4 .

The agreement between the two theories is very satisfactory. The only point at which there is serious disagreement is in the calculation of geminal coupling constants, for which the valence bond approach gave a large positive value for methane [*6*].

A detailed comparison of the valence bond and molecular orbital approaches is difficult to make except that one can say the MO calculation is far easier. Firstly no VB calculation has been made except within the average energy approximation for closing the second-order energy terms. This means that one should really compare the calculations with the MO calculations obtained with the same approximation, that is with the MCCONNELL formula. However, whereas the MCCONNELL formula always gives positive coupling constants this is not true of the corresponding VB calculations.

In the VB calculations on vicinal coupling in ethane and ethylene the following type of structures were considered [*5*].



ψ_0 is the perfect pairing structure, ψ_1 represents an HH bond, and ψ_2 represents bonding between distant carbon and hydrogen atoms with one carbon having its electrons paired. In these calculations exchange integrals between orbitals not on neighbouring atoms were taken to be zero.

A loose analogy can be drawn between our delocalization resonance integrals R, S and T, and the corresponding VB exchange integrals. For example, S is analogous to the VB exchange integral between two hydrogen orbitals $K_{h_1 h_2}$, in the sense that both are zero in the absence of any overlap between the two hydrogen orbitals. Since K is a two electron integral we have $K_{h_1 h_2} \propto S^2$. It follows that the VB calculation is equivalent to our MO calculation in the approximation $R = S = 0$. It should be noted that even though ψ_1 represents an HH bonded structure the interaction between ψ_0 and ψ_1 is not zero if $S = 0$. The agreement between the VB and MO methods can perhaps be attributed to the fact that the most important delocalization term is T, and this corresponds to the most important VB exchange integral.

The VB calculation on geminal coupling [6] gave a very poor agreement with experiment, (at the time it was made the sign of the coupling constant was not known and the result was thought to be very good). It is again difficult to elucidate the point at which the two theories disagree. The following values were used for the VB exchange integrals which result in the breakdown of the perfect pairing approximation.

$$K_{h_1 t_2} = +\,0.233,\ K_{h_1 h_2} = -\,1.00,\ K_{t_1 t_2} = +\,1.01 \text{ ev}\,,$$

which we can compare with R^2, S^2 and T^2 respectively. In the molecular orbital calculations the contributions from R^2 has the opposite sign from the S^2 and T^2 contributions. It does not look as though this type of behaviour arises in the VB approach. Also there is nothing in the method corresponding to our ST term which contributes to negative coupling.

Finally we comment on some results obtained for the benzene molecule. Using a basis of Slater orbitals and including all resonance integrals even between distant atoms ($\beta_{ab} = -\,10\, S_{ab}$ ev) we have obtained by a complete calculation the following result.

$$J_{\text{ortho}} = 7.6 \qquad J_{\text{meta}} = 2.5 \qquad J_{\text{para}} = 1.8 \qquad \text{c.p.s.}$$

Using the approximation to the atom-atom polarizability of expressions (3) and (4) we find

$$J_{\text{ortho}} = 6.2 \qquad J_{\text{meta}} = 0.06 \qquad J_{\text{para}} = 0.06 \qquad \text{c.p.s.}$$

It is clear that whereas the perturbation method is satisfactory for ortho hydrogens it gives a negligible contribution to long range coupling. Preliminary calculations suggest that interaction terms through CC or other CH bonds [c. f. A or B in matrix (5)] will give a contribution to π_{hh} which is of second order in A or B and linear in R, S or T. Further work is in progress to elucidate which of these terms are important for long range coupling, but our general conclusion is in agreement with the VB result that this goes via intermediate CC bonding orbitals [1].

Note added after completion of manuscript. In a paper just published, Pople and Santry have also used a perturbation approach to obtain spin-spin coupling constants. Their expression 5.2 for geminal coupling is identical to our expression (3). For vicinal coupling they include only the delocalization term which is T^2 in our theory [their expression (6.2)]. Although this is the most important contribution to vicinal coupling it is seen from our Fig. 2 and 3 that the other terms are not negligible.

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