

## Comparison of Pople-Santry Type and Hoffmann Type Calculations of Nuclear Spin-Spin Coupling

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The independent electron theories of Pople and Santry and of Hoffmann are used for a calculation of all coupling constants of methane, ethane, ethylene and acetylene. The Hoffmann theory appears to be superior to the Pople-Santry theory in correlating this range of coupling constants. The inclusion of two-centre integrals in the Hoffmann theory gives somewhat better results but is not essential. The results are not improved by the use of an iterative Hoffmann method.

During the last few years the independent electron theory of nuclear spin-spin coupling by Pople and Santry [1, 2] has been applied many times in the interpretation of NMR coupling constants. The MO's are written as a linear combination of all valence AO's.

$$\psi_i = \sum_{\mu} c_{i\mu} \chi_{\mu} \quad (1)$$

The Fermi contact contribution to the coupling constant is

$$J_{AB} = C_{AB} s_A^2(0) s_B^2(0) \pi_{A,B} \quad (2)$$

$C_{AB}$  is a constant for a specific pair of nuclei AB,  $s^2(0)$  is the value of the relevant  $s$ -orbital at the nuclear position and  $\pi_{A,B}$  is the atom-atom polarizability of the  $s$ -orbitals on A and B.

$$\pi_{A,B} = -4 \sum_i^{\text{occ}} \sum_j^{\text{unocc}} (\epsilon_j - \epsilon_i)^{-1} c_{iA} c_{iB} c_{jA} c_{jB} \quad (3)$$

$s^2(0)$  is often evaluated from the best available SCF functions for the atom. As there is not much reason why this gives the correct values for a molecule, they can also be treated as empirical parameters. In the derivation of Eq. (2) only one-centre integrals are retained.

The application of Eq. (2) consists further of a MO calculation of  $\pi_{A,B}$ . The coefficients  $c$  and orbital energies  $\epsilon$  are obtained from the matrix eigenvalue equation

$$(\mathbf{H} - \epsilon \mathbf{S})\mathbf{c} = 0 \quad (4)$$

where  $\mathbf{H}$  is the Hückel matrix and  $\mathbf{S}$  the matrix of overlap integrals. In the theory of Pople and Santry [3, 4] the diagonal elements  $\alpha_{\mu}$  of  $\mathbf{H}$  are taken as the negative valence state ionisation potentials, and the off-diagonal elements are approx-

imated by

$$\beta_{\mu\lambda} = kS_{\mu\lambda} \quad (5)$$

where  $k = -10$  eV. Van Duijneveldt *et al.* [5] used  $k = -7.3$  eV. Although  $S$  is used in Eq. (5), after that in solving Eq. (4) overlap is neglected.

In the extended Hückel theory of Hoffmann [6] the diagonal elements of  $H$  are estimated in the same way; the off-diagonal elements are usually given by

$$\beta_{\mu\lambda} = kS_{\mu\lambda}(\alpha_{\mu} + \alpha_{\lambda})/2 \quad (6)$$

where  $k = 1.75$ . Further in solving Eq. (4) overlap is taken into account. For hydrocarbons Eq. (6) with  $k = 0.75$  gives about the same  $\beta$ -values as Eq. (5) with  $k = -10$ , so the off-diagonal elements are quite different in both theories. The Hoffmann type theory has been applied to the spin-spin coupling problem by Fahey *et al.* [7] and Amos [8].

We calculated all coupling constants of methane, ethane, ethylene and acetylene with both theories, using a basis of Slater orbitals. The results are given in the Table.

The first column of the Table shows that the Pople-Santry method is rather unsuccessful. Two defects are notable: a) the directly bonded CH-coupling con-

Table. Coupling constants of methane, ethane, ethylene and acetylene

	Pople-Santry $k = -10$ eV	Hoffmann $k = 1.75$	Hoffmann <sup>a</sup> 2 centre int.	exp. <sup>b</sup>
<i>One bond</i>				
CH: methane	94	64	83	125
ethane	75	67	84	125
ethylene	113	87	107	156
acetylene	210	139	169	249
CC: ethane	6	22		35
ethylene	4	53		68
acetylene	38	106		172
<i>Two bonds</i>				
HCH: methane	21.8	-18.4	-16.5	-12.5
ethane	26.3	-20.6	-16.7	
ethylene	58.3	-21.5	-15.2	2.3
HCC: ethane	8.3	-3.7	-4.0	-4.5
ethylene	15.2	-7.8	-8.0	-2.4
acetylene	39.5	-7.4	-5.9	49.4
<i>Three bonds</i>				
HCCH: ethane	10.9	5.1	5.2	8.0
cis-ethylene	-7.5	5.0	5.9	11.6
trans-ethylene	57.2	16.3	16.8	19.1
acetylene	54.5	8.8	8.5	9.6

<sup>a</sup> Ref. [7]. <sup>b</sup> Ref. [9].

Slater exponents: Carbon: 1.625, hydrogen: 1.2.

Diagonal elements: Carbon-2s: -21.4 eV, carbon-2p: -11.4 eV, hydrogen-1s: -13.6 eV.

Molecular dimensions: Acetylene:  $r_{CC} = 1.21$  Å,  $r_{CH} = 1.06$  Å; ethylene:  $\angle HCH = 120^\circ$ ,  $r_{CC} = 1.34$  Å,  $r_{CH} = 1.09$  Å; methane, ethane:  $\angle HCH = 129^\circ 28'$ ,  $r_{CC} = 1.54$  Å,  $r_{CH} = 1.10$  Å; ethane in staggered conformation.

stants in methane and ethane differ rather much; b) two-bond coupling constants are all predicted to be positive. In their original paper [2] Pople and Santry got much better results for the same molecules. For the directly bonded coupling constants this is due to the use of an average energy in the denominator of Eq. (3), which is more or less adjusted. For the other coupling constants this is due to the neglect of several contributions, as already noted by Murrell and Gil [10]. Changing  $k$  from  $-10$  to  $-7.3$  eV [5] gives even worse results (except for the directly bonded CH-coupling). It is possible to get better results by adjusting the  $\alpha$  values. This is especially true when the restriction is made to a special class of coupling constants. So Van Duijneveldt *et al.* [5] got very good results for the class of directly bonded CC and CH coupling constants. We do not think this procedure is justified as the parameters now have to be changed in going from one coupling constant to another. Finally we want to mention that the Pople-Santry method is rather unstable under variation of the diagonal elements  $\alpha$ , which places a strong restriction on the validity of the method for general use (see also [11]).

The second column of the Table gives the results from the extended Hückel theory of Hoffmann. Although the absolute values are often not too good, several trends are well reproduced. For methane and ethane the directly bonded CH coupling is about equal, which result is difficult to obtain with Pople-Santry theory [5]. The geminal coupling constants are all negative. Thus the "anomalous" positive geminal coupling constants in ethylene and acetylene are not reproduced. The method is rather stable under variation of the  $\alpha$ 's [11].

To neglect all but one-centre integrals is consistent with the Pople-Santry method where overlap is neglected, but not with the extended Hückel theory. Therefore we quote in column 3 results obtained with the inclusion of some two-centre integrals. Although the absolute values are somewhat better, the general trend is not much improved.

Another possibility to improve the Hoffmann type calculations is to let the diagonal elements  $\alpha_\mu$  depend on the nuclear charge (iterative extended Hückel method). We did these calculations using

$$\alpha_\mu = \alpha_\mu^0 + \Delta\alpha_\mu q \quad (7)$$

where  $q$  is the excess gross charge on the atom on which  $\chi_\mu$  is centered.  $\Delta\alpha_\mu$  is the proportionality constant for the correction due to this charge.  $\Delta\alpha_\mu$  was taken  $-11.90$  eV for carbon and  $-14.00$  eV for hydrogen. The results differ not significantly from those obtained from the normal Hoffmann calculations. The somewhat better results of Polezzi *et al.* [12] with the same type of iterative calculations, are probably due to the use of a basis of SCF atomic orbitals.

In all our calculations we used for  $s_H^2(0)$  and  $s_C^2(0)$  atomic SCF values of 0.5500 resp. 2.767 [1]. Better absolute agreement can probably be obtained by treating these quantities as parameters. We think this is a better procedure than the scaling method of Amos [8]. In the latter case all coupling constants are scaled with the same factor.

Without going into the question of the theoretical justification of the various methods, we conclude that the extended Hückel theory of Hoffmann provides a valuable empirical scheme for correlating this range of coupling constants. In this aspect it is superior to the original Pople-Santry theory.

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