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Molecular Orbital Calculations of Nuclear Spin Coupling Constants. I. Preliminary Results for Proton-Proton Coupling Constants

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Molecular orbital calculations of proton-proton coupling constants are made for simple hydrocarbons and some other compounds with heteroatoms using the equation proposed by Pople and Santry. In the present treatment, a molecular orbital is given by a linear combination of valence atomic orbitals. The calculations for protons separated by two and three bonds lead to positive or negative constants, nearly all of which are compatible with the experimental values.

Most previous theoretical work on the proton-proton spin coupling constants has been carried out by the valence bond theory;¹⁾ this work has been successful in calculating the coupling constants for vicinal protons, but it has led to some erroneous predictions for geminal protons. On the other hand, a molecular orbital theory of the nuclear spin coupling constant has been presented by McConnell.²⁾ In this approximation the second-order perturbation energies are simplified by replacing the electronic excitation energies of all the triplet states by an appropriate average. This theory has, however, the disadvantage of predicting all spin coupling constants to be positive. It has recently been pointed out by Pople and Santry³⁾ that a molecular orbital theory can obtain a proton-proton coupling constant, $J_{\mathrm{HH}'}$, of either sign if the approximation of a "mean excitation energy" is excluded. It has been shown⁴⁾ that Pople and Stantry's treatment is fairly successful for qualitative interpretations of geminal proton-proton coupling constants. They have also recently

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1) M. Karplus and D. H. Anderson, *J. Chem. Phys.*, **30**, 6 (1959); H. S. Gutowsky, M. Karplus and D. M. Grant, *ibid.*, **31**, 1278 (1959).

2) H. M. McConnell, *ibid.*, **24**, 460 (1956).

3) J. A. Pople and D. P. Santry, *Mol. Phys.*, **8**, 1 (1964).

4) J. A. Pople and A. A. Bothner-By, *J. Chem. Phys.*, **42**, 1339 (1965).

extended their MO treatment of the coupling constant to the numerical calculation of the $J_{HH'}$ values of simple hydrocarbons⁵⁾ using a molecular orbital theory of hydrocarbons⁶⁾; it has been shown that the agreement of the calculated values of $J_{HH'}$ with the experimental results is generally satisfactory.

In the present paper, a further calculation is made for proton-proton coupling constants, $J_{HH'}$, between geminal hydrogen atoms and vicinal ones in simple hydrocarbons and some other compounds with heteroatoms, using molecular orbitals different from those used in Pople and Santry's treatment. In our treatment, molecular orbitals are expressed by linear combinations of valence atomic orbitals, taking account of resonance integrals between atomic orbitals on the non-bonded atoms. The present treatment is considered to be more suitable for calculating the $J_{HH'}$ value for a molecule whose structure is complicated and in which hybridization is not certain.

Theoretical

Assuming that the Fermi contact term is most important in the proton-proton coupling mechanisms and that only one-center integrals need be taken into account, the proton-proton coupling constant, $J_{HH'}$, is given by the equations³⁾:

$$J_{HH'} = h(4\beta\gamma_H/3)^2 s_h{}^4(0)\pi_{hh'} \tag{1}$$

$$\pi_{hh'} = -4\sum_{i}^{occ}\sum_{j}^{unocc} C_{ih}C_{ih'}C_{jh}C_{jh'}(\varepsilon_j-\varepsilon_i)^{-1} \tag{2}$$

where β is the Bohr magneton; γ_H, the magnetogyric ratio of a proton, and $s_h(0)$, the magnitude of a hydrogen 1*s* atomic orbital at the nucleus. The notation, $\pi_{hh'}$, is the "mutual polarizability" for the hydrogen 1*s* orbitals, *h* and *h'*. In calculating the value of $\pi_{hh'}$, the molecular orbital coefficients and energies obtained in the following way are substituted into Eq. (2).

The molecular orbitals, φ_i, are approximated by linear combinations of valence atomic orbitals, χ_μ, of all the atoms in a molecule, that is, the 1*s* orbital of a hydrogen atom, the 2*s*, $2p_x$, $2p_y$ and $2p_z$ orbitals of a carbon atom, and so on:

$$\varphi_i = \sum_\mu C_{i\mu}\chi_\mu \tag{3}$$

Molecular orbitals can be obtained by solving the following linear equations without overlap integrals⁷⁾:

$$\sum_\nu (H_{\mu\nu} - \varepsilon_i\delta_{\mu\nu})C_{i\nu} = 0 \tag{4}$$

where ε_i is a root of the secular equation:

$$|H_{\mu\nu} - \varepsilon_i\delta_{\mu\nu}| = 0 \tag{5}$$

The Coulomb integral, $H_{\mu\mu}$, is taken as the negative value of the valence-state ionization potential, $-I_\mu$, which is listed in Table 1, while the resonance integral, $H_{\mu\nu}$, is taken as Eq. (6) and all interactions between the non-bonded atoms are taken into account.

$$H_{\mu\nu} = KS_{\mu\nu}(H_{\mu\mu} + H_{\nu\nu})/2 \tag{6}$$

In Eq. (6) $S_{\mu\nu}$ is the overlap integral between valence atomic orbitals, χ_μ and χ_ν, of the Slater type and the *K* constant is assumed to be unity. The bond angles and distances required for the calculation of $S_{\mu\nu}$ are cited from Sutton's compilation.⁹⁾ In calculating $J_{HH'}$ with Eq. (1), we take $s_h(0)$ to be the central value of a Slater hydrogen 1*s* orbital with Z=1.2.

Results

The calculated values of $J_{HH'}$ are listed in Table 2 and are there compared with the experimental values. These are generally satisfactory with a few exceptions, though the calculated values are rather small, particularly for formaldehyde. The present calculation can lead to a geminal proton-proton coupling constant, $^2J_{HH'}$, of either sign, constants which could not be obtained by the valence bond studies.¹⁾ All the calculated coupling

TABLE 1. COULOMB INTEGRAL OF VARIOUS ATOMIC ORBITALS (eV)

Atom	Orbital				
	1*s*	2*s*	2*p*	3*s*	3*p*
Hydrogen	−13.60	—	—	—	—
Carbon	—	−21.43	−11.42	—	—
Nitrogen	—	−27.50	−14.49	—	—
Oxygen	—	−35.30	−17.76	—	—
Chlorine	—	—	—	−25.26	−15.09

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5) J. A. Pople and D. P. Santry, *Mol. Phys.*, **9**, 311 (1965).

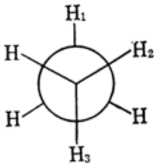
6) J. A. Pople and D. P. Santry, *ibid.*, **7**, 269 (1964); **9**, 301 (1965).

7) If overlap integrals are not neglected, our molecular orbital is exactly equivalent to the extended Hückel orbital given by Hoffmann.⁸⁾ The reason why $S_{\mu\nu}$ is neglected in Eq. (4) will be discussed below.

8) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

9) L. E. Sutton, editor, "Interatomic Distances," The Chemical Society, London (1958).

TABLE 2. CALCULATED AND OBSERVED COUPLING CONSTANTS FOR PROTONS SEPARATED BY TWO AND THREE BONDS

Molecule		J(Calcd.) cps	J(Obs.)[a] cps
Methane	$^2J_{HH'}$	-3.93	-12.4
Methanol	$^2J_{HH'}$	-4.88	-10.8
Ethane (Staggered)	$^3J_{H_1H_2}$	$+0.66$	$+2.5$[b]
	$^3J_{H_1H_3}$	$+8.21$	$+16.0$[b]
Ethylene	$^2J_{HH'}$	-2.02	$+2.5$
	$^3J^{vic}_{cis}$	$+3.79$	$+11.6$
	$^3J^{vic}_{trans}$	$+13.51$	$+19.1$
Vinyl chloride	$^2J_{HH'}$	-3.03	-1.3
	$^3J^{vic}_{trans}$	$+9.91$	$+14.7$
	$^3J^{vic}_{cis}$	$+1.36$	$+7.5$
Formaldehyde	$^2J_{HH'}$	$+2.08$	$+40.2$
Acetylene	$^3J_{HH'}$	$+7.43$	$+9.5$[c]
Cyclopropane	$^2J_{HH'}$	-2.95	-4.5
	$^3J^{vic}_{cis}$	$+1.83$	$+9.2$
	$^3J^{vic}_{trans}$	$+3.83$	$+5.4$
Ethyleneimine	$^2J_{HH'}$	-2.83	$+2.0$
Allene	$^2J_{HH'}$	-11.45	± 9.6[d]
	$^4J_{HH'}$	$+0.02$	—
Methyl acetylene	$^2J_{HH'}$	$+5.80$	—
Acetonitrile	$^4J_{HH'}$	$+0.03$	—
	$^2J_{HH'}$	-5.87	± 16.9

a) Observed values from Ref. 3, or reference therein unless otherwise specified.
b) This value is obtained from empirical relationship between the vicinal coupling constant and the dihedral angle between protons (Ref. 9).
c) R. M. Lynden-Bell and N. Sheppard, *Proc. Roy. Soc.*, **A269**, 385 (1964).
d) The value in $H_2C=C=C-(CH_3)_2$; This is expected to be negative (Ref. 3).

constants of protons separated by three bonds, $^3J_{HH'}$, have a positive sign and reasonable values, values which are in good agreement with the experimental results. Some calculations for the long-range coupling case, $^4J_{HH'}$, give too small values.

Geminal Coupling. The geminal coupling constants, $^2J_{HH'}$, of the methyl group have been calculated for methane, methanol, acetonitrile, and methyl acetylene; all of them are negative. Calculations for the last two compounds have been carried out in order to examine the hyperconjugative effect of the methyl group with adjacent π-bonds on the value of $^2J_{HH'}$. Although the calculated values are rather small, the trend of the negative shift of the calculated $^2J_{HH'}$ values for acetonitrile and methyl acetylene is in accordance with that of the experimental values. This hyperconjugative effect has also been pointed out by Pople and Bothner-By.[4] The geminal coupling constant for the sp^2 hybridized system has either sign, and the values for ethylene and butadiene are calculated to be negative, which is in conformity with the experimental results. However, the trend of the negative shift of $^2J_{HH'}$ from ethylene to vinyl chloride is also in agreement with the observed results. The calculated value of $^2J_{HH'}$ has a tendency to be negative; this is also true for the positive value of the calculated $^2J_{HH'}$ value for formaldehyde, which is too small in comparison with the large positive observed value. The large negative value of $^2J_{HH'}$ for allene may be due to a strong hyperconjugation, as has been expected by an MO interpretation of the geminal coupling constant.[4] For highly-strained three-membered cyclic compounds, the calculated geminal coupling constant is fairly satisfactory for cyclopropane, whereas the constants become too negative for such compounds as ethyleneimine and ethylene oxide with the heteroatom in the ring.

Vicinal Coupling. The calculated values of the vicinal coupling constant, $^3J_{HH'}$, for ethane (staggered), ethylene and vinyl chloride seem satisfactory. The *vic-cis* coupling constant of cyclopropane is too small, and the order of the *vic-cis* coupling, $^3J^{vic}_{cis}$, and the *vic-trans* coupling, $^3J^{vic}_{trans}$, is opposite to the experimental results.

Discussion

Before discussing our results, it should be mentioned that the present treatment becomes just equal to an extended Hückel method when the overlap integral is included.[8] We neglected the overlap integral in the extended Hückel orbital because the values of $J_{HH'}$ calculated using an extended Hückel orbital are too negative, especially in the case of the *gem* coupling constant. This may be due to the disadvantage that the orbital energy of the unoccupied orbital is too high in an extended Hückel orbital[8] and that the difference in the orbital energies in Eq. (2), $\varepsilon_j-\varepsilon_i$, is large. Therefore, the overlap integrals in the secular equation were neglected in order to obtain a favorable value of $\varepsilon_j-\varepsilon_i$,[10] leading to an improved value of $J_{HH'}$. This difficulty has also been fairly well overcome in the recent work by Fahey *et al.* by including the two-center integral in Eq. (1).[11] However, the contribution of the two-center integral is at most a few percent, and one of our aims in this study was to find the main factor contributing to $J_{HH'}$ qualitatively from a theoretical

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[10] When $S_{\mu\nu}$ is neglected, the orbital energies, particularly of unoccupied orbitals, become lower.
[11] R. C. Fahey, G. C. Graham and R. L. Piccioni, *J. Am. Chem. Soc.*, **88**, 193 (1966).

TABLE 3. THE CONTRIBUTION OF ELECTRONIC TRANSITIONS FROM EACH OCCUPIED ORBITAL TO UNOCCUPIED ORBITALS FOR METHANE

Electronic transition[a]		Contribution to $^2J_{HH'}$, cps	Electronic transition[a]		Contribution to $^2J_{HH'}$, cps
Occ	Unocc		Occ	Unocc	
8	4 s → a*	+24.1	6	4 a → a*	−113.2
	3 s → s*	−5.2		3 a → s*	+24.5
	2 s → s*	−6.9		2 a → s*	+32.1
	1 s → s*	−9.6		1 a → s*	+43.9
7	4 s → a*	+56.0	5	4 s → a*	+ 0.6
	3 s → s*	−12.1		3 s → s*	− 0.1
	2 s → s*	−15.9		2 s → s*	− 0.2
	1 s → s*	−21.7		1 s → s*	− 0.2
			Total		− 3.9 (cps)

a) Numbering and symmetry of orbitals are shown in Fig. 1.

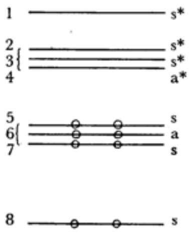

Fig. 1. Molecular orbitals of methane.

point of view, by the aid of the concise expression of Eq. (1). Hence, in the present study we retained only the one-center integral and neglected overlap integrals.

Throughout the numerical calculation of J_{HH} , it has been made clear that the value of $J_{HH'}$ depends to a large extent on the contribution of electronic transitions from the higher-occupied orbital, which is antisymmetric with respect to the hydrogen 1*s* orbitals, *h* and *h'*, to the unoccupied orbitals, with the exception of the case for *vic* coupling constants. The sign of the calculated $J_{HH'}$ value is determined mainly by means of the contribution of this orbital, which is shown for methane, as an example, in Table 3. This is also true for the MO calculation of $J_{HH'}$ of methane, using more exact SCF orbitals, recently given by Loève and Salem.[12] However, in our calculation the contribution of electronic transitions from each occupied orbital to unoccupied orbitals is smaller, probably because in our simple MO treatment the transition energy, $\varepsilon_j - \varepsilon_i$, is rather large, resulting in a small calculated value of $J_{HH'}$.

Now, it seems worthwhile to examine which particular electronic transition, $\varphi_i \rightarrow \varphi_j$, makes the main contribution to the coupling constant in various coupling cases. In the case of the *gem* coupling constant with a minus sign, the main contribution results from the *a*→*a** transition. For formaldehyde with a plus *gem* coupling constant, the *a*→*s** transition contributes greatly. In the *vic* coupling constant with a plus sign for all compounds, the *s*→*a** transition (for *trans* coupling) and the *a*→*s** transition (for *cis* coupling) make the main contributions to the total coupling constant.

Our calculations of $J_{HH'}$ for the compounds with oxygen and nitrogen heteroatoms give unsuccessful values which are too negative. This may be due to the parametrization of $H_{\mu\nu}$ for heteroatoms in our MO calculation. It should also be noted that substantial contributions to the vicinal and long-range coupling constant in the unsaturated system arise by the polarization of the π-electrons,[13] which has not been treated in our study.

The calculations were carried out on the IBM 7090 at the Japan IBM Co., with the permission of the UNICON Committee, whose help we acknowledge.

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[12] P. Loève and L. Salem, *J. Chem. Phys.*, **43**, 3402 (1965).

[13] H. M. McConnell, *J. Mol. Spectry.*, **1**, 11 (1957); M. Karplus, *J. Chem. Phys.*, **33**, 1842 (1960).