Theoret. chim. Acta (Berl.) 1, 222—225 (1963)

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Studies of Delocalized Electron Bonding

II. The Effect of Additional Resonance Structures on the Bonding between Protons in Methane

By

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Valence Bond calculations are made using the methane-type models, CH_2, CH_3, and CH_4. The calculated proton spin-spin coupling constants are found to depend on the complexity of the model. These coupling constants are related to the exchange order and bond order, which are useful as explicit measures of the extent of delocalized electron bonding.

An den Modellen vom Methantyp: CH_2, CH_3 und CH_4 werden Valenzstrukturrechnungen ausgeführt. Es ergibt sich, daß die errechneten Spin-Spin-Kopplungskonstanten der Protonen vom Umfang des Modells abhängen. Diese Kopplungskonstanten werden mit Austausch- und Bindungsordnung verknüpft, die als explizites Maß für die delokalisierte Elektronenbindung von Nutzen sind.

Des calculs sur les modèles du type méthane: CH_2, CH_3 et CH_4 sont faits dans le cadre de la méthode de la mésomérie. On trouve que les constantes de couplage spin-spin protonique dépendent de la complexité du modèle. Ces constantes de couplage sont liées aux indices d'échange et de liaison, quantités qui peuvent servir de mesures explicites de la délocalisation de la liaison électronique.

1. Introduction

A procedure commonly used for the simplification of quantum mechanical calculations is the partitioning of the molecule into various segments, only one of which contains the essential structural features on which attention is focused. For example, this partitioning may take the form of a separation of the electrons into σ and π orbitals, as in the simple molecular orbital calculations of aromatic systems.

Simplified models of a different type have been used recently in valence bond calculations of rotational barriers [*4, 6, 7, 12*] and nuclear spin-spin coupling constants [*1, 5, 10, 11*], in which σ bonding is of predominant interest. Certain atoms and valence electrons have been disregarded in these calculations, thereby reducing the order of the secular determinants which must be solved. This implies that the number of resonance structures contributing to the ground state of the molecule is greatly reduced.

The validity of this approximation for certain calculations has recently been questioned by HECHT [*7*], who suggested that the neglect of contributing resonance structures might have a marked effect on the apparent degree of delocalized bonding. The methane molecule has been chosen to illustrate these effects because, a) the CH_2 fragment has often been used as a model for calculations of magnetic resonance parameters, b) the exchange integrals necessary for the calculations are well known, c) the CH_4 molecule with its eight valence electrons can be easily considered in its entirety, and, d) the experimental nuclear spin-spin coupling constant is available for comparison.

2. Calculations

Three independent calculations, I, II, and III, have been made using standard valence bond techniques. The models used for these calculations are CH_2, CH_3, and CH_4, respectively, as shown in Fig. 1. These models all contain hydrogen atoms tetrahedrally bound to carbon. I and II can be regarded as derived from the usual eight-electron CH_4 model for methane (III) by the abstraction of hydrogen atoms together with the corresponding directly bonded carbon electrons.

Four exchange integrals are necessary for the evaluation of the matrix elements: α, the integral between a hydrogen orbital and a directly bonded carbon orbital (*ab, cd, ef, gh*); β, the integral between hydrogen orbitals (*bd, bf, bh, df, dh, fh*); γ, the integral between carbon orbitals (*ac, ae, ag, ce, cg, eg*); and δ, the integral between a hydrogen orbital and a carbon orbital to which it is not directly bonded (*bc, be, bg, ad, de, dg, af, cf, fg, ah, ch, eh*). The following empirical values found by KARPLUS and ANDERSON [*10*] have been used in the present work: $\alpha = -3.80$ e.v., $\beta = -1.00$ e.v., $\gamma = +1.01$ e.v., $\delta = +0.233$ e.v.

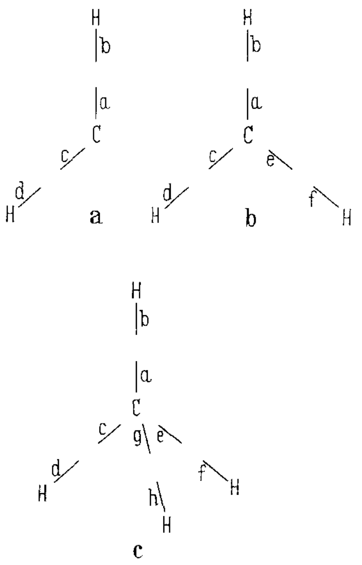

Fig. 1. a Four-electron model used in calculation I, b Six-electron model used in calculation II, c Eight-electron model used in calculation III

In as much as the wave function is independent of the value of the Coulomb integral, the exchange energy, $W = E - Q$, rather than the total energy, E, has been evaluated in each case. The eight-electron calculation, III, has been previously considered. KARPLUS and ANDERSON [*10*] solved the simplified secular equations obtained by a group theoretical treatment of EYRING, FROST, and TURKEVICH [*3*] in terms of a non-canonical set of valence bond structures. These results have been reevaluated in terms of a canonical set, and are listed below together with the results of calculations I and II:

$$
\begin{aligned}
\text{I}:\ & W = -7.8479 \text{ e.v.};\\
& \Psi = 0.9852\,\psi_{ab,\,cd} + 0.0291\,\psi_{ac,\,bd}\\
\text{II}:\ & W = -12.1430 \text{ e.v.};\\
& \Psi = 1.0414\,\psi_{ab,\,cd,\,ef} - 0.0282\,(\psi_{ab,\,cf,\,de} + \psi_{af,\,be,\,cd} + \psi_{ad,\,bc,\,ef}) +\\
& + 0.0000\,\psi_{af,\,bc,\,de}\\
\text{III}:\ & W = -16.6840 \text{ e.v.};\\
& \Psi = 1.0762\,\psi_{ab,\,cd,\,ef,\,gh}\\
& - 0.0249\,(\psi_{ab,\,ch,\,dg,\,ef} + \psi_{af,\,be,\,cd,\,gh} + \psi_{ah,\,bg,\,cd,\,ef} + \psi_{ab,\,cd,\,eh,\,fg} +\\
& + \psi_{ad,\,bc,\,ef,\,gh} + \psi_{ab,\,cf,\,de,\,gh})\\
& - 0.0035\,(\psi_{ah,\,bc,\,dg,\,ef} + \psi_{ab,\,ch,\,de,\,fg} + \psi_{af,\,bc,\,de,\,gh} + \psi_{ah,\,be,\,cd,\,fg})\\
& + 0.0019\,(\psi_{ah,\,bc,\,de,\,fg} + \psi_{ah,\,bg,\,cf,\,de} + \psi_{ad,\,bc,\,eh,\,fg})
\end{aligned}
\tag{1}
$$

3. Discussion

The table summarizes the results of several calculations based on the above mentioned models.

Table

Calculation	Number of Electrons	Number of v. b. structures	$\Delta W_{res.}$ (e. v.)	$J_{HH'}$ (c. p. s.)	$\eta_{HH'}$ (exchange order)	$p_{HH'}$ (bond order)
I	4	2	0.0099	13.71	— 0.4558	0.0295
II	6	5	0.0290	13.10	— 0.4578	0.0282
III	8	14	0.0560	12.38	— 0.4601	0.0266

Column 1 identifies the calculation, and column 2 indicates the number of valence electrons involved in the corresponding model. Column 3 is the number of canonical valence bond structures which must be considered, as given by the well-known formula,

$$\frac{n!}{\frac{n}{2}!\left(\frac{n}{2}+1\right)!}, \tag{2}$$

where n is the number of valence electrons.

An increased resonance stabilization energy is to be expected using additional structures, as shown in column 4 of the table. The term $\Delta W_{res.}$ is the exchange-resonance energy, calculated by

$$\Delta W_{res.} = W_{calc.} - W_{p.p.}, \tag{3}$$

where $W_{calc.}$ is the exchange energy found by solving the appropriate secular determinant, and $W_{p.p.}$ is the exchange energy of the perfect paired structure.

The proton spin-spin coupling constants, $J_{HH'}$, have been calculated as previously described [*7*] using $\Delta E = 9$ e.v., and are shown in the fifth column of the table. It will be observed that there is a significant decrease in the coupling constant calculated using the more complex models, the difference between $J_{HH'}$ for calculations I and III being about 11%. The value obtained using the eight-electron model is essentially the same as that previously calculated by KARPLUS and ANDERSON [*10*] (with the exception that more digits have been retained in the present work), for which the agreement with the experimental value is excellent [*9*].

It has previously been pointed out that the nuclear spin-spin coupling constant is a sensitive measure of deviations from perfect pairing [*8, 10, 13*]. This can be illustrated as follows: The *exchange order* between the two protons, H and H', is defined as

$$\eta_{HH'} = \sum_i \sum_j C_i C_j \frac{1}{2^{n-x_{ij}}} P_{HH'}, \tag{4}$$

where C_i and C_j are coefficients of the various bond structures in the molecular wave function, $\Psi = \sum_i C_i \psi_i$, n is the number of bonds, x_{ij} is the number of islands in the superposition diagram for structures i and j, and $P_{HH'}$ is the appropriate exchange factor between the protons involved. The exchange order thus defined will assume the values: + 1 for complete bonding, — 2 for complete antibonding, and $-1/2$ for no bonding between H and H'. In as much as small deviations from perfect pairing are anticipated, $\eta_{HH'}$ should be very nearly $-1/2$. The calculated values of the exchange order are listed in column 6 of the table.

It is sometimes more convenient to discuss electron delocalization in terms of *bond order,* which varies from 0 for no bonding to $+1$ for complete bonding between the atoms involved. The bond order can be expressed in terms of the exchange order by

$$p_{HH'} = \frac{1 + 2\,\eta_{HH'}}{3}, \tag{5}$$

which is equivalent to the formula given by PENNEY [*2*, *14*] for the bond order between atoms as a result of delocalized π-electron bonding. The bond order between the protons has been calculated for each model using Equation (5). These results are also listed in the table.

It can easily be shown that the bond order as defined in Equation (5) is related to the nuclear spin-spin coupling constant by the following equation:

$$J_{HH'} = \frac{4.185 \times 10^3}{\Delta E\,(\text{e. v.})}\, p_{HH'}. \tag{6}$$

Thus, $J_{HH'}$ can be used as a direct measure of the bond order between the atoms, H and H', by assuming an appropriate value for ΔE.

In conclusion, it has been shown that the calculated bond order (and hence, also the nuclear spin-spin coupling constant) between the protons in methane depends on the number of resonance structures included in the calculation. These results indicate that care must be exercised in using simplified models for calculations of properties which depend directly on delocalized electron bonding. These considerations become particularly important in larger molecules where many more resonance structures are involved. A calculation of the proton spin-spin coupling constants in ethane, for example, should include 429 resonance structures, as seen from Equation (2), rather than the 5 previously considered [*7*, *11*].

References

[*1*] BARFIELD, M., and D. M. GRANT: J. chem. Physics **36**, 2054 (1962).
[*2*] DAUDEL, R., R. LEFEBVRE, and C. MOSER: „Quantum Chemistry, Methods and Applications,“ New York: Interscience Publishers, Inc., 1959.
[*3*] EYRING, H., A. A. FROST, and J. TURKEVICH: J. chem. Physics **1**, 777 (1933).
[*4*] —, D. M. GRANT, and H. G. HECHT: J. chem. Educ. **39**, 466 (1962).
[*5*] GUTOWSKY, H. S., M. KARPLUS, and D. M. GRANT: J. chem. Physics **31**, 1278 (1959).
[*6*] HARRIS, G. M., and F. E. HARRIS: J. chem. Physics **31**, 1450 (1959).
[*7*] HECHT, H. G.: Theoret. chim. Acta **1**, 133 (1963).
[*8*] —, D. M. GRANT, and H. EYRING: Mol. Physics **3**, 577 (1960).
[*9*] KARPLUS, M., D. H. ANDERSON, T. C. FARRAR, and H. S. GUTOWSKY: J. chem. Physics **27**, 597 (1957).
[*10*] —, and D. H. ANDERSON: J. chem. Physics **30**, 6 (1959).
[*11*] — J. chem. Physics **30**, 11 (1959).
[*12*] — J. chem. Physics **33**, 316 (1960).
[*13*] — J. physic. Chem. **64**, 1793 (1961).
[*14*] PENNEY, W. G.: Proc. Roy. Soc. (London) **A 158**, 306 (1937).

(Received January 22, 1963)