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# The Calculation of Directly Bonded $^{13}$C-H and $^{13}$C-$^{13}$C Coupling Constants using Delocalized Molecular Orbital Theory

By

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The Pople-Santry theory of coupling in $\sigma$-electron systems has been applied to directly bonded CH and CC coupling constants. Calculations on normal hydrocarbons, e.g. $CH_4$, $C_2H_6$, $C_2H_4$, $C_2H_2$, show that the theory can give a satisfactory explanation of such coupling constants, although the values are sensitive to the parameters used in the calculation. The theory has been applied with varying success to the larger hydrocarbons methylacetylene, butadiene and benzene, and to the strained molecules cyclopropane and ferrocene. No difficulty arises in applying the theory to hetero-atomic systems (pyridine and pyrimidine) and the results are quite satisfactory.

Die Pople-Santry Theory über Koppelung in $\sigma$-Elektronensystemen wurde auf CH und CC Koppelungskonstanten direkt gebundener Atome angewandt. Rechnungen für einfache Kohlenwasserstoffe, z. B. $CH_4$, $C_2H_6$, $C_2H_4$, $C_2H_2$ zeigen, daß die Theorie eine zufriedenstellende Erklärung solcher Koppelungskonstanten geben kann, obwohl die Werte empfindlich von den in der Rechnung benutzten Parametern abhängen. Die Theorie wurde mit unterschiedlichem Erfolg auf die größeren Kohlenwasserstoffe Methylazetylen, Butadien und Benzol und auf die gespannten Moleküle Cyclopropan und Ferrocen angewandt. Bei Anwendung der Theorie auf Systeme mit Heteroatomen (Pyridin und Pyrimidin) entsteht keine Schwierigkeit und die Ergebnisse sind zufriedenstellend.

La théorie de Pople et Santry sur le couplage dans les systèmes $\sigma$ d'électrons a été appliquée aux constantes de couplage CH et CC entre atomes liés. Les calcules pour quelques simples hydrocarbures, par example $CH_4$, $C_2H_6$, $C_2H_4$, $C_2H_2$, montrent que la théorie explique satisfaisamment ces constantes, bien que les valeurs dépendent sensiblement des paramètres du calcul. La théorie a été appliquée avec succès variable aux hydrocarbures plus grandes: méthylacétylène, butadiène et benzène et aux molecules tendues: cyclopropane et ferrocène. Des systèmes à hétéroatomes (pyridine et pyrimidine) ne prêtent pas de difficultés, et les résultats sont satisfaisants.

## Introduction

In this paper we give a theoretical analysis of $^{13}$C-H and $^{13}$C-$^{13}$C nuclear spin coupling constants between directly bonded atoms using delocalized molecular orbital theory.

$^{13}$C-H coupling constants ($J_{\text{CH}}$) vary from about 100 to 300 c. p. s., the value depending on the number and the nature of the other atoms attached to the $^{13}$C. Some typical results are shown in Tab. 1 and 2. The value for methane is characteristic for the coupling constants associated with an $sp^3$ hybridized atom in many normal (i. e. unstrained, unsubstituted) hydrocarbons. Likewise ethylene and acetylene are typical for normal $sp^2$ and $sp$ hybridized atoms. For cyclic

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hydrocarbons in which there is internal strain, there are deviations from these typical values, $J_{CH}$ being larger when the ring angle is smaller than the normal valence angle [3, 14] (see Tab. 2). $J_{CH}$ is also increased if electronegative substituents are attached to the $^{13}C$. In polysubstituted compounds this substituent effect is roughly additive [11, 12].

There are less data for $^{13}C$-$^{13}C$ coupling constants $J_{CC}$, but again the values for ethane, ethylene and acetylene seem to be typical for the three hybridization states of carbon (Tab. 1) [5].

The first theories of $J_{CH}$ were based on the observation that for $CH_4$, $C_2H_4$ and $C_2H_2$ $J_{CH}$ is almost exactly proportional to the s-character of the carbon hybrids, i.e. $\frac{1}{4}$, $\frac{1}{3}$ and $\frac{1}{2}$ respectively [15, 22]. This correlation was rationalized by Muller and Pritchard using the following approximations: i) only the Fermi contact term contributes to $J_{CH}$, and in calculating this term only the 2s density at the carbon nucleus and the 1s density at the proton are taken into account; ii) the CH bond can be described by a localized molecular orbital; iii) the excitation energy $\Delta E$ from the ground state to a localized CH triplet state is a constant for all CH bonds. With these assumptions they obtained the following expression for $J_{CH}$.

$$J_{CH} = \frac{C}{\Delta E} \varrho_{CH} = 500 \varrho_{CH} \text{ (in c.p.s.) .} \tag{1}$$

$C$ is a constant, $\varrho_{CH}$ is the s-character of the carbon hybrid, and $\Delta E$ is treated as an empirical parameter chosen to fit $J_{CH}$ for $CH_4$. A valence bond treatment using similar assumptions leads to the same relationship [6].

The application of this simple theory to cyclic or substituted molecules encounters several difficulties. For cyclic hydrocarbons one expects that $\varrho_{CH}$ and therefore $J_{CH}$ should increase with decreasing ring angle. Qualitatively this is what is found, but since it is uncertain to what extent the orbital angles actually follow the imposed geometry, quantitative predictions are difficult to make. For example, if orbital following is complete then one predicts $J_{CH} = 264$ c.p.s. for the $C_5H_5$ ring in ferrocene, whereas the observed value is only 175 c.p.s. [16].

Reasonable results have recently been obtained for strained molecules using the criterion of maximum overlap [2,20]. However, this method is not easily extended to encompass heteroatomic systems because it is necessary to introduce ionic structures into the wave function; so far only a deduction of ionic character from the observed $J_{CH}$ has been attempted [2].

In the case of substituted molecules it has been suggested that an electronegative substituent would increase $\varrho_{CH}$ [1], which is in accord with the observed increase in $J_{CH}$. However, these increased s-characters are often at variance with those deduced from the observed bond angles. Thus $J_{CH}$ for the 2 position in pyrimidine would be consistent with $\sphericalangle$ NCN = 114.5°, whereas the observed angle is about 128° [24]. Similarly in fluoro-formaldehyde $J_{CH} = 267$ c.p.s. [16] which requires $\sphericalangle$ FCO = 108° whereas it is 122° [7]. Clearly it is not possible to reconcile the changes in bond angle with the changes in $J_{CH}$ using a theory based on s-character of localized CH bonds.

The localized bond theory also gives a rather poor account of C-C coupling constants; the ratio between the coupling constants of ethane and acetylene

predicted from $s$-character assuming a constant $\Delta E$ is $\frac{1}{4}$ whereas the observed value is nearer $\frac{1}{5}$. If one allows $\Delta E$ to vary, taking a higher $\Delta E$ for a shorter bond, then the prediction is even worse, with a discrepancy of about 20 c.p.s. for ethylene and 80 c.p.s. for acetylene. Part of this discrepancy may be attributed to a $\pi$-electron contribution, but a value of only 5 c.p.s. for this has been thought appropriate for ethylene [10].

POPLE and SANTRY have recently emphasized that it is only within a rather severe set of approximations that the molecular orbitals of a hydrocarbon can be transferred to a set of completely localized orbitals [17]. Assumptions ii) and iii) of the localized orbital theory are therefore difficult to justify. They have shown that a delocalized MO theory can lead to a satisfactory theory of spin-spin coupling constants [18], and it has been shown that this can explain the effect of electronegative substituents on gem H-H coupling constants [19]. We will proceed to apply this theory to the calculation of $J_{\mathrm{CH}}$ and $J_{\mathrm{CC}}$.

## Summary of the Basic Theory

The POPLE and SANTRY theory [18] is based on delocalized molecular orbitals

$$\psi_i = \Sigma_\mu\, C_{i\mu}\, \Phi_\mu \tag{2}$$

which are constructed from all atomic orbitals $\Phi_\mu$ taking part in bonding: for hydrocarbons these are the carbon $2s$ and $2p$ and the hydrogen $1s$ orbitals. The Fermi contact contribution to a coupling constant is

$$J_{ab} = C\,\pi_{a,b} \tag{3}$$

$\Phi_a$ and $\Phi_b$ are either carbon $2s$ or hydrogen $1s$ atomic orbitals depending on what type of coupling constant is being considered.

$C$ is a constant which depends on the magnetic moments of the nuclei and the densities of orbitals $\Phi_a$ and $\Phi_b$ at the nuclei*, and $\pi_{a,b}$ is the atom-atom polarizability which is given by the usual MO expression

$$\pi_{a,b} = -\,4 \sum_i^{\mathrm{occ.}} \sum_j^{\mathrm{unocc.}} (\varepsilon_j - \varepsilon_i)^{-1}\, C_{ia}\, C_{ib}\, C_{ja}\, C_{jb}\ . \tag{4}$$

$\varepsilon$ being the energy of a molecular orbital. If the excitation energies are replaced by an average $\Delta E$, then (3) may be simplified to MCCONNELL's relationship [13]

$$J_{ab} = \frac{C}{\Delta E}\, P_{ab}^2 \tag{5}$$

where $P_{ab}$ is the bond order

$$P_{ab} = 2 \sum_i^{\mathrm{occ.}} C_{ia}\, C_{ib} = -\, 2 \sum_j^{\mathrm{unocc.}} C_{ja}\, C_{jb}\ . \tag{6}$$

With the further assumption of localized orbitals expression (5) reduces to (1). The molecular orbitals are calculated using an extended Hückel model in which all overlap integrals are taken to be zero, and resonance integrals between orbitals on non-adjacent atoms are also zero. The effect of relaxing the latter restriction will be discussed.

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* We used $C = 7.89 \times 10^3$ and $C = 9.98 \times 10^3$ c.p.s. ev for $J_{\mathrm{CH}}$ and $J_{\mathrm{CC}}$ respectively [18].

## Calculations on Small Hydrocarbons

We will begin by showing that the delocalized and localized MO methods i.e. expressions (3) and (4) respectively can lead to quite different results. Consider the following symmetrical $CH_n$ molecules: $CH_4$ tetrahedral; $CH_3$ planar trigonal; $CH_2$ linear. Following POPLE and SANTRY's discussion of $CH_4$ [18] we note that each molecule has only two MO's, one bonding, one antibonding, which belong to the totally symmetric irreducible representation and which therefore contain the carbon $2s$ orbital. It follows that only one term in (4) contributes to $\pi_{s,h}$ namely that for which $i$ and $j$ are both totally symmetric orbitals, and the McCONNELL relationship is equivalent to (3). With the approximation $\alpha_s = \alpha_h$ we have $P_{sh}^2 = 1/n$ and $\Delta E = 2\sqrt{n}\beta_{sh}$, hence $J_{sh} = C/2\beta_{sh}\,n^{3/2}\star$.

The localized bond approach gives $J = C/n\Delta E$. If one fits the parameters for $CH_4$, then the localized orbital calculation gives 167 and 250 c.p.s. for $CH_3$ and $CH_2$, whereas the delocalized orbital calculation gives 192 and 354 c.p.s. respectively.

In the localized orbital theory there is no difference between the $J_{CH}$-values for $CH_3$ and $C_2H_4$, or between those for $CH_2$ and $C_2H_2$. This equivalence does not arise in the delocalized orbital method, except for a very special choice of the parameters; e.g. $J_{CH}$ for $CH_2$ and $C_2H_2$ are equal only if all $\alpha$'s are equal and if all $\beta$'s are equal. From a calculation using the more realistic parameters: $\alpha_h = -13.6$, $\alpha_s = -16.0$, $\alpha_p = -11.2$ ev, $\beta_{\mu\nu} = k\,S_{\mu\nu}$ (which were suggested by POPLE and SANTRY in their first paper on delocalization in paraffins [17]), with $S_{\mu\nu}$ calculated from Slater orbitals ($\zeta_h = 1.2$, $\zeta_s = \zeta_p = 1.625$) and $k = -7.3$ ev one obtains the results shown in the first column of Tab. 1a.

If one considers that for these parameters $J_{CH}$ for $CH_2$ is reduced by only 13 c.p.s., it is surprising to find a decrease of almost 70 c.p.s. for $C_2H_2$. Careful analysis shows that this large decrease is almost entirely due to the exceptionally low value of $\beta_{\sigma\sigma}$, caused by the overlapping of positive and negative regions of the two $2p_\sigma$ orbitals ($\beta_{\sigma\sigma} \simeq 2.0$ ev, whereas all other $\beta$'s have a value of 3.0 to 3.5 ev).

If the overlap integrals are evaluated using SCF atomic orbitals for carbon rather than Slater orbitals, then $\beta_{\sigma\sigma}$ is reduced by a further factor of 2. Calculations using parameters based on these overlap-integrals with $k = -7.3$ ev give the results shown in column 2 of Tab. 1a. There is a further decrease in $J_{CH}$ for $C_2H_2$, and as a result the agreement with experiment is now quite satisfactory. Qualitatively one can say that the $s$-orbitals are being used preferentially for the C-C bond, which leads to a large reduction in $J_{CH}$ relative to the value calculated for $CH_2$. These calculations strongly suggest that the excellent results for $J_{CH}$ given by the localized bond approach must be a coincidence.

Using the same parameters as in the calculations of $J_{CH}$, we have obtained values of $J_{CC}$, which are shown in Tab. 1b. The results using SCF orbitals are

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$\star$ if $\alpha_s \neq \alpha_h$, the result expanded to the first term in $\dfrac{\alpha_s - \alpha_h}{\beta_{sh}}$ is as follows:

$$J_{CH} = \frac{C}{2\,\beta_{sh}\,n^{3/2}}\left[1 - \frac{3}{8}\frac{(\alpha_s - \alpha_h)^2}{n\beta_{sh}^2}\right]$$

For $\alpha_h = -13.6$, $\alpha_s = -16.0$ and $\beta_{sh} = -7.3\,S_{sh}$ (from Slater AO's) this leads to values of 126, 191 and 341 for $CH_4$, $CH_3$ and $CH_2$ respectively.

Table 1 a. *Calculated and observed $J_{CH}$-values* (c.p.s.)

| | 1<br>Slater[a] | 2<br>SCF[a] | 3<br>SCF[b] | 4<br>SCF +<br>l.r.[c] | 5<br>s-char.[d] | 6<br>exp. |
|---|---|---|---|---|---|---|
| methane | (125) | (125) | (125) | 135 | (125) | 125 [15] |
| ethane | 116 | 100 | 115 | 125 | 125 | 125 [10] |
| ethylene | 163 | 134 | 154 | — | 167 | 156 [10] |
| acethylene | 287 | 233 | 252 | 268 | 250 | 249 [10] |

Table 1 b. *Calculated and observed $J_{CC}$-values* (c.p.s.)

| | 1<br>Slater[a] | 2<br>SCF[a] | 3<br>SCF[b] | 4<br>SCF +<br>l.r.[c] | 5<br>s-char.[d] | 6<br>exp. |
|---|---|---|---|---|---|---|
| ethane | 30.4 | 38.2 | 28.4 | 14.7 | (34.6) | 34.6 [10] |
| ethylene | 61.0 | 76.7 | 64.1 | — | 61.5 | 67.6 [10] |
| acethylene | 154 | 186 | 180 | 204 | 138 | 171.5 [10] |

(a) $\alpha_h = -13.6$, $\alpha_s = -16.0$, $\alpha_p = -11.2$, $k = -7.3$ ev.
(b) $\alpha_h = -12.4$, $\alpha_s = -16.0$, $\alpha_p = -13.0$, $k = -7.0$ ev.
(c) as for (b), but including all long range $\beta$'s.
(d) from $J_{CH} = 500\, \varrho_{CH}$, (e) from $J_{CC} = 533\, \varrho_{CC}^2$.

The overlap integrals were evaluated using the following molecular dimensions [23]. Methane and ethane: CH = 1.09, CC = 1.53Å, $\sphericalangle$HCH = 109.5°. Ethylene: CH = 1.08, CC = 1.35Å, $\sphericalangle$HCH = 120°. Acetylene: CH = 1.06, CC = 1.20Å. The carbon and nitrogen SCF AO's used in this paper were taken from [9]; for hydrogen we retained $\zeta_h = 1.2$.

again slightly better than for Slater orbitals. In both cases the results are better than for localized orbital calculations using a constant $\Delta E$ fitted to ethane.

The delocalized orbital calculations give a rather unsatisfactory result for the difference between $J_{CH}$ of $CH_4$ and $C_2H_6$. Presumably if one were willing to treat all the coulomb and resonance integrals as independent empirical parameters one could fit all the experimental data shown in Tab. 1. With the present state of the theory we have not felt that this is worth while. We have, however, examined the effect of varying the coulomb integrals whilst retaining the condition $\beta_{\mu\nu} = k\, S_{\mu\nu}$, and using SCF AO's. We found that the set $\alpha_h = -12.4$, $\alpha_p = -13.0$, $\alpha_s = -16.0$, $k = -7.0$ ev gave the best overall results for $J_{CH}$ and $J_{CC}$ (column 3 of Tab. 1), although there is still an appreciable difference between $J_{CH}$ for $CH_4$ and $C_2H_6$.

Lastly, we have examined the effect of including long range resonance integrals in the calculation. For long range coupling constants, e.g. $J_{HH}$, $J_{CCH}$, $J_{CCCH}$, etc. these long range resonance integrals are important*, and we can anticipate that they may make a contribution of the order of 10 c.p.s. to directly bonded C-C and C-H coupling constants. If one takes the parameters used for column 3 and in addition includes all long range resonance integrals, then the results given in column 4 are obtained. These confirm the sensitivity to long

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* For this reason we have not quoted long range coupling constants, although in our calculation they are obtained along with the directly bonded coupling constants.

range resonance integrals, but the results are rather worse than when the long range terms are neglected, particularly for $J_{CC}$. Further work along these lines must await a detailed study of H-H coupling constants which are more sensitive to the value of the long range resonance integrals and so give a better guide as to the best parameters to use. It is probable that a different value of the constant $k$ may be appropriate for the long range interactions.

We summarize the present position as follows. The delocalized molecular orbital approach can give a satisfactory explanation of $J_{CH}$ and $J_{CC}$ although the quantitative agreement is not better than 10 c.p.s. with the parameters at present examined. The results are sufficiently good to make it worth while extending the calculations to more complicated molecules such as those with heteroatoms or internal bond strain for which the localized bond approach is not very suitable.

## Application to Larger Molecules

Calculations on larger hydrocarbons, based on expression (3) and using the parameters appropriate to columns 1 and 3 of Tab. 1 gave the results shown in Tab. 2; there is little to choose between the two sets of results.

The result for benzene is poor; the theory predicts that $J_{CH}$ should be 20 c.p.s. lower for benzene than for ethylene, whereas the observed values are very similar. This result parallels that for the methane-ethane pair, predicting a lowering of

Table 2. *Calculated and observed coupling constants* (c.p.s.)

| | | $J_{CH}$ | | | | $J_{CC}$ | |
|---|---|---|---|---|---|---|---|
| | | 1 | 3 | exp. | | 1 | 3 |
| methylacetylene | a | 123 | 117 | 132 [15] | i | 57 | 52 |
| | b | 271 | 233 | 248 [15] | ii | 119 | 143 |
| butadiene | a | 157 | 146 | — | i | 54 | 55 |
| | b | 166 | 161 | — | ii | 46 | 43 |
| | c | 152 | 145 | — | | | |
| cyclopropane | | 157 | 161 | 161 [15] | | 8 | 16 |
| ferrocene ($C_5H_5$ ring) | | 158 | 144 | 175 [16] | | 50 | 53 |
| benzene | | 142 | 134 | 159 [15] | | 49 | 51 |
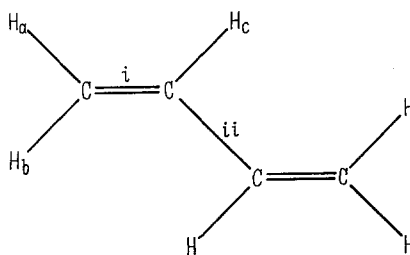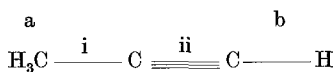


Parameters are the same as in the corresponding column of Tab. 1. Molecular dimensions were as follows [23]. Methylacetylene: $CH_a = 1.09$, $CC_i = 1.46$, $CC_{ii} = 1.20$, $CH_b = 1.06$ Å, $\angle HCH = 109.5°$. Butadiene: $CH = 1.08$, $CC_i = 1.35$, $CC_{ii} = 1.46$ Å, all angles 120°. Cyclopropane: $CH = 1.08$, $CC = 1.53$ Å, $\angle HCH = 118°$. Ferrocene and benzene: $CH = 1.08$, $CC = 1.39$ Å.

$J_{CH}$ when a hydrogen is replaced by a carbon atom which is not observed experimentally.

In view of this weakness of the theory the results for butadiene and methylacetylene must be taken with some caution. For example, the central protons in butadiene are predicted to have a lower $J_{CH}$ than the protons in ethylene, but this is likely to be an artifact of the theory of the type described above. The predicted difference between the two types of outer proton may be more reliable.

Since in the delocalized MO method molecular geometries are reflected in the values taken by the resonance integrals, there are no difficulties in extending the calculations to include strained molecules. The calculated $J_{CH}$ for cyclopropane is in good agreement with experiment, and the increase in $J_{CH}$ for the $C_5H_5$ ring in ferrocene relative to benzene is also satisfactorily reproduced, although the absolute value for $C_5H_5$ is again low. The agreement appears to be as good as for maximum overlap calculations, which give equally good results for cyclopropane [2, 20].

There have been no measured C-C coupling constants for the compounds listed in Tab. 2. The values for benzene, $C_5H_5$ and butadiene all lie between the observed values for ethane and ethylene, which is not unexpected. However, $J_{CC}$ for cyclopropane is predicted to be very low (a result which could also have been obtained from the maximum overlap calculation).
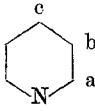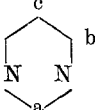
Finally we turn to a calculation on two heteroatomic systems, pyridine and pyrimidine. In Hückel $\pi$-electron theory the dominant effect of replacing CH by N has usually been through the change in the coulomb integral of the atom. Although $\beta_{CN}$ is sometimes taken to be different to $\beta_{CC}$ the results are not usually sensitive to this parameter. For the calculation of coupling constants, however, the situation is quite different, because the results are more sensitive to the values of the resonance integrals than to those of the coulomb integrals. This may be rationalized from the fact that coupling constants are approximately related to bond order, and changes in bond order with coulomb integrals are small (being zero for an alternant system).

Tab. 3 shows C-H coupling constants calculated relative to benzene using the parameters previously discussed. The $\beta_{CN}$ resonance integrals have been taken proportional to the corresponding overlap integrals with the *same* proportionality constant as for $\beta_{CC}$. The coulomb integrals have been taken as 1 ev less than the corresponding carbon coulomb integral\*. This is a value similar to that used in $\pi$-electron theory. The table also shows the results for pyrimidine which are obtained using the same coulomb integrals for carbon and nitrogen (column 4) to illustrate our point that the resonance integrals are the more important parameters. On the whole the results are in qualitative agreement with experiment.

These calculations were based on experimental bond lengths, but with all bond angles taken to be 120°. Experiment suggests that the angles may differ from 120° by a few degrees and if allowance had been made for this, changes in

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\* If one takes the coulomb integrals for nitrogen and carbon equal to the appropriate ionization potential then one is ignoring the effect of electron flow from carbon to nitrogen which tends to smooth out the difference between the core potentials of the carbon and nitrogen. Clearly in a theory which ignores electron repulsion the coulomb integrals must be treated as empirical parameters.

Table 3. $J_{CH}$-values for pyridine and pyrimidine relative to benzene (c.p.s.)

| | | 1 | 3 | 4 | exp. |
|---|---|---|---|---|---|
| (pyridine structure) | a | +27 | +19 | | +20 [12] |
| | b | − 1 | + 5 | | + 4 [12] |
| | c | − 3 | − 3 | | − 7 [12] |
| (pyrimidine structure) | a | +72 | +60 | +43 | +47 [21] |
| | b | +24 | +18 | +20 | +23 [21] |
| | c | 0 | +13 | + 7 | + 9 [21] |

Parameters for columns 1 and 3 see Tab. 1 and text; column 4 as for 3 but with the coulomb integrals for C and N equal. The calculations were performed for simplified geometries: CH = 1.08, CC = 1.39, CN = 1.33 Å, all angles 120°.

the $J_{CH}$-values not greater than 10 c.p.s. would arise. One can therefore say with confidence that the $J_{CH}$-values of these compounds are dominated by a direct effect due to the presence of the hetero-atom, rather than by changes in bond angle. In this context it is interesting to note the similarity between the values in Tab. 3 and the hetero-atom effects suggested by Dischler [3].

The ease with which the delocalized molecular orbital theory tackles the hetero-atomic systems makes it in this respect far superior to the localized bond theories.

## Conclusions

The simple localized bond theories based on the $s$-character of the hybrids are surprisingly successful in explaining the $J_{CH}$-values of the normal hydrocarbons. The results we have obtained on these systems using a delocalised MO theory are definitely poorer, particularly when one compares atoms in the same hybridization state but with different nearest neighbours (e.g. methane-ethane). The delocalized MO theory does seem to be quite successful for the series $CH_4$, $C_2H_4$ and $C_2H_2$, although admittedly the agreement between theory and experiment has only been obtained by a careful choice of some of the empirical parameters involved.

A possible explanation of the methane-ethane discrepancy would be to suppose that the present method overestimates delocalization. Now, although the molecular orbitals obtained by the Pople-Santry method are delocalized, they can always be subjected to an orthogonal transformation which will produce a set of approximately localized bond orbitals [8]. As a measure of the real delocalization present in a molecular orbital scheme one can take the coupling constants between non-neighbouring atoms. For example, with the parameters of column 3 (Tab. 1) we obtain for acetylene $J_{CCH} \simeq 30$ c.p.s. which is to be compared with the experimental value of 50 c.p.s. A localized orbital scheme would give zero. It is clear therefore that the Pople-Santry scheme does give a reasonable amount of delocalization in $\sigma$-electron systems, and that the difficulties encountered probably arise from the choice of parameters, including those for long range interactions.

The most important difference between the Pople-Santry calculations and

those of the localized bond theories is in the sensitivity of $J_{AB}$ in an $ABC$ fragment to the nature of atom $C$.

We stress again the striking difference between our calculations on $CH_2$ and $C_2H_2$, which strongly suggest that the success of the localized bond approach is due to an accidental cancellation between changes in the average excitation energy of a CH bond and deviations of bond order from the $\sqrt{n}$ dependence.

It would appear clear that the delocalized molecular orbital theory cannot at the moment predict coupling constants between directly bonded atoms to better than $10\%$, but deviations of this magnitude can arise from resonance integrals between atoms not directly bonded together, so until these are studied more thoroughly one cannot hope for better. On the other hand the superiority of the theory over the localized bond theories lies in its ability to deal with the coupling between atoms not bonded together, and the ease with which it accounts for substituent effects.

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