following observations about ^{13}C relaxation in small molecules. 1. The relaxation is primarily due to ^1H–^{13}C dipole–dipole interaction if ^{13}C is bonded directly to one or more protons. 2. Spin rotation can be expected to contribute in small molecules, especially at temperatures near the boiling point, and to be a dominant relaxation mechanism for CH_3 groups due to the free internal rotation about the CH_3–R bond. 3.

Chemical shift anisotropy is, in general, not a significant relaxation mechanism. 4. Scalar relaxation only rarely contributes to R_1 and then only when ^{13}C is bonded to an appropriate quadrupolar nucleus, such as ^{79}Br and ^{81}Br, but probably never ^{127}I.

Molecular Orbital Theory of the Electronic Structure of Organic Compounds. IX. A Study of n → π* Transition Energies in Small Molecules[1a]

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Abstract: *Ab initio* minimal basis SCF–CI calculations have been performed on a series of small molecules possessing uv bands which may be attributed to n → π* excitations. The calculated results show that this level of theory can give an adequate description of such transition energies. The changes in transition energies produced by substitution on four chromophores are analyzed in detail.

Organic molecules which contain nitrogen or oxygen in an unsaturated group often possess low-energy uv absorption bands of rather low intensity. These bands are known to be due to the excitation of non-bonding (n) electrons into antibonding π orbitals and have been called n → π* bands by Kasha.[2] Experimental studies of such excitations have led to many correlations between transition energy and the nature and environment of the absorbing group, and there have been many theoretical attempts to explain these data. The earliest theoretical studies were all based on approximate theories which neglected electron interaction.[3] At this level, transition energies are given by the difference of the n and π* one-electron orbital energies, and substituent effects are discussed in terms of the way in which a particular substituent raises or lowers the energies of these orbitals. Although a theory which neglects electron interaction cannot give an overall correct picture of electronic spectra, it has been useful in rationalizing trends within restricted classes of compounds. At the semiempirical level, improvements were obtained by incorporating electron interaction into the theory, but this was usually done in an approximate manner.[4]

Although there have been several *ab initio* molecular orbital studies of n → π* excited states,[5,6] there

has been no systematic study at a uniform level of approximation. The aim of this work is to present such a study of n → π* excited singlet states for a group of small molecules containing the chromophores $>C=O$, $>C=N-$, $-N=N-$, and $-N=O$ and which (1) are acyclic; (2) contain only H, C, N, O, and F; (3) contain up to three heavy atoms (C, N, O, or F); and (4) may be represented in the ground state by a classical valence structure with no formal charges or unpaired electrons associated with any atom. The group of carbonyl compounds has been enlarged to include a greater variety of monosubstituted compounds and some disubstituted molecules, since these are particularly appropriate for examining substituent effects.

For this study each ground state is described by a single determinant of doubly occupied molecular orbitals, ψ_i, each of which is constructed from a minimal basis of Gaussian-fitted Slater-type atomic orbitals ϕ_μ. Wave functions, $\Psi_i{}^l$, describing singly excited configurations are formed from the ground-state wave function by promoting electrons from doubly occupied orbitals ψ_i to virtual orbitals ψ_l. Some allowance for electron reorganization on excitation is then made by permitting mixing of configurations representing different singly excited virtual states.

Quantum Mechanical Method

The quantum mechanical method used is that given in detail in ref 7. The closed-shell ground-state Ψ is rep-

(1) (a) Acknowledgment is made of partial support under National Science Foundation Grant No. GP-9338; (b) NIH Postdoctoral Fellow.
(2) M. Kasha, *Discuss. Faraday Soc.*, No. 9, 14 (1950).
(3) See J. D. Roberts, "Notes on Molecular Orbital Calculations," W. A. Benjamin, New York, N. Y., 1961; or A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961.
(4) See R. G. Parr, "The Quantum Theory of Molecular Electronic Structure," W. A. Benjamin, New York, N. Y., 1964; or O. Sinanoglu and K. B. Wiberg, "Sigma Molecular Orbital Theory," Yale University Press, New Haven, Conn., 1970.

(5) (a) H. Basch, M. B. Robin, and N. A. Kuebler, *J. Chem. Phys.*, 47, 1201 (1967); (b) *ibid.*, 49, 5007 (1968).
(6) J. L. Whitten and M. Hackmeyer, *ibid.*, 51, 5584 (1969).
(7) J. Del Bene, R. Ditchfield, and J. A. Pople, *ibid.*, 55, 2236 (1971).

resented by a single determinant of molecular orbitals ψ_i

$$\Psi = (1/\sqrt{2n!})|\psi_1\bar{\psi}_1\psi_2\bar{\psi}_2\ldots\psi_n\bar{\psi}_n| \qquad (1)$$

each of which is written as a linear combination of atomic orbitals ϕ_μ(LCAO)

$$\psi_i = \sum_\mu c_{\mu i}\phi_\mu \qquad (2)$$

The ϕ functions used in this work are closely related to a minimal basis set of Slater-type atomic orbitals (STO). Each STO is replaced by a sum of four Gaussian-type functions, with exponents and contraction coefficients determined by least-squares methods.[8] The resulting basis set is briefly described as STO-4G. The molecular scale factors are chosen as a standard set,[8] taken as an average of optimized values for the ground states of small organic molecules. As was shown previously,[7] the STO-4G basis set gives excitation energies close to the limit appropriate to pure STO functions.

The LCAO coefficients $c_{\mu i}$ are determined for the ground state by solving the Roothaan equations.[9] The virtual-orbital solutions of these equations are then used to construct representations of the excited states of the molecule. For example, the singlet wave function $^1\Psi_i^l$ describing the configuration in which one electron is promoted from an occupied orbital ψ_i to an unoccupied one ψ_l is given by

$$^1\Psi_i^l = \{|\psi_1\bar{\psi}_1\ldots\psi_i\bar{\psi}_l\ldots\psi_n\bar{\psi}_n| - $$
$$|\psi_1\bar{\psi}_1\ldots\bar{\psi}_i\psi_l\ldots\psi_n\bar{\psi}_n|\}/\sqrt{2} \qquad (3)$$

This description of excited states is then improved by allowing for the mixing of configurations corresponding to different electronic excitations (CI). As a first approximation, the excited-state wave functions can be written as linear combinations of single excitation functions Ψ_i^l

$$^1\Phi = \sum_i^{occ} \sum_l^{unocc} B_{il}{}^1\Psi_i^l \qquad (4)$$

where the coefficients B_{il} are determined by the variation principle. It is important to note that if the ground-state wave function is truly self-consistent, there will be no mixing between it and any single excitation function $^1\Psi_i^l$. Since for many organic molecules, it is not possible to include all such singly excited configurations in the CI expansion, it is necessary to limit the number of configurations considered. Recently, we proposed[7] a well-defined method for selecting a subset of configurations in terms of an expansion parameter M. This subset consists of all singly excited configurations formed from the M highest occupied and the M lowest energy virtual orbitals. For minimal basis calculations on some of the smaller molecules, M is determined by the number of virtual molecular orbitals (an upper limit of $M = 8$ has been set). It was shown in our earlier work[7] that this method gives results close to those of a full first-order CI calculation and is capable of giving reliable results for n → π* transition energies.

(8) W. J. Hehre, R. F. Stewart, and J. A. Pople, J. Chem. Phys., 51, 2657 (1969).
(9) C. C. J. Roothaan, Rev. Mod. Phys., 23, 69 (1951).

Table I. Calculated and Observed Vertical Singlet n → π* Transition Energies and One-Electron Orbital Energies (eV)

Molecule	ϵ_n	ϵ_{π^*}	ΔE(n → π*) Calcd	ΔE(n → π*) Obsd[a,b]
HCHO	−9.84	7.48	4.05	4.20
CH₃CHO	−9.31	7.79	4.23	4.28
NH₂CHO	−8.88	9.18	5.46	5.66[c]
OHCHO	−9.89	7.97	5.37	5.64
FCHO	−10.61	7.31	5.14	5.64
CH₃CH₂CHO[g]	−9.22	7.83	4.27	4.23
CH₂CHCHO (trans)	−9.42	5.86	3.86	3.72
(CHO)₂ (trans)	−9.39	4.98	3.10	2.72
CHCCHO	−10.29	5.95	3.86	3.71
(CH₃)₂CO	−8.84	7.99	4.37	4.44
CH₃NH₂CO	−8.41	9.38	5.57	
CH₃(OH)CO[h]	−9.35	8.31	5.20	5.89[d]
CH₃(F)CO	−9.97	7.71	5.40	
(NH₂)₂CO	−8.08	10.71	6.75	
NH₂(OH)CO[i]	−8.83	9.68	6.52	
NH₂(F)CO	−9.49	9.06	6.34	
(OH)₂CO[j]	−9.72	8.56	6.18	
OH(F)CO[k]	−10.51	7.89	5.97	
F₂CO	−11.22	7.18	5.85	6.49
HNO	−9.24	5.80	1.69	(1.61–2.25)
CH₃NO	−8.69	6.16	1.78	(1.75–2.10)
NH₂NO	−9.19	6.36	2.90	
OHNO	−9.47	5.68	2.79	(3.22–3.94)
FNO	−10.66	4.89	3.03	(3.70–4.77)
HNNH (cis)	−9.66	6.40	4.37	
CH₃NNH (cis)	−9.30	6.68	4.63	
NH₂NNH (cis)	−9.92	6.83	5.72	
OHNNH (cis)	−10.05	6.42	5.54	
FNNH (cis)	−11.14	5.67	5.75	
HNNH (trans)	−8.98	6.61	3.37	3.55[e]
CH₃NNH (trans)	−8.64	6.88	3.58	3.57[f]
NH₂NNH (trans)	−9.04	7.12	4.42	
OHNNH (trans)	−9.98	6.32	4.37	
FNNH (trans)	−10.05	5.87	4.22	
CH₂NH	−9.99	7.36	5.83	
CH₂NCH₃	−9.70	7.48	5.96	
CH₂NNH₂	−10.47	7.71	6.89	
CH₂NOH	−9.75	7.34	6.23	
CH₂NF	−10.54	7.21	6.35	
CH₃CHNH (cis)	−9.50	7.61	5.88	
NH₂CHNH (cis)	−9.28	8.47	6.85	
OHCHNH (cis)	−9.94	7.86	6.72	
FCHNH (cis)	−10.47	7.21	6.50	
CH₃CHNH (trans)	−9.65	7.62	6.03	
NH₂CHNH (trans)	−9.17	8.53	6.74	
OHCHNH (trans)	−9.96	7.81	6.66	
FCHNH (trans)	−10.26	7.22	6.19	

[a] Observed data are λ_{max} energies. Band widths are given in parentheses. [b] Except where noted, experimental data are taken from G. Herzberg, "Electronic Spectra of Polyatomic Molecules," Van Nostrand, Inc., Princeton, N. J., 1967. [c] Reference 5b. [d] E. E. Barnes and W. T. Simpson, J. Chem. Phys., 39, 670 (1963). [e] A. Trombetti, Can. J. Phys., 46, 1005 (1968). [f] H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," Wiley, New York, N. Y., 1964. [g] CCCO cis. [h] HOCO trans; HCCO cis. [i] HOCO cis. [j] H₁OCO cis; H₂OCO trans. [k] HOCO trans. All other conformations are those of lowest energy from ref 10 and 11.

Results and Discussion

For this study we have taken the geometry of both ground and excited states to be that defined by the standard geometrical model for ground states presented elsewhere.[10,11] Thus, our calculated excitation energies are to be compared with experimental *vertical* excitation energies corresponding to the maximum of the Franck–Condon envelope. In Table I we present

(10) J. A. Pople and M. S. Gordon, J. Amer. Chem. Soc., 89, 4253 (1967).
(11) L. Radom, W. J. Hehre, and J. A. Pople, ibid., 93, 289 (1971).

calculated vertical n → π* excitation energies and the available experimental data for molecules containing the chromophores >C=O, >C=N-, -N=N-, and -N=O. The results show that calculated n → π* excitation energies are in good overall agreement with experimental values. The results for each type of chromophore are discussed in some detail in the following sections.

(a) Molecules Containing the >C=O Group. General substituent effects in a series of carbonyl compounds are well reproduced by these calculations as shown in Table I. In particular, for XCHO molecules, the excitation energies are found to decrease in the order X = NH_2, OH, F, CH_3. In this connection we note the following points. (1) As X varies, σ withdrawal by X (as measured by appropriate Mulliken populations[12] in CHO) increases in the order

$$CH_3 < NH_2 < OH < F$$
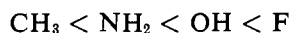
(2) as X varies, π donation by X increases in the order

$$CH_3 < F < OH < NH_2$$
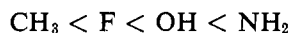
It is of interest to examine the effects of σ withdrawal and π donation on the one-electron orbital energies ϵ_n and $\epsilon_{\pi*}$ which are also listed in Table I. The single configuration result for the singlet excitation energy is

$$\Delta E_i^1 = \epsilon_l - \epsilon_i - J_{il} + 2K_{il} \qquad (5)$$

where J and K are appropriate Coulomb and exchange two-electron integrals. It is found that for XCHO, variation of $\epsilon_l - \epsilon_i$ is greater than variation of the two-electron part of (5), suggesting that substituent effects, for the case where X is not an unsaturated group, can be rationalized mainly in terms of changes of the orbital energies. There are two effects associated with π donation by X. The first and more direct effect is an increase of the π* one-electron orbital energy. The second effect is a consequence of the fact that π donation by X increases the negative charge on the carbonyl oxygen relative to HCHO. This indirectly causes the oxygen lone-pair orbital to be less tightly bound (relative to HCHO) due to the lowering of the oxygen effective nuclear charge. On the other hand, the primary effect of σ withdrawal by X is a stabilization of the n orbital. There is, however, a further effect of σ withdrawal. On σ withdrawal by X, the effective nuclear charges of carbon and oxygen increase, and this leads to a stabilization of the π* orbital. Thus the changes in n → π* transition energy as X is varied are determined by a competition among these four effects. In many cases the more direct effects predominate, but in some cases the secondary effects become quite large. For example, the energy of the π* orbital in HFCO is less than that in HCHO in contrast to the order expected by considering the π-donating ability of F.

Thus it is worthy of note that although the n → π* transition energies decrease as the π-donating ability of X decreases, the small range of values for X = NH_2, OH, and F and the detailed changes of the energies of the n and π* orbitals suggest that all four effects mentioned above must be considered in explaining the calculated values for monosubstituted carbonyl compounds of this type.

(12) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955).

The replacement of one hydrogen in HCHO by an unsaturated substituent produces a bathochromic shift in the n → π* excitation energy, as shown in Table I. Although our calculations reflect a lowering of the energy of the π* orbital (relative to HCHO) in these molecules, in agreement with the usual arguments based on the effect of conjugation on the lowest antibonding π orbital, we find that it is not possible to explain the n → π* transition energies of these molecules on this basis alone. In fact, the calculated single configuration transition energies are significantly larger than the n → π* excitation in HCHO, in marked disagreement with experiment. To explain this discrepancy, we consider glyoxal as an extreme case. If there were no interaction between the two C=O groups, then the four transitions possible between the pair of degenerate n orbitals and the pair of degenerate π* orbitals would occur at the same energy. However, interaction between the two groups produces a splitting of the nonbonding orbitals and a splitting of the π* orbitals, resulting in four possible n → π* transitions of different energy. Because of this type of interaction, a significant electron reorganization occurs upon excitation to the lowest n → π* state. An adequate description of such states is then impossible in terms of any one-electron or single configuration description and can only be obtained from a more flexible multiconfiguration wave function which allows at least mixing of the configurations describing the four different n → π* states. Thus, after allowing for such configurational mixing, the calculated n → π* transition energy is in good agreement with experiment. Similar ideas may be used to explain the n → π* excitation energy in any XCHO compound where the substituent X contains an unsaturated group.

Calculated results for disubstituted carbonyl compounds are also given in Table I. It is interesting to note that for a given first substituent X, the order of the n → π* transition energies in the XCYO series (Y = CH_3, NH_2, OH, and F) is usually identical with the order in the monosubstituted carbonyl compounds. The only exception is when X = CH_3, in which case the order for Y = OH and Y = F is reversed. Thus it appears that the order of the n → π* transition energies in the XCYO series is in general independent of the nature of the first substituent. Quantitatively, however, we note that the second substituent in X_2CO molecules does not produce as large a shift in the n → π* transition energy, relative to XCHO, as that observed in going from HCHO to XCHO.

The highest n → π* transition energy observed in all the carbonyl compounds is that of $(NH_2)_2CO$. We attribute this to the strong π-donating ability of the NH_2 substituent, which leads to a destabilization of both the π* and the n orbitals. This shows that in this case, the secondary π effect is large enough to offset the σ-withdrawing effect of NH_2, with the result that the n orbital in $(NH_2)_2CO$ lies at a higher energy than the n orbital in HCHO.

(b) Molecules Containing the -N=O Group. The low-energy uv absorption bands associated with X—N=O compounds (X = H, CH_3, NH_2, OH, and F) are adequately described as involving electron excitation from an oxygen lone-pair orbital to an antibonding π orbital. Experimentally, these transitions are found

to occur at very low energies in hyponitrous acid and nitrosomethane and at higher energies in other members of this series. The calculated results are in good agreement with this observation, although absolute values are probably too small. Although HO—N=O can exist in cis or trans forms, we report calculated values for the trans isomer only, since this is found to have a lower ground-state energy than the cis compound. This latter result is in good agreement with the experimental results of Jones and Thompson.[13]

A comparison of HNO with HCHO shows that the n orbital is slightly raised in energy, while the π^* orbital is considerably lowered. This is probably due to the fact that the N=O part of the molecule has a larger effective nuclear charge than >C=O. This would have a somewhat larger effect on the π^* orbital which is spread over both N and O and would lead to stabilization. The n orbital, which is almost completely localized on oxygen (gross orbital charge = 1.97), would be affected to a much smaller extent. Also, since the n orbital is more localized in HNO, this would tend to destabilize it relative to HCHO.

The lowest n → π^* transition energies in the X—N=O compounds (X = CH₃, NH₂, OH, and F) can be rationalized using the arguments based on σ withdrawal and π donation presented in section a. However, in changing the chromophore from >C=O to -N=O, the absorbing group is less polarized, and this influences the π-donating and σ-withdrawing effects of X. The fact that N has a lower positive charge than C in C=O will make π donation less likely. Also, considerations of electronegativity suggest that σ withdrawal will be reduced. In particular, for NH₂NO, the π^* orbital is only raised by 0.56 eV (relative to HNO), while the corresponding destabilization in NH₂CHO is 1.70 eV. The secondary π effect will also be smaller, and in NH₂NO this is apparently canceled by the stabilization of the n orbital associated with σ withdrawal. This is in marked contrast to the 0.97-eV destabilization of the n orbital in NH₂CHO. For FNO we find that the n orbital is stabilized by 1.43 eV compared with a value of 0.77 eV in FCHO. For the X—N=O series, the secondary σ effect is observed for both X = OH and X = F and is very pronounced in the latter case. Thus, as in the XCHO series, all four effects must be considered in explaining the trends in the X—N=O n → π^* transition energies. The main difference from the XCHO series is the relative importance of the four effects, although the overall result is a similar order of n → π^* transition energies.

(c) Molecules Containing the >C=N- Group. There are three series of compounds containing the >C=N- chromophore, the cis and trans imines and the N-substituted formaldimines. Ground-state calculations predict that trans imines are more stable than the cis isomers.

As in the carbonyl and nitroso series, the trends in the n → π^* excitation energies may be rationalized in terms of the π-donating and σ-withdrawing abilities of X. Modifications of the arguments presented in section a are expected because of the change of the nature of the chromophore. For example, for imines, π donation of the type

(13) E. W. Jones and H. W. Thompson, *Proc. Roy. Soc., Ser. A*, **228**, 50 (1965).
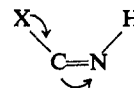
is expected to be reduced because NH is less able than O to accept electrons. Thus, destabilization of the π^* orbital when X is changed from H to NH₂ is smaller in this series.

In moving from X—CH=NH to X—N=CH₂, π-electron donation by X is further reduced, perhaps because X is now attached to the negative end of the C=N dipole and the primary π effect, which is shown by a destabilization of the π^* orbital, is very small in these compounds. However, since X is now bonded to the atom that has the lone pair of electrons, it produces fairly large effects on the n orbitals. The secondary effect of σ withdrawal is also observed in a stabilization of the π^* orbital, particularly in F—N=CH₂.

(d) Molecules Containing the -N=N- Group. Azo compounds may exist either as cis or trans isomers, and we have included data for both forms in Table I. For the ground states we calculate the trans isomer to be more stable than the cis compound in all cases, although the energy difference between the two forms decreases in the order

$$CH_3 > H > NH_2 > OH > F$$

Since the azo group contains two pairs of nonbonding electrons, there are two possible n → π^* transitions, although only one low-energy uv band is generally observed. The accepted explanation for the appearance of a single band assumes that these compounds exist in the trans form, in which there is a strong interaction between the lone pairs. As a result, there is a large splitting in the energies of the two n orbitals. These two orbitals then give rise to two n → π^* transitions of very different energies.[14,15] We find that this explanation is supported by our calculations. The splitting between the two n orbitals is found to be approximately 5–6 eV in the trans compounds, while it is only of the order of 2.5–3.5 eV in the cis isomers. The two n → π^* transitions in the trans compounds are separated by about 6 eV, whereas the corresponding difference in the cis compounds is only about 2 eV. These results indicate that the second n → π^* transition in the trans isomers will be in a far different region of the uv spectrum. Hence, the strong interaction between trans lone pairs in azo compounds has quite important spectral consequences. The same type of effect was observed in HO—N=CH₂, where the n orbital was calculated to be at a much higher energy than expected in view of the σ-withdrawing ability of OH.

In both cis and trans azo compounds, the lowest n → π^* transition is shifted to higher energy when hydrogen is replaced by the various substituents. As expected, π-donating effects are quite small in this series, and the changes of the n and π^* orbital energies resulting from σ withdrawal are more important. For example, the n orbital in *trans*-NH₂N=NH is slightly more stable than that in *trans*-NH=NH. For all other chromophores, the secondary π effect of the NH₂ group has

(14) M. B. Robin, R. R. Hart, and N. A. Kuebler, *J. Amer. Chem. Soc.*, **89**, 1564 (1967).

(15) J. R. Lombardi, W. Klemperer, M. B. Robin, H. Basch, and N. A. Kuebler, *J. Chem. Phys.*, **51**, 33 (1969).

been large enough to produce an overall raising of the n orbital (relative to the parent compound). The secondary σ effect stabilizes the π^* orbitals of *trans*-HO–N=NH and -F—N=NH, with the result that they occur at lower energies than the π^* orbital in *trans*-HN=NH. Thus, although the order of the n $\rightarrow$ π^* transition energies in the trans compounds is identical with the order in the substituted carbonyls, the effect of substituents on the n and π^* orbitals is quite different for the two chromophores.

Conclusions

Ab initio minimal basis SCF–CI calculations have been performed on a series of small molecules possessing uv bands which may be attributed to n $\rightarrow$ π^* excitations. The calculated results show that this level of theory can give an adequate description of such transition energies. The changes of transition energy produced by substituents show very similar trends for four different chromophores and follow the order of the π-donating ability of the substituents. However, an analysis of each series suggests that this is somewhat misleading. There are two effects associated with both π donation and σ withdrawal, and the transition energy depends on a balance among these four effects. For molecules containing unsaturated substituents which can conjugate with the chromophore, inclusion of CI was found to be necessary for an adequate description of the n $\rightarrow$ π^* excited singlet states. The interaction between the two nitrogen lone pairs in azo compounds was found to be much larger in the trans isomers and consequently the two n $\rightarrow$ π^* states are split to a greater extent in the trans isomers than in the cis compounds.

Localized Molecular Orbitals in Methane and Ethane and the Transferability of the Chemical Bond between These Molecules

David Peters

Contribution from the Department of Chemistry, Royal Holloway College, University of London, Englefield Green, Surrey, England. Received March 18, 1971

Abstract: The localized molecular orbitals (MO's) of the self-consistent-field wave functions of methane and ethane are examined in order to compare the calculated carbon-hydrogen bonds of the two molecules and to see how nearly identical are these two bonds. The results show that in many ways the two carbon-hydrogen bonds are indeed very alike and not far removed from Pauling's description of them. The general question of the choice of the localization route is discussed and illustrated.

In some earlier work,[1] the localized molecular orbitals (MO's) which correspond to chemical bonds and lone pairs were examined in an effort to establish a simple but rigorous theoretical description of these bonds and lone pairs. It must not be felt that these results are final or definitive, because there are some improvements which could be made in them.

The two molecules methane and ethane are treated separately from the main group of molecules for several reasons. First, they are the prototype of the whole class of saturated organic compounds. Second, this pair of molecules is the natural testing ground for ideas about the transferability of the chemical bond from one molecule to another.[2] Third, these two molecules exemplify many of the ideas developed earlier[1] and, in particular, they are a useful exercise in some aspects of the localization problem. Fourth, it is interesting to see just how much information may be derived from such wave functions as these.

The wave functions at the all-electron, all-integral self-consistent field level of approximation were computed for methane and ethane by the writer[3] and by Pitzer and Lipscomb,[4] respectively. There are several other methane computations available.[5]

Summary of Procedure

The methane results may be taken directly from the literature.[3] The ethane results are obtained as follows. We consider a $2n$-electron, closed-shell molecule with n doubly occupied MO's which are taken in real form throughout. Then we follow Coulson, Lennard-Jones, and others[6] by replacing the Slater determinant Ψ' of delocalized MO's (ϕ') by the determinant Ψ of localized MO's (ϕ), where the row vector of the delocalized MO's and that of the localized MO's are related by[1a]

$$\phi = \phi'A \tag{1}$$

The matrix A is an $n \times n$ orthogonal matrix, and it is chosen in such a way as to localize the MO's into regions of space.

Given the forms of the localized MO's we can read off the hybridizations in the valence atomic orbitals

(1) (a) D. Peters, *J. Chem. Soc.*, 2003 (1963); (b) 2015 (1963); (c) 4017 (1963); (d) 2901 (1964); (e) 2908 (1964); (f) 2916 (1964); (g) 3026 (1965); (h) 644 (1966); (i) 652 (1966); (j) 656 (1966).
(2) T. L. Allen and H. Shull, *J. Chem. Phys.*, 35, 1644 (1961); C. Edmiston and K. Ruedenberg, *Rev. Mod. Phys.*, 34, 457 (1963).

(3) D. Peters, *J. Chem. Phys.*, 51, 1559, 1566 (1969).
(4) R. M. Pitzer and W. Lipscomb, *ibid.*, 39, 1995 (1963).
(5) *Cf.* O. Sinanoğlu and D. F. Tuan, *Annu. Rev. Phys. Chem.*, 15, 260 (1964); J. Sinai, *J. Chem. Phys.*, 39, 1575 (1963).
(6) C. A. Coulson, *Trans. Faraday Soc.*, 38, 433 (1942); J. Lennard-Jones, *Proc. Roy. Soc., Ser. A*, 198, 1, 14 (1949).