Thermodynamic Functions.—The complete thermodynamics of the vaporization process requires a knowledge of the values of ΔH_v and ΔS_v as functions of the temperature. The heat of vaporization is expressed by the relationship

$$\Delta H_v = \Delta H_0 + \int_0^T \Delta C_p T$$

If it is assumed that the change in the difference between the heat capacities of the two phases is small over the temperature range under consideration, then the influence of the coefficients of the higher order temperature factors $\Delta\beta$, $\Delta\gamma$, $\Delta\delta\ldots$ of Kirchhoff's equation becomes small and the following simplified expressions may be written.

$$\Delta H_v = \Delta H_0 + \Delta C_p T \qquad (5)$$

$$\Delta S_v = \frac{\Delta H_0}{T} + \Delta C_p \qquad (6)$$

By substituting the value for ΔH in the Clausius–Clapeyron equation, one obtains an expression for the liquid–vapor equilibrium.

$$\frac{\mathrm{d}\ln P}{\mathrm{d}\,(1/T)} = \frac{-T}{P(V_v - V_l)}(\Delta H_0 + \Delta C_p T) \qquad (7)$$

The differentiated experimental equation is similar in form

$$\frac{\mathrm{d}\ln P}{\mathrm{d}\,(1/T)} = B - CT \qquad (8)$$

By equating the coefficients in equations (7) and (8) expressions for ΔH and ΔC_p are obtained.

$$\Delta H_0 = \frac{-P(V_v - V_l)}{T} B \qquad (9)$$

$$\Delta C_p = \frac{P(V_v - V_l)}{T} C \qquad (10)$$

Statistical values for B and C are -8716 ± 62 and -4.41, respectively. The liquid molal volume V_l is taken directly from the liquid density data, and the vapor molal volume V_v may be calculated by the van der Waals equation. By using the rules proposed by Brewer and Searcy[5] for calculating the values of the van der Waals constants, ΔH_0 and ΔC_p are evaluated

$$\Delta H_0 = 16{,}800 \pm 120 \text{ cal. mole}^{-1} \qquad (11)$$

$$\Delta C_p = -8.5 \text{ cal. deg.}^{-1} \text{ mole}^{-1} \qquad (12)$$

and from equations (5) and (6) expressions for the primary thermodynamic functions are obtained

$$\Delta H_v = (16{,}800 - 8.5T) \pm 120 \text{ cal. mole}^{-1}$$

$$\Delta S_v = \frac{16{,}800}{T} - 8.5$$

While these equations are subject to some uncertainty, they do represent the best estimates which can be made from currently available data.

General Comments.—Niobium pentafluoride appears to be more stable to hydrolysis than either uranium hexafluoride or ruthenium pentafluoride. In a dry box with a dew point of −40° the niobium fluoride may be transferred with no appreciable decomposition or fuming, while the ruthenium compound decomposes slowly even at a dew point of −50°. There was no evidence of dissociation of the niobium pentafluoride up to a temperature of 255°.

(5) Leo Brewer and Alan W. Searcy, *J. Chem. Ed.*, **26**, 548 (1949).

OAK RIDGE, TENNESSEE

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, PURDUE UNIVERSITY]

Chemical Valency Theory and the Electronic Structure of the Methane Molecule[1]

BY CHARLES R. MUELLER

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Two principal methods, the atomic and molecular orbital methods, have been used in attacking the problems of chemical valency theory. An alternative method, the semi-localized orbital approach has been developed and includes both of the previous methods as special cases. A semi-localized orbital calculation of the binding energy and electronic structure of methane is made. The bond energy from such a calculation is 160 kcal. greater than that for the atomic orbital method. The latter gives a negative bond energy. The electronic structure of the methane molecule obtained from the semi-localized orbital method is quite different from that of either simpler approach. It is shown that the method gives a natural description of steric effects, resonance, heteropolar binding, inductive effect and has a formal analogy with classical valency theory. This is the first full scale quantum mechanical treatment of the methane molecule as a 10-electron problem.

Introduction

Two principal methods of attacking the problems of chemical valency theory have been utilized. Both of these methods, the atomic and molecular orbital methods, as well as the semi-localized orbital approach used in this paper, postulate that a reasonably good molecular eigenfunction (a good approximate solution of the Schrödinger equation for the molecule) can be formed from a linear combination of all the product of all the one-electron orbitals in the molecule. In all three cases this linear combination must be formed in such a way as to obey the Pauli Exclusion Principle and the Uncertainty Principle. The individual products differ only in that different electrons are assigned to the orbitals.

The three methods differ in the way the one-electron orbitals are formed. In the atomic orbital method the electrons are assigned to orbitals which are approximate solutions of the Schrödinger wave equation for individual atoms (atomic orbitals). Such a theory gives poor description of heteropolar binding.

There are two variations of the second approach, the molecular orbital method. In one case the one-electron orbitals move over the entire molecule. In the second form, localized molecular orbitals, the one-electron orbitals cover only two atoms which form a chemical bond. Since Lennard-

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Jones[2] has proved the equivalence of the two methods for methane we need consider only the localized molecular orbital method.

For computational purposes the one-electron orbitals are almost invariably composed of atomic orbitals, and, in the calculations which follow, we have used Slater atomic orbitals,[3] except that the carbon $1 - s$ orbitals have the form $\varphi_{1s} = (Z^{3/2}\sqrt{\pi})e^{-Z\gamma}$; $Z = 5.688$. The carbon orbitals used in the molecule in the one-electron orbitals of the valence electrons have tetrahedral hybridization.

In the atomic orbital method one of the valence electrons of a C–H bond is assigned to a tetrahedral carbon atomic orbital φc, and one to a hydrogen atomic orbital φ_n.

In the localized molecular orbital method the valence electrons are assigned to two orbitals of exactly the same form, $(\varphi_c + \lambda\varphi_h)$. λ is a parameter which is selected by the variation principle. λ has that value which gives the *maximum* total energy for the molecule.

In the semi-localized orbital method the two electrons are assigned, one to the orbital $(\varphi_c + \lambda_1\varphi_h)$, the other to $(\lambda_2\varphi_c + \varphi_h)$. Now if λ_1 and λ_2 are zero these orbitals are simply atomic orbitals. If $\lambda_1\lambda_2 = 1$, these orbitals become molecular orbitals. A semi-localized orbital treatment of the methane molecule is particularly interesting because it is the first calculation of this type for heteronuclear covalent binding. Calculations for a homonuclear molecule, the hydrogen molecule, have been previously made.[4] In this case the semi-localized orbitals bore a strong resemblance to atomic orbitals, even though the calculated binding energy is about 10% better for the semi-localized orbital treatment.

The reverse was found to be true for hydrogen fluoride[5] where the semi-localized orbital method was closer energetically to the molecular orbital method. A 10% improvement in binding energy again results, and the calculated dipole moment using semi-localized orbitals shows a very striking improvement over that obtained from molecular orbitals.

In the intermediate region one might expect that both of the simpler methods would be bad. This would have important repercussions in any interpretation of heteronuclear covalent binding on the basis of atomic or molecular orbital theory. These repercussions would be particularly important in organic chemistry.

Calculations of Binding Energy and Molecular Eigenfunctions.—The binding energy of a molecule is by definition the difference between the total energy of the molecule and the total energy of the separated atoms which combine to form the molecule.

Applying the Dirac vector model[6] to the $2s^2\ 2p^2$ ground state of the carbon atom the total energy is given by

$$E = \frac{(Q - 2K_{1s,2s} - K_{Px,1s} - K_{Py.1s} - K_{Px.2s} - K_{Py.2s} - K_{Px,Py})}{(1 - 2S^2_{1s,2s} - S^2_{Px,1s} - S^2_{Py.1s} - S^2_{Px,2s} - S^2_{Py.2s} - S^2_{Px.Py})} \qquad (1)$$

Q represents the coulombic (electrostatic) energy of the atom. $K_{1s,2s}$ is, for example, the exchange integral between the 1s and 2s states, H is the quantum mechanical Hamiltonian, φ_{ij} is a carbon atomic orbital. In a sense the K's are resonance energies between two states differing only in the electrons assigned to the orbitals, in this case between states where electrons 1 and 3 have exchanged orbitals. The expression $d\tau_1 \ldots d\tau_6$ indicates that the integration is carried out over the coördinates of 6 electrons, S_{ij} is the overlap integral between the i^{th} and j^{th} orbitals.

$$\int \varphi_{1s}(1)\,\varphi_{1s}(2)\,\varphi_{2s}(3)\,\varphi_{2s}(4)\,\varphi_{Px}(5)\,\varphi_{Py}(6)\,H\varphi_{1s}(3)\,\varphi_{1s}(2)\,\varphi_{2s}(1)\,\varphi_{2s}(4)\,\varphi_{Px}(5)\,\varphi_{Py}(6)\,d\tau_1..d\tau_6$$

In the semi-localized orbital method, again applying the Dirac Vector Model, the total molecular energy is given by

$$E = \frac{Q + 4K_{CH} - 6K_{CH'} - 3K_{HH'} - 3K_{CC'} - 4K_{C.1s} - 4K_{H,1s}}{1 + 4S^2_{CH} - 6S^2_{CH'} - 3S^2_{HH'} - 4S^2_{C.1s} - 4S^2_{H.2s} - 3S^2_{CC'}} \qquad (2)$$

K_{ch} represents the exchange integral between the semi-localized carbon orbital $(\varphi_c + \lambda_1\varphi_h)$ and the adjacent hydrogen orbital $(\lambda_2\varphi_c + \varphi_h)$. K_{ch} represents the exchange integral between a semi-localized carbon orbital and a hydrogen atom which is to the rear of the direction in which the orbital is pointed, etc.

We find the values of λ_1 and λ_2 which give the greatest total molecular energy, obtaining simultaneously a calculated binding energy and the best molecular eigenfunction of this type. Essentially we have simply given the electrons greater freedom in choice of eigenfunctions than they had in either the molecular or atomic orbital methods.

For λ_1 and λ_2 equal to zero (atomic orbital method) we obtain a total electronic energy of 53.4204 atomic units (1 atomic unit = 27.205 electron volts = 627.08 kcal.). After subtracting from this the energy of nuclear repulsion and the energy of the free atoms, we obtain a binding energy of −0.1022 atomic unit, or a bond energy of about −16 kcal. (−20 kcal. if corrected for zero point energy).

Using the semi-localized orbital method we find that $\lambda_1 = 1.063$, $\lambda_2 = 0.534$ and the total electronic energy is 54.442 atomic units. The bond energy is 140 kcal. after correction for zero point energy.

While the bond energy for the C–H bond is subject to considerable discussion, this value is probably too high. We suspect this is due to a slight improvement in the accuracy of the molecular eigenfunctions over the atomic eigenfunctions. In addition some of the integrals must be approximated for the molecule and small indeterminate errors may arise. The eigenfunctions obtained in this way depend only on the total electronic energy and should be reliable. It should be noted that for molecular orbitals $\lambda_1\lambda_2 = 1$. Here $\lambda_1\lambda_2 = 0.568$. This is therefore a very great deviation from the molecular orbital form of eigenfunction.

All of the above calculations were made at a carbon–hydrogen internuclear distance of two atomic

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[2] J. Lennard-Jones, *Proc. Roy. Soc.* (*London*), **A197**, 14 (1949).

[3] J. Slater, *Phys. Rev.*, **36**, 57 (1930).

[4] C. Mueller and H. Eyring, *J. Chem. Phys.*, **19**, 1495 (1951).

[5] C. Mueller, *ibid.*, **19**, 1498 (1951).

[6] E. Corson, "Perturbation Methods in the Quantum Mechanics of *n*-Electron Systems," Hafner Publishing Co., New York, N. Y., 1951, Chap. 10.

units. In preliminary calculations it was found that the treatment of methane necessarily involves the effect of inner shell electrons. The kinetic energy of the 2s electrons is only one-third of the value of the 2p electrons and this is compensated by inner-shell outer-shell interaction.

Discussion

The semi-localized orbital method has now been applied to three different types of molecules, homonuclear covalent, heteronuclear covalent and heteronuclear semi-ionic. The results from semi-localized orbitals are consistently better quantitatively than those from either molecular orbital methods. In molecules of the heteropolar covalent type, the more general semi-localized orbitals bear little resemblance to either molecular or atomic orbitals. Because of this discrepancy it would appear that these simpler methods should not be used in interpretation of organic compounds.

We should like to extend this argument a little further to show that some of the simpler methods are incapable of complete theoretical interpretations of the reactions of organic molecules.

First of all it is preferable that any theory has a formal analogy with classical valence theory. The interpretative success of this theory is surely not an accident. The formal analogy is illustrated in equation (2). For each bond there appears in the numerator an exchange integral having a coefficient of plus one. This advantage is shared by the atomic orbital method.

Secondly the theory must give an adequate description of heteropolar binding. The semi-localized orbital and molecular orbital methods do this. The atomic orbital method gives an explanation only of covalent binding. A number of writers have sought to overcome this deficiency by adding to the covalent terms in the atomic orbital methods, some ionic terms and interpreting heteropolar binding as resulting from resonance between ionic and covalent states. There are two objections to this method. It involves resonance between states separated by large energy differences, while the semi-localized orbital method involves resonance between states of equal energy only.[4] In addition the method is extremely clumsy. An equivalent calculation giving the same binding energy as the present semi-localized orbital method would require 240 ionic and partially ionic states.

Thirdly, any theory of organic reactivity must give an adequate explanation of steric strain, repulsion between non-bonded atoms. In the semi-localized orbital method these appear as exchange integrals, such as $K_{\mathrm{hh}'}$ in eq. (2), between non-bonding electrons, having coefficients of minus one-half. This advantage is shared with the atomic orbital method, and the localized molecular orbital method.

Fourthly the general idea of benzenoid resonance must be retained. This comes directly from the use of a general quantum mechanical formalism such as the Dirac vector method and is possessed jointly by the atomic orbital, semi-localized orbital method, and by the localized molecular orbital method.

Finally the inductive effect finds a natural description in the semi-localized orbital method. We shall assume that induction results from charge transfer within a bond, and not between bonds. If the latter occurs, this can also be accomplished by a slight modification of the orbital. The charge transfer within a bond is accomplished simply by a change in λ_1 and λ_2. The inductive effect can also be described by the molecular orbital method. Unfortunately dipole moments calculated by such a method are extremely poor,[7] and would probably give a useless result.

All five factors are necessary for an adequate explanation of organic reactivity. Where explanations of these factors are shared with simpler theories, the semi-localized orbital method still possesses a great quantitative advantage.

It would not be objective to conclude this section without raising a question whether the improved accuracy of the semi-localized orbitals is sufficient to give useful results. One can point out the binding energy is quite high for methane. It must be conceded that the present form of the semi-localized orbitals using Slater atomic orbitals is not good enough for this purpose. The free atoms and the resultant molecule are too different for adequate comparison. One may however hope that in calculation of dissociation energies, where the difference is much less, adequate accuracy will be forthcoming.

Evaluation of Integrals.—The two-center integrals in this calculation were either evaluated by the author using the standard methods of expanding in elliptic coördinates or, with the exception of those integrals involving interelectronic distances, were calculated from the formulas of Kotani, Amemiya and Simose.[8]

The two center integrals involving interelectronic distances were obtained from the tables of Kotani and Amemiya[9] by central difference interpolation or were evaluated by the author.

Three and four center integrals involving the interelectronic differences were approximated by Mulliken's[10] overlap average approximation with some slight extension by Mueller and Eyring.[11]

The other three center integrals not involving carbon orbitals were evaluated using the method of Massey.[12]

Finally the three center integrals involving carbon atomic orbitals, but not interelectronic distances, were approximated by the point charge[13] approximation.

The integral $\int \frac{\varphi_{\mathrm{C2s}}\,\varphi_{\mathrm{h}}}{\gamma_{\mathrm{h}'}}\,d\gamma$ was checked using a method of Coulson.[14] The point charge approximation gave a value of 0.2266 atomic units for this integral. Coulson's method gave a value of 0.230 correct to the third decimal place for the first five terms of an infinite series in half-order Bessel functions.

LAFAYETTE, INDIANA

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(7) R. Mulliken, *J. chim. phys.*, **46**, 497 (1949).

(8) M. Kotani, A. Amemiya and F. Simose, *Proc. Phys. Math. Soc. Japan.*, **20**, Ext. No. 1 (1938).

(9) M. Kotani and A. Amemiya, *ibid.*, **22**, Ex. No. (1940).

(10) R. Mulliken, *J. chim. phys.*, **46**, 497 (1949), eq. (104)-(106).

(11) C. Mueller and H. Eyring, *J. Chem. Phys.*, **19**, 934 (1951).

(12) N. Massey, *Proc. Camb. Phil. Soc.*, **27**, 451 (1931).

(13) J. Mulligan, *J. Chem. Phys.*, **19**, 347 (1951).

(14) C. A. Coulson, *Proc. Camb. Phil. Soc.*, **33**, 104 (1937).