Polar Structures in the VB-Theory of Conjugated Molecules

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Introduction

The parameters appearing in the semi-empirical valence bond (VB) calculation of the electronic structure of molecules, have been estimated on the basis of thermochemical data of molecules. For instance, the value of the exchange integral for π-electrons between adjacent atoms r and s,

$$\alpha=\int\cdots r(i)s(j)\cdots H\cdots s(i)r(j)\cdots \mathrm{d}\tau$$
$$=-1.92\,\mathrm{eV.}, \tag{1}$$

was determined from the heat of hydrogenation of unsaturated hydrocarbons by Sklar[1]. However, two improprieties are inevitable in his procedure; one is the underestimation of the ionic contribution and the other is the disregard of the compression energy resulting from bond compression in molecules. Recently Craig[2], adopting this value for α, evaluated three more quantities which enter in a rather detailed theory including polar structures,

$$\eta=\int\cdots r(i)r(j)\cdots H\cdots r(i)s(j)\cdots \mathrm{d}\tau \tag{2}$$

$$\xi=\int\cdots r(i)r(j)\cdots H\cdots r(i)r(j)\cdots \mathrm{d}\tau$$
$$-\int\cdots r(i)s(j)\cdots H\cdots r(i)s(j)\cdots \mathrm{d}\tau \tag{3}^*$$

$$\zeta=\int\cdots r(i)r(j)\cdots H\cdots s(i)s(j)\cdots \mathrm{d}\tau \tag{1'}$$

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[1] A.L. Sklar, *J. Chem. Phys.*, 5, 669 (1937).

[2] D.P. Craig, *Proc. Roy. Soc.*, A **200**, 390 (1950).

* This is recognized to be the difference between Coulomb integral of polar structure Q′ and that of non-polar one Q.

as —0.54, 4.28 and —0.48 eV. respectively, from the consideration of the spectrum of ethylene. On the other hand inconsistent with Craig's evaluation, Mulliken's approximation formula[3] claims that

$$\alpha=\int r(i)s(j)H\,s(i)r(j)\mathrm{d}\tau_{ij}$$

$$=S_{rs}\int r(i)r(j)H\,r(i)s(j)\mathrm{d}\tau_{ij}=S_{rs}\eta\ , \qquad (4)$$

where S_{rs} is the overlap integral between atomic orbitals of atoms r and s. This great discrepancy occurs clearly from the adoption of the above large value of α without any criticism. Keeping this fact in mind, we shall attain a new set of the semi-empirical values of integrals, making use only of spectroscopically observed results of ethylene, and examine the applicability of them to the calculation of *trans*-butadiene. In the last part of this paper, the role of η and α will be discussed in connection with the importance of the ionic character of conjugated molecules.

Evaluation of Integrals

First, the wave functions of ethylene as following are used;

$$^1\mathrm{A_g}\ (\text{ground})\quad \Psi_0=a\psi_a+\frac{b}{\sqrt{2}}(\psi_b+\psi_{b'}), \qquad (5)$$

with a relation between the coefficients $a^2+b^2=1$, and

$$^1\mathrm{B_{1u}}\ (\text{excited})\quad \Psi_1=\frac{1}{\sqrt{2}}(\psi_b-\psi_{b'}), \qquad (6)$$

in which ψ_a is written for the non-polar structure and ψ_b, $\psi_{b'}$ for the two polar ones (see Fig. 1). Then ignoring overlap, these lead to a formula for the $^1\mathrm{A_g}-{}^1\mathrm{B_{1u}}$ excitation energy ΔE,

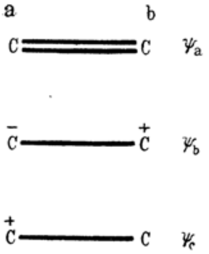

Fig. 1.

$$\Delta E=-2\alpha+\frac{\xi}{2}+\sqrt{\xi^2/4+4\eta^2}\,. \qquad (7)$$

Another representation of this is

$$\Delta E=\xi-2b^2\xi-2\alpha-4\sqrt{2}\,ab\eta-2b^2\alpha. \qquad (7')$$

In order to determine the numerical values for a and b, the oscillator strength,

$$f=1.085\times10^{11}\omega\Big(\int\Psi_0\vec{r}\,\Psi_1\,\mathrm{d}\tau\Big)^2 \qquad (8)$$

$$=1.085\times10^{11}\omega(R^2\times10^{-16}b^2)$$

may be turned to use, where ω is the frequency of the transition in cm^{-1}, $\vec{r}$ is the sum of the position vectors of π-electrons and R is the C=C bond distance in ethylene of ground state. Information on experimental results (ΔE=7.6 eV., f=0.25, bond length =1.35Å) makes it possible to calculate a, b, and with a further assumption of the relation (4), α, ξ and η numerically. If 0.28 is employed for S in equation (4), then we have

$$\left.\begin{aligned}a&=0.889\\ b&=0.498\end{aligned}\right\}\ (9)$$

$$\left.\begin{aligned}\eta&=-2.15\ \text{eV.}\\ \xi&=3.51\ \text{eV.}\\ \alpha&=-0.60\ \text{eV.}\end{aligned}\right\}(10)$$

Much attention must be paid to the comparison of the present set of η, ξ and α with that given by Craig[2,*]. Moreover, a striking fact is that the values attained here allow the VB calculation to come very near the semi-empirical molecular orbital (MO) method which was developed quite successfully by Pariser and Parr[5] in recent years. η has a comparable numerical value as the resonance integral β (=2.75 eV.) in the semi-empirical MO calculation. This is owing to the fact that these are quite similar quantities by nature. That is, if overlap is put equal to zero,

$$\eta=\int r(i)r(j)H\,r(i)s(j)\mathrm{d}\tau_{ij}\doteqdot\int r(j)H'\,s(j)\mathrm{d}\tau_j=\beta.$$

On the other hand, ξ can be approximated as

$$\xi=(\mathrm{aa:aa})-(\mathrm{aa:bb}) \qquad (11)$$

where,

$$(\mathrm{rr:ss})=\int r(i)s(j)\frac{e^2}{r_{ij}}r(i)s(j)\mathrm{d}\tau_{ij}. \qquad (12)$$

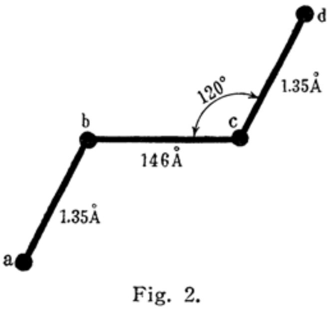

Fig. 2.

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[3] R.S. Mulliken, *J. Chem. Phys.*, 46, 497 (1949).

* ζ is set equal to α, like the treatment by Sklar (reference 1).

[5] R. Pariser and R.G. Parr, *J. Chem. Phys.*, 21, 466, 766 (1953)

According to the reference 5, this difference is predicted to be 10.53−7.38=3.15 eV. being close to the present value.

Another set of parameters which can be determined from the consideration of the singlet-triplet separation of ethylene, is not useful, because of the small value of ξ*.

Application to *trans*-Butadiene

In order to examine the applicability of the new set of η, ξ and α to other molecules, *trans*-butadiene is chosen. All the polar and non-polar structures are taken into account, but a simplification of considering only single exchange integrals between adjacent atoms is allowed. Corrections for η, ξ, α should be made, corresponding to the change of the internuclear distances (Fig. 3). These are done according to the following procedures**.

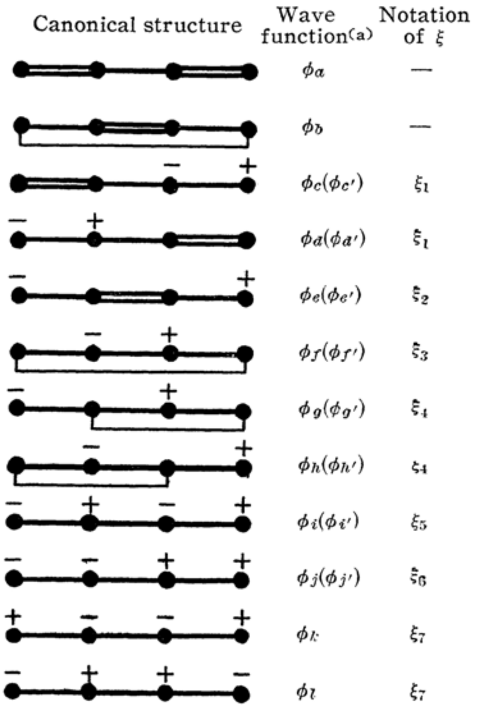

Fig. 3.

(a) $\phi_{c'}$'s are given by inversion respect to the center of molecule from ϕ_c's.

$$\left.\begin{aligned}\eta_{rs}&=\int\cdots r)i)r(j)\cdots H\cdots r(i)s(j)\cdots\mathrm{d}\tau=S=_{rs}\eta_0\\ \alpha_{rs}&=S_{rs}\eta_{rs}=S^2_{rs}\eta_0.\end{aligned}\right\}\quad(13)$$

where η_0 is a constant to be determined by insertions of η_{rs} and S_{rs} for ethylene into (13). So, if $S_{ab}=0.27$ and $S_{bc}=0.23$ are used*,

$$\eta_{ab}=-2.07,\ \eta_{bc}=-1.77\ \text{eV.};\ \alpha_{ab}=-0.56,\ \alpha_{bc}=-0.41\ \text{eV.}\quad(14)$$

Moreover as to ξ next relation holds;

$$\xi=Q'-Q=(\Sigma I+\Sigma K)_{Q'}-(\Sigma I+\Sigma K)_{Q\mathrm{i}}\quad(15)$$

where I and K are respectively core and Coulomb type repulsion integrals,

$$I=\int r(i)\sum_{p\neq r}U_{\mathrm{p}}(i)r(i)\mathrm{d}\tau_i$$

$$K=\int r(i)r(i)\frac{e^2}{r_{ij}}s(j)s(j)\mathrm{d}\tau_{ij}=(\mathrm{rr:ss}).$$

$U_p(i)$ signifies the potential of electron i in the field of the p-th carbon atom less its $2p\pi$-electron. Being used the Sklar type potential,

$$U_p(i)=U^0_p(i)-\int s(j)^2\frac{e^2}{r_{ij}}\mathrm{d}\tau_{ij}$$

and zero $U^0_p(i)$(i. e., the potential of electron i in the field of the neutral p-th carbon atom) asumed, the problem is reduced to an estimation of Coulomb type repulsion integrals (rr : ss) only. In the case of $r=s$, i. e., (rr : rr), by a simple approximation it can be set equal to the difference between the ionization potential and the electron affinity of carbon atom (=10.53 eV.)$^{5)}$. When this is accepted, (rr : ss) corresponding to 1.34Å ($r-s$ separation for ethylene) is obtainable to be 10.53−3.51=7.02 eV., from the value of ξ. Repulsion integrals at arbitrary separations, may then be easily found supposing a linear relation to Pariser and Parr's result. Seven ξ's required are estimated by this procedure as follows (see Fig. 3).

$$\left.\begin{aligned}\xi_1&=(\mathrm{aa:aa})-(\mathrm{aa:bb})=3.53\ \text{eV.}\\ \xi_2&=(\mathrm{aa:aa})-(\mathrm{aa:dd})=6.97\ \text{eV.}\\ \xi_3&=(\mathrm{aa:aa})-(\mathrm{bb:cc})=3.74\ \text{eV.}\\ \xi_4&=(\mathrm{aa:aa})-(\mathrm{aa:cc})=5.45\ \text{eV.}\\ \xi_5&=2\xi_1+2(\mathrm{aa:cc})-(\mathrm{aa:dd})\\ &\quad-(\mathrm{bb:cc})=6.87\ \text{eV.}\\ \xi_6&=2\xi_4+2(\mathrm{aa:bb})-(\mathrm{aa:dd})\\ &\quad-(\mathrm{bb:cc})=14.63\ \text{eV.}\\ \xi_7&=2\xi_1-2(\mathrm{aa:cc})+(\mathrm{aa:dd})\\ &\quad+(\mathrm{bb:cc})=7.25\ \text{eV.}\end{aligned}\right\}\quad(17)$$

The calculated energy diagram is shown in Fig. 4 together with results by several other methods.

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* See reference 2.

** These formulae which contain S explicitly, never mean the inclusion of S in the actual calculation. Here, S should be recognized as a parameter defining the integrals in a function of internuclear distances.

* These values are obtained conveniently using the calculated bond orders p by the simple LCAO method, according to

$$S=0.080p+0.115$$

(N. Müller et al., *J. Am. Chem. Soc.*, **76**, 4770 (1954)).

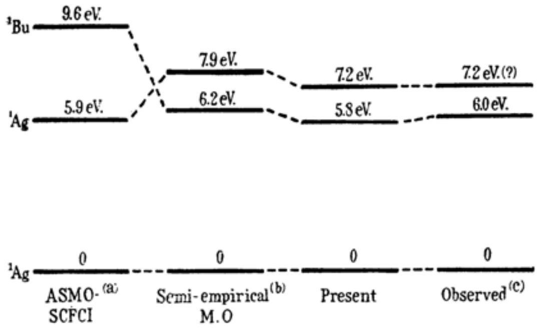

Fig. 4. Energy diagrams

(a) Y. Mori, This Bulletin, **28**, 291 (1955).

(b) Reference 5.

(c) R. S. Mulliken, Rev. Mod. Phys., **14**, 265 (1942).

The wave functions of the ground state and the first excited singlet state are

$$\left.\begin{aligned}(^1\mathrm{A_g})\quad \Phi_0=&0.671\phi_a+0.062\phi_b+0.305(\phi_c+\phi_{c'})\\&+0.337(\phi_d+\phi_{d'})+0.044(\phi_e+\phi_{e'})\\&+0.103(\phi_f+\phi_{f'})+0.074(\phi_g+\phi_{g'})\\&+0.070(\phi_h+\phi_{h'})+0.153(\phi_i+_{i'})\\&+0.009(\phi_j+\phi_{j'})+0.131\,\phi_k\\&+0.153\,\phi_l,\\(^1\mathrm{B_u})\quad \Phi_1=&0.366(\phi_c-\phi_{c'})+0.376(\phi_d-\phi_{d'})\\&+0.204(\phi_e-\phi_{e'}+0.131(\phi_f-\phi_{f'})\\&+0.176(\phi_g-\phi_{g'})+0.173(\phi_h-\phi_{h'})\\&+0.323(\phi_i-\phi_{i'})+0.034(\phi_j-\phi_{j'}).\end{aligned}\right\}\quad(17)$$

Finally the oscillator strength of the transition $^1\mathrm{A_g}-^1\mathrm{B_u}$ is calculated to be 0.62 (observed 0.53).

These agreements with experimental observations are sufficient to confirm the conclusion that our first evaluation of quantities η, ξ, α is not at all an irresponsible one. The resemblance to the semi-empirical MO is a natural consequence of our arrangement of the integral values.

Discussion

The most marked point in our method exists, of course, in an estimation of a great deal of ionic contribution to electronic structures. On the contrary, the semi-empirical VB-method heretofore in use, estimates little about this but a great amount of the interaction between non-polar configurations. Now, it will be worth while to study the signification of our evaluation of the quantities η and α. If the Mulliken's approximation is allowable, the extent of contribution of interaction between polar and non-polar structures may be measured by the degree of overlapping. A large overlap suggests much contribution of polar structures and vice versa. So, we shall try a VB calculation of ethylene, studying the influence of the overlap integral. The wave function are

$$\left.\begin{aligned}&^1\mathrm{A_g}(\text{ground})\\&\qquad \Psi_0=a\Psi_a+\frac{b}{\sqrt{2(1+S^2)}}(\psi_b+\psi_{b'})\\&^1\mathrm{B_{lu}}(\text{excited})\quad \Psi_1=\frac{1}{\sqrt{2(1-S^2)}}(\psi_b-\psi_{b'}).\end{aligned}\right\}(18)$$

where ψ_a, ψ_b and $\psi_{c'}$ are normalized.

The secular equation for $_1\mathrm{A_g}$ state is

$$\begin{vmatrix}\frac{1}{1+S^2}(Q+\alpha)-E_1 & \frac{2}{1+S^2}(\eta-SE^1)\\ \frac{2}{1+S^2}(\eta-SE_1) & \frac{1}{1+S^2}(Q+\xi+\alpha)-E_1\end{vmatrix}=0 \quad (19)$$

$$\frac{1}{1-S^2}(Q+\xi-\alpha)-E_2=0. \quad (20)$$

Here, we shall try to express η and α in functions of S. Coulomb integral Q is given by direct integration.

$$\begin{aligned}Q&=2W_{2p\pi}+2(U_a:\mathrm{bb})+(\mathrm{aa}:\mathrm{bb})\\&=2W_{2p\pi}+(U_a:\mathrm{bb})+(U_a^0:\mathrm{bb})\end{aligned}$$

where, $W_{2p\pi}$ is the energy of $2_{p\pi}$ electron of carbon atom. Consequently

$$QS=2W_{2p\pi}S+(U_a:\mathrm{bb})S+(U_a^0:\mathrm{bb})S \quad (22)$$

while η is

$$\begin{aligned}\eta&=2W_{2p\pi}S+(U_a:\mathrm{bb})S+(U_a:\mathrm{ab})+(\mathrm{aa}:\mathrm{ab})\\&=2W_{2p\pi}S+(U_a:\mathrm{bb})S+(U_a^0:\mathrm{ab}).\end{aligned} \quad (22)$$

Then from equations (21) and (22) it is seen that

$$QS=\eta-(U_a^0:\mathrm{ab})+(U_a^0:\mathrm{bb})S. \quad (23)$$

Furthermore, $(U_a^0:\mathrm{ab})$ is approximated by the method of Sklar, thus*

$$(U_a^0:\mathrm{ab})=S(U_a^0:\mathrm{b'b'}). \quad (24)$$

Numerical values of the penetration integrals $(U_a^0:\mathrm{b'b'})$ and $(U_a^0:\mathrm{bb})$, i.e., -8.739 and -1.091 eV.** respectively, give

$$\left.\begin{aligned}&\eta=SQ-7.648S\\ \text{and}\\&\alpha=S^2Q-7.648S^2.\end{aligned}\right\}(25)$$

Inserting Eqs. (25) and an adequate numerical value of ξ into Eqs. (19) and (20), one can calculate the excitation energy ΔE in function of S. Fig. 5 shows the results of calculations in the cases of $\xi=3.51$ and 7.69 eV. The latter is true in the non-empirical calculation. The amount of ionic contribution is accounted for by the ratio b/a, and also by the ratio of the calculated stabilization

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* b′ is a $2p\pi$ function located midway between a and b atoms.

** Calculated from the paper of R. G. Parr and B. L. Crawford, *J. Chem. Phys.*, 18, 1049 (1948).

energy of the ground state including polar structures to that excluding them. These ratios are seen in Fig. 5. The experimental excitation energy is attainable at the value of the overlap integral by 0.3, consistent with our first assumption (S=0.28). When the overlap integral is small like this, η causes the most part of the stabilization energy and as S becomes large, the importance of polar structures of the molecule, consequently the contribution of η, decreases to the ground state.

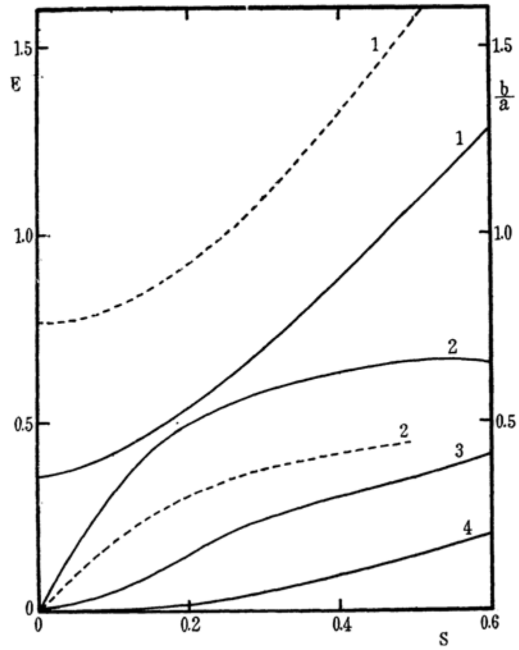

Fig. 5. Ionic Character of Ethylene.

1. Excitation energy ΔE
2. Ratio of b to a
3. Binding energy calculated from (18)
4. Binding energy calculated using ψ_a only

Broken lines show results of using ξ=7.69 eV.

Conjugated molecules, so far as we are dealing only with the π-electron system, have small S in general. Concerning this fact, one may understand that the simple MO method, which ignores the exchange and overlap integrals and includes a large amount of polar structures, is reliable in the calculation of π-electron systems and the good agreement with experiments of the results obtained by Pariser and Parr[5)] may not be accidental. In the present calculation of *trans*-butadiene, the small value of α does not cause the contravention to the experiments and furthermore the disregard of the exchange integrals will cause the results of the calculation to come near those by the method of Pariser and Parr.

However, in the treatment of σ-bond, say like a hydrogen molecule, in which the overlap of atomic orbitals is large that it can never be excluded from the calculation, the approximation we have used here will not fit. In such cases, non-polar configurations will play an important role.

Conclusion

The usual VB-method, in spite of its theoretical infirmity that all or at least the large part of ionic influence is entirely ignored, has been served for predications and interpretations of electronic phenomena. But from a different point of view, we have described another direction of the VB-theory, and applying that to butadiene, we have shown that excellent agreements with experiments can be realized. A further study on the polar character of conjugated molecules could give an assurance to the propriety of our procedure. Our method was found to be very near the semi-empirical MO-method, but a large complication accompanies the practical calculation*. In this point, VB-method must fall below the MO-method.

Finally, from the present study, it was pointed out that the old VB-method in the semi-empirical theory of conjugated molecules, although it sometimes could lead to a good result, never represents the essential figure of a molecule and also that its agreement with experimental facts was accidental.

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* Benzene is a rather simple and important object in the discussion of the propriety of a theory of electronic structures. But it is almost impossible to represent the wave function of benzene by VB-theory, since in order to expect a statisfactory result it requires inclusion of all kind polar structures, even triply-polar ones.