Theoret. chim. Acta (Berl.) 23, 93—97 (1971)

Relationes

β Parameters for Non-Nearest Neighbors*

KARL JUG
Department of Chemistry, Saint Louis University, Missouri 63156, USA

Received April 19, 1971

Formulas for non-nearest neighbor β parameters over orthogonal orbitals are derived and discussed for the $2p\pi$-orbitals of benzene and *cis*- and *trans*-butadiene.

In recent years it has become attractive to establish an improved basis for semiempirical molecular orbital methods by searching for improved approximate formulas for parameters. In particular, the bonding parameter β, which is defined as the integral of an effective single-electron Hamiltonian over atomic orbitals on different atoms, seems to lend itself to such an investigation.

Based on the Heisenberg equation of motion[1]

$$\boldsymbol{p} = [\boldsymbol{r}, h], \tag{1}$$

Linderberg [1] derived a formula for β over symmetrically orthogonalized atomic $2p\pi$-orbitals [2]. It was shown later [3] that Linderberg's formula can be regarded as the main term in an expansion of integrals defined over operator equation (1):

$$\boldsymbol{p}_{\mu\nu} = \sum_{\lambda} (\boldsymbol{r}_{\mu\lambda} h_{\lambda\nu} - h_{\mu\lambda} \boldsymbol{r}_{\lambda\nu}), \tag{2}$$

where $\boldsymbol{p}_{\mu\nu} = \langle \mu | \boldsymbol{p} | \nu \rangle$, $\boldsymbol{r}_{\mu\lambda} = \langle \mu | \boldsymbol{r} | \lambda \rangle$, $h_{\lambda\nu} = \langle \lambda | h | \nu \rangle$, μ, ν are atomic orbitals and λ is taken over a complete orthogonal set.

An extension of the formula to $2s$- and $2p\sigma$-orbitals was also presented. The truncation effect was investigated [4]. The result showed that more terms than just the main ones were needed for a proper account of the coupling between $2s$- and $2p\sigma$-orbitals through the effective Hamiltonian. All these investigations were limited to diatomic molecules. Linderberg and Öhrn [5] also presented a modification of their approximation which dealt with $\bar{\beta}$ over non-orthogonal Slater orbitals and emphasized the nearest neighbor character of their approach.

This seems to limit the applicability of the formalism since polyatomic molecules are most interesting and their non-nearest neighbor interaction might be important. We wish to show, therefore, with the examples of benzene and butadiene that it is indeed possible to find simple formulas for non-nearest neighbors β's whose values are in agreement with those reported in the literature.

---

* Presented in part at the van Vleck-Symposium on Atomic, Molecular and Solid State Theory and Quantum Biology, Sanibel Island, Florida, January 18–23, 1971.

[1] We assume atomic units; $\boldsymbol{r}$ is the position vector of an electron, h the effective Hamiltonian, $\boldsymbol{p}$ the momentum conveniently taken as antihermitian.

The benzene atoms are labeled as usual. Atomic $2p\pi$-orbitals are centered on each of the atoms i and denoted by χ_i. The transformation to symmetrically orthogonal orbitals λ_i is given by the following set of equations.

$$\lambda_i = \sum_{k=1}^{6} A_{ik}\chi_k \qquad i=1\ldots 6 \tag{3}$$

with

$$A = \begin{pmatrix} A & B & C & D & C & B \\ B & A & B & C & D & C \\ C & B & A & B & C & D \\ D & C & B & A & B & C \\ C & D & C & B & A & B \\ B & C & D & C & B & A \end{pmatrix}.$$

We then use the following notation

$$\begin{aligned} \beta &= \beta_{12} = \langle \lambda_1 | h | \lambda_2 \rangle \\ \beta' &= \beta_{13} = \langle \lambda_1 | h | \lambda_3 \rangle \\ \beta'' &= \beta_{14} = \langle \lambda_1 | h | \lambda_4 \rangle . \end{aligned} \tag{4}$$

We denote integrals over λ's and momentum operator by $\boldsymbol{p}_{ij}$ and position operator by $\boldsymbol{r}_{ij}$.

We then proceed to establish approximate relations for $\boldsymbol{p}_{12}$, $\boldsymbol{p}_{13}$ and $\boldsymbol{p}_{14}$ by using as expansion functions in Eq. (2) only the six equivalent orbitals λ_i. In this framework it follows that

$$\begin{aligned} \boldsymbol{p}_{12} &= (\boldsymbol{r}_{11} - \boldsymbol{r}_{22} + \boldsymbol{r}_{13} - \boldsymbol{r}_{26})\beta + (\boldsymbol{r}_{16} - \boldsymbol{r}_{32} + \boldsymbol{r}_{14} - \boldsymbol{r}_{25})\beta' + (\boldsymbol{r}_{15} - \boldsymbol{r}_{24})\beta'' \\ \boldsymbol{p}_{13} &= (\boldsymbol{r}_{12} - \boldsymbol{r}_{23} + \boldsymbol{r}_{14} - \boldsymbol{r}_{36})\beta + (\boldsymbol{r}_{11} - \boldsymbol{r}_{33} + \boldsymbol{r}_{15} - \boldsymbol{r}_{35})\beta' + (\boldsymbol{r}_{16} - \boldsymbol{r}_{34})\beta'' \\ \boldsymbol{p}_{14} &= (\boldsymbol{r}_{13} - \boldsymbol{r}_{24} + \boldsymbol{r}_{15} - \boldsymbol{r}_{46})\beta + (\boldsymbol{r}_{12} - \boldsymbol{r}_{34} + \boldsymbol{r}_{16} - \boldsymbol{r}_{45})\beta' + (\boldsymbol{r}_{11} - \boldsymbol{r}_{44})\beta'' . \end{aligned} \tag{5}$$

We simplify these equations by keeping only terms of comparable magnitude

$$\begin{aligned} \boldsymbol{p}_{12} &= (\boldsymbol{r}_{11} - \boldsymbol{r}_{22})\beta \\ \boldsymbol{p}_{13} &= (\boldsymbol{r}_{11} - \boldsymbol{r}_{33})\beta' + (\boldsymbol{r}_{12} - \boldsymbol{r}_{23})\beta \\ \boldsymbol{p}_{14} &= (\boldsymbol{r}_{11} - \boldsymbol{r}_{44})\beta'' + (\boldsymbol{r}_{12} - \boldsymbol{r}_{34} + \boldsymbol{r}_{16} - \boldsymbol{r}_{45})\beta' + (\boldsymbol{r}_{13} - \boldsymbol{r}_{24} + \boldsymbol{r}_{15} - \boldsymbol{r}_{46})\beta . \end{aligned} \tag{6}$$

The expression for $\boldsymbol{p}_{14}$ remains unchanged. Now we transform the integrals over orthogonal orbitals λ_i to integrals over non-orthogonal orbitals χ_i denoted by a bar: $\bar{\boldsymbol{p}}_{12}$, $\bar{\boldsymbol{r}}_{11}$ etc. We invoke the following approximations by keeping only the largest terms of equal magnitude.

$$\begin{aligned} \boldsymbol{p}_{12} &= A^2\bar{\boldsymbol{p}}_{12} \\ \boldsymbol{p}_{13} &= A^2\bar{\boldsymbol{p}}_{13} + AB(\bar{\boldsymbol{p}}_{12} + \bar{\boldsymbol{p}}_{23}) \\ \boldsymbol{p}_{14} &= A^2\bar{\boldsymbol{p}}_{14} + AB(\bar{\boldsymbol{p}}_{13} + \bar{\boldsymbol{p}}_{15} + \bar{\boldsymbol{p}}_{24} + \bar{\boldsymbol{p}}_{64}) \\ &\quad + B^2\bar{\boldsymbol{p}}_{23} + AC(\bar{\boldsymbol{p}}_{12} + \bar{\boldsymbol{p}}_{16} + \bar{\boldsymbol{p}}_{34} + \bar{\boldsymbol{p}}_{54}) \\ \boldsymbol{r}_{11} - \boldsymbol{r}_{22} &= A^2(\bar{\boldsymbol{r}}_{11} - \bar{\boldsymbol{r}}_{22}) \end{aligned} \tag{7}$$

$$\begin{aligned}
r_{11}-r_{33}&=A^2(\bar{r}_{11}-\bar{r}_{33})\\
r_{11}-r_{44}&=A^2(\bar{r}_{11}-\bar{r}_{44})\\
r_{12}-r_{23}&=A^2(\bar{r}_{12}-\bar{r}_{23})+AB(\bar{r}_{11}+\bar{r}_{22}-\bar{r}_{22}-\bar{r}_{33})\\
r_{13}-r_{24}&=A^2(\bar{r}_{13}-\bar{r}_{24})+AB(\bar{r}_{12}+\bar{r}_{23}-\bar{r}_{23}-\bar{r}_{34})\\
&\quad+B^2(\bar{r}_{22}-\bar{r}_{33})+AC(\bar{r}_{11}+\bar{r}_{33}-\bar{r}_{22}-\bar{r}_{44})\,.
\end{aligned}\tag{7}$$

If we insert (7) into (6) we find that terms with A^2, AB, B^2, AC on both sides are equal and lead to

$$\begin{aligned}
\bar{p}_{12}&=(\bar{r}_{11}-\bar{r}_{22})\,\beta\\
\bar{p}_{13}&=(\bar{r}_{11}-\bar{r}_{33})\,\beta'+(\bar{r}_{12}-\bar{r}_{23})\,\beta\\
\bar{p}_{14}&=(\bar{r}_{11}-\bar{r}_{44})\,\beta''+(\bar{r}_{12}-\bar{r}_{34}+\bar{r}_{16}-\bar{r}_{45})\,\beta'+(\bar{r}_{13}-\bar{r}_{24}+\bar{r}_{15}-\bar{r}_{46})\,\beta\,.
\end{aligned}\tag{8}$$

We finally use the Mulliken approximation

$$\bar{r}_{ij}=\frac{1}{2}S_{ij}(\bar{r}_{ii}+\bar{r}_{jj})\tag{9}$$

to obtain the following formulas for β's in benzene

$$\begin{aligned}
\beta&=\frac{1}{R}\frac{dS}{dR}\\
\beta'&=\frac{1}{R'}\frac{dS'}{dR'}-\frac{1}{2}S\beta\\
\beta''&=\frac{1}{R''}\frac{dS''}{dR''}-\frac{3}{2}S\beta'-\frac{1}{2}S'\beta
\end{aligned}\tag{10}$$

where the R's are the corresponding distances between the atoms and the S's the overlap integrals over χ's.

In cases of lower symmetry these formulas have to be modified. To show that these changes do not affect the major idea we have also calculated the corresponding formulas for β's in butadiene which are as follows

$$\begin{aligned}
\beta_{\mathrm{C=C}}&=\frac{1}{R_{\mathrm{C=C}}}\frac{dS_{\mathrm{C=C}}}{dR_{\mathrm{C=C}}}\\
\beta_{\mathrm{C-C}}&=\frac{1}{R_{\mathrm{C-C}}}\frac{dS_{\mathrm{C-C}}}{dR_{\mathrm{C-C}}}\\
\beta'&=\frac{1}{R'}\frac{dS'}{dR'}-\frac{1}{4}(S_{\mathrm{C-C}}\beta_{\mathrm{C=C}}+S_{\mathrm{C=C}}\beta_{\mathrm{C-C}})\\
\beta''&=\frac{1}{R''}\frac{dS''}{dR''}-\frac{1}{2}(1+P)\,S_{\mathrm{C=C}}\beta'-\frac{1}{2}(1-P)\,S'\beta_{\mathrm{C=C}}
\end{aligned}\tag{11}$$

with

$$P=\boldsymbol{R}_{\mathrm{C-C}}\cdot\boldsymbol{R}''/(R'')^2\,.$$

Table 1. *Values of β parameters (in* eV) *over orthogonalized $2p\pi$-orbitals for benzene* ($R = 1.40$ Å) *and butadiene* ($R_{C=C} = 1.35$ Å, $R_{C-C} = 1.46$ Å, $\alpha = 124°$)

Molecule	ζ	$\beta_{C=C}$	β_{C-C}	β'	β''
Benzene	1.59[a]	−2.27	−2.27	0.05	−0.08
	1.29[b]	−2.47	−2.47	0.02	−0.13
cis-butadiene	1.59[a]	−2.51	−2.02	0.07	−0.06
	1.29[b]	−2.67	−2.26	0.06	−0.13
trans-butadiene	1.59[a]	−2.51	−2.02	0.07	0.001
	1.29[b]	−2.67	−2.26	0.06	0.01

[a] Slater's exponents. [b] Silverstone *et al.* [6].

Cis- and *trans*-butadiene can be distinguished in this framework of approximations only through β''. The difference is due to a difference of bond length R'' and of projection P of R_{C-C} on R''.

We have calculated β's for benzene and butadiene and collected the results in the Table 1.

We see from this table that the β's for benzene alternate in sign from nearest to next nearest neighbors and again to the following neighbor. This pattern is preserved if we use more diffuse orbitals than Slater's rules prescribe. However the difference from Linderberg's results is striking. Linderberg's paper contains the result $\beta' = 0$ for benzene. This must be a first-order approximation because the original formula [1] would yield a negative value for β'. Our improved formula yields a positive value. This and the order of magnitude for both β' and β'' are in agreement with a calculation by Chong [7] who found $\beta' = 0.07$ eV, $\beta'' = -0.05$ eV. For butadiene non-nearest neighbor β's were calculated by Parr and Mulliken [8]. Their values refer to an SCF Hamiltonian, rather than to the core Hamiltonian of the usual semiempirical π-electron methods. Thus their values are not comparable to ours. Semiempirical methods have usually neglected non-nearest neighbor β's [9], but their neighbor β's are of the same magnitude as those reported in this work. The difference in magnitude of β'' for *cis*- and *trans*-butadiene is due to the difference in distance between the end atoms. The change in sign occurs because of the rapid decrease of the first term in (11) compared to the third, the two having opposite signs.

We have also investigated these approximations for $2s$- and $2p\sigma$-orbitals. β values for $2s$-orbitals show the same pattern of alternation. However, more recent studies [10] suggest caution with regard to the interpretation of the underlying single-electron Hamiltonian of β's over orthogonal $2s$- and $2p\sigma$-orbitals. The reason for a failure of this simple approach might be the neglect of interaction terms between $2s$- and $2p\sigma$-orbitals.

Acknowledgement. I thank Professor T. J. Curphey for helpful comments on the presentation of the manuscript.

References

1. Linderberg, J.: Chem. Physics Letters **1**, 39 (1967).
2. Löwdin, P. O.: J. chem. Physics **18**, 365 (1950).
3. Jug, K.: Theoret. chim. Acta (Berl.) **16**, 95 (1970).

4. — Theoret. chim. Acta (Berl.) **19**, 391 (1970).
5. Linderberg, J., Öhrn, Y.: Chem. Physics Letters **3**, 119 (1969).
6. Silverstone, H. J., Joy, H. W., Orloff, M. K.: J. Amer. chem. Soc. **88**, 1325 (1966).
7. Chong, D. P.: Molecular Physics **10**, 67 (1965).
8. Parr, R. G., Mulliken, R. S.: J. chem. Physics **18**, 1338 (1950).
9. Mori, Y.: Bull. chem. Soc. Japan **28**, 291 (1955).
10. Jug, K.: Operator equations in approximate molecular orbital theories. Theoret. chim. Acta (Berl.), in press.

Prof. Karl Jug
Department of Chemistry
Saint Louis University
Saint Louis, Missouri 63156, USA