

Determination of α and β Parameters in Approximate SCF MO Theories

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The formula proposed by Linderberg for the evaluation of the resonance integral is further investigated. Consistency requirements for the α parameters lead to an explanation of the Wolfsberg-Helmholz form for β . The simple assumption that β is proportional to the overlap integral is improved. The dependency of α and β values on the distance in a diatomic molecule in this approximation is presented and discussed.

Linderbergs Formel zur Berechnung des Resonanzintegrals wird weiter untersucht. Konsistenzforderungen für die α -Parameter führen zu einer Erklärung der Wolfsberg-Helmholz-Form für β . Die einfache Annahme, daß β dem Überlappungsintegral proportional ist, wird verbessert. Die Abhängigkeit von α - und β -Werten vom Atomabstand in einem zweiatomigen Molekül wird in dieser Näherung angegeben und diskutiert.

Etude de la formule proposée par Linderberg pour le calcul de l'intégrale de résonance. Des nécessités de cohérence pour les paramètres α conduisent à une explication de la formule de Wolfsberg-Helmholz pour β . L'hypothèse simple selon laquelle β est proportionnel à l'intégrale de recouvrement est améliorée. On présente en la discutant la dépendance à la distance des valeurs de α et de β dans une molécule diatomique dans cette approximation.

1. Introduction

Recently Linderberg [1] has shown that the equivalence of dipole length and velocity forms of oscillator strengths places a condition on the parameters used in the Pariser-Parr model. Under the ZDO assumption for the matrix elements of the operators in the Hamiltonian certain simplifications hold which allow to establish a connection between the gradient of the overlap integral and the resonance integral β , which is defined over the core operator H_{core} .

In the case of two orbitals in a diatomic molecule, centered at positions μ and ν with vanishing gradient perpendicular to the axis connecting μ and ν , the following formula has been derived

$$\beta_{\mu\nu} = \frac{1}{R_{\mu\nu}} \frac{dS_{\mu\nu}}{dR_{\mu\nu}}. \quad (1.1)$$

As is well known, the ZDO assumption may, in the Pariser-Parr model, be interpreted on a basis of symmetrically orthogonalized atomic orbitals [2]. This device has been used by Linderberg to calculate β_{π} for ethylene and benzene. He could not only reproduce the commonly used values, but obtained the surprising result that the slope of the overlap for Slater type orbitals and SCF orbitals is the same, although their overlap values differ by 20%.

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In Linderberg's paper a further assumption was tentatively made to represent the overlap in a certain range of interest in an exponential form

$$S_{\mu\nu} = S_0 \exp(-(\zeta_\mu + \zeta_\nu) R_{\mu\nu}/2). \quad (1.2)$$

This leads to the following form for β

$$\beta_{\mu\nu} = -\frac{1}{2}(\zeta_\mu + \zeta_\nu) S_{\mu\nu}/R_{\mu\nu}. \quad (1.3)$$

Wratten [3] used this idea to explain the form of β which was used by Pople and Segal [4]

$$\beta_{AB} = \frac{1}{2}(\beta_A^0 + \beta_B^0) S_{\mu\nu}. \quad (1.4)$$

A comparison of (3) and (4) suggests

$$\beta_A^0 = -\frac{\zeta_A}{R} \quad (1.5)$$

if all the orbital exponents at the same atom are equal.

As Linderberg's formula has already drawn attention for application to molecular systems [5], some remarks on the derivation and range of applicability should be worthwhile, in particular, because there seems to be some confusion about the formula.

Firstly, it has been mentioned that form (1.1) implies the PPP-formalism [5]. This is certainly not the case. The connection is only established if the basis set for PPP-calculations is assumed as symmetrically orthogonalized. Secondly, there is a remark by Linderberg which could be misinterpreted. He stated that even if the overlap is zero, the slope of the overlap need not vanish. This is certainly true, e.g. for $2p\sigma$ -orbitals, but does not yield a satisfactory description of the situation. Derivation of Eq. (1.1) implies that the overlap is defined over *non-orthogonal* orbitals, β however over orthogonalized orbitals. For π -orbitals, which are the examples of Linderberg's paper, the overlap does not vanish at any finite distance. Wratten [3] has taken Linderberg's remark and concluded that Pople's formula [4] for β suffers a defect because S has been neglected in all other parts of the SCF matrix elements. The objection has, as it stands, little meaning, because on transformation from orthogonalized to non-orthogonal sets, overlap integrals defined over the latter basis do occur [6]. We shall show later, that Pople's form of β is in principle correct, because in both, orthogonal and non-orthogonal, basis sets proportionality of β and $S^{\text{non-orthogonal}}$ occur. A decision as to whether Pople's formula is inconsistent with the other assumptions of the CNDO method can only be made through parameter values. This point will be discussed later. But Wratten's form [5] suffers from the defect that β cannot converge to the proper limit α for vanishing distance.

In the following, we center attention on diatomic molecules. This cannot give correctly the higher order effects in overlap expansions for larger systems [7]. But we know that nearest neighbour effects are the dominant ones and we therefore prefer to simplify this aspect to a topological theory. This device yields some new qualitative results.

2. Derivation of the Basic Equation

To get a better insight into formula (1.1), let us go through the derivation more explicitly. We start with Heisenberg's equation of motion [8] for the position vector

$$\mathbf{p} = [\mathbf{r}, H] \quad (2.1)$$

where \mathbf{p} has been defined for convenience as antiermitian. This cancels the imaginary i , and we have to observe that $\mathbf{p}_{ab} = -\mathbf{p}_{ba}$. For many-electron systems \mathbf{p} and \mathbf{r} are sums over the single electron parts

$$\mathbf{p} = \sum_i \mathbf{p}_i, \quad \mathbf{r} = \sum_i \mathbf{r}_i. \quad (2.2)$$

We can simplify the formalism by the observation that the electronic motion commutes with the position vector and that expectation values of the \mathbf{p}_i can be defined over molecular orbitals

$$\langle \mathbf{p}_i \rangle = \langle \psi_i | \mathbf{p}_i | \psi_i \rangle.$$

Expansion over atomic orbitals yields

$$\langle \mathbf{p}_i \rangle = \sum_{\mu, \nu} c_{i\mu}^* c_{i\nu} \langle \chi_\mu | \mathbf{p}_i | \chi_\nu \rangle$$

so that (2.1) essentially results in

$$\langle \chi_\mu | \mathbf{p}_i | \chi_\nu \rangle = \langle \chi_\mu | [\mathbf{r}_i, h_i] | \chi_\nu \rangle \quad (2.3)$$

where h_i is the one-electron core operator.

In the following, we shall omit brackets and indices i and use for (2.3) the notation

$$\mathbf{p}_{\mu\nu} = [\mathbf{r}, h]_{\mu\nu}. \quad (2.4)$$

The product of operators on the right side of (2.4) can be expanded in any complete and orthogonal set $\{\lambda\}$ by using Dirac's resolution of the identity [9]

$$\sum_i |\lambda_i\rangle \langle \lambda_i| = 1.$$

It yields a general form of relation between momentum vector, position vector and core elements:

$$\mathbf{p}_{\mu\nu} = \sum_\lambda (\mathbf{r}_{\mu\lambda} h_{\lambda\nu} - h_{\mu\lambda} \mathbf{r}_{\lambda\nu}). \quad (2.5)$$

3. Symmetrical Expansion

We define now symmetrically orthogonalized orbitals λ from two equivalent Slater orbitals χ by

$$\begin{aligned} \lambda_a &= A\chi_a + B\chi_b, \\ \lambda_b &= B\chi_a + A\chi_b, \end{aligned} \quad (3.1)$$

where A and B fulfill the relations

$$\begin{aligned} A^2 + B^2 &= 1/(1 - S_{ab}^2), \\ 2AB &= -S_{ab}/(1 - S_{ab}^2), \\ (A^2 - B^2)^2 &= A^2 + B^2. \end{aligned} \quad (3.2)$$

For convenience, we give the relations between α and β in the orthogonal and non-orthogonal (with bar) set

$$\begin{aligned} \alpha &= (A^2 + B^2)\bar{\alpha} + 2AB\bar{\beta}, \\ \beta &= (A^2 + B^2)\bar{\beta} + 2AB\bar{\alpha}, \end{aligned} \quad (3.3a)$$

or

$$\begin{aligned} \bar{\alpha} &= \alpha + S\beta, \\ \bar{\beta} &= \beta + S\alpha. \end{aligned} \quad (3.3b)$$

Now we are able to derive Linderberg's formula as follows. We take a set of two orthogonal orbitals λ_a and λ_b only

$$\begin{aligned} p_{ab} &= r_{aa}h_{ab} - h_{aa}r_{ab} \\ &\quad + r_{ab}h_{bb} - h_{ab}r_{bb} \\ &= (r_{aa} - r_{bb})h_{ab} + r_{ab}(h_{bb} - h_{aa}). \end{aligned} \quad (3.4)$$

Under the assumption of equal exponents for χ_a and χ_b and using definition (3.1) and (3.2) we obtain

$$p_{ab} = (A^2 - B^2)(r_{\bar{a}\bar{a}} - r_{\bar{b}\bar{b}})\bar{\beta}_{ab}.$$

As p has been defined as antihermitian, we can use the relation

$$p_{ab} = (A^2 - B^2)p_{\bar{a}\bar{b}}$$

and obtain

$$p_{\bar{a}\bar{b}} = -\beta_{ab}R, \quad R = r_{\bar{b}\bar{b}} - r_{\bar{a}\bar{a}}, \quad (3.5)$$

or

$$\beta_{ab} = \frac{1}{R} \frac{dS_{\bar{a}\bar{b}}}{dR}; \quad R = |R|. \quad (3.6)$$

From the symmetrical expansion, we can get only information about β , but not about α . If we would take for instance $\lambda_a = \frac{1}{2}(\chi_a + \chi_b)/\sqrt{1 + S^2}$, $\lambda_b = \frac{1}{2}(\chi_a - \chi_b)/\sqrt{1 - S^2}$, we would obtain the same result (3.5). We need another relation to overcome the lack of information about α , $\bar{\alpha}$ and $\bar{\beta}$. This can be obtained when we leave the molecular symmetry property and start with an asymmetrical atomic expansion.

4. Asymmetrical Expansion

We define the p -integral over non-orthogonal orbitals \bar{a} and \bar{b} and take as expansion function a complete set of atomic orbitals centered at atom A

$$\{\lambda\} = \bar{a}, \bar{a}', \bar{a}'' \dots$$

Then we rewrite (2.5)

$$\begin{aligned} p_{\bar{a}\bar{b}} &= r_{\bar{a}\bar{a}}h_{\bar{a}\bar{b}} - h_{\bar{a}\bar{a}}r_{\bar{a}\bar{b}} \\ &+ r_{\bar{a}\bar{a}'}h_{\bar{a}'\bar{b}} - h_{\bar{a}\bar{a}'}r_{\bar{a}'\bar{b}} \\ &+ r_{\bar{a}\bar{a}''}h_{\bar{a}''\bar{b}} - h_{\bar{a}\bar{a}''}r_{\bar{a}''\bar{b}} \dots \end{aligned} \quad (4.1)$$

Relation (2.5), and in consequence (4.1), has to be independent of the choice of the origin of the coordinate system. For the left side of (4.1) this is obviously fulfilled, for the right we may take advantage of this invariance property by choosing a proper origin. Furthermore, we take the orbitals \bar{a} and \bar{b} as equivalent: $2s_a - 2s_b$, $2p\sigma_a - 2p\sigma_b$, $2p\pi_a - 2p\pi_b$ etc. So they have a moment only along the axis of the diatomic molecule.

a) Coordinate system origin at atom A:

$$\begin{aligned} p_{\bar{a}\bar{b}} &= -\frac{1}{2}\bar{\alpha}RS_{\bar{a}\bar{b}} - \bar{\alpha}'r' - \bar{\alpha}''r'' \dots \\ \bar{\alpha} &= h_{\bar{a}\bar{a}'}, \quad r' = r_{\bar{a}'\bar{b}} \quad \text{etc.} \end{aligned} \quad (4.2)$$

We have used the property that the moment vanishes: $z_{ab} = 0$, if the origin is in the middle between atoms A and B. This is valid for equal exponents.

b) Coordinate system origin in the middle between atom A and B

$$p_{\bar{a}\bar{b}} = -\frac{1}{2}\bar{\beta}R - \bar{\alpha}'\tilde{r}' - \bar{\alpha}''\tilde{r}'' \dots \quad (4.3)$$

Between r' and \tilde{r}' the relation holds

$$r' = \frac{1}{2}RS' + \tilde{r}'. \quad (4.4)$$

A closer inspection of (4.2) and (4.4) yields that \tilde{r}' is a small quantity in comparison to r' . So we regard it as of second order in $S_{\bar{a}\bar{b}}$ and neglect it. Besides, $\bar{\alpha}'$ etc. are smaller quantities than $\bar{\beta}$. This yields the reasonable approximations

$$p_{\bar{a}\bar{b}} = -\frac{1}{2}R(\bar{\alpha}S + \bar{\alpha}'S' + \bar{\alpha}''S'' \dots), \quad (4.5a)$$

$$p_{\bar{a}\bar{b}} = -\frac{1}{2}R\bar{\beta}. \quad (4.5b)$$

A comparison of (4.5a) and (4.5b) yields

$$\bar{\beta} = \bar{\alpha}S + \bar{\alpha}'S' + \bar{\alpha}''S'' \dots$$

which is nothing else than Ruedenberg's asymmetrical expansion [10]

$$\chi_b = S_{ab}\chi_a + S_{a'b}\chi_{a'} + S_{a''b}\chi_{a''} \dots$$

This means that we still have a consistent relation between $\bar{\alpha}$ and $\bar{\beta}$, although form (4.5b) for $\bar{\beta}$ is only approximately valid. Together with (3.3) and (3.5), (4.5b)

yields

$$\bar{\beta} = 2\beta, \quad (4.6a)$$

$$\beta = S\alpha, \quad (4.6b)$$

$$\bar{\beta} = \frac{2}{1+S^2} S\bar{\alpha}. \quad (4.6c)$$

The last equation is obviously most interesting. It gives an explanation of the Wolfsberg-Helmholz factor [11] K

$$K = \frac{2}{1+S^2}. \quad (4.7)$$

K is unity for vanishing distance and two for infinite separation. It is always smaller than two which eliminates the choice of values $K=3$ which was taken by several investigators. In π -electron systems with $S=0.25$ the value $K=1.88$ comes close to the generally adopted value $K=1.75$ [12]. To be more correct, we would have to adopt three K -values, e.g. in benzene¹

$$K_s = 1.70, \quad K_\sigma = 1.80, \quad K_\pi = 1.88.$$

The choice of a single K value was obviously successful only because the three K -values are very close.

At this point, we are also able to make a comparison with Pople's formula for β . If Pople's basis set is regarded as non-orthogonal we obtain

$$\bar{\beta}_A^0 = \frac{2}{1+S^2} \bar{\alpha}_s \quad (4.8)$$

whereas an identification with the orthogonalized set would yield

$$\beta_A^0 = \alpha_s. \quad (4.9)$$

From our derivation we obtain (Table)

$$\bar{\beta}_A^0 = -12.76 \text{ eV}, \quad \beta_A^0 = -6.38 \text{ eV}.$$

This reveals that the actual choice of the parameter value $\beta_C^0 = -21 \text{ eV}$ can only be ascribed to the non-orthogonal set.

From the definition in Pople's papers [4, 13], it should be clear that this author assumed a non-orthogonal set. It is not quite clear, however, that the neglect of overlap of certain electronic *two-center* integrals is consistent with this assumption. In a paper by McWeeny [14], we already find a remark about an inconsistency in the CNDO basis. A way out of this dilemma is only in the conclusion that the neglect of electronic two-center integrals is too minor to influence the interpretation of the basis set; the dominant effect is in β .

Consequently the set has to be regarded as non-orthogonal. We should not be confused by the ZDO assumption in connection with the invariance question. The invariance is discussed only for orbitals at the same center and does not concern the two-center non-orthogonality problem.

¹ With Slater exponents.

5. Two Different Shielding Exponents

With the same device, we shall attack now the difficult case of different exponents for the two orbitals at atom A and B. The Eqs. (3.3) take now the form

$$\begin{aligned}\beta &= (A^2 + B^2) \bar{\beta} + AB(\bar{\alpha}_a + \bar{\alpha}_b), \\ \alpha_a &= A^2 \bar{\alpha}_a + B^2 \bar{\alpha}_b + 2AB \bar{\beta}, \\ \alpha_b &= B^2 \bar{\alpha}_a + A^2 \bar{\alpha}_b + 2AB \bar{\beta},\end{aligned}\tag{5.1 a}$$

or

$$\begin{aligned}\bar{\beta} &= \beta + \frac{1}{2} S(\alpha_a + \alpha_b), \\ \bar{\alpha}_a &= \frac{1}{2} (\alpha_a + \alpha_b) + \frac{1}{2(A^2 - B^2)} (\alpha_a - \alpha_b) + S\beta, \\ \bar{\alpha}_b &= \frac{1}{2} (\alpha_a + \alpha_b) - \frac{1}{2(A^2 - B^2)} (\alpha_a - \alpha_b) + S\beta.\end{aligned}\tag{5.1 b}$$

Again we may start with a truncated symmetrical expansion. Analogous to (3.5), we obtain the relation

$$p_{\bar{a}\bar{b}} = -R\beta + \left[\frac{AB}{A^2 - B^2} (r_{\bar{a}\bar{a}} + r_{\bar{b}\bar{b}}) + \frac{A^2 + B^2}{A^2 - B^2} r_{\bar{a}\bar{b}} \right] (\alpha_b - \alpha_a).\tag{5.2}$$

We know that the term in the brackets has to be independent of the coordinate origin². In addition, we know that the dipole moment of a charge distribution $\chi_a \chi_b$ vanishes if we take the center of charge as the origin of the coordinate system. For symmetry reasons, this center of charge has to be on the axis between atoms A and B. In the case of equal exponents it is in the middle: $r_{ab}(\frac{1}{2}R) = 0$. In the case of unequal exponents we can assume:

$$r_{ab}(R_0) = 0\tag{5.3}$$

where R_0 is different from $\frac{1}{2}R$. R_0 is defined to have the same direction as R , i.e. from atom A to atom B.

Then (5.2) can be simplified

$$p_{\bar{a}\bar{b}} = -R\beta - \frac{AB}{A^2 - B^2} (2R_0 - R) (\alpha_b - \alpha_a).\tag{5.4}$$

$(2R_0 - R)$ is negative if the center of charge is moved towards atom A.

The asymmetrical expansion with the expansion functions centered at atom A

$$\{\lambda\} = \bar{a}, \bar{a}', \bar{a}'' \dots$$

yields under assumption of coordinate origin in R_0

$$p_{\bar{a}\bar{b}} = -R_0 \bar{\beta} - \bar{r}' \alpha' - \bar{r}'' \alpha'' \dots\tag{5.5}$$

If we neglect now all terms with the exception of the dominant one, we obtain

$$p_{\bar{a}\bar{b}} = -R_0 \bar{\beta}.$$

² That this is indeed the case can be proved by inserting the explicit expressions for AB and $(A^2 + B^2)$ in the bracket.

This form is unfortunately not invariant under exchange of atoms A and B. If we take an expansion set with origin at atom B, we would obtain

$$p_{\bar{a}\bar{b}} = -(\mathbf{R} - \mathbf{R}_0) \bar{\beta}.$$

The invariance is guaranteed, if we take the average of both expansions

$$p_{\bar{a}\bar{b}} = -\frac{1}{2} \mathbf{R} \bar{\beta}. \quad (5.6)$$

To keep the invariance and to derive a simple formula, we have to make a compromise. This is probably a weak point in this derivation. So we can expect (5.6) to be reasonably valid only if the exponents of the orbitals at atoms A and B do not differ too much. What this means quantitatively is a difficult question. At any rate, it is more justified to use a consistent form as (5.6) and then search for correction terms than to use a restrictive approximation. From a comparison of (5.4) and (5.6) we obtain

$$\bar{\beta} = 2\beta + \frac{2AB}{A^2 - B^2} \left(\frac{2R_0}{R} - 1 \right) |\alpha_b - \alpha_a|. \quad (5.7)$$

Substitution of (5.7) in (5.1b) yields for the orthogonalized set

$$\begin{aligned} \beta &= \frac{1}{2} S [(\alpha_a + \alpha_b) + \kappa |\alpha_a - \alpha_b|], \\ \kappa &= 2 \left(1 - \frac{2R_0}{R} \right) / \sqrt{1 - S^2}. \end{aligned} \quad (5.8)$$

For the non-orthogonal set we obtain

$$\begin{aligned} \bar{\beta} &= \frac{1}{2} KS [(\bar{\alpha}_a + \bar{\alpha}_b) + \kappa |\bar{\alpha}_a - \bar{\alpha}_b|], \\ K &= \frac{2}{1 + S^2}, \quad \kappa = 1 - \frac{2R_0}{R}. \end{aligned} \quad (5.9)$$

6. Results and Discussion

The dependence of K -, α - and β -values on the distance, under special consideration of benzene, is collected in Figs. 1–3 and the Table.

Let us concentrate on the π -orbitals first. Linderberg [1] had already shown that the PPP β -value can be quantitatively reproduced. We can show in addition that both β - and $\bar{\beta}$ -values are almost insensitive to large changes in the orbital exponent for distances larger than 2 a.u. The second remarkable result is that the curves for α - and $\bar{\beta}$ -values intersect at about 2 a.u., so that the closeness of these values in the literature [15] is not at all accidental. In addition it may be observed that for distances larger than 3 a.u. α approaches $\bar{\alpha}$ rapidly.

Another case for comparison is Berthier's [16] relation for π -electron hydrocarbons

$$\beta_{\mu\nu} = -8.53 S_{\mu\nu},$$

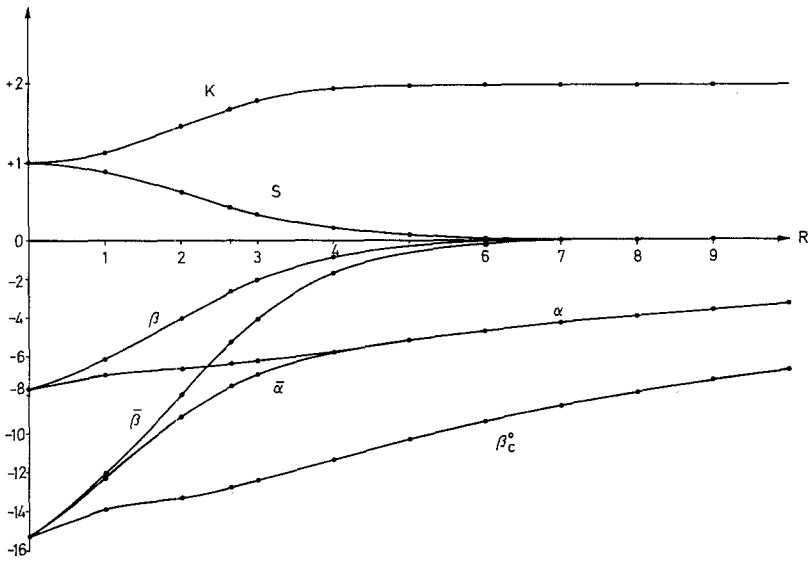


Fig. 1. Dependence of K -, S -, α - and β -values for $2s$ -orbitals on the distance R

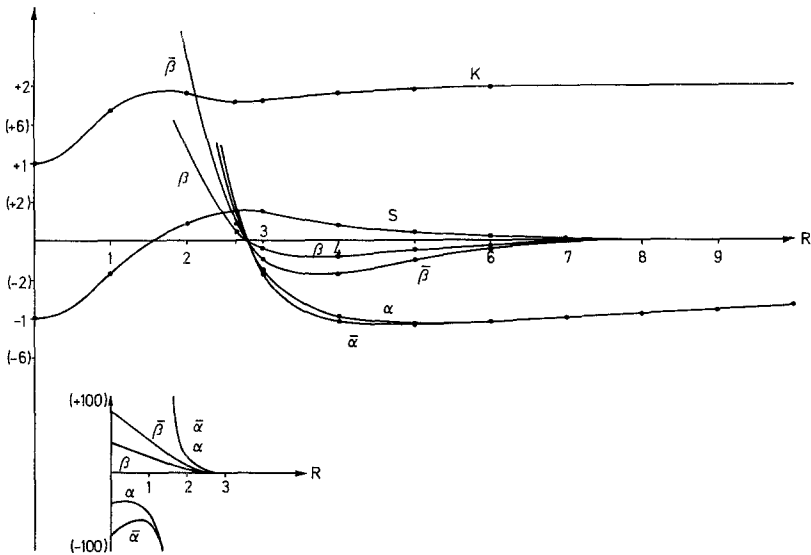


Fig. 2. Dependence of K -, S -, α - and β -values for $2p\sigma$ -orbitals on the distance R . Scale in parentheses apply to α - and β -values only

fitted for benzene. From (4.6b) the coefficient can be identified with α . The Table yields $\alpha = -8.85$ eV resp. -6.40 . For Slater exponents only the first is in agreement with Berthier's choice.

Finally, we are unable with the above formalism to explain choices where the $\bar{\alpha}$ -value has been set equal to the carbon ionization potential [15]. Indeed, the split between α and $\bar{\alpha}$ is larger in the literature values [15] than in the present work.

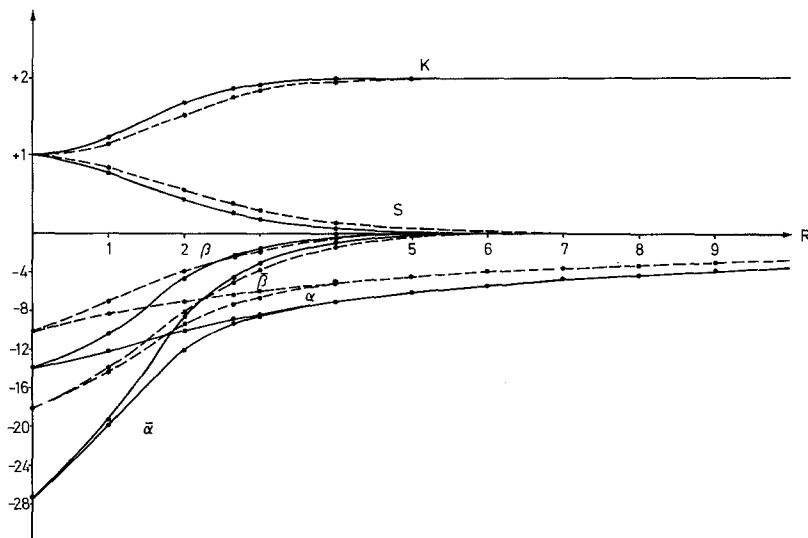


Fig. 3. Dependence of K -, S -, α - and β -values for $2p\pi$ -orbitals on the distance R . Dashed curves with Silverstone's exponents

Table. α - and β -values for benzene ($R = 1.40 \text{ \AA}$)

	$2s$	$2p\sigma$	$2p\pi$	$2p\pi$
ζ	1.59 ^a	1.59 ^a	1.59 ^a	1.29 ^b
S	0.42	0.329	0.256	0.385
K	1.70	1.80	1.88	1.74
β	-2.68	0.52	-2.27	-2.47
$\bar{\beta}$	-5.36	1.03	-4.53	-4.93
α	-6.38	1.57	-8.85	-6.40
$\bar{\alpha}$	-7.50	1.74	-9.43	-7.35

^a Slater: *Physic. Rev.* **36**, 57 (1930).

^b Silverstone *et al.*: *J. Amer. chem. Soc.* **88**, 1325 (1966).

We have already mentioned that we would have to take three K -values in the Wolfsberg-Helmholz approximation instead of one in all valence electron calculations. From Figs. 1–3 and the Table we obtain that the K -values are very close together for distances larger than 2 a.u. In addition, the K_π -value is almost insensitive to large changes in the orbital exponent. This explains, at least in part, the success of Hoffmann's [12] results with a single K -value 1.75. We would like to mention that an explicit form of the Wolfsberg-Helmholz factor K has already been given by Cusachs [17]

$$K = 2 - |S_{\mu\nu}|$$

which compares favorably with our formula (4.7).

A closer inspection of the α - and β -parameters for σ -electrons reveals that the quantitative agreement with values in the literature is not so satisfactory, e.g. Pople's absolute value for $\beta_C^0 = -21 \text{ eV}$ is much larger than our value $K\bar{\alpha}_s = -12.76 \text{ eV}$. However, it must be added that the slope of the curve is small.

This is in qualitative agreement with Pople's claim that β_C^0 should be constant. The qualitative feature of the other curves for $2s$ -orbitals are very similar to those of the π -orbitals.

The greatest difficulty is the interpretation of Fig. 2 for $2p\sigma$ -orbitals. There are large changes in all the parameter values for distances smaller than 3 a.u. However, it is not surprising that changes in sign occur. For the reference distance 2.65 a.u. in benzene, β and $\bar{\beta}$ are positive. As some features are due to our approximation, it must be concluded that a pure β -value over $2p\sigma$ -orbitals has to be regarded with much caution. This leads us finally to the shortcomings of our simplified approach. Our formalism would be improved by more expansion functions. In particular, there is a coupling between the $2s$ - and $2p\sigma$ -orbitals which probably cannot be neglected. It could shift the parameter values for s - and $p\sigma$ -orbitals considerably. How important this coupling is, can be seen for $2p\sigma$ -orbitals. Formulas (4.6b) and (4.6c) yield singularities for α and $\bar{\alpha}$ if S vanishes. This is due to approximation (4.5b) which yields $\bar{\beta} = 2\beta$, regardless of the overlap, whereas the correct form (3.3b) yields $\bar{\beta} = \beta$ for $S = 0$. The maximum error occurs in this case of vanishing overlap.

To the author's knowledge, so far all formulas³ which have established a connection between α and β resp. $\bar{\alpha}$ and $\bar{\beta}$ suffer this defect for the same reason: Any approximation which is based on a power series expansion in S is basically improper. One would think that this impropriety could be easily removed by a functional dependency on S which accounts for the cases $S = 0$ and $S = 1$. Yet, the author was unable to find a simple interpolation formalism which is still consistent. The basic difficulty is that for $S = 0$, α and $\bar{\alpha}$ cannot be determined through (3.3). Trial and error attempts are not very helpful; for instance, formulas like $\bar{\beta} = (1 + S)\beta$ would yield $\alpha = \beta$ and $\bar{\beta} = (1 + S^2)\beta$ even yields $\alpha = S\beta$. It might be worthwhile to mention that some methods avoid the singularity by arbitrarily defining an α -value. They consequently obtain $\beta = 0$ for $S = 0$. This is of little advantage, because the inaccuracy is shifted from α to β . Despite some negative quantitative results, we may conclude that the choice of β -parameters in the literature can be explained on the basis of simple approximations. However, a quantitative application has to be regarded with much caution. To improve the formulas we have at least to include the largest coupling terms, e.g. between s - and $p\sigma$ -orbitals, in an expansion. This might lead to complicated formulas where the underlying features are less visible.

Also the choice of hybrids would have to be discussed more extensively. Our formulas (3.6) and (4.6) are not covariant under hybridization.

Finally, our diatomic approach neglects higher order corrections which would occur in polyatomic molecules. It might be objected that in this case we would have to neglect also the higher order terms in (4.6c). But these are necessary for consistency between $\bar{\alpha}$ and $\bar{\beta}$.

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³ We do not include those formulas which do not yield the proper limit; their range of applicability is much more limited.

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