Theoret. chim. Acta (Berl.) 19, 301—309 (1970)

Commentationes

Formulas for $\bar{\beta}$ Parameters and Their Limitations

KARL JUG

Department of Chemistry, Saint Louis University, Saint Louis, Missouri 63156

Received July 31, 1970

The operator relationship $\boldsymbol{p} = [\boldsymbol{r}, h]$ between linear momentum, position vector and Hamiltonian is the basis for an investigation of formulas for $\bar{\beta}$ parameters in extended Hückel [1] and CNDO [2] type methods. The gauge problem of this equation in connection with truncated expansions of matrix elements $\langle\chi|\boldsymbol{p}|\chi'\rangle$ over atomic orbitals is discussed. Formulas for $\bar{\beta}$ parameters useful in extended Hückel methods are presented.

Die Operatorengleichung $\boldsymbol{p} = [\boldsymbol{r}, h]$ zwischen Impuls, Ortsvektor und Hamiltonoperator ist die Grundlage für eine Untersuchung von Formeln für $\bar{\beta}$-Parameter in der erweiterten Hückel[1]- und CNDO[2]-Methode. Das Eichproblem dieser Gleichung in Verbindung mit abgebrochenen Entwicklungen für Matrixelemente $\langle\chi|\boldsymbol{p}|\chi'\rangle$ über Atomfunktionen wird diskutiert. Nützliche Formeln für die erweiterte Hückel-Methode werden abgeleitet.

La relation entre opérateurs moment linéaire, position et hamiltonien: $\boldsymbol{p} = [\boldsymbol{r}, h]$ sert de base à une étude de formules pour les paramètres $\bar{\beta}$ dans les méthodes de type Hückel étendu [1] et CNDO [2]. Le problème de jauge de cette équation est discuté par rapport au développement limité des éléments de matrice $\langle x|\boldsymbol{p}|x'\rangle$ dans une base d'orbitales atomiques. Présentation de formules pour les paramètres $\bar{\beta}$ utiles dans les méthodes Hückel étendu.

1. Introduction

Formulas for β parameters [4] in molecular frameworks can be divided in two categories: $\bar{\beta} = \langle\chi|h_{\text{eff}}|\chi'\rangle$ defined over non-orthogonal atomic Slater orbitals χ, χ' at different atoms, $\beta = \langle\lambda|h_{\text{eff}}|\lambda'\rangle$ defined over orthogonalized orbitals λ, λ'. In this paper we shall deal primarily with the former. $\bar{\alpha}$ parameters refer to a single atom. The orbitals on which we concentrate are those occuring in σ-frameworks: $2s$ and $2p\sigma$. In the following we shall refer to them as s, z for one atom and s', z' for another atom. Further distinction arises from the fact that the effective Hamiltonian h_{eff} for the representative one-electron problem of the SCF MO formalism is different for different levels of approximation. h_{eff} is usually assumed as the SCF Hamiltonian in the extended Hückel method [1], whereas a core without electronic interaction is used in Pople's CNDO method [2]. We denote those $\bar{\beta}$ parameters which refer to the former h_{eff} as $\bar{\beta}_{\text{Hückel}}$ and to the latter as $\bar{\beta}_{\text{core}}$.

In a previous paper [3], generalizing a suggestion by Linderberg [5], we discussed how the operator relationship $\boldsymbol{p}_i = [\boldsymbol{r}_i, h_i]$ for linear momentum, position vector and Hamiltonian of a single electron i in a molecular framework can be used to establish approximate formulas for $\overline{\beta}$ parameters. Despite a number of illuminating results about the nature of Wolfsberg-Helmholz [6] type approximations [1, 7] and other semiempirical suggestions [8, 9], shortcomings of the approach become obvious upon closer inspection. These are essentially the following:

i) $\overline{\alpha}_z = \langle z | h_{\text{eff}} | z \rangle$ has a singularity for the finite interatomic distance R for which the overlap $S_z = \langle z | z' \rangle$ vanishes.

ii) All $\overline{\alpha}$ values vanish for $R \rightarrow \infty$ with the order $1/R$.

iii) β values approach α values for $R \rightarrow 0$. An improved formula should take care of the fact that $\beta \rightarrow \frac{1}{2}(\overline{\alpha} - \varepsilon)$, $\alpha \rightarrow \frac{1}{2}(\overline{\alpha} + \varepsilon)$ for $R \rightarrow 0$, where ε comes from the antisymmetric part $[2(1-S)]^{1/2}(\chi - \chi')$ of the symmetrically orthogonalized orbitals.

iv) There is no unique recipe for obtaining results independent of the coordinate origin, in a truncated atomic expansion.

v) $\overline{\alpha}$ and $\overline{\beta}$ parameters depend on the shielding exponents ζ of the atomic orbitals. If we assume that the AO's are "good" expansion functions for the MO's then we have to assume their dependence on the molecular framework. The ζ's are consequently dependent on the interatomic distance R.

vi) There is no *a priori* knowledge of how the approximations plus the orbital exponents influence the interpretation of the Hamiltonian h in $\boldsymbol{p} = [\boldsymbol{r}, h]$.

It can be shown that problems i) and iii) can be avoided by taking more terms in the expansions than just the main terms. In particular we have to use expansion functions $2s$ to determine $\overline{\beta}_z$ and $\overline{\alpha}_z$. We call this case the *coupled* formalism, in contrast to the *uncoupled* formalism where $\overline{\beta}_z$ and $\overline{\alpha}_z$ were determined by z orbitals only. We shall comment on it briefly later. iv) was taken care of by using the symmetry of the molecule, or more generally the property that reflections in the plane perpendicular to and through the middle point of the nuclear axis either leave the quantities considered unchanged or change their sign. We shall apply this recipe also in this paper, but wish to emphasize that this is not the only way to ensure invariance under translations of the coordinate origin. Problem v) is still unsolved in a sense that few data are available where exponents in molecular frameworks are determined [10–12]. For the few quantitative results, we have used Slater's exponents, which for σ-electrons at intermediate distances seem not to be significantly different from the molecular framework exponents [10–12] and so do not disturb the qualitative conclusions.

Our main concern shall be points ii) and vi). To avoid the vanishing $\overline{\alpha}$'s for large internuclear distances we adopt an alternative point of view which is concerned with an investigation of the effective Hamiltonian and thus connected with vi). We shall show that a form $\overline{\beta} = KS\overline{\alpha}$ leaves some freedom in the interpretation of h_{eff}. In particular, since it does not exclude that $\overline{\alpha}_s$ and $\overline{\alpha}_z$ are "atomic" parameters, where the potential term of h_{eff} refers to a single atom, we shall *postulate* for practical purposes later $\overline{\alpha}_s = \overline{\alpha}_s$ (atom) and $\overline{\alpha}_z = \overline{\alpha}_z$ (atom). In the final section we extend the expansion to the *coupled* formalism between s- and z-orbitals. We discuss how correction terms to the Wolfsberg-Helmholz term for $\overline{\beta}$ influence these quantities.

2. Gauge Invariance and Effective Hamiltonian

In our previous paper [3] we derived approximate formulas, but did not concentrate on implications which are closely connected with their derivation. In this section, we want to obtain some idea about the effective Hamiltonian with which we are dealing. Therefore, we go back to our starting point, the Heisenberg equation of motion [13]

$$\boldsymbol{p} = [\boldsymbol{r}, h] . \tag{2.1}$$

We realize that the commutation rules allow for an infinite number of Hamiltonians which differ only by a potential term $V(r)$. We call this property of the Heisenberg equation of motion *gauge invariance.* The linear momentum on the left side (2.1) should not depend on a particular choice of an effective Hamiltonian. This is guaranteed only in a infinite expansion of the type [14]

$$\boldsymbol{p}_{\mu\nu} = \sum_{\lambda} (\boldsymbol{r}_{\mu\lambda} h_{\lambda\nu} - h_{\mu\lambda} \boldsymbol{r}_{\lambda\nu}) \tag{2.2}$$

where λ is a complete, orthogonal set and $\boldsymbol{p}_{\mu\nu}$, $\boldsymbol{r}_{\mu\nu}$, $h_{\mu\nu}$ are matrix elements of the operators over orbitals μ and ν. In a truncated expansion this invariance is partly or completely lost.

Let us consider for example a special case, where we take for λ only s and z at the same atom. Then the following equality should hold approximately

$$\boldsymbol{p}_{sz} = \boldsymbol{r}_{sz} (\bar{\alpha}_z - \bar{\alpha}_s) . \tag{2.3}$$

Eq. (2.3) is well known in the semiclassical theory of radiation, where the transition moment for dipole radiation is defined in either the momentum or coordinate representation. We know that (2.3) holds *exactly* if $\bar{\alpha}_z$ and $\bar{\alpha}_s$ are eigenvalues of an *effective* Hamiltonian $h = h_{\text{eff}}$ with

$$h_{\text{eff}} \chi(\zeta) = \bar{\alpha}(\zeta) \, \chi(\zeta) . \tag{2.4}$$

In this context, we understand that we are not free in interpreting the effective Hamiltonian once we assign values to $\bar{\alpha}_z$ and $\bar{\alpha}_s$. Eq. (2.4) is the generalization of the Pariser-Parr approximation [15]

$$(T + U_p) \, \chi_p = W_p \chi_p$$

in a molecular framework. To be consistent, we have to use (2.3) to assign a value to $r_{sz} \equiv |\boldsymbol{r}_{sz}| = \langle s | z | z \rangle$

$$r_{sz} = (2\sqrt{3})^{-1} \zeta / (\bar{\alpha}_z - \bar{\alpha}_s) . \tag{2.5}$$

The theory on this level of approximations is free of singularities only if there is no crossing of the $\bar{\alpha}_z$ and $\bar{\alpha}_s$ curves, for any distance R between the two atoms.

To simplify our investigation on the underlying effective Hamiltonian in truncated expansions, we shall compare the Linderberg formula [5] and the Wolfsberg-Helmholz formula [3] for $\bar{\beta}$. For this purpose we rewrite the Linderberg formula similarly to Linderberg and Öhrn's [16] procedure, for a homonuclear diatomic molecule

$$\bar{\beta}=S\bar{\alpha}+(1-S^2)\frac{1}{R}\frac{dS}{dR}, \tag{2.6}$$

$$\bar{\beta}=\frac{2S}{1+S^2}\bar{\alpha}. \tag{2.7}$$

The last term $\frac{1}{R}\frac{dS}{dR}$ is β over symmetrically orthogonalized orbitals [3, 5]. We recognize that β is given in a gauge invariant form. However, the exact equation $\beta=(\bar{\beta}-S\bar{\alpha})/(1-S^2)$ proves that β is gauge invariant only to the first order in S. $\bar{\beta}$ is not gauge invariant. It is obvious that Eqs. (2.6) and (2.7) have different transformation properties. This suggests that the effective Hamiltonian of the two formulas are different. Some information may be obtained by looking at $\bar{\beta}$ and $\bar{\alpha}$ values of the Hamiltonian

$$h_{\mathrm{eff}}=T+\frac{Z_{\mathrm{eff}}}{r_a}+\frac{Z_{\mathrm{eff}}}{r_b}$$

of a diatomic molecule. The asymptotic behaviour of $\bar{\beta}/\bar{\alpha}$ for large R calculated exactly with Roothaan's [17] formulas yields

$$\bar{\beta}\to KS\bar{\alpha}, \qquad \bar{\alpha}\to\bar{\alpha}\ \text{(atom)}$$

$$K\to\frac{1}{Z_{\mathrm{eff}}/\zeta-1} \qquad \text{for } 2p\text{-orbitals}$$

$$K\to\frac{1}{Z_{\mathrm{eff}}/\zeta-1/3} \qquad \text{for } 2s\text{-orbitals}.$$

It suggests $Z_{\mathrm{eff}}=2\zeta$ (resp. $\frac{4}{3}\zeta$) to yield $K\to 1$ and $Z_{\mathrm{eff}}=\frac{3}{2}\zeta$ (resp. $\frac{5}{6}\zeta$) for $K\to 2$. So Linderberg's formula which approaches $\bar{\beta}=S\bar{\alpha}$ represents a situation with a larger effective charge than the Wolfsberg-Helmholz formula. This suggests that in the Wolfsberg-Helmholz case there is accounted for more shielding than the core parameter $\bar{\beta}_{\mathrm{core}}$ represents. Thus Wolfsberg-Helmholz type formulas might be used better for Hückel-type methods than for Pariser-Parr-Pople type calculations. Dahl and Ballhausen [18] have reached similar conclusions in a different context. On the other hand, we may identify Linderberg's effective Hamiltonian with the core Hamiltonian of Pople's CNDO form [9] of

$$\bar{\beta}=S\beta_A.$$

From (2.6) we obtain

$$\beta_A=\bar{\alpha}+\frac{(1-S^2)}{SR}\frac{dS}{dR} \tag{2.8}$$

$\bar{\alpha}$ and S have to be taken over s orbitals. This identification has the right behaviour for large and small R, which was not the case for Wratten's [19] derivation. For practical purposes we can take $\bar{\alpha}=\bar{\alpha}_s$(atom) and regard the second term in (2.8) as a molecular correction term.

We have seen in the preceding paragraphs that the Wolfsberg-Helmholz form $\bar{\beta}=KS\bar{\alpha}$ can yield non-vanishing $\bar{\alpha}$ values for $R\to\infty$ and that it refers to different effective Hamiltonians for different K values. This opens the way to an alternative view of our previous formulas [3]. We recall that a truncated atomic expansion with the main term yielded

$$\frac{dS}{dR}=\frac{1}{2}R\bar{\beta}. \tag{2.9}$$

Whereas the left side of (2.9) is the correct evaluation of the linear momentum matrix element, the right side is an approximate representation of the commutator $[r,h]$. $\bar{\beta}$ decreases with the order $1/R$ too fast for large interatomic distances R. This is not serious in molecular calculations, but prevents a formulation of $\bar{\beta}=KS\bar{\alpha}$ with an $\bar{\alpha}\to\bar{\alpha}$ (atom) for large R. On the other hand, the main term of the orthogonal expansion [20]

$$\frac{dS}{dR}=R\beta \tag{2.10}$$

is a more flexible approximation which is still invariant to the first order in S.

We therefore suggest the following procedure. We use truncated asymmetrical atomic expansions of type (2.9) and truncated symmetrical expansions of type (2.10) to establish equalities between β and $\bar{\beta}$, where slopes of overlaps dS/dR are used only as intermediates. This leaves some freedom for $\bar{\alpha}$ values. Then we can *assume* $\bar{\alpha}$ values which have the proper atomic limits as outlined above. In other words, we suggest not to determine the gauge by slopes of overlap according to (2.9), but by the *requested* asymptotic behaviour of $\bar{\alpha}$.

In the next section we want to investigate which correction terms occur to the Wolfsberg-Helmholz form of $\bar{\beta}$ in the coupled formalism of s- and z-orbitals.

3. Relations between $\bar{\alpha}$ and $\bar{\beta}$ Parameters over $2s$- and $2p\sigma$-Orbitals in the Coupled Approximation

We use a coordinate system x, y, z at atom A and x', y', z' at atom B in a homonuclear diatomic molecule with the following conventions: $x'=x$, $y'=y$, $z'=z-R$ where R is the internuclear distance between A and B. (This is different from the coordinates in our previous paper [3] where we used $z'=R-z$.) We define the six parameters

$$\begin{aligned}
\bar{\alpha}_s&=\langle s|h_{\mathrm{eff}}|s\rangle, & \bar{\beta}_s&=\langle s|h_{\mathrm{eff}}|s'\rangle;\\
\bar{\alpha}_z&=\langle z|h_{\mathrm{eff}}|z\rangle, & \bar{\beta}_z&=\langle z|h_{\mathrm{eff}}|z'\rangle;\\
\bar{\alpha}_{sz}&=\langle s|h_{\mathrm{eff}}|z\rangle, & \bar{\beta}_{sz}&=\langle s|h_{\mathrm{eff}}|z'\rangle.
\end{aligned} \tag{3.1}$$

We shall also use the following notation for the overlap integrals

$$S_s=\langle s|s'\rangle, \quad S_z=\langle z|z'\rangle, \quad S_{sz}=\langle s|z'\rangle.$$

In the following we want to derive equations which relate $\bar{\beta}$ parameters to $\bar{\alpha}$ parameters. We use the same approach as previously [3] starting with Eq. (2.2).

For the symmetric expansion we use four expansion functions for λ, namely $\lambda_1 = N_1(s+s')$, $\lambda_2 = N_2(s-s')$, $\lambda_3 = N_3(z-z')$, $\lambda_4 = N_4(z+z')$. Here we have neglected all terms with S_{sz} which would be necessary to make λ_1 exactly orthogonal to λ_3 and λ_2 to λ_4. An investigation has shown that their importance is minor for a qualitative discussion of the final results. This yields *three* non-redundant relations between $\boldsymbol{p}$, $\boldsymbol{r}$ and h matrix elements in the orthogonal basis. Subsequent substitution of the orthogonal functions by the non-orthogonal s, z, s', z' functions yields essentially relations of the type

$$\begin{gathered}\frac{dS_i}{dR} = f_i(R, r_{sz}, \bar{\alpha}_s, \bar{\beta}_s, \bar{\alpha}_z, \bar{\beta}_z, \bar{\alpha}_{sz}, \bar{\beta}_{sz}),\\ S_i = S_s, S_z \text{ or } S_{sz}.\end{gathered} \tag{3.2}$$

We use an asymmetrical atomic expansion with two orbitals s and z to obtain *three* additional equations of the type

$$\begin{gathered}\frac{dS_i}{dR} = g_i(R, r_{sz}, \bar{\alpha}_s, \bar{\beta}_s, \bar{\alpha}_z, \bar{\beta}_z, \bar{\alpha}_{sz}, \bar{\beta}_{sz}),\\ S_i = S_s, S_z \text{ or } S_{sz}.\end{gathered} \tag{3.3}$$

The atomic expansions are symmetrized, similar to Ruedenberg's suggestion [21], i.e. they are averaged over expansions s, z at atom A and s' and z' at atom B. Both should yield the same results for dS_i/dR.

We use Eqs. (3.2) and (3.3) to establish three relations $f_i = g_i$ between the six $\bar{\alpha}$ and $\bar{\beta}$ parameters. This allows us to establish a dependence of the three $\bar{\beta}$ parameters on the $\bar{\alpha}$ parameters. There are only minor approximations necessary to obtain the final equations

$$\bar{\beta}_s = \frac{2S_s}{1+S_s^2}\bar{\alpha}_s + \frac{r_{sz}}{R}\frac{1-S_s^2}{1+S_s^2}(S_s+S_z)\bar{\alpha}_{sz}, \tag{3.4}$$

$$\bar{\beta}_z = \frac{2S_z}{1+S_z^2}\bar{\alpha}_z + \frac{r_{sz}}{R}\frac{1-S_z^2}{1+S_z^2}(S_s+S_z)\bar{\alpha}_{sz}, \tag{3.5}$$

$$\bar{\beta}_{sz} = \frac{S_z-S_s}{1-S_sS_z}\bar{\alpha}_{sz} + \frac{r_{sz}}{R}\frac{(1-S_s)(1-S_z)}{1-S_sS_z}[(S_s-S_z)\bar{\alpha}_z - 2S_s(1-S_s)\bar{\alpha}_s]. \tag{3.6}$$

The first terms are the Wolfsberg-Helmholz terms $\bar{\beta}_{\mathrm{WH}}$, the second terms are the next higher order corrections. A qualitative study for small and large R reveals the following:

The second terms on the right sides vanish for $R \to 0$. This can be proven by using that $S \approx 1 - aR^2$ for small R. The numerators are proportional to R^3 resp. R^6, the denominators proportional to R resp. R^3. In the limit $R \to 0$ the left sides and the first terms on the right side of (3.4) and (3.5) converge to the corresponding $\bar{\alpha}$-values. In (3.6) $\bar{\beta}_{sz}$ approaches $-0.687\,\bar{\alpha}_{sz}$. This is not strange if we consider that $\bar{\alpha}_{sz}$ is zero for the atomic case. Our coordinate system implies that $\bar{\beta}_{sz}$ is not bonding, so it should be positive, whereas $\bar{\alpha}_{sz}$ is the interaction between the electronic distribution sz at atom A and the effective core of atom B, hence it is expected to be negative. For large R, the first terms on the right side of $\bar{\beta}_s$, $\bar{\beta}_z$ and $\bar{\beta}_{sz}$ have coefficients proportional to S the second terms to S/R.

Table. *$\overline{\beta}$ values (eV) and correction terms $\Delta\overline{\beta}$ (%) dependent on the interatomic distance R (a.u.)*

R	$\overline{\beta}_s$	$\Delta\overline{\beta}_s$[a]	$\overline{\beta}_z$	$\Delta\overline{\beta}_z$[a]	$\overline{\beta}_{sz}$	$\Delta\overline{\beta}_{sz}$[a]
0.1	−21.408	0.000	−11.447	0.004	0.162	−0.001
0.3	−21.475	0.004	−11.798	0.036	0.503	−0.009
1.0	−21.837	0.029	−11.393	0.289	1.974	−0.032
1.6[b]	−20.915	0.034	− 1.393	1.531	2.946	0.025
2.0	−19.178	0.023	3.951	−0.206	3.030	0.103
2.65[c]	−14.966	0.004	6.730	−0.011	2.312	0.279
3.0	−12.408	−0.0002	6.693	0.0004	1.753	0.389
4.0	− 6.069	−0.0016	4.594	0.002	0.574	0.703
5.0	− 2.460	−0.0004	2.271	0.004	0.152	0.905
10.0	− 0.008	−0.0000	0.010	0.000	0.0001	1.000

[a] $\Delta\overline{\beta} = (\overline{\beta} - \overline{\beta}_{\mathrm{WH}})/\overline{\beta}$.

[b] $S_z(1.55) = 0$.

[c] Nearest neighbour distance in benzene.

To obtain some quantitative information about the coupling in a C–C framework, we introduce, for practical reasons, the following drastic assumptions: ζ shall be taken, as Slater's rules prescribe, as $\zeta_C = 1.625$, and $\overline{\alpha}_s$ and $\overline{\alpha}_z$ are the negative atomic valence state ionization potentials −21.4 eV and −11.4 eV [1]. These numerical values are well in agreement with the qualitative argumentation of asymptotic behaviour of $\overline{\alpha}$ values in the previous chapter. The Wolfsberg-Helmholz form (2.7) yields $Z_{\mathrm{eff}} = \frac{5}{6}\zeta = 1.4$ for *s*-orbitals and $Z_{\mathrm{eff}} = \frac{3}{2}\zeta = 2.4$ for *p*-orbitals. Calculation of Z_{eff} from the $\overline{\alpha}_s = \frac{1}{6}\zeta^2 - \frac{1}{2}Z_{\mathrm{eff}}\zeta$ and $\overline{\alpha}_z = \frac{1}{2}\zeta^2 - \frac{1}{2}Z_{\mathrm{eff}}\zeta$ with the use of the above ionization potentials and Slater exponents results in $Z_{\mathrm{eff}} = 1.5$ for *s*-orbitals and $Z_{\mathrm{eff}} = 2.1$ for *p*-orbitals. r_{sz} is determined by (2.5) and is constant. This means, we take the infinite distance as representative for all distances. This meets with the usual assumptions of Hückel type methods and is not unreasonable for intermediate distances which we encounter in aromatic systems. For the limit $R \to 0$, carbon valence state potentials and carbon ζ values would have, however, no physical significance. We calculate $\overline{\alpha}_{sz}$ tentatively by

$$\overline{\alpha}_{sz} = -\tfrac{1}{2}S_{sz}(S_s\overline{\alpha}_s - S_z\overline{\alpha}_z)\,. \tag{3.7}$$

This is based on expansion of orbitals s, z in s' and z' and application of the virial theorem for atoms, an idea similarly expressed by Cusachs [7]. (3.7) is approximately valid for small and intermediate distances. The table shows $\overline{\beta}$ values and the influence of the correction terms in (5.1) for various distances. We conclude that corrections to the Wolfsberg-Helmholz form for $\overline{\beta}$ can be neglected for *s*-orbitals. For *z*-orbitals they are important at distances where S_z vanishes. They effect a shift of the node of $\overline{\beta}_z$. For $\overline{\beta}_{sz}$ they cannot be neglected but represent an essential part of the formula. In particular, the magnitude of $\overline{\beta}_{sz}$ is not negligible for intermediate distances when compared with $\overline{\beta}_s$ and $\overline{\beta}_z$.

One final comment might be appropriate with regard to the singularity of $\overline{\alpha}_z$ in the uncoupled approximation [3]. We could have removed this singularity in the coupled formalism by extending our previous procedure of determining the three $\overline{\alpha}$'s by a combination of slopes of overlap with the help of (3.1) or (3.2). We have checked that the key quantity r_{sz}, when chosen according to (2.5), fulfills an inequality arising in the procedure. We have preferred not to present details of this way since the wrong behaviour of $\bar{\alpha}$ for large R when determined through dS/dR terms cannot be removed even in the coupled approximation.

4. Conclusion

We have used truncated expansions for the matrix elements of the operator relation $\boldsymbol{p} = [\boldsymbol{r}, h]$ over atomic orbitals to establish approximate relations between $\bar{\alpha}$ and $\bar{\beta}$ parameters in extended Hückel methods. Some clarification about h_{eff} underlying these parameters was given through an investigation of gauge properties of truncated expansions. It was shown that the gauge invariance of h in $\boldsymbol{p} = [\boldsymbol{r}, h]$ is partly or completely lost in a truncated expansion and that we are dealing with effective Hamiltonians $h = h_{\text{eff}}$ which depend on the approximation. We showed an alternative viewpoint of the formulas previously derived [3] which allows the $\bar{\alpha}$'s to converge properly to atomic parameters for large internuclear distances. Our main concern then was the coupling between matrix elements over s- and z-orbitals. This gave rise to parameters $\bar{\alpha}_{sz}$ and $\bar{\beta}_{sz}$. The influence of these parameters in the formulas [(3.4)–(3.6)] was estimated by *assuming* atomic parameters $\bar{\alpha}_s = \bar{\alpha}_s$ (atom) and $\bar{\alpha}_z = \bar{\alpha}_z$ (atom) and subsequently *calculating* $\bar{\beta}_s, \bar{\beta}_z, \bar{\beta}_{sz}, \bar{\alpha}_{sz}$. We found the usual Wolfsberg-Helmholz term sufficient for $\bar{\beta}_s$, but insufficient for $\bar{\beta}_z$ and $\bar{\beta}_{sz}$. In particular, the magnitude of $\bar{\beta}_{sz}$ is not negligible compared to $\bar{\beta}_s$ and $\bar{\beta}_z$ at intermediate distances.

Note. In Ref. [3], the absolute signs in formulas (5.7) to (5.9) should be replaced by parentheses, since the polarity is taken care of by the definition of R_0. We thank Prof. D. P. Chong for pointing this out to us.

Acknowledgement. We greatly appreciate comments and suggestions by Prof. F. E. Harris on contents and presentation of this paper. We thank also Prof. W. Rhodes for reading the manuscript.

References

1. Hoffmann, R.: J. chem. Physics **39**, 1397 (1963).
2. Pople, J. A., Santry, D. P., Segal, G. A.: J. chem. Physics **43**, S129 (1965).
3. Jug, K.: Theoret. chim. Acta (Berl.) **16**, 95 (1970).
4. — Theoret. chim. Acta (Berl.) **14**, 124 (1969).
5. Linderberg, J.: Chem. Physics Letters **1**, 39 (1967).
6. Wolfsberg, M., Helmholz, L.: J. chem. Physics **20**, 837 (1952).
7. Cusachs, L. C.: J. chem. Physics **43**, S157 (1965).
   — Cusachs, B. B.: J. physic. Chem. **71**, 1060 (1967).
8. Berthier, G.: Molecular orbitals in chemistry, physics and biology, p. 57, Ed. by P. O. Löwdin and B. Pullmann. New York-London: Academic Press 1964.
9. Pople, J. A., Segal, G. A.: J. chem. Physics **43**, S136 (1965).
10. Silverstone, H. J., Joy, H. W., Orloff, M. K.: J. Amer. chem. Soc. **88**, 1325 (1966).
    — — J. chem. Physics **47**, 1384 (1967).
    Joy, H. W., Silverstone, H. J.: Molecular Physics **13**, 149 (1967).
11. Hermann, R. B., Lykos, P. G., Sharp-Ritter, J. D., Moccia, R.: Quantum theory of atoms, molecules and the solid state, p. 335, ed. by P. O. Löwdin. New York-London: Academic Press 1966.
    Sharp-Ritter, J., Lykos, P. G.: J. chem. Physics **47**, 1384 (1967).

12. Hehre, W. J., Pople, J. A.: Chem. Physics Letters **2**, 379 (1968).
Lathan, W. A., Hehre, W. J., Pople, J. A.: Chem. Physics Letters **3**, 579 (1969).
Hehre, W. J., Stewart, R. F., Pople, J. A.: J. chem. Physics **51**, 2657 (1969).
13. Schiff, L. I.: Quantum mechanics, p. 170—171, third ed. New York: McGraw 1968.
14. Dirac, P. A. M.: The principles of quantum mechanics, fourth edition, p. 63. Oxford: University Press 1959.
15. Linderberg, J., Öhrn, Y.: Chem. Physics Letters **3**, 119 (1969).
16. Pariser, R., Parr, R.: J. chem. Physics **21**, 466, 767 (1953).
17. Roothaan, C. C. J.: J. chem. Physics **19**, 1445 (1951).
18. Dahl, J. P., Ballhausen, C. J.: Advances quant. Chem. **4**, 170 (1968).
19. Wratten, R. J.: Chem. Physics Letters **1**, 667 (1968).
20. Löwdin, P. O.: J. chem. Physics **18**, 365 (1950).
21. Ruedenberg, K.: J. chem. Physics **19**, 1433 (1951).

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