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Operator Equations in Approximate Molecular Orbital Theories*

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Commutator equations of type $[t, x] = u$ involving hermitian and antihermitian operators are studied with regard to possible use in MO methods. Their advantage for adoption in semiempirical methods is demonstrated in truncated diatomic expansions involving integrals over $[\boldsymbol{r}, \boldsymbol{p}] = -1$ and $[\boldsymbol{r}, h] = \boldsymbol{p}$. Approximate and exact formulas for both slope of overlap and effective core Hamiltonian parameters are compared. A generalization to polyatomics is suggested.

Kommutatorgleichungen vom Typ $[t, x] = u$ mit hermitischen und antihermitischen Operatoren werden im Hinblick auf mögliche Anwendung in MO Methoden studiert. Der Vorteil ihrer Verwendung in semiempirischen Methoden wird anhand von abgebrochenen zweiatomigen Entwicklungen für Integrale über $[\boldsymbol{r}, \boldsymbol{p}] = -1$ und $[\boldsymbol{r}, h] = \boldsymbol{p}$ demonstriert. Approximative und exakte Formeln für sowohl Überlappungsgradient als auch Parameter des effektiven Core-Hamiltonoperators werden verglichen. Eine Verallgemeinerung zu polyatomaren Molekülen wird angeregt.

Etude d'équations opératorielles à commutateurs: $[t, x] = u$ portant sur des opérateurs hermitiques ou anti hermitiques, en vue de leur utilisation possible dans les méthodes d'orbitales moléculaires. Démonstration de leur avantage pour les méthodes semi-empiriques dans les développements diatomiques tranqués comportant des intégrales sur $[\boldsymbol{r}, \boldsymbol{p}] = -1$ et $[\boldsymbol{r}, h] = \boldsymbol{p}$. Comparaison de formules approchées et exactes pour les paramètres de pente du recouvrement et d'hamiltonien de coeur effectif. Suggestion d'une généralisation aux molécules polyatomiques.

1. Introduction

In the last few years, there has been considerable interest in semiempirical methods of structure and bonding whose formalisms have some theoretical justification [1, 2]. The attractiveness comes from the fact that such a method should be more reliable in its predictiveness. Sometimes this has been misunderstood to mean that such a method can and should produce better results than an empirical method. Since this frequently is not the case, there is an inclination to give up searching for theoretically satisfactory improvements. However, one should bear in mind that results of a theoretically sound method in any form of approximation should resemble results of its unapproximated form, not an empirical set of data. Thus approximations to a SCF method can be compared in a meaningful way only to SCF theory itself.

Let us call a method without empirical ingredients an approximate molecular orbital method. To get away from empirical adjustment, one has to investigate the consequences of approximations in the underlying theory. In particular, the search for simple formulas for the integrals retained in the approximate method, called parameters in semiempirical methods, seems to be promising.

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The two kinds of parameters which are most interesting are α and β parameters. Theoretically, they are defined as integrals over an effective core Hamiltonian h and a set of atomic orbitals. In the following, we denote parameters with a bar: $\bar{\alpha}_a = \langle \chi_a | h | \chi_a \rangle$, $\bar{\beta}_{ab} = \langle \chi_a | h | \chi_b \rangle$ for non-orthogonal orbitals χ and without a bar: $\alpha_a = \langle \lambda_a | h | \lambda_a \rangle$, $\beta_{ab} = \langle \lambda_a | h | \lambda_b \rangle$ for orthogonalized atomic orbitals λ.

The most recent formulas for β parameters are based on the use of the commutator relation $[\boldsymbol{r}, h] = \boldsymbol{p}$ between position vector $\boldsymbol{r}$, linear momentum $\boldsymbol{p}$ (here defined as antihermitian by the inclusion of the imaginary unit i), and effective Hamiltonian h of a single electron. Various formulas have been proposed for β's over orthogonalized orbitals and $\bar{\beta}$'s over non-orthogonal orbitals in diatomic [3–6] and polyatomic molecules [7].

In this paper we present a study of general commutator relations. In Sect. 2 we derive relations between integrals of operators in a diatomic first-order expansion over non-orthogonal and symmetrically orthogonalized orbitals [8]. In Sect. 3 we apply these formulas to the slope of overlap dS/dR (R is the internuclear distance). Three approximations are compared to the exact calculation of this quantity for $2s$-, $2p\sigma$-, and $2p\pi$-orbitals. Sect. 4 gives the same comparison for $\bar{\beta}$ parameters for varying effective charges Z. Sect. 5 discusses values of Linderberg's form of β in comparison to an exact calculation of β, also for varying effective charges Z.

2. Approximate Formulas from General Commutator Equations

Let us start with a general operator equation of the form

$$[t, x] = u \tag{2.1}$$

where t is a hermitian operator and x and u are hermitian or anti-hermitian single-electron operators. The equivalent of this equation in integral form is an expansion of an element $u_{\mu\nu} = \langle \mu | u | \nu \rangle$ as follows [9]

$$u_{\mu\nu} = \sum_{\lambda} (t_{\mu\lambda} x_{\lambda\nu} - x_{\mu\lambda} t_{\lambda\nu}) \tag{2.2}$$

where μ, ν are arbitrary (orthogonal or non-orthogonal) orbitals and λ is taken over a complete orthogonal set. Elements $t_{\mu\lambda}$, $x_{\lambda\nu}$, etc., are integrals defined in the same way as $u_{\mu\nu}$.

An expansion in a non-orthogonal set χ takes the form

$$u_{\mu\nu} = \sum_{\chi, \chi'} [t_{\mu\chi} (F^2)_{\chi'\chi} x_{\chi'\nu} - x_{\mu\chi} (F^2)_{\chi'\chi} t_{\chi'\nu}] \tag{2.3}$$

where $\boldsymbol{F}$ is a transformation matrix from the non-orthogonal to an orthogonal set. For symmetrically orthogonalized orbitals in molecules [8], $\boldsymbol{F}^2 = \boldsymbol{S}^{-1}$ holds, where $\boldsymbol{S}$ is the overlap matrix.

In a truncated expansion, only the few main terms are used. This is particularly useful if matrix elements of two of the operators are easy to calculate so that an element of the third operator can essentially be represented as a combination of a few terms of elements of the first two operators. For example, we can approximately represent an element of operator x as a combination of other elements of x, elements of operator t, and a single element of operator u.

Let us consider matrix elements over non-orthogonal atomic orbitals in diatomics. They will be denoted by a bar. A non-diagonal element $\langle \chi_a | u | \chi_b \rangle$ over orbital χ_a on atom A and χ_b on atom B will be written $\bar{u}_{ab}$.

The simplest type of approximation for $\bar{u}_{ab}$ is the one suggested by Ruedenberg [10] where only a single orbital is used in the expansion (2.2). One assumes that the expansion is equally valid if either orbital χ_a or χ_b is used. $\bar{u}_{ab}$ is represented as the average of the single orbital expansions over χ_a and χ_b. Non-diagonal elements $\bar{x}_{ab}$ are then approximately obtained as

$$\bar{x}_{ab} = \frac{\bar{t}_{ab}}{\bar{t}_{aa} - \bar{t}_{bb}} (\bar{x}_{aa} - \bar{x}_{bb}) + \frac{2}{\bar{t}_{aa} - \bar{t}_{bb}} \bar{u}_{ab} \,. \tag{A}$$

The next improved approximation uses two orbitals in the expansion (2.2) of $\bar{u}_{ab}$. If we take orthogonalized orbitals λ_a and λ_b from a symmetrical orthogonalization [8] of χ_a and χ_b, we obtain

$$\bar{x}_{ab} = \frac{1}{2} S_{ab} (\bar{x}_{aa} + \bar{x}_{bb}) + \frac{\bar{t}_{ab} - \frac{1}{2} S_{ab} (\bar{t}_{aa} + \bar{t}_{bb})}{\bar{t}_{aa} - \bar{t}_{bb}} (\bar{x}_{aa} - \bar{x}_{bb}) + \frac{1 - S_{ab}^2}{\bar{t}_{aa} - \bar{t}_{bb}} \bar{u}_{ab} \tag{B}$$

with $S_{ab} = \langle \chi_a | \chi_b \rangle$.

If we consider approximate relations between elements over orthogonalized orbitals, we denote them without a bar: $u_{ab} = \langle \lambda_a | u | \lambda_b \rangle$. The two-orbital expansion comparable to (B) is an expansion using again λ_a and λ_b in (2.2). The non-diagonal element x_{ab} can be approximately represented as

$$x_{ab} = \frac{t_{ab}}{t_{aa} - t_{bb}} (x_{aa} - x_{bb}) + \frac{1}{t_{aa} - t_{bb}} u_{ab} \,. \tag{B'}$$

In the following section, we make use of the relations (A), (B) and (B') and their possible modifications. It has to be remembered, however, that we have excluded cases where $t_{aa} - t_{bb} = 0$. Also we cannot expect meaningful results if all the expansion terms in t and x vanish or cancel each other.

3. Overlap and Slope of Overlap

An operator equation which is both basic to quantum mechanics and easy to analyze is the Heisenberg uncertainty principle

$$[\boldsymbol{r}, \boldsymbol{p}] = -1 \tag{3.1}$$

where $\boldsymbol{r}$ is the position vector and $\boldsymbol{p}$ the linear momentum in the direction of $\boldsymbol{r}$. From the preceding section, we identify $t = \boldsymbol{r}$, $u = -1$ hermitian, $x = \boldsymbol{p}$ antihermitian. In this case (A) yields[1]

$$\frac{dS}{dR} = -\frac{2}{R} S \tag{3.2}$$

where $S = \langle \chi_a | \chi_b \rangle$ and R is the internuclear distance. To keep the form of the formulas invariant with respect to a change of orbital exponents ζ, we define $\varrho = \zeta R$ and rewrite (3.2) as

$$\frac{dS}{d\varrho} = -\frac{2}{\varrho} S \,. \tag{A}$$

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[1] The vector character of $\boldsymbol{r}$ and $\boldsymbol{p}$ does not cause any difficulty and can be eliminated.

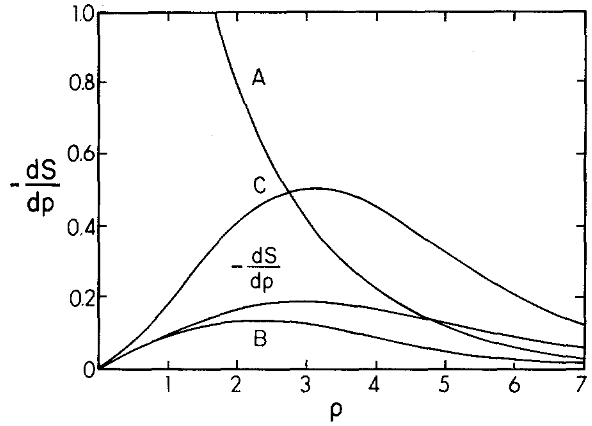

Fig. 1. Exact $(-dS/d\varrho)$ and approximate (A, B, C) curves for slope of overlap over 2*s*-orbitals in dependence of $\varrho = \zeta R$ in a diatomic molecule; ζ shielding exponent, R internuclear distance (in atomic units)

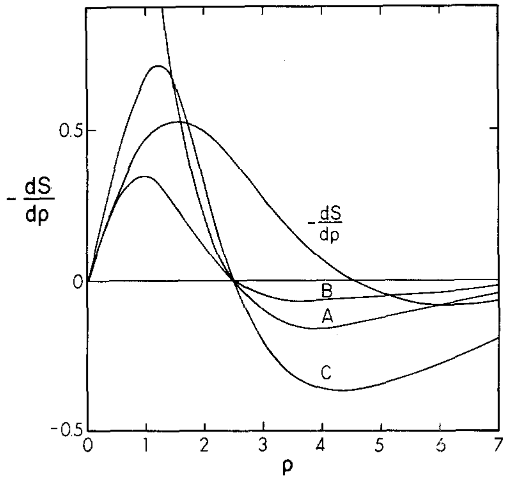

Fig. 2. Same curves as in Fig. 1 for $2p\sigma$-orbitals; local axes on the two atoms are parallel

The analogous formula for (B) is

$$\frac{dS}{d\varrho} = -\frac{(1-S^2)}{\varrho} S. \tag{B}$$

In the following we investigate these approximations for 2*s*-, $2p\sigma$-, and $2p\pi$-orbitals in diatomics. The discussion is not restricted to equal exponents if we define $\varrho = \frac{1}{2}(\zeta_a + \zeta_b) R$. Our forms (A) and (B) lend themselves to such a generalization. To check the validity, we compare (A) and (B) with the correct form of $dS/d\varrho$ obtained by Roothaan [11]. Here, we discuss only overlap integrals of the type $\langle 2s_a | 2s_b \rangle$, $\langle 2p\sigma_a | 2p\sigma_b \rangle$, $\langle 2p\pi_a | 2p\pi_b \rangle$. Qualitatively, we can make statements about the behavior at small and large ϱ. For $\varrho = 0$ (A) diverges, whereas (B)

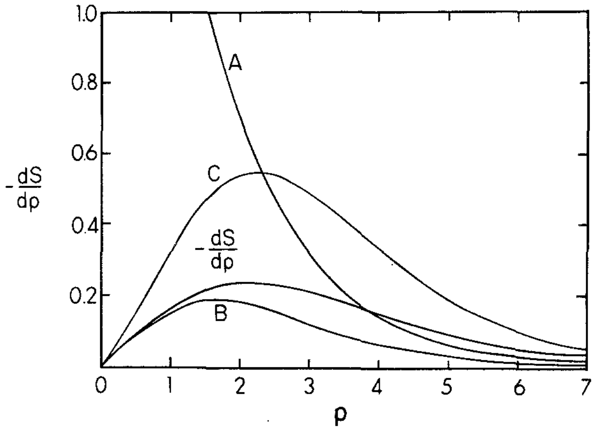

Fig. 3. Same curves as in Fig. 1 for $2p\pi$-orbitals

approaches $dS/d\varrho = 0$ as the exact formulas prescribe. For large ϱ both representations (A) and (B) of the slope of overlap vanish by an order of ϱ too fast: For $\varrho \to \infty$ (A) $dS/d\varrho \to -2S/\varrho$, (B) $dS/d\varrho \to -S/\varrho$ whereas $(dS/d\varrho)_{\text{exact}} \to -S$. To obtain the proper limit, we modify formula (B) in the following way

$$\frac{dS}{d\varrho} = -\frac{(1-S^2)(1+\varrho)}{\varrho} S. \tag{C}$$

Any further discussion has to rely on quantitative evaluation of approximations (A), (B), and (C) and comparison to the exact curves over the whole range of ϱ. Figs. 1–3 contain this information. The results are particularly simple for $2s$- and $2p\pi$-orbitals. Approximation (B) provides a lower bound for $-dS/d\varrho$ and approximation (C) provides an upper bound, with (B) being by far the better approximation to the exact curve. To be correct we have to point out that (B) is not an exact lower bound. For $\varrho < 0.5$ it intersects the exact curve, but stays so close that the two curves are indistinguishable. Approximation (A) is poor for small ϱ. Surprisingly, however, it approaches the exact curve more closely for $\varrho > 4$ and remains a better approximation than either (B) or (C) in the range of interest in molecular binding. Unfortunately, such promising results are not obtained for $2p\sigma$-orbitals. In particular the proportionality to S in (A), (B), and (C) forces the approximative curves through a common node at $\varrho = 2.5$, whereas the exact curve has a node at $\varrho = 4.5$. In the range $2.5 \leqq \varrho \leqq 4.5$, values of the approximate curves even have the wrong sign. For $\varrho < 2$ and $\varrho > 5$, either (B) and (C) or (B) and (A) become acceptable approximations.

4. $\bar{\alpha}$ and $\bar{\beta}$ Parameters

The commutator equation which is most advantageous in determining $\bar{\beta}$ and β parameters is

$$[\boldsymbol{r}, h] = \boldsymbol{p} \tag{4.1}$$

where $\boldsymbol{r}$ is the position vector, $\boldsymbol{p}$ the linear momentum in the direction of $\boldsymbol{r}$ and h the effective Hamiltonian of a single electron.

Here the identification $t=\boldsymbol{r}$, $x=h$, and $u=\boldsymbol{p}$ leads to direct application of the formulas in Sect. 2.

For non-orthogonal orbitals χ_a and χ_b on the two atoms of a diatomic molecule approximation (A) is

$$\beta_{ab}=\frac{2}{\varrho}\,\frac{dS}{d\varrho} \tag{A}$$

whereas (B) yields

$$\bar{\beta}_{ab}=\frac{1}{2}S_{ab}(\bar{\alpha}_a+\bar{\alpha}_b)+\frac{\Delta\varrho}{\varrho}(\bar{\alpha}_a-\bar{\alpha}_b)+\frac{(1-S_{ab}^2)}{\varrho}\,\frac{dS_{ab}}{d\varrho}$$

where $\varrho=\frac{1}{2}(\zeta_a+\zeta_b)R$ and $\Delta\varrho$ accounts for the shift of the center of density $\chi_a\chi_b$ from the midpoint between the two nuclei [5]. $\bar{\alpha}$ and $\bar{\beta}$ are calculated in units of $\frac{1}{4}(\zeta_a+\zeta_b)^2$. Since we will discuss only the case where $\zeta_a=\zeta_b$ and χ_a and χ_b are the equivalent orbitals $2s_a$ and $2s_b$, $2p\sigma_a$ and $2p\sigma_b$ or $2p\pi_a$ and $2p\pi_b$, we shall recast (B) in the form

$$\bar{\beta}_{ab}=S_{ab}\bar{\alpha}_a+\frac{(1-S_{ab}^2)}{\varrho}\,\frac{dS_{ab}}{d\varrho}\,. \tag{B}$$

This form lends itself to a comparison with Pople's form of $\bar{\beta}_{ab}=S_{ab}\beta^\circ$ if we set

$$\beta^\circ=\bar{\alpha}_a+\Delta\bar{\alpha} \tag{4.2}$$

with

$$\Delta\bar{\alpha}=\frac{(1-S_{ab}^2)}{S_{ab}\varrho}\,\frac{dS_{ab}}{d\varrho}\,.$$

It should be mentioned at this point that Linderberg and Öhrn [4] have proposed a formula similar to (B). But they emphasized the nearest-neighbor character of their approximation and dropped higher terms in S which are necessary for the proper limits. Their basis of expansion was essentially (2.3) with $\boldsymbol{F}^2=\boldsymbol{S}^{-1}$.

To avoid confining our results for large ϱ to a single limit $\bar{\beta}\to S\bar{\alpha}$, we also use modification (C) similar to the one in Sect. 3.

$$\bar{\beta}_{ab}=S_{ab}\bar{\alpha}_a+\frac{(1-S_{ab}^2)(1+\varrho)}{\varrho}\,\frac{dS_{ab}}{d\varrho} \tag{C}$$

We have calculated $\bar{\beta}$ values (in units ζ^2) in approximations (A), (B), and (C) with exact and approximate $\bar{\alpha}$ values (in units ζ^2). To obtain an idea of how good these approximations are, we compared them with the exact $\bar{\beta}$ values calculated with Roothaan's formulas [11]. We used an effective Hamiltonian of the form

$$h_\varrho=-\frac{1}{2}\nabla_\varrho^2-\frac{Z}{\varrho_a}-\frac{Z}{\varrho_b} \tag{4.3}$$

where $\varrho_a=\zeta r_a$, $\varrho_b=\zeta r_b$, $Z=Z_{\mathrm{eff}}/\zeta$. This yields a convenient invariance of the results to changes in exponents ζ. The energy quantities $\bar{\alpha}$ and $\bar{\beta}$ are given in units of ζ^2. The effective charge Z is in units of ζ.

$\bar{\beta}$ values over $2s$-, $2p\sigma$-, and $2p\pi$-orbitals for various choices of Z are given in Figs. 4–6. Here we have calculated $\bar{\alpha}$ values for all cases exactly, *i.e.*, the approximate $\bar{\beta}$ parameters in these figures are all based on exact $\bar{\alpha}$ parameters. These $\bar{\alpha}$ parameters are given in Figs. 7–9.

The resemblance of the behavior of $\bar{\beta}$ parameters in approximations (A), (B), and (C) to the corresponding results for $dS/d\varrho$ discussed in Sect. 2 is striking. Again (B) and (C) provide lower and upper bounds for $-\bar{\beta}_{\text{exact}}$ over $2s$- and $2p\pi$-orbitals for large ranges of ϱ. Although there is a dependence of this boundary range on Z, the essence of the above conclusion holds for $Z=0$ (pure kinetic energy) to $Z=3$ which covers effective charges up to $Z_{\text{eff}}=4.8$ in carbon with the usual Slater exponents. Approximation (B) is indeed very good for the whole range of interest of parameters ϱ and Z. Approximation (A) refers to a specific choice of Z which is of the order of 0.5 to 0.8. Hence it refers in molecular calculations to a strongly shielded Hamiltonian. We have attributed (A) previously [5] to extended Hückel methods [12] which is herewith justified. For $2p\sigma$-orbitals neither (B) nor (C) have the simple behavior which could classify them as lower and upper bounds. Simplifying, we could say both provide mostly upper bounds for $-\bar{\beta}_{\text{exact}}$ (B) is again an acceptable approximation. Approximation (A), for this case, fails to provide a basis for a meaningful interpretation. For $3<\varrho<5$ which includes the benzene distance ($\varrho=4.30$), it refers to a strongly shielded situation.

Form (B) lends itself to an extension to polyatomics. Let us suppose we have a third atom which generates a potential $\frac{Z}{r_c}$. If we approximate matrix elements of potential terms involving atomic orbitals χ_a and χ_b on two atoms and potential energy operator $\frac{Z}{r_c}$ of a third (or further) atom by the Mulliken approximation

$$\left\langle \chi_a \left| \frac{Z}{r_c} \right| \chi_b \right\rangle = \frac{1}{2} S_{ab} \left[\left\langle \chi_a \left| \frac{Z}{r_c} \right| \chi_a \right\rangle + \left\langle \chi_b \left| \frac{Z}{r_c} \right| \chi_b \right\rangle \right] \tag{4.4}$$

we can keep form (B) or its more general expression with several different $\bar{\alpha}$ values for polyatomics. This would mean that any $\bar{\beta}$ values, even those involving three-center integrals, can be calculated approximately by two-center integrals only. Further investigation of this point could be gratifying.

We conclude this section with two remarks on $\bar{\alpha}$ parameters. In Figs. 7–9, $\bar{\alpha}_H$ is the value of the carbon ionization potential in units of ζ_C^2 ($\zeta_C=1.625$). We can say that for distances of the order of the nearest-neighbor distance in benzene ($\varrho=4.30$) $\bar{\alpha}_H$ refers to a charge $Z=0.5$ to 0.8. This is in agreement with our above conclusions about $\bar{\beta}$ parameters in extended Hückel methods. We may say that consistency in the choice of parameters K and $\bar{\alpha}$ in the extended Hückel method [12] is a matter of meaningful empirical adjustment for a small range of distances. The conclusions about $\bar{\alpha}_H$ are also in agreement with the assumptions made for a preliminary investigation of coupling effects between $2s$- and $2p\sigma$-orbitals [6]. Pople has introduced in the CNDO method a parameter β° which we have interpreted in Eq. (4.2). We find some justification for Pople's claim that β° can be taken as constant. In particular, for intermediate distances the decrease in $\bar{\alpha}$ is

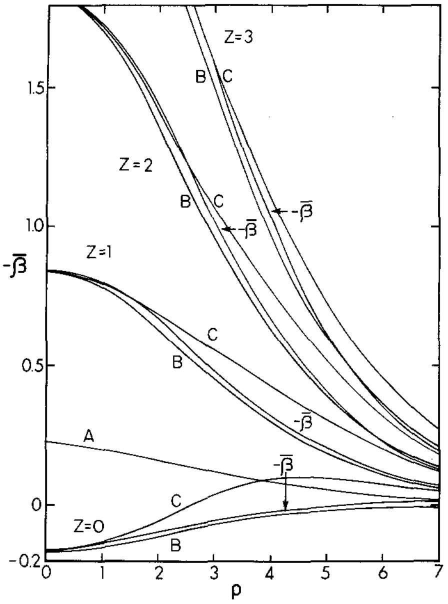

Fig. 4

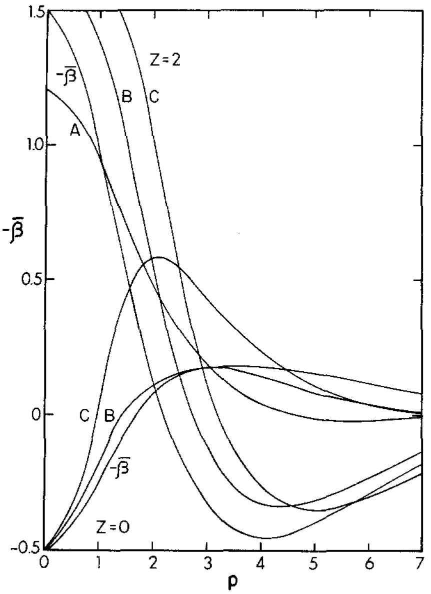

Fig. 5

Fig. 4. Exact ($-\bar{\beta}$) and approximate (A, B, C) curves for non-diagonal effective core elements over 2*s*-orbitals in dependence of $\varrho = \zeta R$ and $Z = Z_{\text{eff}}/\zeta$ in a homonuclear diatomic molecule (in atomic units/ζ^2); ζ orbital shielding exponent, Z_{eff} effective core charge, R internuclear distance (in atomic units)

Fig. 5. Same curves as in Fig. 4 for $2p\sigma$-orbitals; axes as in Fig. 2

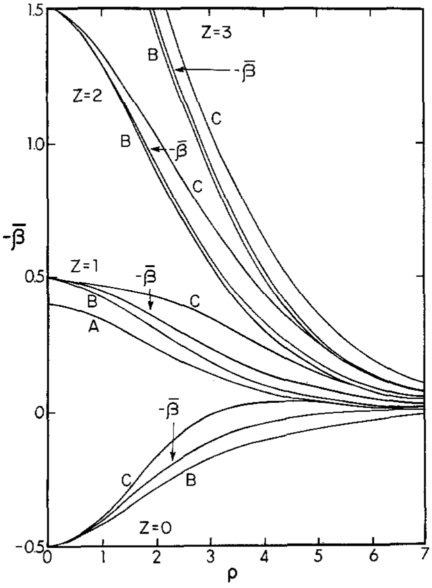

Fig. 6. Same curves as in Fig. 4 for $2p\pi$-orbitals

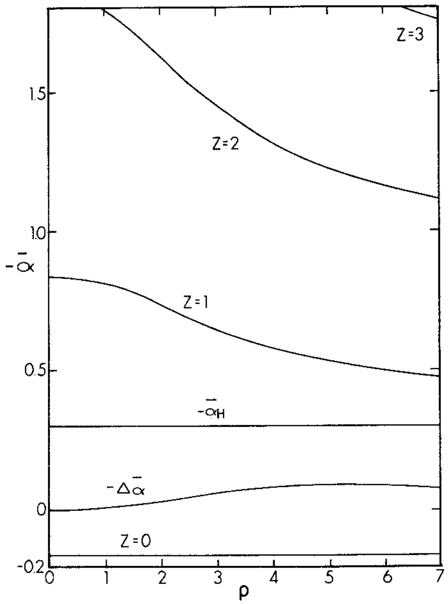

Fig. 7

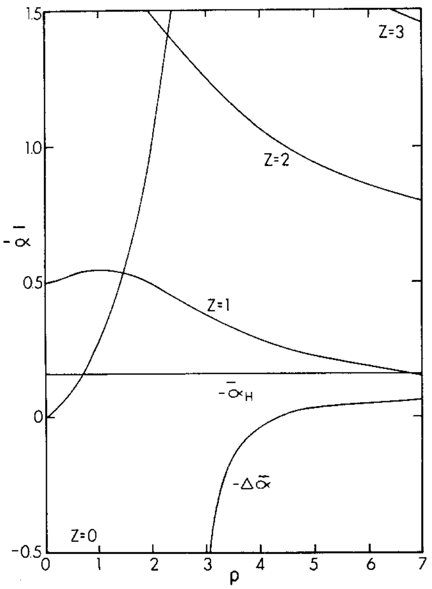

Fig. 8

Fig. 7. Exact ($-\bar{\alpha}$) curves for diagonal effective core elements over 2*s*-orbitals in dependence of $\varrho = \zeta R$ and $Z = Z_{\mathrm{eff}}/\zeta$ in a homonuclear diatomic molecule (in atomic units/ζ^2); also semiempirical ($-\bar{\alpha}_H$) and shift ($-\Delta\bar{\alpha}$) curves; ζ orbital shielding exponent, Z_{eff} effective core, R internuclear distance (in atomic units)

Fig. 8. Same curves as in Fig. 7 for $2p\sigma$-orbitals; axes as in Fig. 2

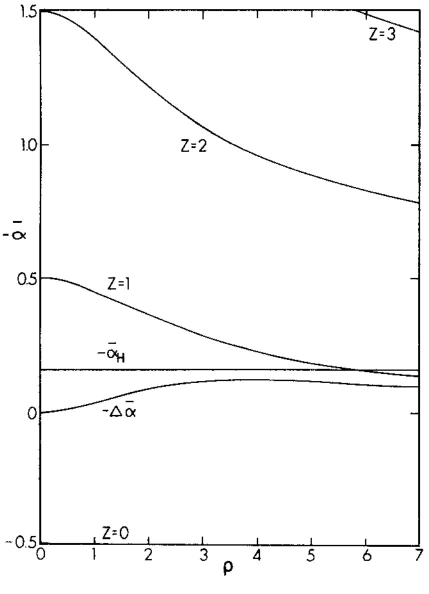

Fig. 9. Same curves as in Fig. 7 for $2p\pi$-orbitals

balanced somewhat by the increase of $\Delta\bar{\alpha}$, so that the sum is fairly constant, although care has to be taken for $2p\sigma$-orbitals. For $\varrho < 3.5$ (4.2) fails to be satisfactory in this case.

However, if we compare the actual values of β°, *e.g.*, for ethylene -21 eV, with our exact calculations of $\bar{\alpha}$ and $\Delta\bar{\alpha}$, we can attribute Pople's values of β° only to strongly shielded cases where $Z_{\text{eff}} = 1$ or even smaller. In no way can we interpret Pople's choice of β° parameter values on the basis of his own statement that Z_{eff} is the core charge with all valence electrons removed, *e.g.*, $Z_{\text{eff}} = 4$ for carbon. In fact, to our knowledge, the close resemblance of $\bar{\beta}$ values for π-electrons in the extended Hückel method and CNDO method has not been emphasized. We understand the CNDO method in such a way that the formal neglect of a part of electronic interaction is balanced by a decrease of the effective charge in the core Hamiltonian. Finally, one might object that it would be better to consider the CNDO method as based on orthogonal orbitals. Our investigation of β parameters over symmetrically orthogonalized orbitals in the next section cannot substantiate this reasoning.

5. β Parameters

From Eq. (4.1) we can also obtain formulas for β parameters over symmetrically orthogonalized atomic orbitals. In this case (B′) of Sect. 2 take the form

$$\beta_{ab} = \frac{1}{(1 - S_{ab}^2)^{\frac{1}{2}}} \frac{\Delta\varrho}{\varrho} (\alpha_a - \alpha_b) + \frac{1}{\varrho} \frac{dS_{ab}}{d\varrho}.$$

For $\alpha_a = \alpha_b$ this can be simplified to

$$\beta_{ab} = \frac{1}{\varrho} \frac{dS_{ab}}{d\varrho}. \qquad \text{(B')}$$

This is the formula used first by Linderberg [2] in a slightly different form. We have calculated values with (B′) and compared them with the exact β's from Roothaan's formulas [11]. The Hamiltonian used was the same as in (4.3).

The results for $2s$-, $2p\sigma$-, and $2p\pi$-orbitals are in Figs. 10–12. Whereas form (B′) suggests gauge invariance, *i.e.*, invariance with respect to a change of Z, the exact curves for β are *not* gauge invariant. The exact curves for $2s$-orbitals all intersect at $\varrho = 4.75$. For $\varrho < 4.75$ the kinetic energy curve ($Z = 0$) is the lowest. The approximate curve (B′) for this range would refer to a repulsive potential. At larger distances the inversion of the curves allows for physical interpretation. But there is no single Z to which (B′) could be referred for any interval of the ϱ axis. Our conclusion can only be that (B′) is not a meaningful approximation for β over $2s$-orbitals. The same conclusion holds for $2p\sigma$-orbitals. There is no inversion point for exact β curves over $2p\pi$-orbitals. But only for $\varrho > 4$ values of (B′) can be identified with values of exact β's for physically significant Z's. If we want to interpret semiempirical values for benzene, the value $\beta = -2.39$ eV [13] refers to an effective charge of about $Z_{\text{eff}} = 5$. This is a rather large effective charge if one considers that $Z_{\text{eff}} = 1$ is usually considered as underlying semiempirical methods. Fischer-Hjalmars [14] has calculated $\beta = -3.8$ eV for $Z_{\text{eff}} = 3.25$

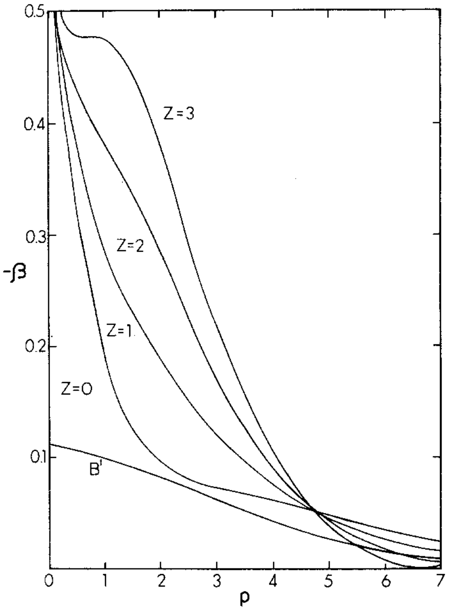

Fig. 10

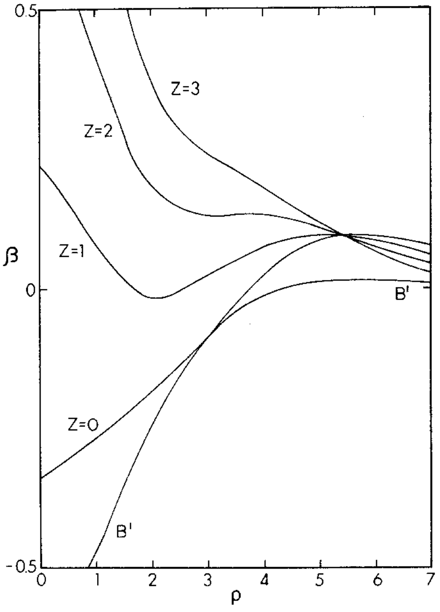

Fig. 11

Fig. 10. Exact ($-\beta$) and approximate (B′) curves of non-diagonal effective core elements over symmetrically orthogonalized 2*s*-orbitals in dependence of $\varrho = \zeta R$ and $Z = Z_{\mathrm{eff}}/\zeta$ in a homonuclear diatomic molecule (in atomic units/ζ^2); orbital shielding exponent, Z_{eff} effective core charge, R internuclear distance (in atomic units)

Fig. 11. Same curves as in Fig. 10 for $2p\sigma$-orbitals; axes as in Fig. 2

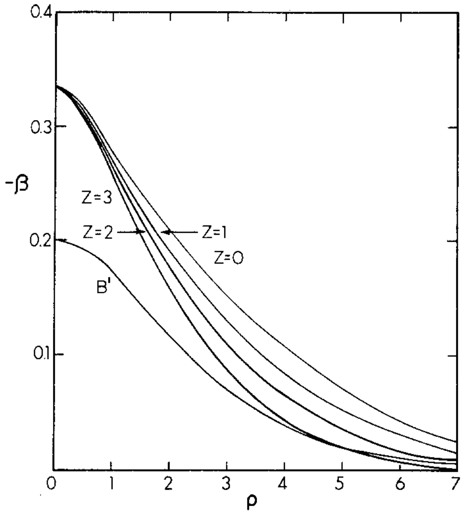

Fig. 12. Same curves as in Fig. 10 for $2p\pi$-orbitals

which is in agreement with our findings. The exact β's increase in absolute value with decreasing Z.

If we try to interpret the consequences of Pople's value of CNDO β° for carbon on the basis of orthogonalized orbitals, it would require for $2s$-orbitals $Z_{\text{eff}} \gg 5$, for $2p\pi$-orbitals $Z_{\text{eff}} \approx 1.6$, and for $2p\sigma$-orbitals $Z_{\text{eff}} \approx 2.0$ to obtain β's. Not only is this set of Z_{eff}'s inconsistent, but it is difficult to attach physical significance to a value $Z_{\text{eff}} \gg 5$.

6. Conclusion

We have investigated the possibility of using operator equations of the type $[t, x] = u$ in molecular calculations. In particular, we were interested in reducing matrix elements of operators x to elements of x, t, and u which are easier to calculate. Our general approximations (A), (B), (C), and (B′) were based on truncated expansions of integrals over the commutator relation. The general formulas were applied to two commutator relations of particular interest $[\boldsymbol{r}, \boldsymbol{p}] = -1$ and $[\boldsymbol{r}, h] = \boldsymbol{p}$. Slopes of overlap $dS/d\varrho$ and parameters of core Hamiltonians $\bar{\beta}$ and β were calculated exactly and approximately. Our investigations support the adoption of a single approximation (B) for parameters over non-orthogonal orbitals. In particular $\bar{\beta}$ parameters can be reduced to $\bar{\alpha}$ parameters and slopes of overlap $dS/d\varrho$. The form (B) lends itself to generalization to polyatomics. For $2p\sigma$-orbitals the approximations would be improved by taking also expansion terms of $2s$-orbitals as suggested previously [6]. Finally, we find β parameters in the original form by Linderberg less satisfactory than the first studies seemed to suggest.

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