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Theoretical and Practical Aspects of the ZDO Approximation

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An investigation of the multicentre terms in energy expressions for alternant hydrocarbons results in a refinement of the argument for the overall correctness of the ZDO-approximation in empirical methods. Correction formulae are derived for cases where the neglect of multicentre integrals is not justified. A revised definition of γ_{12} offers an explanation for the irregularity occurring near $r = 1.4$ Å in many empirical $\gamma - r$ curves.

Aus einer Untersuchung der Rolle der Mehrzentrenintegrale in den Energieformeln für alternierende Kohlenwasserstoffe ergibt sich eine Verfeinerung des Beweises der Anwendbarkeit der ZDO-Näherung in empirischen Methoden. In einigen Fällen aber ist die Vernachlässigung der Mehrzentrenintegrale nicht korrekt; für solche Fälle wird die Korrektur mit einfachen Formeln bestimmt. Weiter ergibt sich eine neue Definition von γ_{12} mit einer Erklärung für die Unregelmäßigkeit, die in vielen empirischen $\gamma - r$-Kurven bei $r = 1{,}4$ Å gefunden wird.

Une investigation de l'importance des intégrales polycentriques dans les expressions d'énergie pour les hydrocarbures conjugués conduit à une revision de la preuve de l'applicabilité de l'approximation ZDO pour la plupart des cas d'importance pratique. En quelques cas les erreurs dues à l'approximation ZDO ne sont pas négligeables; les corrections nécessaires sont déterminées par des formules simples. La définition du paramètre γ_{12} est revisée; il s'ensuit une explication pour l'irrégularité observée près de $r = 1.4$ Å dans les courbes $\gamma - r$ empiriques.

1. The ZDO Approximation

In a recent investigation ([1]; cf. [10]) we found that an empirical calculation of parameter values from the benzene spectrum with detailed consideration of π-electron correlation results in an unacceptable set of γ-values ($\gamma_{12} < \gamma_{14}$) if the simplifications of the PPP-method are rigorously maintained. This led us to reconsider the foundations of the zero differential overlap (ZDO) approximation. The analysis, given in the present paper, shows why the ZDO-assumption, in spite of some probable deficiencies, is on the whole entirely satisfactory for calculations on large conjugated systems; at the same time it becomes clear that in calculations on small molecules the ZDO-approximation may involve large errors.

In the LCAO–MO–SCF π-electron treatment of alternant conjugated systems the most convenient general expression for the π-electron energy of the ground configuration N is the one given by Pople [2]:

$$E_\pi^N = \sum_p \sum_q P_{pq}^N h_{pq} + \sum_p \sum_q \sum_r \sum_s P_{pq}^N P_{rs}^N \left\{ \frac{1}{2} (pq|rs) - \frac{1}{4} (pr|qs) \right\} \tag{1}$$

where

$$h_{pq} = \int \chi_p^*(1) \left\{ \frac{-\hbar^2}{2m} \nabla^2(1) + V_{\text{core}}^+(1) \right\} \chi_q(1)\, d\tau_1 \,, \tag{2}$$

$$(pq|rs) = \int \int \chi_p^*(1)\, \chi_q(1) \frac{e^2}{r_{12}} \chi_r^*(2)\, \chi_s(2)\, d\tau_1\, d\tau_2 \,, \tag{3}$$

and

$$P_{pq}^N = \sum_{i=1}^{2n} m_i^N c_{ip} c_{iq} \,, \tag{4}$$

m_i being the occupation number of the i^{th} MO; c_{ip} is the coefficient of χ_p in the MO φ_i, and χ_p is taken to be a Slater $2p_z$-AO, centered on the p^{th} C-atom.

Eq. (1) and the related eigenvalue equations are usually simplified by the assumptions of zero overlap and zero differential overlap (ZDO):

$$S_{pq} = \delta_{pq} \,, \tag{5}$$

$$(pq|rs) = \delta_{pq}\delta_{rs}(pp|rr) \,. \tag{6}$$

These approximations, introduced as useful simplifications in the original work of Pople [2] and of Pariser and Parr [3], were shown to be largely justified by an investigation of Fischer-Hjalmars [4]: if the basic AO's are taken to be Löwdin orthogonalised orbitals (OAO) ${}^{\lambda}\chi$ instead of the Slater orbitals χ

$${}^{\lambda}\underline{\chi} = \underline{S}^{-1/2}\underline{\chi} \,, \tag{7}$$

(5) follows directly, and (6) is correct up to terms in S^2 if the Mulliken approximation [5]

$$(pq|rs) = \tfrac{1}{4} S_{pq} S_{rs} \{(pp|rr) + (pp|ss) + (qq|rr) + (qq|ss)\} \tag{8}$$

is exactly valid. Now from a comparison [6] of the exact values of $(pq|rs)$ with those obtained from the Mulliken approximation it is seen that for many multicentre integrals over $2p_z$ – AO's (8) is a very good approximation, so that the ZDO-assumption, though neglecting terms of several eV, is largely justified. However, we may adopt a less grateful attitude towards the ZDO-approximation, and state that it involves first-order errors proportional to the inaccuracy of (8), which amounts to about 0.1 eV for a few multicentre integrals. The idea that such errors may be expected is supported by Chong's calculation of ${}^{\lambda}(pq|rs)$ [7]. He found that ${}^{\lambda}(pp|pq) = -0.10$, ${}^{\lambda}(rr|pq) = -0.05$ and ${}^{\lambda}(pq|pq) = 0.09$ eV, where p, q and r are consecutive C-atoms along a chain. If such multicentre integrals happen to occur with large coefficients in excitation energies they may cause unpleasant complications when we try to devise π-electron calculation methods which should be reliable within 0.1 eV.

In the present paper we investigate the influence of some multicentre integrals on the energy levels of alternant hydrocarbons. Starting from the assumption that Chong's values for ${}^{\lambda}(pp|pq)$, ${}^{\lambda}(rr|pq)$ and ${}^{\lambda}(pq|pq)$ are of the correct order of magnitude, even if π-electron correlation is considered, we wish to show that:

1. The contribution of the multicentre integrals to the state energies is not neglegibly small.

2. In *empirical* methods it can often be largely or completely accounted for by a judicious choice of parameter values. This implies that in many cases the ZDO-approximation gives good results; its justification, however, depends partly on (7) and (8), and partly on a revision of the definitions of some parameters which were introduced in [3] and [4].

3. In a few cases, specially in small molecules, the application of the ZDO involves considerable errors. Because a calibration of empirical methods is usually based on calculations on such molecules the neglect of the multicentre integrals may affect the choice of the parameter values, and through the latter influence calculations on larger molecules for which the ZDO is a valid approximation within an empirical scheme.

2. Configuration Energies in Alternant Hydrocarbons

Before simplifying (1) by means of the neglect of many or all multicentre integrals we recall that in an alternant hydrocarbon the C-atoms can be divided into two classes, "starred" and "unstarred", such that neighbouring atoms always belong to different classes. If the SCF-MO's are arranged in the order of increasing ε_i the AO-coefficients in the MO's φ_i and $\varphi_{i'}$ $(i' = 2n + 1 - i)$ are coupled by the relation

$$c_{ip} = \pm c_{i'p}\,, \tag{9}$$

where the upper sign is valid for atoms in one class, (starred, say) and the lower sign for the atoms in the other class. It was shown by Pople and Brickstock [8] that for all configurations x_0 and $x_i^{i'}$[1] and for the plus- and minus combinations of the alternation-degenerate configurations $x_i^{j'}$ and $x_j^{i'}$.

$$P_{pr} = \delta_{pr}\,, \tag{10}$$

if p and r are in the same class. We remark that, though (9) and (10) are correct for both real and complex AO coefficients, the validity of some of the subsequent conclusions is restricted to the case where all c's are *real.*

We substitute (6) into the OAO-version of (1) and collect in a constant E_0 all terms which depend on P_{pp} only, and are therefore state-independent because of (10). If further the integrals ${}^{\lambda}h_{pq}$ and ${}^{\lambda}(pp|qq)$ are replaced by the parameters $\beta_{pq}(\beta_{pq} = 0$ unless $q = p \pm 1)$ and γ_{pq}, we find that in the ZDO-scheme E_π^N is given by

$$E_\pi^N = E_0 + \sum_p \sum_{q=p\pm 1} P_{pq}^N \beta_{pq} - \frac{1}{4} \sum_p \sum_q{}' P_{pq}^{\overset{2}{N}} \gamma_{pq}\,. \tag{11}$$

A similar expression can be derived for the expectation values of E_π for the singlet component V and the triplet component T of a singly excited configuration x_k^l:

$$E_\pi^{V,T} = \sum_p \sum_q P_{pq}^V\,{}^{\lambda}h_{pq} + \sum_p \sum_q \sum_r \sum_s P_{pq}^V P_{rs}^V \left\{ \frac{1}{2}\,{}^{\lambda}(pq|rs) - \frac{1}{4}\,{}^{\lambda}(pr|qs) \right\} \tag{12}$$

$$- \frac{1}{4} J_{kk} - \frac{1}{4} J_{ll} + \frac{1}{2} K_{kl} \pm K_{kl}\,,$$

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[1] We use the notation introduced by Murrell and McEwen [9].

where the upper sign refers to V and the lower sign to T, and

$$J_{kl} = \sum_p \sum_q \sum_r \sum_s c_{kp} c_{kq} c_{lr} c_{ls} \, {}^{\lambda}(pq|rs)\,, \tag{13}$$

$$K_{kl} = \sum_p \sum_q \sum_r \sum_s c_{kp} c_{lq} c_{kr} c_{ls} \, {}^{\lambda}(pq|rs)\,. \tag{14}$$

For $l = k'$ we simplify (12) in the ZDO-scheme:

$$\begin{aligned} E_{\pi}^{VT}(x_k^{kx}) = E_0 + \sum_p \sum_{q=p\pm 1} P_{pq}^{V} \beta_{pq} - \frac{1}{4} \sum_p {\sum_q}' P_{pq}^{V^2} \gamma_{pq} \\ - \frac{1}{4} J_{kk}^0 - \frac{1}{4} J_{k'k'}^0 + \frac{1}{2} K_{kk'}^0 \pm K_{kk'}^0\,, \end{aligned} \tag{15}$$

where J^0 and K^0 are obtained on simplifying (13) and (14) by (6).

On the other hand, if we modify the ZDO-scheme by assuming in principle non-zero values for the multicentre integrals ${}^{\lambda}(rr|pq)$, ${}^{\lambda}(pp|pq)$ and ${}^{\lambda}(pq|pq)$ for for $q = p \pm 1$, we find slightly more complicated formulae for E_{π}. We make use of (9) and of (10), from which equations it follows that $P_{pr} . P_{qr} = 0$ if p and q are neighbours; also we take into account that, for a given p, q, e.g. ${}^{\lambda}(pp|pq)$ occurs with a weight factor 4 in the fourfold summation in (1), and with a weight factor 1 in a twofold summation. The expressions obtained for E_{π} are now:

$$\begin{aligned} E_{\pi}^{N} = E_0' + \sum_p {\sum_q}' P_{pq}^{N} \left\{ {}^{\lambda}h_{pq} + \sum_{r \neq q} {}^{\lambda}(rr|pq) \right\} \\ - \frac{1}{4} \sum_p {\sum_q}' \{ {}^{\lambda}(pp|qq) - 3\, {}^{\lambda}(pq|pq) \} P_{pq}^{\overset{2}{N}}\,, \end{aligned} \tag{16}$$

$$\begin{aligned} E_{\pi}^{V,T} = E_0' + \sum_p {\sum_q}' P_{pq}^{V} \left\{ {}^{\lambda}h_{pq} + \sum_{r \neq q} {}^{\lambda}(rr|pq) \right\} \\ - \frac{1}{4} \sum_p {\sum_q}' P_{pq}^{\overset{2}{V}} \{ {}^{\lambda}(pp|qq) - 3\, {}^{\lambda}(pq|pq) \} - \frac{1}{4} J_{kk} - \frac{1}{4} J_{k'k'} + \frac{1}{2} K_{kk'} \pm K_{kk'}\,, \end{aligned} \tag{17}$$

where advantage has been taken of the assumption that ${}^{\lambda}(pq|pq) = 0$ unless p and q are neighbours. E_0' is given by:

$$E_0' = E_0 - \frac{1}{4} \sum_p {\sum_q}' \, {}^{\lambda}(pq|pq)\,. \tag{18}$$

For the following calculations of excitation energies the difference between E_0 and E_0' is not relevant. It is seen that, apart from possible differences between J^0, K^0 and J, K, (16) and (17) become formally identical with the ZDO-formulae (11) and (15), if we make the following identifications:

$$\beta_{pq} = {}^{\lambda}h_{pq} + \sum_{r \neq q} {}^{\lambda}(rr|pq) \qquad (q = p \pm 1)\,, \tag{19}$$

$$\gamma_{pq} = {}^{\lambda}(pp|qq) \qquad (q \neq p \pm 1)\,, \tag{20}$$

$$\gamma_{pq} = {}^{\lambda}(pp|qq) - 3\, {}^{\lambda}(pq|pq) \quad (q = p \pm 1)\,. \tag{21}$$

Further we may expand J and K in terms of the γ's, defined by (20) and (21), and of the multicentre integrals; the relevant expressions are:

$$\frac{1}{4}(J_{kk}+J_{k'k'})=\frac{1}{4}J^0_{kk}+\frac{1}{4}J^0_{k'k'}+\frac{5}{2}\sum_p\sum_q{}^* c^2_{kp}c^2_{kq}\,{}^\lambda(12|12), \tag{22}$$

$$K_{kk'}=K^0_{kk'}-3\sum_p\sum_q{}^* c^2_{kp}c^2_{kq}\,{}^\lambda(12|12), \tag{23}$$

where the asterisk denotes that the summation extends over $q=p\pm 1$.

The final results are formulated most conveniently by writing

$$E_\pi=E_Z+E_D, \tag{24}$$

where E_Z is found by combining the ZDO-expression for E_π with the definitions (19), (20) and (21), and E_D is a correction term, depending on ${}^\lambda(12|12)$ only. From (11), (15), (16), (17) and (19)–(24) it follows that for the ground configuration

$$E^N_D=0, \tag{25}$$

whereas for the configurations $x^{k'}_k$

$$E^V_D=-7\sum_p\sum_q{}^* c^2_{kp}c^2_{kq}\,{}^\lambda(12|12), \tag{26a}$$

$$E^T_D=-\sum_p\sum_q{}^* c^2_{kp}c^2_{kq}\,{}^\lambda(12|12). \tag{26b}$$

From a similar calculation for the combinations of $x^{l'}_k$ and $x^{k'}_l$ it is found that

$$E_D=-2\sum_p\sum_q{}^* (c^2_{kp}c^2_{lq}+6c_{kp}c_{kq}c_{lp}c_{lq})\,{}^\lambda(12|12) \tag{27a}$$

for a singulet-plus configuration,

$$E_D=0 \tag{27b}$$

for a singulet-minus configuration,

$$E_D=-2\sum_p\sum_q{}^* c^2_{kp}c^2_{lq}\,{}^\lambda(12|12) \tag{27c}$$

for a triplet plus-configuration, and

$$E_D=-4\sum_p\sum_q{}^* (c^2_{kp}c^2_{lq}-c_{kp}c_{kq}c_{lp}c_{lq})\,{}^\lambda(12|12) \tag{27d}$$

for a triplet minus configuration.

In a hydrocarbons with $2n$ C-atoms the AO-coefficients are of the order of $(2n)^{-1/2}$, so that the expressions in (26) and (27) are roughly proportional to n^{-2}; the number of pairs p, q over which the summation is extended is proportional with n, so that E_0 is roughly proportional with n^{-1}. For the lower excited configuration of naphthalene and anthracene we found that $|E_D|\leqq 0.05$ eV; for larger molecules the neglect of E_D seems to be justified. It follows then from the argument underlying (19) and (21) that in empirical calculations on large conjugated systems any deficiency of the ZDO-approximation can be quantitatively accounted for by the choice of β and γ_{12}. For small molecules, however, E_D should be taken quantitatively into account.

It is further seen that in all cases E_D depends on ${}^{\lambda}(12|12)$ alone. Because this exchange integral is certainly non-negative the sign of E_D can always be found by the substitution of the AO-coefficients into (26) and (27).

The efficiency of the present procedure in accounting for the effects of differential overlap may be judged by the fact that for the lowest $x_k^{k'}$ in naphthalene the term in ${}^{\lambda}(12|12)$ included in the summation of P_{pq}^2 in (17) is 2.6 ${}^{\lambda}(12|12)$, whereas the corrections E_D are only 0.7 ${}^{\lambda}(12|12)$ (singlet) and 0.1 $(12|12)$ (triplet).

3. Calculations and Conclusions

3.1. *First-Order Calculations of Excitation Energies*

It follows from (25) that for excitation energies calculated from one-configurational functions the differential overlap correction equals the value of E_D for the considered excited state. However, some care should be exercised in applying (26) and (27) to molecules in which degenerate MO's occur. As an exemple we mention the lowest ${}^1B_{1u}$ state of benzene. It was stated above that the derivation of E_D is valid only if all AO-coefficients are real. Now in terms of configurations based on real MO's the benzene B_{1u}-states can only be written as a linear combination of two configurations of type $x_k^{k'}$; (26) and (27) do not apply to such a function. In this case it is necessary to combine the E_D-terms for the two configurations, as given by (26), with the multicentre contribution due to the crossterm.

The calculation of E_D for the lower benzene states gives:

$$\begin{gathered}E_D({}^1B_{2u})=0, \quad E_D({}^1B_{1u})=-\tfrac{11}{3}{}^{\lambda}(12|12), \quad E_D({}^1E_{1u})=\tfrac{1}{6}{}^{\lambda}(12|12), \\ E_D({}^3B_{1u})=\tfrac{1}{3}{}^{\lambda}(12|12).\end{gathered} \tag{28}$$

3.2. *Multicentre Integrals in* CI-*Calculations*

In a theoretical investigation of the benzene spectrum [1] we duplicated Karwowski's conclusion [10] that in the strict ZDO-approximation it is impossible to find a physically acceptable set of parameter values from which the experimental benzene spectrum is reproduced by means of a CI-calculation with all configurations which are no more than triply excited with respect to the ground configuration. An extension of the calculation by introducing more highly excited configurations does not modify the results [11]. The introduction of the correction (28), with the estimated value 0.07 eV for ${}^{\lambda}(12|12)$, enabled us to give a consistent interpretation of the benzene UV-spectrum. From a more detailed investigation it followed that the explicit inclusion of ${}^{\lambda}(12|12)$ in the off-diagonal elements of the CI-matrix is marginally worthwhile for those elements which are responsible for second order corrections of more than about 0.2 eV on the energy value for the considered state. More explicity, the correction for differential overlap in interaction matrix elements modifies the calculated energy of the ${}^1B_{2u}$-state by +0.04 eV, and does not affect the other transitions investigated in [1].

The parameter values which may be used in CI-calculations were found to be:

$$\begin{gathered}\beta = -2.65, \quad \gamma_{11} = 10.50, \quad \gamma_{12} = 6.90, \quad \gamma_{13} = 5.55, \\ \gamma_{14} = 5.00, \quad {}^{\lambda}(12|12) = 0.07\ \text{eV},\end{gathered} \tag{29}$$

where β and γ_{12} are defined by (19) and (21).

It is seen that the γ-values are quite close to those found by Pariser [12] from a spectral matching procedure without CI. This can be explained if we recall that in such procedures the γ-values are largely determined by the *differences* between the spectroscopic energies. It follows from Koutecky's calculations [13] that for any reasonable set of γ-values the omission of CI implies the neglect of considerable negative energy terms for all states except ${}^1B_{1u}$; for this state, however, the strict application of the ZDO-approximation involves the neglect of a rather large negative term. Thus a spectral matching procedure which accounts for both π-electron correlation and differential overlap may well give γ-values which differ but slightly from those proposed by Pariser. The differences between the two schemes make themselves mainly felt in the respective β-values, which differ by almost 0.3 eV.

3.3. An Irregularity in γ-r Curves

In many empirical relations between γ_{pq} and r_{pq}, derived on the basis of the ZDO assumption, it is found that γ_{12} is slightly lower than the value estimated from a smooth interpolation between γ_{11} and the γ-r curve for $r > 2.4$ Å. The "buckle" in the γ-function, regarded as unphysical by Ruedenberg [14], was recognised by Simmons [15] as a common feature of γ-r-relations obtained from spectral matching procedures. It seems now that (21) offers at least a qualitative explanation of the irregularity, as ${}^{\lambda}(12|12)$ is non-negative. Also the value -0.21 eV, suggested by (29) for the correction term in (21), is of the correct magnitude to reduce the slightly irregular γ-r-curve outlined in (29) to a smooth ${}^{\lambda}(pp|qq) - r_{pq}$ curve. Thus the explicit consideration of some multicentre integrals provides through (19) and (21) an additional argument for the applicability of the ZDO-approximation for large molecules; at the same time it explains one detail of the γ-values which at first sight seems to lack a physical base.

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