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An analysis of the zero differential overlap approximation. Towards an improved semiempirical MO method beyond it

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Summary. Some systematic errors of the zero differential overlap (ZDO) approximation in semiempirical molecular orbital (MO) methods are discussed. In π electron methods, a power series expansion of the inverse square root $\boldsymbol{S}^{-1/2}$ of the overlap matrix and application of the Mulliken approximation to the two-electron integrals show that the ZDO Hamiltonian coincides with the Hamiltonian obtained by explicit performance of the Löwdin transformation up to first-order terms of diatomic overlap densities. Higher than first-order terms lead to a systematic up-shift of the canonical MO energies. Although a power series expansion of $\boldsymbol{S}^{-1/2}$ is no longer possible in all-valence-electron methods, the MO levels resulting from the ZDO approximation are also systematically placed at too low energies, especially the low-lying occupied and the virtual MOs. A method based on explicit performance of the Löwdin transformation and retaining the simplicity of the ZDO approach for the calculation of Fock matrix elements is developed. The parameters of this method are obtained by very simple manipulations of the original ZDO parameters. Numerical calculations show that a considerable improvement of the MO energy spectrum in the inner valence region can be obtained in this way

Key words: Zero differential overlap – Semiempirical MO methods – Löwdin transformation – Overlap density – Mulliken approximation

1 Introduction

Some of the most common semiempirical molecular orbital (MO) methods like CNDO (complete neglect of differential overlap) [1], INDO (intermediate neglect of differential overlap) [1], MINDO/1–3 (modified intermediate neglect of differential overlap) [2] as well as MNDO (modified neglect of differential overlap) [3] and AM1 (Austin Model 1) [4] use the zero differential overlap (ZDO) approximation, i.e., overlap densities $\phi_\mu^* \phi_\nu$ with ϕ_μ and ϕ_ν being orbitals localized on different atoms are neglected whenever they appear in an integral or matrix element except for the so-called resonance integral $\beta_{\mu\nu}$ which is indispensable for the description of chemical bonding. In contrast to these approaches, the most simple semiempirical all-valence-electron MO formalism, the extended Hückel method [5], operates with a full-overlap basis. A full-overlap semiempirical Hartree–Fock (HF) method based on the two-electron integrals used in CNDO has been developed by Yonezawa et al. [6]. Another interesting approach is the Hartree–Fock π electron model of Berthier et al. [7] in which the Löwdin transformation from the nonorthogonal atomic orbital (AO) to a symmetrically orthogonalized basis [8] is performed explicitly and the ZDO approximation for the two-electron integrals is only used after the transformation. Several semiempirical methods employing orthogonality correction terms in the diagonal elements of the Fock matrix have also been reported [9–12].

The validity of the ZDO approximation gave rise to some discussion in the sixties and seventies [13–22]. Most of these analyses start from the assumption that the basis used in ZDO methods consists of symmetrically orthogonalized Löwdin orbitals [8] rather than the nonorthogonal AOs and rely heavily on a power series expansion of the inverse square root $\boldsymbol{S}^{-1/2}$ of the overlap matrix $\boldsymbol{S}$. This leads to a justification of the ZDO method in π electron theories as has been shown by Fischer-Hjalmars [13]. However, second-order overlap terms missing in the ZDO scheme seriously affect the resonance integrals β_{13} between nonnearest neighbors in π systems as has been discussed by de Bruijn [14]. He also showed that there is a decrease of the nearest-neighbor resonance integral in small atomic clusters which cannot be consistently parametrized in a ZDO scheme [14]. The analysis of Fischer-Hjalmars has been extended by Brown and Roby [15] to all-valence-electron methods of the CNDO, INDO and NDDO (neglect of diatomic differential overlap) [23] type. However, it has been pointed out by Gray and Stone [16] that even for such simple molecules as e.g. methane some elements of the overlap matrix can get quite large (> 0.5) leading to eigenvalues of the overlap matrix bigger than 2 so that a power series expansion of $\boldsymbol{S}^{-1/2}$ no longer converges. In that case the conclusions based on such an expansion break down. Thus, the arguments of Brown and Roby [15] have been reexamined by Chandler and Grader [17] using a different $\boldsymbol{S}$ expansion technique. In agreement with Brown and Roby, they arrived at the conclusion that the one-electron Hamiltonian matrix elements of the ZDO method cannot be identified with those obtained after explicit performance of the Löwdin transformation but that there is some justification for neglecting diatomic differential overlap in the two-electron repulsion integrals if the latter are calculated in the Löwdin basis. Roby [18] attempted to justify the ZDO approximation without having recourse to a power series expansion of $\boldsymbol{S}^{-1/2}$. His arguments have been criticized by King et al. [19].

The evaluation of the two-electron integrals poses the most serious problems in the design of an appropriate NDO method based on explicit performance of the Löwdin transformation. Actually, the difficulty in handling the two-electron part of the Fock matrix in a full-overlap basis is probably the most compelling reason for the widespread use of the ZDO approximation in semiempirical SCF MO approaches. On the other hand, the simpler extended Hückel method [5] does not encounter this problem and can therefore be easily formulated in a full-overlap basis. Since the two-electron part of the Fock matrix is much better approximated by the usual NDO expression than the one-electron part [15] it might be tempting to calculate the latter explicitly in a Löwdin basis and to treat the former like in traditional NDO theories. However, this leads to an imbalance between rather large electron–core attraction and electron–electron repulsion terms [20]. Thus, the two-electron part of the Fock matrix should be dealt with in the same way as the one-electron part, i.e., both should be subjected to the Löwdin transformation simultaneously. However, not much is gained by such a procedure. Even if the NDO approximation, i.e., the neglect of two-electron integrals containing diatomic differential overlap, is justified to some extent in the Löwdin basis [15, 17] the whole set of two-electron integrals in the AO basis has to be evaluated before the Löwdin transformation can be performed. Note that in an AO basis there is no justification for neglecting diatomic differential overlap terms within the multitude of two-electron repulsion integrals, the number of which increases roughly as N^4 if N is the dimension of the AO basis. To avoid evaluation of such an abundant number of integrals one often uses the Mulliken [24] (in the case of CNDO) or Ruedenberg [25] (NDDO) approximations for replacement of diatomic differential overlap terms by mono-center terms in the AO basis. Recently, Koch [26] suggested to explicitly perform the transformation only for two-electron integrals containing orbitals on atoms located within a certain radius and to identify the remaining integrals to those of the AO basis. Sometimes, the two-electron integrals in the Löwdin basis are related to those of the AO basis in a crude fashion by using scaling factors [27]. Extensive efforts to circumvent the N^4 problem without serious loss in accuracy have been performed in the PRDDO (partial retention of diatomic differential overlap) [28] and AAMOM (an approximate molecular orbital theory) [29] approaches. An intuitively appealing strategy based on explicit performance of the Löwdin transformation but retaining both the above-mentioned balance between electron–core attraction and electron–electron repulsion terms and the simplicity of NDO methods in the treatment of two-electron integrals has been outlined by Spanget-Larsen [20a]. This elegant setup has been used in calculations of conjugated hydrocarbons [20b–e].

The most serious deficiency inherent in the ZDO methods mentioned at the beginning (CNDO, INDO, etc.) is that they must pretend to operate with a Löwdin basis but parametrize all matrix elements and two-electron integrals as if an AO basis were used. Hence, they do not take into account the fact that a Löwdin orbital associated with a certain atom also depends on the surroundings of that atom. Thus, there is no guarantee that matrix elements calculated in the Löwdin basis are transferable from one molecule to another [13, 14]. In the present contribution we will make some efforts to overcome this inconsistency. We will focus on the transformation of given ZDO parameters to an AO basis which are subsequently subjected to the Löwdin transformation. Although a careful reparametrization of existing ZDO methods might be unavoidable if one wants to benefit quantitatively from such an improved formalism we will show that a rather simple modification of ZDO parameters leads already to quite reasonable results and eliminates some systematic errors inherent in the ZDO approximation. For example, the most bonding and antibonding MOs are consistently found at too low energies in ZDO methods which give reasonable MO energies only for the frontier orbitals near the HOMO-LUMO region. Our objective is to retain the simplicity of existing ZDO formalisms and to base them on explicit performance of the Löwdin transformation.

As already mentioned most of the theoretical contributions to our understanding of semiempirical MO methods have been published in the sixties and seventies while recent approaches are quite sparse. This change in scientific emphasis has its technical origin in the increasing availability of high-speed computers allowing high-quality *ab initio* calculations also on larger molecules. The necessity to study electronic structure properties of molecules by approximate MO techniques therefore had been reduced in the past years. Nevertheless, there exist challenging problems where efficient non-*ab initio* electronic structure approaches are prerequisites for theoretical investigations. *Ab initio* Hartree–Fock methods which have their roots in the techniques of quantum chemistry cannot be employed in investigations of solid-state electronic structures of complex materials. For these systems one can choose only between band-structure methods based on the local density functional (LDF) approximation [30, 31] and crystal orbital formalisms based on approximate ZDO Hamiltonians. But as documented in the literature [32–34] the latter lead to inner valence bands which are much too broad. LDF methods also have intrinsic shortcomings in the reproduction of experimental properties. Band gaps are predicted to be too small. By adopting the improvements discussed below previous ZDO deficiencies can be eliminated. Furthermore, we expect that improved LCAO (linear combination of atomic orbitals) models should be of some utility in combination with quantum Monte Carlo (QMC) simulation methods. Most of the previous QMC work had been restricted to simple model Hamiltonians of the Hubbard or extended Hubbard type [35, 36]. A previous PPP (Pariser–Parr–Pople) [37] extension can also be found in the literature [38, 39]. In combination with Green's function QMC techniques, improved model Hamiltonians avoiding certain ZDO errors should be very useful. Apart from this motivation, the present theoretical analysis has a didactic aim, too, i.e., to clarify problems of the ZDO approach in as transparent a manner as possible.

In Sect. 2 we examine the relationship of ZDO parameters with the corresponding parameters in an AO basis. This section has to some extent the character of a review but also covers new aspects. Section 3 will be devoted to numerical calculations which illustrate some of the theoretical arguments. A theoretical resume and suggestions for future work are presented in Sect. 4.

2 Deficiencies of ZDO approximations

Self-consistent-field (SCF) MO calculations in a full-overlap, i.e., the AO basis $\{\phi_\mu\}$ are based on an iterative solution of the following secular equation:

$$\boldsymbol{FC} = \boldsymbol{SC\varepsilon}, \tag{1}$$

where $\boldsymbol{S}$ is the overlap matrix, $\boldsymbol{C}$ the matrix of the eigenvector coefficients, $\boldsymbol{\varepsilon}$ a diagonal matrix containing the canonical MO energies, and $\boldsymbol{F}$ the Fock matrix which can be divided into a one-electron part $\boldsymbol{h}$ and a two-electron part $\boldsymbol{G}$:

$$\boldsymbol{F} = \boldsymbol{h} + \boldsymbol{G}. \tag{2}$$

For closed shell systems, the matrix elements of $\boldsymbol{h}$ and $\boldsymbol{G}$ read

$$\begin{aligned} h_{\mu\nu} &= \langle \phi_\mu | \hat{h} | \phi_\nu \rangle, \\ G_{\mu\nu} &= \sum_\lambda \sum_\sigma P_{\lambda\sigma}\left((\phi_\mu\phi_\nu|\phi_\sigma\phi_\lambda) - \tfrac{1}{2}(\phi_\mu\phi_\lambda|\phi_\sigma\phi_\nu)\right), \end{aligned} \tag{3}$$

with the bond order matrix $\boldsymbol{P}$ having the following matrix elements:

$$P_{\lambda\sigma} = 2 \sum_{i(\text{occ. MOs})} C_{\lambda i} C^*_{\sigma i}. \tag{4}$$

The two-electron integrals are abbreviated as follows:

$$(\phi_\mu\phi_\nu|\phi_\sigma\phi_\lambda) = \int \phi^*_\mu(1)\phi^*_\sigma(2)\frac{e^2}{r_{12}}\phi_\nu(1)\phi_\lambda(2)\,\mathrm{d}v_1\,\mathrm{d}v_2, \tag{5}$$

where r_{12} is the distance between electrons 1 and 2. The electron charge is symbolized by e. Since we are dealing with real orbitals the asterisks indicating the complex conjugate in Eq. (5) can be omitted in the following. $\hat{h}$ is the core Hamiltonian which can be partitioned into the kinetic energy and the potential energy in the electrostatic field of all the atom cores; each core consists of the bare nucleus and those electrons which are not being explicitly considered, i.e., the inner shell electrons in the case of all-valence-electron methods. Denoting the cores by the capital letter A we obtain

$$\hat{h} = -\tfrac{1}{2}\Delta + \sum_{A} V_A. \tag{6}$$

In contrast to full-overlap methods the ZDO approaches use the following secular equation:

$${}^{\mathrm{ZDO}}\boldsymbol{F}\,{}^{\mathrm{ZDO}}\boldsymbol{C} = {}^{\mathrm{ZDO}}\boldsymbol{C}\boldsymbol{\varepsilon}. \tag{7}$$

It has been shown by Löwdin [8] that Eq. (1) can be brought to the form of Eq. (7) by the following transformation:

$$\begin{aligned} {}^{\lambda}\boldsymbol{F} &= \boldsymbol{S}^{-1/2}\boldsymbol{F}\boldsymbol{S}^{-1/2}, \\ {}^{\lambda}\boldsymbol{C} &= \boldsymbol{S}^{1/2}\boldsymbol{C}, \end{aligned} \tag{8}$$

resulting in

$${}^{\lambda}\boldsymbol{F}\,{}^{\lambda}\boldsymbol{C} = {}^{\lambda}\boldsymbol{C}\boldsymbol{\varepsilon}. \tag{9}$$

It should be noted that the Löwdin basis represents just one particular choice out of an infinite multitude of possible orthogonal basis sets. Necessary condition for the transformation is only the conservation of the functional space spanned by the genuine AOs. However, the Löwdin orbitals have some special properties responsible for their importance in quantum chemistry. First, they resemble the initial AOs as closely as possible and, second, they have the same transformation properties as the AOs under symmetry operations of the molecular point group [8].

It is clear that the utility of ZDO methods depends on the fact that observable quantities like charge distributions, dipole moments, ionization potentials, etc. calculated in the ZDO approximation are not too different from those resulting either from Eq. (1) or Eq. (9). This does not imply ${}^{\lambda}\boldsymbol{F} \approx {}^{\mathrm{ZDO}}\boldsymbol{F}$. Although Eqs. (7) and (9) are formally identical the Fock matrix of the latter has been obtained in a completely different way by explicitly performing the Löwdin transformation. We will see shortly that an approximate relationship ${}^{\lambda}\boldsymbol{F} \approx {}^{\mathrm{ZDO}}\boldsymbol{F}$ only holds in π electron methods.

2.1 The ZDO approximation in π electron methods

The ZDO approximation in π electron methods has been discussed by Fischer-Hjalmars [13]. Here we present a somewhat different analysis with two main objectives. We discuss (a) the consistency of the ZDO approximation with the neglect of penetration integrals appearing in the diagonal elements of the core Hamiltonian and (b) the transferability of matrix elements from one molecular environment to another one.

Since the overlap integrals between π orbitals on neighboring carbon centers are not too large ($S \approx 0.3$) and since there is just one π orbital per center, a power series expansion of the inverse square root of the overlap matrix does converge in this case:

$$\boldsymbol{S}^{-1/2} = (1 + \boldsymbol{d})^{-1/2} = 1 - \tfrac{1}{2}\boldsymbol{d} + \tfrac{3}{8}\boldsymbol{d}^2 + \cdots, \tag{10}$$

where $\boldsymbol{d}$ is a matrix containing zeros in the diagonal and the overlap integrals in the off-diagonal:

$$d_{\mu\nu} = S_{\mu\nu} - \delta_{\mu\nu}. \tag{11}$$

We first consider the one-electron part of the Fock Hamiltonian:

$$^{\lambda}\boldsymbol{h} = \boldsymbol{S}^{-1/2}\boldsymbol{h}\boldsymbol{S}^{-1/2}. \tag{12}$$

Let us split $\boldsymbol{h}$ into diagonal and off-diagonal parts denoted as $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$, respectively, as follows:

$$\alpha_{\mu\nu} = h_{\mu\nu}\delta_{\mu\nu},$$

$$\beta_{\mu\nu} = h_{\mu\nu}(1 - \delta_{\mu\nu}). \tag{13}$$

Using Eq. (13), applying the expansion (10) in Eq. (12) and restricting ourselves to terms containing overlap densities $\phi_\mu\phi_\nu$ ($\mu \neq \nu$) in first order we obtain

$$^{\lambda}\boldsymbol{h} \approx (1 - \tfrac{1}{2}\boldsymbol{d})\boldsymbol{\alpha}(1 - \tfrac{1}{2}\boldsymbol{d}) + \boldsymbol{\beta} \tag{14}$$

or

$$^{\lambda}h_{\mu\mu} \equiv {}^{\lambda}\alpha_{\mu} \approx \alpha_{\mu},$$

$$^{\lambda}h_{\mu\nu} \equiv {}^{\lambda}\beta_{\mu\nu} \approx \beta_{\mu\nu} - \tfrac{1}{2}S_{\mu\nu}(\alpha_\mu + \alpha_\nu) \quad (\mu \neq \nu). \tag{15}$$

Note that only the leading term of the power series expansion (10) has to be considered in the case of the off-diagonal matrix $\boldsymbol{\beta}$ because the matrix elements $\beta_{\mu\nu}$ themselves contain diatomic overlap densities $\phi_\mu\phi_\nu(\mu \neq \nu)$ thus representing first-order terms. This definition of "order" deviates from the one used by Brown and Roby [15] who consider only the powers of the overlap integrals whereas we consider overlap densities no matter if they occur in an overlap integral or in a Hamiltonian matrix element. Thus, the matrix $\boldsymbol{\beta d}$ containing products of resonance and overlap integrals is first order in the sense of Roby and Brown but second order in the present definition. Please note that a resonance integral β is of the same order of magnitude as a product of the type αS both being first order in terms of overlap densities. It is important to note that the second relation of Eq. (15) represents the resonance integral used in the Pariser–Parr–Pople (PPP) method [37] which must therefore not be identified with the corresponding integral $\beta_{\mu\nu}$ in the AO basis.

In contrast to the AOs which have the same form for two different atoms of the same type the Löwdin orbitals depend on the surroundings and may thus differ from e.g. one carbon atom to a neighboring one. This raises the question of transferability of matrix elements calculated in the Löwdin basis from one molecule to another. Equations (15) show that transferability is guaranteed to first order in the overlap because the matrix elements in Eq. (15) are only functions of the AOs ϕ_μ and ϕ_ν. In principle, however, a matrix element in the Löwdin basis is a function of the whole AO basis set. It can be seen that the magnitude of the diagonal matrix elements of the core Hamiltonian is approximately the same in both the AO and the Löwdin basis whereas the absolute magnitude of the off-diagonal matrix elements is considerably reduced in the latter.

Now let us turn to the integrals appearing in the two-electron part G (Eq. (3)) of the Hamiltonian. Before starting our analysis we would like to mention that the first derivation of the two-electron integrals in the Löwdin basis has been given by Julg [40]. He has shown that orthogonalization effects are of second order in the overlap and thus rather weak for π systems of conjugated hydrocarbons. Denoting the AO and Löwdin basis as $\{\phi_\mu\}$ and $\{\chi_\mu\}$, respectively, we obtain

$$(\chi_\mu\chi_\nu|\chi_\sigma\chi_\lambda) = \sum_{\mu'}\sum_{\nu'}\sum_{\sigma'}\sum_{\lambda'}(\phi_{\mu'}\phi_{\nu'}|\phi_{\sigma'}\phi_{\lambda'})S^{-1/2}_{\mu'\mu}S^{-1/2}_{\nu'\nu}S^{-1/2}_{\sigma'\sigma}S^{-1/2}_{\lambda'\lambda}. \tag{16}$$

In the AO basis only Coulomb integrals of the type $(\phi_{\mu'}\phi_{\mu'}|\phi_{\sigma'}\phi_{\sigma'})$, i.e., those which contain charge densities $|\phi_\mu|^2$ are easily available if the AOs are represented by Slater orbitals. However, the remaining ones which represent the vast majority can be reduced to those of the simple type using the Mulliken approximation for overlap densities [24]:

$$\phi_\mu\phi_\nu = \tfrac{1}{2}S_{\mu\nu}(\phi_\mu\phi_\mu + \phi_\nu\phi_\nu). \tag{17}$$

Note that Eq. (17) can only be used if the overlap densities appear in a Coulomb integral but not as an approximation to the overlap densities themselves [21, 41]. Inserting Eq. (17) in Eq. (16) results in a considerable simplification:

$$(\chi_\mu\chi_\nu|\chi_\sigma\chi_\lambda) = \frac{1}{4}\sum_{\mu'}\sum_{\sigma'}(S^{-1/2}_{\mu'\mu}S^{+1/2}_{\mu'\nu} + S^{+1/2}_{\mu'\mu}S^{-1/2}_{\mu'\nu})\gamma_{\mu'\sigma'}(S^{-1/2}_{\sigma'\sigma}S^{+1/2}_{\sigma'\lambda} + S^{+1/2}_{\sigma'\sigma}S^{-1/2}_{\sigma'\lambda}) \tag{18}$$

with

$$\gamma_{\mu'\sigma'} = (\phi_{\mu'}\phi_{\mu'}|\phi_{\sigma'}\phi_{\sigma'}). \tag{19}$$

Thus, the vast summation in Eq. (16) involving four sum indices has been reduced to two sum indices in Eq. (18). The two-electron integrals in the Löwdin basis have an interesting property. Contrary to overlap densities in the AO basis an overlap density $\chi_\mu\chi_\nu$ appearing in an integral in the Löwdin basis is of second order in terms of AO overlap densities rather than of first order [40], i.e., integrals containing overlap densities in the Löwdin basis are much smaller than the corresponding ones of the AO basis. To verify this we use again the power series expansion of Eq. (10) and a corresponding expansion of $\boldsymbol{S}^{+1/2}$:

$$\boldsymbol{S}^{+1/2} = \mathbf{1} + \tfrac{1}{2}\mathbf{d} - \tfrac{1}{8}\boldsymbol{d}^2 + \cdots \tag{20}$$

Inserting Eqs (10) and (20) into Eq. (18) we obtain to second order [40]:

$$(\chi_\mu\chi_\nu|\chi_\sigma\chi_\lambda) \approx \gamma_{\mu\sigma}\delta_{\mu\nu}\delta_{\sigma\lambda} + \frac{1}{8}\delta_{\sigma\lambda}\sum_{\mu'(\neq\mu,\nu)} S_{\mu'\mu}S_{\mu'\nu}(\gamma_{\mu\sigma} + \gamma_{\nu\sigma} - 2\gamma_{\mu'\sigma})$$
$$+ \frac{1}{8}\delta_{\mu\nu}\sum_{\sigma'(\neq\sigma,\lambda)} S_{\sigma'\sigma}S_{\sigma'\lambda}(\gamma_{\mu\sigma} + \gamma_{\mu\lambda} - 2\gamma_{\mu\sigma'}). \tag{21}$$

It is easily seen that this expression does not contain first-order terms. Moreover, the Coulomb integrals in the brackets on the right-hand side of Eq. (21) are of the same order of magnitude so that they cancel each other to some extent. Restricting ourselves again to first-order terms like in Eqs. (14) and (15) we end up with

$$(\chi_\mu\chi_\nu|\chi_\sigma\chi_\lambda) = \delta_{\mu\nu}\delta_{\sigma\lambda}\gamma_{\mu\sigma}, \tag{22}$$

It can be seen from Eq. (22) that the Coulomb integrals $\gamma_{\mu\sigma}$ are approximately the same in both the Löwdin and the AO basis, whereas Coulomb integrals containing diatomic overlap densities are strongly reduced in the Löwdin basis so that they may be neglected thus justifying the zero differential overlap approximation.

It is important to note that the Mulliken approximation [24] must not be applied to ${}^{\lambda}\beta_{\mu\nu}$ in Eq. (15) which would then vanish. This is a consequence of the presence of the kinetic energy operator Δ in the core Hamiltonian $\hat{h}$. It has been demonstrated by Cook [42] that the resonance integral ${}^{\lambda}\beta_{\mu\nu}$ as given by Eq. (15) in the Löwdin basis is largely dominated by the kinetic energy contribution because the Mulliken approximation can still be applied to the potential energy part of the one-electron Hamiltonian $\hat{h}$ which then vanishes. Thus, the zero differential overlap approximation in the Löwdin basis holds in first order for the two-electron integrals but not for the resonance integral. We emphasize this point because ZDO methods are often accused of arbitrarily retaining diatomic overlap densities in the resonance integrals which cannot be skipped because they are essential for chemical bonding and neglecting the same overlap densities elsewhere. This cannot be considered as an inconsistency of ZDO methods. Actually, it seems more plausible to replace the expression "zero differential overlap approximation" by "differential overlap in first-order approximation", at least in the context of π electron methods.

We would like to find a relationship between parameters of a given ZDO approach and the corresponding parameters in an AO basis subsequently subjected to the Löwdin transformation. This is very simple for π electron methods. Considering the core Hamiltonian matrix $\boldsymbol{h}$ we have already seen that the diagonal elements need not be changed (the neglect of rather small penetration integrals in ZDO parameters will be discussed below). The absolute magnitude of the resonance integrals, on the other hand, has to be enhanced by the arithmetic mean of the corresponding diagonal matrix elements multiplied by the overlap integral. Subsequent Löwdin transformation will then reduce the magnitude of the resonance integral approximately to the ZDO value as can be seen from Eq. (15). Thus, AO and ZDO matrix elements are related as follows:

$$\begin{aligned} h_{\mu\mu} &= \alpha_\mu \approx {}^{\mathrm{ZDO}}\alpha_\mu, \\ h_{\mu\nu} &= \beta_{\mu\nu} \approx {}^{\mathrm{ZDO}}\beta_{\mu\nu} + \tfrac{1}{2}S_{\mu\nu}(\alpha_\mu + \alpha_\nu) \quad (\mu \neq \nu), \end{aligned} \tag{23}$$

or in matrix form using Eq. (11):

$$\begin{aligned} {}^{\mathrm{ZDO}}\boldsymbol{h} &= \boldsymbol{\alpha} + {}^{\mathrm{ZDO}}\boldsymbol{\beta}, \\ \boldsymbol{h} &= \boldsymbol{\alpha} + {}^{\mathrm{ZDO}}\boldsymbol{\beta} + \tfrac{1}{2}(\boldsymbol{\alpha d} + \boldsymbol{d\alpha}) = \tfrac{1}{2}(\boldsymbol{\alpha S} + \boldsymbol{S\alpha}) + {}^{\mathrm{ZDO}}\boldsymbol{\beta}. \end{aligned} \tag{24}$$

Performing the Löwdin transformation we obtain

$${}^{\lambda}\boldsymbol{h} = \boldsymbol{S}^{-1/2}\boldsymbol{h}\boldsymbol{S}^{-1/2} = \tfrac{1}{2}(\boldsymbol{S}^{-1/2}\boldsymbol{\alpha}\boldsymbol{S}^{+1/2} + \boldsymbol{S}^{+1/2}\boldsymbol{\alpha}\boldsymbol{S}^{-1/2}) + \boldsymbol{S}^{-1/2}\,{}^{\mathrm{ZDO}}\boldsymbol{\beta}\boldsymbol{S}^{-1/2}. \tag{25}$$

Using the power series expansions (10) and (20) we obtain the expected result that ${}^{\lambda}\boldsymbol{h}$ and ${}^{\mathrm{ZDO}}\boldsymbol{h}$ are identical up to first order:

$${}^{\lambda}\boldsymbol{h} \approx \boldsymbol{\alpha} + {}^{\mathrm{ZDO}}\boldsymbol{\beta} = {}^{\mathrm{ZDO}}\boldsymbol{h}. \tag{26}$$

It can be seen from Eq. (23) that the resonance integral $\beta_{\mu\nu}$ in the AO basis is considerably larger in absolute magnitude than the resonance integral ${}^{\mathrm{ZDO}}\beta_{\mu\nu}$ of the Pariser–Parr–Pople method. The two-electron part $\boldsymbol{G}$ of the Fock matrix $\boldsymbol{F}$ can be adopted directly from the ZDO basis because the Löwdin transformation does not change these integrals up to first order in the overlap densities.

If second- and higher-order terms of overlap densities are included ${}^{\lambda}\boldsymbol{h}$ and ${}^{\mathrm{ZDO}}\boldsymbol{h}$ are no longer identical. It is illustrative to consider the second-order terms in some more detail because they are crucial in answering the question of the transferability of matrix elements. Using the power series expansion (10) and (20) we obtain from Eq. (25) up to second order:

$$ {}^{\lambda}\boldsymbol{h} \approx {}^{\mathrm{ZDO}}\boldsymbol{h} + \boldsymbol{\Delta}^{\alpha} + \boldsymbol{\Delta}^{\beta} \tag{27} $$

with

$$ \begin{aligned} \boldsymbol{\Delta}^{\alpha} &= -\tfrac{1}{4}\boldsymbol{d\alpha d} + \tfrac{1}{8}(\boldsymbol{d}^2\boldsymbol{\alpha} + \boldsymbol{\alpha d}^2), \\ \boldsymbol{\Delta}^{\beta} &= -\tfrac{1}{2}({}^{\mathrm{ZDO}}\boldsymbol{\beta d} + \boldsymbol{d}\,{}^{\mathrm{ZDO}}\boldsymbol{\beta}). \end{aligned} \tag{28} $$

Considering a particular matrix element of Δ^{α} we have

$$ \Delta^{\alpha}_{\mu\nu} = \frac{1}{4} \sum_{\sigma(\neq\mu,\nu)} S_{\mu\sigma} S_{\sigma\nu} \left(-\alpha_{\sigma} + \frac{1}{2}\alpha_{\nu} + \frac{1}{2}\alpha_{\mu} \right). \tag{29} $$

The bracket on the right-hand side of Eq. (29) contains terms of opposite sign. The matrix elements of Δ^{α} may therefore be positive or negative and do not indicate clear-cut trends in their magnitude and sign. We would like to show that they may be neglected if the π system does not involve heteroatoms and excess charges. First, let us cast the matrix elements α_{μ} into a somewhat different form. The core Hamiltonian has already been given in Eq. (6). Since each atom contributes one π orbital to the conjugated system we may number the atoms in the same way as the π AOs themselves for the convenience of notation. Thus, we replace the capital letter A in Eq. (6) by greek indices. Using this convention and Eq. (6) we obtain for the diagonal elements:

$$ \alpha_{\mu} = U_{\mu} + \sum_{\sigma(\neq\mu)} \langle \phi_{\mu} | V_{\sigma} | \phi_{\mu} \rangle \tag{30} $$

with

$$ U_{\mu} = \langle \phi_{\mu} | -\tfrac{1}{2}\Delta + V_{\mu} | \phi_{\mu} \rangle \tag{31} $$

The terms in the sum on the right-hand side of Eq. (30) can be rewritten as follows:

$$ \langle \phi_{\mu} | V_{\sigma} | \phi_{\mu} \rangle = -(\sigma; \mu\mu) - Z_{\sigma}\gamma_{\mu\sigma}. \tag{32} $$

Z_{σ} is the number of π electrons contributed by atom σ. $(\sigma; \mu\mu)$ is the penetration integral first introduced by Goeppert-Mayer and Sklar [43] and represents the Coulomb interaction of a charge distribution $|\phi_{\mu}|^2$ with the *neutral* atom σ. Note that this interaction is always attractive. The penetration integral itself is defined in such a way that it is positive so that a minus sign has to be added in Eq. (32). Since the penetration integrals are quite small for π orbitals and all of the same sign they are often considered to represent a simple shift of the zero of the energy scale and are thus neglected. We will see below that there might be a more systematic reason for neglecting penetration effects in ZDO methods. Using Eqs. (30) and (32) and neglecting penetration integrals we can rewrite Eq. (29) as follows:

$$ \begin{aligned} \Delta^{\alpha}_{\mu\nu} = \frac{1}{4} \sum_{\sigma(\neq\mu,\nu)} S_{\mu\sigma} S_{\sigma\nu} \Bigg(-U_{\sigma} + \frac{1}{2}U_{\nu} + \frac{1}{2}U_{\mu} - \Bigg(-\sum_{\lambda(\neq\sigma)} Z_{\lambda}\gamma_{\sigma\lambda} \\ + \frac{1}{2} \sum_{\lambda(\neq\nu)} Z_{\lambda}\gamma_{\nu\lambda} + \frac{1}{2} \sum_{\lambda(\neq\mu)} Z_{\lambda}\gamma_{\mu\lambda} \Bigg)\Bigg). \end{aligned} \tag{33} $$

In the following we assume that no heteroatoms contribute to the π system. Taking into account that the on-site repulsion integrals $\gamma_{\mu\mu}$ and the valence state energies

U_μ are all identical in this case we obtain from Eq. (33)

$$\Delta^{\alpha}_{\mu\nu} = -\frac{1}{4} \sum_{\sigma(\neq \mu,\nu)} S_{\mu\sigma} S_{\sigma\nu} \sum_{\lambda} Z_{\lambda} \left(-\gamma_{\sigma\lambda} + \frac{1}{2}\gamma_{\nu\lambda} + \frac{1}{2}\gamma_{\mu\lambda} \right). \tag{34}$$

Even if there is no obvious reason for neglecting this term completely, it can be shown that it is approximately compensated by a corresponding term of opposite sign arising from the two-electron matrix $\boldsymbol{G}$. This matrix may be split into a Coulomb and an exchange part:

$$^{\lambda}G_{\mu\nu} = {}^{\lambda}G^{\mathrm{c}}_{\mu\nu} + {}^{\lambda}G^{\mathrm{cx}}_{\mu\nu}. \tag{35}$$

Using Eq. (3) and keeping in mind that we are dealing with matrix elements in the Löwdin basis we obtain

$$\begin{aligned} {}^{\lambda}G^{\mathrm{c}}_{\mu\nu} &= \sum_{\lambda} \sum_{\sigma} P_{\lambda\sigma} (\chi_\mu \chi_\nu | \phi_\sigma \phi_\lambda), \\ {}^{\lambda}G^{\mathrm{cx}}_{\mu\nu} &= \sum_{\lambda} \sum_{\sigma} -\frac{1}{2} P_{\lambda\sigma} (\chi_\mu \phi_\lambda | \phi_\sigma \chi_\nu). \end{aligned} \tag{36}$$

Using the Mulliken approximation for the AO overlap densities occurring in the first of Eqs. (36) we can rewrite the Coulomb part as follows:

$$^{\lambda}G^{\mathrm{c}}_{\mu\nu} = \sum_{\lambda} N_{\lambda\lambda} (\chi_\mu \chi_\nu | \phi_\lambda \phi_\lambda), \tag{37}$$

where $N_{\lambda\lambda}$ represents the *gross* atomic population as introduced by Mulliken [44]:

$$N_{\lambda\lambda} = \sum_{\sigma} P_{\lambda\sigma} S_{\lambda\sigma}. \tag{38}$$

Expanding the Löwdin orbitals χ_μ, χ_ν in Eq. (37) in terms of AOs, using again the Mulliken approximation and including overlap terms up to second order we obtain in the same manner which led us to Eq. (21):

$$(\chi_\mu \chi_\nu | \phi_\lambda \phi_\lambda) \approx \gamma_{\mu\lambda} \delta_{\mu\nu} + \frac{1}{4} \sum_{\sigma(\neq \mu,\nu)} S_{\mu\sigma} S_{\sigma\nu} (-\gamma_{\sigma\lambda} + \tfrac{1}{2}\gamma_{\nu\lambda} + \tfrac{1}{2}\gamma_{\mu\lambda}). \tag{39}$$

Inserting Eq. (39) into Eq. (37) we obtain

$$^{\lambda}G^{\mathrm{c}}_{\mu\nu} = \delta_{\mu\nu} \sum_{\lambda} N_{\lambda\lambda} \gamma_{\mu\lambda} + \frac{1}{4} \sum_{\sigma(\neq \mu,\nu)} S_{\mu\sigma} S_{\sigma\nu} \sum_{\lambda} N_{\lambda\lambda} (-\gamma_{\sigma\lambda} + \tfrac{1}{2}\gamma_{\nu\lambda} + \tfrac{1}{2}\gamma_{\mu\lambda}). \tag{40}$$

Comparing Eqs. (34) and (40) we recognize that the second-order correction terms in these expressions cancel if $Z_\lambda = N_{\lambda\lambda}$, i.e., if the charge distribution is uniform as is the case in neutral alternant hydrocarbons [45]. Even if the charge distribution shows some inhomogenity the terms still compensate each other to a large extent.

We have just shown that the matrix Δ^{α} is completely negligible in neutral systems if no heteroatoms are involved and provides for correction terms of varying sign otherwise. The sums occurring in the matrix elements of Δ^{β}, on the other hand, consist of products of resonance and overlap integrals which are always negative because resonance and overlap integrals are of opposite sign. Hence, they provide for a cumulative effect. Since the matrix elements of Δ^{β} are all of the same sign their influence on the parameters can be clearly analyzed.

Neglecting Δ^{α} we obtain the following matrix elements in the Löwdin basis from Eqs. (27) and (28):

$$
\begin{aligned}
{}^{\lambda}h_{\mu\mu} &\approx \alpha_{\mu} - \sum_{\sigma(\neq\mu)} {}^{\mathrm{ZDO}}\beta_{\mu\sigma} S_{\sigma\mu}, \\
{}^{\lambda}h_{\mu\nu} &\approx {}^{\mathrm{ZDO}}\beta_{\mu\nu} - \frac{1}{2} \sum_{\sigma(\neq\mu,\nu)} ({}^{\mathrm{ZDO}}\beta_{\mu\sigma} S_{\sigma\nu} + S_{\mu\sigma}\, {}^{\mathrm{ZDO}}\beta_{\sigma\nu}) \quad (\mu \neq \nu).
\end{aligned} \tag{41}
$$

It is easily seen that all second-order correction terms add a positive contribution to the matrix elements, thus diminishing them in absolute magnitude. Addition of a positive contribution to all diagonal matrix elements leads to an up-shift of the MO energy levels. But we can go further in our analysis showing that the second-order correction term in the diagonal matrix elements compensates to some extent the neglect of penetration effects in ZDO methods. Neglecting penetration effects in the ZDO diagonal elements, the integrals $-(\sigma;\mu\mu)$ contained in the AO parameters α_{μ} (see Eq. (32)) have to be subtracted so that we obtain instead of the first of Eqs. (23):

$$
{}^{\mathrm{ZDO}}\alpha_{\mu} = \alpha_{\mu} + \sum_{\sigma(\neq\mu)} (\sigma;\mu\mu) \tag{42}
$$

Thus, the diagonal matrix elements of the ZDO method are slightly up-shifted in energy as compared to the corresponding AO parameters. Note that a similar up-shift has also been obtained for the diagonal matrix elements of the Löwdin basis represented by the second-order correction term in the first relation of Eqs. (41). Inserting Eq. (42) into the first relation of Eq. (41) gives

$$
{}^{\lambda}h_{\mu\mu} = {}^{\mathrm{ZDO}}\alpha_{\mu} - \sum_{\sigma(\neq\mu)} ((\sigma;\mu\mu) + {}^{\mathrm{ZDO}}\beta_{\mu\sigma} S_{\mu\sigma}). \tag{43}
$$

Assuming the resonance integral to be approximately proportional to the overlap integral we obtain

$$
{}^{\lambda}h_{\mu\mu} = {}^{\mathrm{ZDO}}\alpha_{\mu} - \sum_{\sigma(\neq\mu)} ((\sigma;\mu\mu) + k_{\mu\sigma} S_{\mu\sigma}^{2}). \tag{44}
$$

The proportionality factor $k_{\mu\sigma}$ has been defined to be negative. Setting the resonance integral proportional to the overlap integral is quite common in semiempirical MO methods and sufficient to support the plausibility arguments presented in this paper. However, it must be considered as a rather crude approximation [46].

The terms in brackets on the right-hand side of Eq. (44) are of opposite sign. If they compensate each other approximately the diagonal elements of the Löwdin basis are very close to the corresponding ZDO parameters thus justifying the neglect of penetration effects in the ZDO parametrization. It is quite obvious that both terms behave very similar as a function of the interatomic distance both decreasing rapidly with increasing distance between the atoms σ and μ. Numerical values for penetration integrals as a function of distance have been calculated by Parr and Crawford [47]. According to this work the decrease of the penetration integrals is much closer to that of S^2 than to that of S.

In the following it proves useful to distinguish between nearest and second-nearest-neighbor interactions. We introduce the following notation for nearest and second-nearest-neighbor resonance and overlap integrals:

$$\begin{aligned} S_{\mu,\mu+1} &\equiv S_1, \\ S_{\mu,\mu+2} &\equiv S_2, \\ {}^{\mathrm{ZDO}}\beta_{\mu,\mu+1} &\equiv \beta_1, \\ {}^{\mathrm{ZDO}}\beta_{\mu,\mu+2} &\equiv \beta_2. \end{aligned} \tag{45}$$

All quantities given in Eq. (45) are in principle a function of the carbon–carbon bond lengths. For the present order-of-magnitude considerations it is justified to disregard the details of this dependence setting all nearest-neighbor overlap integrals equal to S_1, etc. It is important to note that S_1, β_1 are one order of magnitude larger than S_2, β_2. In the following we take into account only second-order correction terms of the type $\beta_1 S_1$ neglecting all the other ones. Thus, we can rewrite the first of Eq. (41) as follows:

$$^{\lambda}h_{\mu\mu} = \alpha_\mu - n_\mu \beta_1 S_1. \tag{46}$$

n_μ represents the number of nearest-neighbor carbon atoms ranging from 1 to 3 in systems consisting of sp^2-hybridized carbons. Thus, the diagonal matrix elements of the core Hamiltonian in the Löwdin basis depend on the number of nearest-neighbor carbon atoms as has already been found by Fischer-Hjalmars [13]. This indicates the dependence of these matrix elements on the molecular environment and their nontransferability if second-order terms are included.

The second-order correction terms in Eq. (46) account approximately for the penetration integrals of carbon nearest neighbors. However, there might be also hydrogen nearest neighbors which provide for penetration integrals of roughly the same magnitude as those of carbon [13]. These are not compensated by second-order correction terms as in Eq. (44) where we included only carbon atoms. This argument clearly shows that second-order correction terms of the Löwdin basis cannot compensate the neglect of penetration integrals in ZDO parameters in a consistent way.

We discussed this point in some detail because in the very first version of CNDO denoted as CNDO/1 penetration effects were included [1b]. It turned out that the bond lengths calculated by this method were too small. Neglect of penetration effects in the next version CNDO/2 corrected this error [1c]. This gives empirical support to the hypothesis that the neglect of penetration integrals is consistent with the ZDO approximation. However, the analysis just given can in general not be extended to all-valence-electron methods because it rests on a power series expansion which is only possible for sufficiently small overlap integrals. We will come back to this point below.

Now let us discuss the influence of second-order correction terms on the off-diagonal elements. For topological reasons no terms of the type $\beta_1 S_1$ occur in the second-order correction terms for the off-diagonal matrix elements between nearest neighbors so that we obtain from the second relation of Eq. (41) and Eq. (45):

$$^{\lambda}h_{\mu,\mu+1} = \beta_1. \tag{47}$$

Thus, nearest-neighbor resonance integrals are correctly represented in the ZDO approximation and transferability is guaranteed even in second order. There is one notable exception, however. This is the cyclopropenyl ring consisting of an equilateral triangle of three carbons forming a conjugated π system. Obviously, there are only nearest-neighbor carbons in this triangular molecule so that all overlap and resonance integrals are equal to S_1 and β_1, respectively. We therefore obtain

$$ {}^{\lambda}h_{12} = {}^{\mathrm{ZDO}}\beta_{12} - \tfrac{1}{2}({}^{\mathrm{ZDO}}\beta_{13}S_{32} + S_{13}{}^{\mathrm{ZDO}}\beta_{32}) = \beta_1 - \beta_1 S_1. \tag{48} $$

Comparison with Eq. (47) shows that the resonance integral is reduced for a cyclopropenyl ring. This demonstrates the dependence of resonance integrals in the Löwdin basis on the environment so that a consistent parametrization is not possible. The particular case of the cyclopropenyl ring corresponds to the equilateral triangle of hydrogen atoms discussed by de Bruijn [14a] who also considered the case of four nearest-neighbor hydrogens, i.e., a tetrahedral arrangement with no central atom where the resonance integral is diminished even further than in the equilateral triangle. This led him to the more general conclusion that the ZDO approximation is bound to fail for small molecules with many nearest-neighbor pair interactions. De Bruijn pointed to the fact that MINDO/3 calculations underestimate the strain energy in small rings [2c].

Nevertheless, in general the second-order correction terms do not enter into nearest-neighbor resonance integrals of the π system in conjugated hydrocarbons which might be one of the reasons for the success of the PPP method. More troublesome is the case of second-nearest-neighbor resonance integrals. From the second relation of Eq. (41) and Eq. (45) we obtain

$$ {}^{\lambda}h_{\mu,\mu+2} = {}^{\mathrm{ZDO}}\beta_{\mu,\mu+2} - \tfrac{1}{2}({}^{\mathrm{ZDO}}\beta_{\mu,\mu+1}S_{\mu+1,\mu+2} + S_{\mu,\mu+1}{}^{\mathrm{ZDO}}\beta_{\mu+1,\mu+2}) = \beta_2 - \beta_1 S_1. \tag{49} $$

The second-nearest-neighbor resonance integral β_2 is quite small and of the same order of magnitude as the product $\beta_1 S_1$ so that the two terms in Eq. (49) compensate each other to a large extent making this matrix element negligibly small. De Bruijn commented somewhat ironically that this lends support to "π electron theoreticians who have maintained for nearly fifty years that β_{13} is negligible" [14a]. Note that our analysis is a generalization of the one of de Bruijn who discussed the special case of three centers with one s orbital on each center.

In the abundant literature on ZDO methods no attention has been paid to the systematic errors in the MO energy spectrum due to this approximation, at least as far as we know. This might be due to the fact that the MO energies of the frontier orbitals in the HOMO-LUMO region are reproduced reasonably well whereas the remaining part of the MO energy spectrum is often thought to be of minor chemical relevance. It is evident, however, that the MO energy spectrum should bear at least some resemblance to the photoelectron spectrum. The systematic errors in MO energies of ZDO approaches are mainly due to the difference between the core Hamiltonians ${}^{\lambda}\boldsymbol{h}$ and ${}^{\mathrm{ZDO}}\boldsymbol{h}$ caused by second- and higher-order overlap terms. In π electron methods, these errors might not lead to large shifts of MO energy levels provided we are concerned with smaller π networks. We will see in Sect. 3, however, that these shifts are by no means negligible for σ levels in all-valence-electron methods. Even in π systems, the magnitude of the MO energy shifts depends sensitively on the size of the π system. In extended π networks (for example graphite) with a broad MO energy spectrum the shifts of the innermost occupied and outermost virtual MOs are enhanced. We would like to illustrate our point by using ethylene as a simple example. Each of the two carbons contributes one p_π orbital. We thus obtain a bonding and an antibonding π MO with energies

$E = \alpha \pm {}^{\mathrm{ZDO}}\beta$ in a simple Hückel model [48], i.e., the MO energies are symmetrically split around α in the ZDO method. In a full-overlap basis, however, the MO energies are given by $E = (\alpha \pm \beta)/(1 \pm S)$. Thus, the splitting is asymmetric, the energetic up-shift of the antibonding MO with respect to α being more pronounced than the corresponding down-shift of the bonding MO [49]. This asymmetry in MO energy splittings plays an important role in qualitative MO theories [49]. It is a second-order effect in terms of overlap densities which is missing in the ZDO scheme.

To observe the general trends of the MO shifts we choose a π system involving only carbons using a simple Hückel model [48]. We assume again the resonance integrals to be proportional to the corresponding overlap integrals. Since no heteroatoms are involved the proportionality factor denoted as k is the same for all resonance integrals. We therefore obtain the following Hückel secular matrix:

$$ {}^{\mathrm{ZDO}}\boldsymbol{h} = \boldsymbol{\alpha} + {}^{\mathrm{ZDO}}\boldsymbol{\beta} = \alpha\mathbf{1} + k\boldsymbol{d}. \tag{50} $$

Thus, using $\boldsymbol{S} = \mathbf{1} + \boldsymbol{d}$ we obtain from Eq. (25)

$$ {}^{\lambda}\boldsymbol{h} = \alpha\mathbf{1} + k(\mathbf{1} + \boldsymbol{d})^{-1/2}\boldsymbol{d}(\mathbf{1} + \boldsymbol{d})^{-1/2} = \alpha\mathbf{1} + k(\mathbf{1} + \boldsymbol{d})^{-1}\boldsymbol{d}. \tag{51} $$

It is easily seen that both Hamiltonian matrices (50) and (51) commute with the overlap matrix $\boldsymbol{S} = \mathbf{1} + \boldsymbol{d}$ or $\boldsymbol{d}$ itself. It has been pointed out by Löwdin [8] that this simplifies the analysis considerably. Both the overlap matrix and the Hermitian matrices (50) and (51) are then diagonalized by the same unitary matrix $\boldsymbol{C}$. Introducing the diagonal matrix

$$ \boldsymbol{D} = \boldsymbol{C}^{+}\boldsymbol{d}\boldsymbol{C} \tag{52} $$

we obtain the following diagonal eigenvalue matrices from Eqs. (50) and (51):

$$ \begin{aligned} {}^{\mathrm{ZDO}}\boldsymbol{\varepsilon} &= \boldsymbol{C}^{+}\,{}^{\mathrm{ZDO}}\boldsymbol{h}\boldsymbol{C} = \alpha\mathbf{1} + k\boldsymbol{D}, \\ {}^{\lambda}\boldsymbol{\varepsilon} &= \boldsymbol{C}^{+}\,{}^{\lambda}\boldsymbol{h}\boldsymbol{C} = \alpha\mathbf{1} + k(\mathbf{1} + \boldsymbol{D})^{-1}\boldsymbol{D}. \end{aligned} \tag{53} $$

In Eq. (53) we have used the fact that the unitary matrix $\boldsymbol{C}$ not only diagonalizes $\boldsymbol{d}$ but also any function $f(\boldsymbol{d})$ resulting in a diagonal matrix $f(\boldsymbol{D})$. The eigenvalues in the ZDO and in the Löwdin basis can now be written as follows:

$$ \begin{aligned} {}^{\mathrm{ZDO}}\varepsilon_i &= \alpha + kD_i, \\ {}^{\lambda}\varepsilon_i &= \alpha + k\frac{D_i}{1 + D_i}. \end{aligned} \tag{54} $$

D_i are the eigenvalues of the matrix $\boldsymbol{d} = \boldsymbol{S} - \mathbf{1}$. Note that the eigenvalue spectrum (54) of ${}^{\mathrm{ZDO}}\boldsymbol{h}$ has the same structure as the eigenvalue spectrum $S_i = 1 + D_i$ of the overlap matrix $\boldsymbol{S}$ in this simple case. In π systems we have $|D_i| < 1$ which is a necessary condition for convergence of the power series expansions (10) and (20). The bonding and antibonding MOs correspond to positive and negative eigenvalues D_i, respectively, of the overlap matrix. From Eq. (54) we obtain

$$ {}^{\lambda}\varepsilon_i = {}^{\mathrm{ZDO}}\varepsilon_i - k\frac{D_i^2}{1 + D_i} \tag{55} $$

The constant k is negative because overlap and resonance integrals are always of opposite sign. Thus, there is an up-shift of all canonical MO energies in the Löwdin basis which is most pronounced for the most antibonding levels, i.e., those with D_i being large and negative. It is also relatively large for strongly bonding levels

(D_i large and positive) whereas the energy levels near the HOMO and LUMO (D_i small) are not much affected. It is now clear that the magnitude of the MO energy shifts depends on the breadth of the MO energy spectrum which is closely related to the spectrum of eigenvalues of the overlap matrix. Although the eigenvalues of ${}^{\lambda}\boldsymbol{h}$ and ${}^{\mathrm{ZDO}}\boldsymbol{h}$ are different their eigenvectors are the same being simply represented by the coefficient matrix $\boldsymbol{C}$. This would no longer be the case if heteroatoms were involved because then the overlap matrix does not commute with the Hamiltonian matrices. Note that the present analysis does not rely on a power series expansion.

Even if this simple analysis cannot be generalized we will see later that the shifts in the MO energy spectrum show the same trends in considerably more sophisticated all-valence-electron Hartree–Fock MO methods.

A Hartree–Fock π electron method based on explicit performance of the Löwdin transformation has been developed by Berthier *et al.* [7]. The two-electron integrals in this method are evaluated according to Eq. (18) in the Löwdin basis neglecting those containing overlap densities $\chi_\mu \chi_\nu$ $(\mu \neq \nu)$.

2.2 The ZDO approximation in all-valence-electron methods

In π electron methods the relationship between ZDO parameters of the one-electron Hamiltonian and the corresponding parameters in an AO basis was given by Eq. (23). This choice was based on a power series expansion of the inverse square root of the overlap matrix. Unfortunately, an expansion as given by Eq. (10) or Eq. (20) is in general not possible in all-valence-electron methods. It has been shown by Gray and Stone [16] that the matrix $\boldsymbol{d}$ has eigenvalues exceeding 1 for methane which cannot be considered as a particularly exotic molecule. In this case a power series expansion according to Eq. (10) or Eq. (20) does not converge so that one can no longer rely on arguments based on a truncated expansion.

If the possibility of a power series expansion of $\boldsymbol{S}^{-1/2}$ has to be discarded there is no obvious justification of the ZDO approximation and thus no obvious relationship between ZDO parameters and the corresponding parameters in an AO basis as given by Eq. (23). In a first approximation we nevertheless retain Eq. (23) which turns out to be a reasonable choice as we will see later. However, in contrast to π electron methods, Eq. (26) no longer holds, i.e., the one-electron Hamiltonian in a true Löwdin basis cannot even approximately be identified with the corresponding ZDO Hamiltonian in all-valence-electron methods.

Even if a rigorous justification of Eq. (23) might be difficult we will try to show that it is the most plausible choice. Let us assume that the electrostatic potential in a molecule is changed by exposing it to an electrostatic field corresponding to an electrostatic potential ΔV. The one-electron Hamiltonian $\hat{h}$ has then to be replaced by $\hat{h} + \Delta V$ leading to the following change of the one-electron Hamiltonian matrix elements in an AO basis:

$$\alpha'_\mu = \langle \phi_\mu | \hat{h} + \Delta V | \phi_\mu \rangle \approx \alpha_\mu + \Delta V_\mu,$$

$$\beta'_{\mu\nu} = \langle \phi_\mu | \hat{h} + \Delta V | \phi_\nu \rangle \approx \beta_{\mu\nu} + \Delta V_{\mu\nu} S_{\mu\nu}. \tag{56}$$

Here we have assumed that the electrostatic potential varies only slowly within the region where the density $\phi_\mu \phi_\nu$ is nonnegligible. ΔV_μ and $\Delta V_{\mu\nu}$ are, respectively, the values of the potential ΔV at the atom to which ϕ_μ belongs and in the overlap region between the orbitals ϕ_μ and ϕ_ν. In the Löwdin basis a similar equation is obtained:

$$
\begin{aligned}
{}^{\lambda}\alpha'_\mu &= \langle \chi_\mu | \hat{h} + \Delta V | \chi_\mu \rangle \approx {}^{\lambda}\alpha_\mu + \Delta V_\mu, \\
{}^{\lambda}\beta'_{\mu\nu} &= \langle \chi_\mu | \hat{h} + \Delta V | \chi_\nu \rangle \approx {}^{\lambda}\beta_{\mu\nu}.
\end{aligned}
\tag{57}
$$

Comparison of Eqs. (56) and (57) shows that the resonance integrals $\beta_{\mu\nu}$ are only in the orthogonal basis approximately invariant against a change of the electrostatic potential, not, however, in the AO basis. Consequently, the resonance integrals in an AO basis are not transferable from one molecule to another. E.g., if a hydrogen atom with core charge $+1$ is replaced by fluorine with core charge $+7$ (nuclear charge shielded by two inner shell electrons) with the rest of the molecule being unchanged the resulting change of the electrostatic potential will affect all resonance integrals in the molecule.

It is clear that the electrostatic potential does not enter into the parametrization of the resonance integrals ${}^{\mathrm{ZDO}}\beta_{\mu\nu}$ in any semiempirical MO method so that these integrals are invariant against a change of the electrostatic potential caused by a source exterior to the atoms on which the orbitals ϕ_μ and ϕ_ν are localized, e.g. replacement of a third atom by another one. Thus, the ZDO parameters ${}^{\mathrm{ZDO}}\alpha_\mu$ and ${}^{\mathrm{ZDO}}\beta_{\mu\nu}$ obey Eq. (57). If we are looking for a relationship to the corresponding parameters in an AO basis we have to take care that the latter transform according to Eq. (56). Now it is obvious that Eqs. (23) represent the most plausible choice with respect to this requirement. From Eqs. (23) and (57) we obtain

$$
\begin{aligned}
\alpha'_\mu &= {}^{\mathrm{ZDO}}\alpha'_\mu = {}^{\mathrm{ZDO}}\alpha_\mu + \Delta V_\mu = \alpha_\mu + \Delta V_\mu, \\
\beta'_{\mu\nu} &= {}^{\mathrm{ZDO}}\beta'_{\mu\nu} + \tfrac{1}{2}S_{\mu\nu}(\alpha'_\mu + \alpha'_\nu) = {}^{\mathrm{ZDO}}\beta_{\mu\nu} + \tfrac{1}{2}S_{\mu\nu}(\alpha_\mu + \Delta V_\mu + \alpha_\nu + \Delta V_\nu) \\
&= \beta_{\mu\nu} + \tfrac{1}{2}S_{\mu\nu}(\Delta V_\mu + \Delta V_\nu).
\end{aligned}
\tag{58}
$$

Provided that

$$
\Delta V_{\mu\nu} \approx \tfrac{1}{2}(\Delta V_\mu + \Delta V_\nu) \tag{59}
$$

we recognize that AO parameters obtained from Eq. (23) transform correctly according to Eq. (56). Since we assume the gradient of ΔV to be sufficiently small Eq. (59) will be fulfilled if the atoms on which the orbitals ϕ_μ and ϕ_ν are localized are not too distant from each other. For distant atoms, on the other hand, $S_{\mu\nu}$ will be negligible so that Eqs. (58) are equivalent to Eqs. (56), even in this case. To summarize, the second term on the right-hand side of the second of Eqs. (23) is necessary to insure the correct transformation properties with respect to changes of the electrostatic potential.

Again the question of penetration effects arises. The most common semiempirical methods [1–4] neglect penetration integrals although there has been an effort to include them in the CNDO and INDO method [50, 51]. As already mentioned, Pople [1c] found that neglect of penetration integrals led to improved bond lengths, at least in his original CNDO parametrization. Numerical calculations of Coffey [52] for C_2 seem to confirm this. He found that neglect of both penetration integrals and an additional pseudopotential accounting for the effects of core-valence orthogonality [53] leads to a surprising numerical agreement of CNDO core attraction integrals with the corresponding parameters in the Löwdin basis over the whole range of carbon–carbon distances. However, it is by no means evident how this analysis might be generalized to polyatomic molecules. We have shown in the previous section that neglect of penetration integrals might be justified for π electron methods because the Löwdin transformation provides for a second-order term in the diagonal elements which is opposite in sign to the penetration integral and shows a similar behavior as a function of the interatomic distance. If a power series expansion according to Eqs. (10) and (20) were possible this analysis could be extended to all-valence-electron methods. Unfortunately, this is not fulfilled. In any case, if penetration effects are neglected in ${}^{\mathrm{ZDO}}\alpha_\mu$ they should nevertheless be included in the AO basis, i.e., the first of Eqs. (23) should be replaced by Eq. (42). We will show that explicit transformation of matrix elements to the Löwdin basis leads on the average to an energetic up-shift of the diagonal elements of the core Hamiltonian ${}^{\lambda}\boldsymbol{h}$ as compared to the corresponding AO matrix elements thus giving at least the same trend as the neglect of penetration integrals in ZDO matrix elements (Eq. (42)). Since the ZDO matrix elements must be compared to the corresponding matrix elements in the true Löwdin basis the diagonal elements of the ZDO core Hamiltonian would be too negative in energy if we simply set them equal to the corresponding matrix elements in the AO basis according to the first of Eqs. (23). Consequently, the total electronic energy would also be too negative. Neglect of penetration integrals in ZDO matrix elements (see Eq. (42)) may partially correct this error although it remains unclear to what extent. To support this very crude argument, it remains to be shown that the Löwdin transformation increases the average of the diagonal matrix elements ${}^{\lambda}h_{\mu\mu}$. From Eqs. (24) and (25) we obtain

$$\operatorname{tr}{}^{\mathrm{ZDO}}\boldsymbol{h} = \operatorname{tr}\boldsymbol{\alpha},$$
$$\operatorname{tr}{}^{\lambda}\boldsymbol{h} = \operatorname{tr}\boldsymbol{\alpha} + \operatorname{tr}(\boldsymbol{S}^{-1/2}\,{}^{\mathrm{ZDO}}\boldsymbol{\beta}\boldsymbol{S}^{-1/2}). \tag{60}$$

In the second of Eqs. (60) we have used the fact that the trace of a matrix product is invariant under cyclic permutation of the factors. The reasonance integrals can again be assumed to be approximately proportional to the corresponding overlap integrals. The proportionality factor will of course depend on the atoms involved. To show the general trend it might be sufficient to replace the different proportionality constants by an average value so that we obtain in analogy to Eq. (50):

$${}^{\mathrm{ZDO}}\boldsymbol{\beta} = k\boldsymbol{d}. \tag{61}$$

Using Eq. (61) we obtain

$$\operatorname{tr}(\boldsymbol{S}^{-1/2}\,{}^{\mathrm{ZDO}}\boldsymbol{\beta}\boldsymbol{S}^{-1/2}) = k\operatorname{tr}(1+\boldsymbol{d})^{-1}\boldsymbol{d}. \tag{62}$$

The Hermitian matrix $\boldsymbol{d}$ is brought to diagonal form by the unitary transformation (52) which leaves the trace invariant so that we obtain

$$\operatorname{tr}(\boldsymbol{S}^{-1/2}\,{}^{\mathrm{ZDO}}\boldsymbol{\beta}\boldsymbol{S}^{-1/2}) = k\sum_i \frac{D_i}{1+D_i}. \tag{63}$$

Since $\operatorname{tr}\boldsymbol{d} = \operatorname{tr}\boldsymbol{D} = 0$ there must be positive and negative values D_i summing up to zero. We obtain

$$\frac{D_i}{1+D_i} \langle D_i \quad \text{if } D_i \rangle -1 \tag{64}$$

The case $D_i < -1$ has to be excluded because in that case the overlap matrix $\boldsymbol{S}$ no longer represents a positive-definite metric for the vector space spanned by the AOs. Note that the AOs are no longer linearily independent if there are eigenvalues $D_i = -1$ corresponding to zero eigenvalues of the overlap matrix $\boldsymbol{S}$ [54].

Since $\operatorname{tr} \boldsymbol{d} = \operatorname{tr} \boldsymbol{D} = 0$ and $k < 0$ it is easily seen from Eqs. (63) and (64) that

$$\operatorname{tr}(\boldsymbol{S}^{-1/2}\,{}^{\mathrm{ZDO}}\boldsymbol{\beta}\boldsymbol{S}^{-1/2}) > 0. \tag{65}$$

Thus, the Löwdin transformation can be expected to lead to an energetic up-shift of the diagonal elements of the core Hamiltonian, at least on the average. An analogous up-shift is obtained in the ZDO diagonal elements if penetration effects are neglected, i.e., if the first of Eqs. (23) is replaced by Eq. (42).

Now let us turn to the two-electron integrals. The transformation according to Eq. (16) still holds but the Mulliken approximation [24] can no longer be used because we now have several AOs on the same center. It has been shown by Ruttink [55] that invariance of multicenter integrals against rotation of the local coordinate axes or hybridization is only guaranteed if the Ruedenberg approximation [25] is used instead of the Mulliken approximation. In the Ruedenberg approximation diatomic overlap densities are replaced by monocenter terms as follows:

$$\phi^*_{\mu_A}\phi_{\nu_B} = \tfrac{1}{2}\left(\sum_{\kappa_A} S_{\kappa_A\nu_B}\phi^*_{\mu_A}\phi_{\kappa_A} + \sum_{\rho_B} S_{\mu_A\rho_B}\phi^*_{\rho_B}\phi_{\nu_B}\right). \tag{66}$$

The additional subindices A, B symbolize the atomic centers on which the corresponding orbitals are located. Please note that Eq. (66) is not a good approximation to the overlap densities themselves but should only be used when appearing in a Coulomb integral. In the original paper of Ruedenberg [25] it was shown that an orbital on one center can be expanded in a complete basis set on the neighboring center but in our case an interpretation in that sense is not possible because the basis sets on a distinct center are much too limited.

In the following we discuss the transformation of two-electron integrals from the AO to the Löwdin basis. In the AO basis only two-electron integrals retained in the NDDO method are needed explicitly, the remaining ones being calculated by the Ruedenberg approximation. It will be helpful to employ a matrix notation in the following. Thus, we introduce the charge density matrix

$$\boldsymbol{\Omega} = \boldsymbol{\phi}^+\boldsymbol{\phi}. \tag{67}$$

Here the AO basis vectors have been collected into the row matrix $\boldsymbol{\phi} = (\phi_1, \phi_2, \ldots, \phi_n)$. Using Eq. (67), Eq. (66) can be rewritten as follows:

$$\boldsymbol{\Omega} = \tfrac{1}{2}(\boldsymbol{\Omega}^0\boldsymbol{S} + \boldsymbol{S}\boldsymbol{\Omega}^0). \tag{68}$$

$\boldsymbol{\Omega}^0$ is a block diagonal matrix containing only charge densities localized on a distinct center, i.e., the mono-center terms in an NDDO approach:

$$\Omega^0_{\mu_A\nu_B} = \delta_{AB}\phi^*_{\mu_A}\phi_{\nu_B}. \tag{69}$$

In the following it will be useful to introduce a block notation for the matrices resulting from a division of all matrices $\boldsymbol{X}$ into submatrices $\boldsymbol{X}_{AB}$ of dimension $d_A \times d_B$ with d_A and d_B being the dimension of the AO basis sets on centers A and B, respectively. Thus, Eqs. (68) and (69) can be rewritten as follows:

$$\begin{aligned} \boldsymbol{\Omega}_{AB} &= \tfrac{1}{2}(\boldsymbol{\Omega}^0_{AA}\boldsymbol{S}_{AB} + \boldsymbol{S}_{AB}\boldsymbol{\Omega}^0_{BB}), \\ \boldsymbol{\Omega}^0_{AB} &= \delta_{AB}\boldsymbol{\Omega}^0_{AA}. \end{aligned} \tag{70}$$

Note that any submatrix $\boldsymbol{S}_{AA}$ on the block diagonal is a unit matrix of dimension d_A:

$$\boldsymbol{S}_{AA} = \mathbf{1}_A \tag{71}$$

Inserting Eq. (71) into the first of Eqs. (70) confirms that the block diagonal elements of $\boldsymbol{\Omega}$ and $\boldsymbol{\Omega}^0$ are identical:

$$\boldsymbol{\Omega}_{AA} = \boldsymbol{\Omega}^0_{AA}. \tag{72}$$

Using the Ruedenberg approximation (68) we obtain for the charge density in the Löwdin basis:

$${}^{\lambda}\boldsymbol{\Omega} = \boldsymbol{S}^{-1/2}\boldsymbol{\Omega}\boldsymbol{S}^{-1/2} = \tfrac{1}{2}(\boldsymbol{S}^{-1/2}\boldsymbol{\Omega}^0\boldsymbol{S}^{+1/2} + \boldsymbol{S}^{+1/2}\boldsymbol{\Omega}^0\boldsymbol{S}^{-1/2}) \tag{73}$$

or in block notation:

$${}^{\lambda}\boldsymbol{\Omega}_{AB} = \tfrac{1}{2}\sum_{C}(\boldsymbol{S}_{AC}^{-1/2}\boldsymbol{\Omega}^0_{CC}\boldsymbol{S}_{CB}^{+1/2} + \boldsymbol{S}_{AC}^{+1/2}\boldsymbol{\Omega}^0_{CC}\boldsymbol{S}_{CB}^{-1/2}). \tag{74}$$

Equation (74) indicates that e.g. the charge density ${}^{\lambda}\Omega_{\mu_A\mu_A} = |\chi_{\mu_A}|^2$ on atom A in the Löwdin basis involves contributions from AOs of all atoms in the molecule. Upon integration over the whole space we obtain from Eq. (74)

$$\int {}^{\lambda}\Omega_{\mu_A\mu_A}\,\mathrm{d}v = \int |\chi_{\mu_A}|^2\,\mathrm{d}v = \sum_{C} q^C_{\mu_A} = 1 \tag{75}$$

with

$$q^C_{\mu_A} = \sum_{\sigma_C} \boldsymbol{S}^{-1/2}_{\mu_A\sigma_C}\boldsymbol{S}^{+1/2}_{\mu_A\sigma_C}. \tag{76}$$

$q^C_{\mu_A}$ indicates the charge contribution from AOs on atom C to the charge of an electron in the Löwdin orbital χ_{μ_A}. From Eq. (75) one might suspect that the charge distribution $|\chi_{\mu_A}|^2$ is less well localized than the corresponding charge density $|\phi_{\mu_A}|^2$ in the AO basis because the former contains contributions from AOs of all atom centers. However, this is not the case. In fact, the Löwdin orbitals are even more localized than the corresponding AOs as has been discussed previously [13]. Thus, $q^A_{\mu_A} > 1$ in Eq. (75), whereas the remaining terms $q^C_{\mu_A}$ $(C \neq A)$ are negative. The fact that the Löwdin orthogonalization leads to a concentration of charge density on the atom centers is also indicated by an increase of the one-center two-electron integrals in the Löwdin basis as compared to the corresponding integrals in the AO basis.

The four-dimensional array of two-electron integrals can now be written by forming the tensor product of the charge density matrix $\boldsymbol{\Omega}$ with itself and subsequent integration:

$$(\boldsymbol{\Omega}|\boldsymbol{\Omega}) = \int \boldsymbol{\Omega}(1) \otimes \boldsymbol{\Omega}(2)\frac{e^2}{r_{12}}\,\mathrm{d}v_1\,\mathrm{d}v_2. \tag{77}$$

For the two-electron integrals in the Löwdin basis we obtain using Eq. (74):

$$\begin{aligned}({}^{\lambda}\boldsymbol{\Omega}_{AB}|{}^{\lambda}\boldsymbol{\Omega}_{EF}) = \frac{1}{4}\sum_{C}\sum_{D}&(\boldsymbol{S}_{AC}^{-1/2}\boldsymbol{S}_{CB}^{+1/2} + \boldsymbol{S}_{AC}^{+1/2}\boldsymbol{S}_{CB}^{-1/2})(\boldsymbol{\Omega}^0_{CC}|\boldsymbol{\Omega}^0_{DD})\\ &\times(\boldsymbol{S}_{ED}^{-1/2}\boldsymbol{S}_{DF}^{+1/2} + \boldsymbol{S}_{ED}^{+1/2}\boldsymbol{S}_{DF}^{-1/2}).\end{aligned} \tag{78}$$

Considering a distinct integral from the four-dimensional array given by Eq. (78) we obtain the following expression:

$$(\chi_{\mu_A}\chi_{\nu_B}|\chi_{\sigma_E}\chi_{\lambda_F}) = \frac{1}{4}\sum_{C}\sum_{\mu_C}\sum_{\nu_C}\sum_{D}\sum_{\sigma_D}\sum_{\lambda_D}(S^{-1/2}_{\mu_A\mu_C}S^{+1/2}_{\nu_C\nu_B} + S^{+1/2}_{\mu_A\mu_C}S^{-1/2}_{\nu_C\nu_B})$$
$$\times(\phi_{\mu_C}\phi_{\nu_C}|\phi_{\sigma_D}\phi_{\lambda_D})(S^{-1/2}_{\sigma_E\sigma_D}S^{+1/2}_{\lambda_D\lambda_F} + S^{+1/2}_{\sigma_E\sigma_D}S^{-1/2}_{\lambda_D\lambda_F}). \tag{79}$$

Applying the NDDO approximation in the Löwdin basis we neglect diatomic differential overlap terms:

$$({}^{\lambda}\boldsymbol{\Omega}_{AB}|{}^{\lambda}\boldsymbol{\Omega}_{EF})_{\mathrm{NDDO}} = \delta_{AB}\delta_{EF}({}^{\lambda}\boldsymbol{\Omega}_{AA}|{}^{\lambda}\boldsymbol{\Omega}_{EE}). \tag{80}$$

The reliability of NDDO calculations rests on the validity of the approximation (80). The two-electron matrix ${}^{\lambda}\boldsymbol{G}$ in the Löwdin basis is represented by an expression analogous to Eq. (3) with the AOs ϕ_μ replaced by Löwdin orbitals χ_μ and with the bond order matrix $\boldsymbol{P}$ replaced by

$${}^{\lambda}\boldsymbol{P} = \boldsymbol{S}^{1/2}\boldsymbol{P}\boldsymbol{S}^{1/2}. \tag{81}$$

Using the NDDO approximation (80) and splitting the two-electron matrix into a Coulomb and an exchange part in analogy to Eq. (36), we obtain

$${}^{\lambda}G^{\mathrm{c}}_{\mu_A\nu_B} = \delta_{AB}\sum_{C}\sum_{\sigma_C}\sum_{\lambda_C}{}^{\lambda}\boldsymbol{P}_{\lambda_C\sigma_C}(\chi_{\mu_A}\chi_{\nu_B}|\chi_{\sigma_C}\chi_{\lambda_C}),$$
$${}^{\lambda}G^{\mathrm{cx}}_{\mu_A\nu_B} = -\frac{1}{2}\sum_{\sigma_B}\sum_{\lambda_A}{}^{\lambda}\boldsymbol{P}_{\lambda_A\sigma_B}(\chi_{\mu_A}\chi_{\lambda_A}|\chi_{\sigma_B}\chi_{\nu_B}). \tag{82}$$

Note that the two-electron integrals in Eq. (82) have been obtained by explicitly performing the Löwdin transformation (Eq. (79)) thus being adapted to the molecular environment.

If it were possible, a power series expansion of the matrices $\boldsymbol{S}^{-1/2}$ and $\boldsymbol{S}^{+1/2}$ would again show us the justification of Eq. (80) up to first order in complete analogy to the reasoning given in the previous section for π electron methods. An attempt to justify the NDDO approximation without reference to a power series expansion has been made by Roby [18]. It is based on the assumption that the basis sets on the distinct atom centers are sufficiently large so that the Ruedenberg approximation (Eq. (66) or (68)) can be considered as a good approximation to the charge densities themselves instead of just a method for approximating two-electron integrals containing diatomic overlap densities. This leads to the commutation relation $[\boldsymbol{\Omega}^0, \boldsymbol{S}] = 0$ which is crucial for Roby's reasoning [18]. It is easily seen that this relation does not hold for small AO basis sets including only valence orbitals. If we consider, e.g., two p_π orbitals denoted as π_A and π_B on neighboring centers A and B the commutation relation $[\boldsymbol{\Omega}^0, \boldsymbol{S}] = 0$ would give $|\pi_A|^2 S = |\pi_B|^2 S$ with S being the overlap integral between the orbitals π_A and π_B. Thus, a two-electron integral $(\pi_A\pi_B|\pi_A\pi_A)$ could be approximated by either $S(\pi_A\pi_A|\pi_A\pi_A)$ or $S(\pi_B\pi_B|\pi_A\pi_A)$ implying $(\pi_A\pi_A|\pi_A\pi_A) = (\pi_B\pi_B|\pi_A\pi_A)$ which is clearly a very poor approximation. The critical reexamination of Roby's arguments by King et al. [19] is also based on the assumption of complete basis sets on the atom centers which leads to infinite degeneracies of the eigenvalues of the overlap matrix not considered by Roby [18] and invalidating some of his conclusions. Again we would like to stress the limitation of basis sets in practical calculations preventing the occurrence of such degeneracies except those imposed by the symmetry of a molecule.

The mono-center charge distributions appearing in $\boldsymbol{\Omega}^0$ may be expanded in spherical harmonics around the respective centers [56] giving the corresponding multipole moments. Distinguishing between the monopole term $\boldsymbol{\Omega}^{00}$ and the higher multipole moments summarized under the symbol $\boldsymbol{\Omega}^{01}$ we obtain:

$$\boldsymbol{\Omega}^0_{CC} = \boldsymbol{\Omega}^{00}_{CC} + \boldsymbol{\Omega}^{01}_{CC}. \tag{83}$$

The isotropic monopole contribution has a particularly simple form:

$$\boldsymbol{\Omega}^{00}_{CC} = \rho^0_C \mathbf{1}_C. \tag{84}$$

ρ^0_C is an AO charge density with spherical symmetry around center C. Note that the two-electron integrals retained in the CNDO method are just those arising from the monopole term. Thus, even charge densities involving AOs with orbital quantum numbers $l > 0$ which do not have spherical symmetry are replaced by ρ^0_C in the CNDO approach. In the original CNDO and INDO versions [1] the charge density of a valence s orbital was taken for ρ^0_C but frequently it is not necessary to specify these charge densities because the two-electron integrals in which they appear are parametrized by using either the Dewar–Sabelli–Ohno–Klopman relation [57] or the Mataga–Nishimoto approximation [58]. It should also be noted that the Ruedenberg approximation (68) reduces to the Mulliken approximation if only the monopole terms are taken into account. Neglecting the contributions from higher multipoles we obtain from Eqs. (78) and (84):

$$({}^{\lambda}\boldsymbol{\Omega}_{AB}|{}^{\lambda}\boldsymbol{\Omega}_{EF}) = \frac{1}{4}\sum_C\sum_D (\boldsymbol{S}_{AC}^{-1/2}\boldsymbol{S}_{CB}^{+1/2} + \boldsymbol{S}_{AC}^{+1/2}\boldsymbol{S}_{CB}^{-1/2})\gamma_{CD}(\boldsymbol{S}_{ED}^{-1/2}\boldsymbol{S}_{DF}^{+1/2} + \boldsymbol{S}_{ED}^{+1/2}\boldsymbol{S}_{DF}^{-1/2}) \tag{85}$$

with γ_{CD} being the two-electron integrals of the CNDO method:

$$\gamma_{CD} = (\rho^0_C|\rho^0_D). \tag{86}$$

Since the monopole–monopole interactions in Eq. (85) are long-range interactions they are all quite large and we may replace the different Coulomb integrals γ_{CD} by their average value. The integrals (85) then vanish for $A \neq B$ or $E \neq F$ because

$$\sum_C \boldsymbol{S}_{AC}^{-1/2}\boldsymbol{S}_{CB}^{+1/2} = \mathbf{1}_A\delta_{AB}. \tag{87}$$

Even if this is a very crude approximation the different terms in the sum (85) are likely to average out to some extent for $A \neq B$, $E \neq F$, thus providing some justification for the neglect of diatomic overlap in the Coulomb integrals of the Löwdin basis according to Eq. (80). However, applying the NDDO scheme (Eq. (80)) one might well neglect contributions which could be of the same order of magnitude as many of those retained, especially those arising from higher multipole moments which are essential in distinguishing the NDDO from the CNDO method.

Note that there is no justification for neglecting diatomic differential overlap in the AO basis, especially in all-valence-electron methods where the overlap integrals can get quite large. This becomes evident if we write the two-electron integrals in the AO basis in block form using Eq. (70):

$$(\boldsymbol{\Omega}_{AB}|\boldsymbol{\Omega}_{EF}) = \tfrac{1}{4}\boldsymbol{S}_{AB}\boldsymbol{S}_{EF}((\boldsymbol{\Omega}^0_{AA}|\boldsymbol{\Omega}^0_{EE}) + (\boldsymbol{\Omega}^0_{AA}|\boldsymbol{\Omega}^0_{FF}) + (\boldsymbol{\Omega}^0_{BB}|\boldsymbol{\Omega}^0_{EE}) + (\boldsymbol{\Omega}^0_{BB}|\boldsymbol{\Omega}^0_{FF})) \tag{88}$$

It has been shown by Ruttink [55] that the charge density matrix (68) transforms correctly under a local transformation of orbitals on the same center (hybridization or rotation of local coordinate axes), i.e., if the transformation matrix has the same diagonal block structure as $\boldsymbol{\Omega}^0$ itself. It may be shown in an analogous manner that the charge density matrix ${}^\lambda\boldsymbol{\Omega}$ in the Löwdin basis as represented by Eq. (73) also transforms correctly under such a transformation. Thus, no invariance problems of the integrals with respect to local transformations arise in an NDDO approach. However, some care is necessary in CNDO or INDO methods. If we apply the CNDO approach in the AO basis, i.e., retain only the monopole contribution, the charge density matrix $\boldsymbol{\Omega}^0_{CC}$ is diagonal (Eq. (84)). However, this does not imply that the charge density matrix ${}^\lambda\boldsymbol{\Omega}_{CC}$ in the Löwdin basis is also diagonal. It can be easily seen from Eq. (74) that this is not the case. It does not help to simply neglect the off-diagonal terms in ${}^\lambda\boldsymbol{\Omega}_{CC}$ because this would violate the invariance requirements with respect to rotation of local coordinate axes or hybridization. In order to apply the CNDO scheme to the integrals in the Löwdin basis an averaging procedure is necessary:

$$ {}^\lambda\bar{\boldsymbol{\Omega}}_{CC} = \omega_C \mathbf{1}_C \tag{89} $$

with

$$ \omega_C = \frac{1}{d_C} \sum_{\mu_C} {}^\lambda\Omega_{\mu_C\mu_C}. \tag{90} $$

Remember that d_C is the dimension of the AO basis set on center C. If we now apply a local unitary transformation

$$ \begin{aligned} \phi'_C &= \phi_C U_C \\ \chi'_C &= \chi_C U_C \end{aligned} \tag{91} $$

to the orbitals on a center C the trace of the local charge density matrix contained in Eq. (90) remains invariant so that the correct transformation properties are now insured. Remember that such a unitary transformation operates on both the Löwdin and the AO basis in the same way [8]. Thus, the two-electron integrals in a CNDO approach are calculated as follows:

$$ (\omega_A | \omega_B) = \frac{1}{d_A d_B} \sum_{\mu_A} \sum_{\nu_B} ({}^\lambda\Omega_{\mu_A\mu_A} | {}^\lambda\Omega_{\nu_B\nu_B}) \tag{92} $$

In the INDO scheme such an averaging is only applied to two-center integrals ($A \neq B$) whereas all one-center integrals are retained. Nevertheless, a complication arises. In an AO basis consisting of s and p orbitals only Coulomb integrals $(\phi_i\phi_i|\phi_j\phi_j)$ and exchange integrals $(\phi_i\phi_j|\phi_j\phi_i)$ need to be considered. All other one-center integrals vanish due to the spherical symmetry of an atom. This is no longer the case in a Löwdin basis where all one-center integrals are nonvanishing and need to be taken into account if the invariance requirements are to be met. If d orbitals are included there are quite a few one-center integrals which vanish for symmetry reasons in an AO basis but not in the Löwdin basis. This indicates again the inconsistency of ZDO methods pretending to operate in a Löwdin basis but determining the parameters as if an AO basis were used. Using Eqs. (78) and (80) the two-electron integrals are calculated in the Löwdin basis rather than in the AO basis but the simplicity of the NDDO approach is retained due to Eq. (80).

If one wants to avoid the disadvantage of neglecting two-electron integrals there is an alternative. One could calculate the Fock matrix elements in the AO basis according to Eqs. (2) and (3) using the Ruedenberg approximation for those two-electron integrals containing diatomic differential overlap. Thus, only the NDDO integrals are explicitly needed. Such a procedure dispenses with the need to store the complete four-dimensional array of two-electron integrals as in ab initio methods. However, there is a price to pay for this saving of computer memory apart from possible inaccuracies of the Ruedenberg approximation. The evaluation of the Fock matrix elements which has to be repeated in each iteration step is then considerably more time consuming than in a method based on the storage of the complete set of two-electron integrals. Let us rewrite the two-electron part of the Fock matrix elements (3) as follows:

$$G_{\mu_A \nu_B} = \sum_C \sum_D \sum_{\sigma_C} \sum_{\lambda_D} P_{\lambda_D \sigma_C} \left((\phi_{\mu_A} \phi_{\nu_B} | \phi_{\sigma_C} \phi_{\lambda_D}) - \tfrac{1}{2} (\phi_{\mu_A} \phi_{\lambda_D} | \phi_{\sigma_C} \phi_{\nu_B}) \right). \tag{93}$$

Splitting the two-electron matrix $\boldsymbol{G}$ into a Coulomb and an exchange part in analogy to Eq. (36) and inserting the Ruedenberg approximation in Eq. (93) we obtain

$$\begin{aligned} G^{\mathrm{c}}_{\mu_A \nu_B} = {} & \frac{1}{2} \sum_C \sum_D \sum_{\sigma_C} \sum_{\lambda_D} P_{\lambda_D \sigma_C} \sum_{\sigma'_C} S_{\sigma'_C \lambda_D} \Bigg(\sum_{\mu'_A} S_{\mu'_A \nu_B} (\phi_{\mu_A} \phi_{\mu'_A} | \phi_{\sigma_C} \phi_{\sigma'_C}) \\ & + \sum_{\nu'_B} S_{\mu_A \nu'_B} (\phi_{\nu'_B} \phi_{\nu_B} | \phi_{\sigma_C} \phi_{\sigma'_C}) \Bigg) \\ G^{\mathrm{ex}}_{\mu_A \nu_B} = {} & -\frac{1}{8} \sum_C \sum_D \sum_{\sigma_C} \sum_{\lambda_D} P_{\lambda_D \sigma_C} \Bigg(\sum_{\lambda'_D} \sum_{\sigma'_C} S_{\mu_A \lambda'_D} S_{\sigma'_C \nu_B} (\phi_{\lambda'_D} \phi_{\lambda_D} | \phi_{\sigma_C} \phi_{\sigma'_C}) \\ & + \sum_{\lambda'_D} \sum_{\nu'_B} S_{\mu_A \lambda'_D} S_{\sigma_C \nu'_B} (\phi_{\lambda'_D} \phi_{\lambda_D} | \phi_{\nu'_B} \phi_{\nu_B}) \\ & + \sum_{\mu'_A} \sum_{\sigma'_C} S_{\mu'_A \lambda_D} S_{\sigma'_C \nu_B} (\phi_{\mu_A} \phi_{\mu'_A} | \phi_{\sigma_C} \phi_{\sigma'_C}) \\ & + \sum_{\mu'_A} \sum_{\nu'_B} S_{\mu'_A \lambda_D} S_{\sigma_C \nu'_B} (\phi_{\mu_A} \phi_{\mu'_A} | \phi_{\nu'_B} \phi_{\nu_B}) \Bigg). \end{aligned} \tag{94}$$

It is easily seen that the Coulomb part may be further simplified. We obtain

$$G^{\mathrm{c}}_{\mu_A \nu_B} = \frac{1}{2} \sum_C \sum_{\sigma_C} \sum_{\sigma'_C} N_{\sigma_C \sigma'_C} \left(\sum_{\mu'_A} S_{\mu'_A \nu_B} (\phi_{\mu_A} \phi_{\mu'_A} | \phi_{\sigma_C} \phi_{\sigma'_C}) + \sum_{\nu'_B} S_{\mu_A \nu'_B} (\phi_{\nu'_B} \phi_{\nu_B} | \phi_{\sigma_C} \phi_{\sigma'_C}) \right). \tag{95}$$

Here we have introduced the bond order matrix as defined by Chirgwin and Coulson [59]:

$$\boldsymbol{N} = \tfrac{1}{2} (\boldsymbol{PS} + \boldsymbol{SP}). \tag{96}$$

Note that the diagonal elements of the matrix (96) represent the gross populations defined by Mulliken [44]. It can be seen from Eq. (81) that this matrix is related to the bond order matrix in the Löwdin basis as follows:

$$\boldsymbol{N} = \tfrac{1}{2} (\boldsymbol{S}^{-1/2}\, {}^{\lambda}\boldsymbol{P} \boldsymbol{S}^{+1/2} + \boldsymbol{S}^{+1/2}\, {}^{\lambda}\boldsymbol{P} \boldsymbol{S}^{-1/2}). \tag{97}$$

It is obvious that Eq. (94) takes into account the complete set of two-electron integrals although only the NDDO integrals appear explicitly. Since no integrals are neglected the only approximation involved being the Ruedenberg approximation, this procedure is more accurate than the NDDO approach based on Eqs. (78)

and (80) after transformation of the two-electron integrals to the Löwdin basis. However, it is less economic due to the extensive sums in Eq. (94). The Coulomb part of the two-electron matrix can be simplified according to Eq. (95) so that these matrix elements can be calculated rather efficiently but the exchange part remains complicated involving a double sum over the atomic centers.

Equation (94) simplifies considerably if we neglect the higher multipole moments of the charge distributions thus retaining only the two-electron integrals of the CNDO method. The Ruedenberg approximation then reduces to the Mulliken approximation and Eq. (94) is replaced as follows:

$$G^{c}_{\mu_A\nu_B} = \frac{1}{2}\sum_{C}\sum_{D}\sum_{\sigma_C}\sum_{\lambda_D} P_{\lambda_D\sigma_C} S_{\sigma_C\lambda_D} S_{\mu_A\nu_B}(\gamma_{AC} + \gamma_{BC}) = \frac{1}{2}\sum_{\mathrm{C}}\sum_{\sigma_C} N_{\sigma_C\sigma_C} S_{\mu_A\nu_B}(\gamma_{AC} + \gamma_{BC}),$$

$$G^{\mathrm{ex}}_{\mu_A\nu_B} = -\frac{1}{8}\sum_{C}\sum_{D}\sum_{\sigma_C}\sum_{\lambda_D} P_{\lambda_D\sigma_C} S_{\mu_A\lambda_D} S_{\sigma_C\nu_B}(\gamma_{DC} + \gamma_{AB} + \gamma_{AC} + \gamma_{DB}). \tag{98}$$

This is the procedure suggested by Yonezawa et al. [6].

Let us briefly summarize how to proceed from a given ZDO method to an improved method based on explicit performance of the Löwdin transformation. The matrix elements of the core Hamiltonian in an AO basis can be obtained according to Eq. (23) from the ZDO matrix elements except that penetration integrals usually neglected in ZDO methods should be added to the diagonal matrix elements. Concerning the two-electron matrix $\boldsymbol{G}$ we have two possibilities. One could transform the complete four-dimensional array of two-electron integrals to the Löwdin basis using the Ruedenberg approximation for integrals containing diatomic overlap densities in the AO basis (Eq. (78)) and apply the NDDO approximation to the *transformed* integrals in the Löwdin basis (Eq. (80)). Then the two-electron matrix ${}^{\lambda}\boldsymbol{G}$ is calculated (Eq. (82)) and added to the transformed core Hamiltonian matrix ${}^{\lambda}\boldsymbol{h}$. Once the two-electron integrals in the Löwdin basis have been calculated this procedure is not more time-consuming than the usual NDDO method based on the ZDO approximation. A second possibility is to calculate the two-electron matrix $\boldsymbol{G}$ in the AO basis according to Eqs. (94) and (95) using again the Ruedenberg approximation, adding it to the core Hamiltonian matrix $\boldsymbol{h}$ and transforming the complete Fock matrix $\boldsymbol{F}$ to the Löwdin basis. This second approach is more accurate but also more time-consuming.

3 Numerical results

In the following numerical results obtained by an improved CNDO method are presented. In the previous section we referred in general to the NDDO approximation but the simplifications leading to CNDO or INDO approaches are straightforward. Our emphasis is on shifts of the canonical MO energies in the improved method. To obtain the general trends it is sufficient if we restrict ourselves to the simple CNDO method using the ZDO parametrization of Ref. 51. Let us summarize the basic steps. First we calculate the matrix elements of the core Hamiltonian in the AO basis according to Eq. (23):

$$h_{\mu\mu} = {}^{\mathrm{ZDO}}h_{\mu\mu},$$

$$h_{\mu\nu} = {}^{\mathrm{ZDO}}h_{\mu\nu} + \tfrac{1}{2}S_{\mu\nu}(h_{\mu\mu} + h_{\nu\nu}) \quad (\mu \neq \nu).$$

Now we may proceed in two different ways as described in the previous section. We denote the alternatives as method A and B in the following. In method A the core Hamiltonian matrix is immediately subjected to the Löwdin transformation:

$$^{\lambda}\boldsymbol{h} = \boldsymbol{S}^{-1/2}\boldsymbol{h}\boldsymbol{S}^{-1/2}.$$

Next, we transform the two-electron integrals to the Löwdin basis according to Eq. (79). Adopting the simplifications of the CNDO method, we obtain

$$(\chi_{\mu_A}\chi_{\mu_A}|\chi_{\nu_B}\chi_{\nu_B}) = \sum_{C}\sum_{\sigma_C}\sum_{D}\sum_{\lambda_D} S^{-1/2}_{\mu_A\sigma_C} S^{+1/2}_{\mu_A\sigma_C} (\phi_{\sigma_C}\phi_{\sigma_C}|\phi_{\lambda_D}\phi_{\lambda_D}) S^{-1/2}_{\nu_B\lambda_D} S^{+1/2}_{\nu_B\lambda_D}.$$

Note that we only require invariance of the two-electron integrals against rotation of the local coordinate axes, not, however, against hybridization. Thus, the two-electron integrals may still depend on the quantum number l of the angular momentum [50]. To fulfill the same invariance criterion in the Löwdin basis, an averaging procedure has to be employed (see Eq. (92)). If we do not require invariance against hybridization it is not necessary to average over the whole basis set of an atom but only over AOs with the same angular quantum number l. Denoting the AOs on centers A and B by their angular quantum numbers l_A and l_B and additional indices m_A and m_B distinguishing AOs with the same angular quantum number l, Eq. (92) is replaced as follows:

$$^{\lambda}\gamma_{l_A l_B} = \frac{1}{(2l_A + 1)(2l_B + 1)} \sum_{m_A}\sum_{m_B} (\chi^{m_A}_{l_A}\chi^{m_A}_{l_A}|\chi^{m_B}_{l_B}\chi^{m_B}_{l_B}).$$

Now the elements of the two-electron matrix are obtained as in the usual CNDO procedure:

$$^{\lambda}G^{\mathrm{c}}_{\mu\nu} = \delta_{\mu\nu}\sum_{\sigma} {}^{\lambda}P_{\sigma\sigma}\,{}^{\lambda}\gamma_{\mu\sigma},$$

$$^{\lambda}G^{\mathrm{ex}}_{\mu\nu} = -\tfrac{1}{2}\,{}^{\lambda}P_{\mu\nu}\,{}^{\lambda}\gamma_{\mu\nu}.$$

The Fock matrix $^{\lambda}\boldsymbol{F} = {}^{\lambda}\boldsymbol{h} + {}^{\lambda}\boldsymbol{G}$ may now be diagonalized by the well-known iteration procedure.

In method B which corresponds to the approach suggested by Yonezawa et al. [6] the two-electron matrix $\boldsymbol{G}$ is calculated in the AO basis using the Mulliken approximation [24] for replacement of diatomic overlap densities in the two-electron integrals. If we require again only invariance against rotation of local coordinate axes Eq. (98) is replaced as follows:

$$G^{\mathrm{c}}_{\mu\nu} = \frac{1}{2} S_{\mu\nu} \sum_{\sigma}\sum_{\lambda} P_{\lambda\sigma} S_{\sigma\lambda}(\gamma_{\mu\sigma} + \gamma_{\nu\sigma}) = \frac{1}{2} S_{\mu\nu} \sum_{\sigma} N_{\sigma\sigma}(\gamma_{\mu\sigma} + \gamma_{\nu\sigma}),$$

$$G^{\mathrm{ex}}_{\mu\nu} = -\frac{1}{8}\sum_{\sigma}\sum_{\lambda} P_{\lambda\sigma} S_{\mu\lambda} S_{\sigma\nu}(\gamma_{\lambda\sigma} + \gamma_{\lambda\nu} + \gamma_{\mu\nu} + \gamma_{\mu\sigma}).$$

Now the matrix $\boldsymbol{F} = \boldsymbol{h} + \boldsymbol{G}$ is formed and subjected to the Löwdin transformation:

$$^{\lambda}\boldsymbol{F} = \boldsymbol{S}^{-1/2}\boldsymbol{F}\boldsymbol{S}^{-1/2}.$$

The eigenvalue problem is again solved iteratively.

Let us compare the MO energies obtained by the CNDO realization of Ref. 51 with those obtained by the improved methods A and B for some simple hydrocarbons. The examples considered are methane (CH_4), acetylene (C_2H_2), ethylene (C_2H_4) and ethane (C_2H_6) in staggered conformation. We have chosen experimental bond lengths which are $l_{\text{C-H}} = 1.094$ Å for CH_4, $l_{\text{C-C}} = 1.205$ Å, $l_{\text{C-H}} = 1.059$ Å for C_2H_2, $l_{\text{C-C}} = 1.339$ Å, $l_{\text{C-H}} = 1.086$ Å for C_2H_4 and $l_{\text{C-C}} = 1.536$ Å, $l_{\text{C-H}} = 1.091$ Å for C_2H_6. In addition, we performed minimal basis set ab initio calculations (STO-3G basis) [60] for these molecules using the same geometry data. Since the parametrization of Ref. 51 is designed to match the results of ab initio calculations a comparison is legitimate. For the simple molecules studied ab initio calculations with much better basis sets would not pose any difficulties. But as emphasized above it is the aim of the present work to analyze general trends in the modification of canonical MO energies when avoiding the ZDO approximation in model Hamiltonians. And for this general purpose the minimal basis set results are a sufficient reference. The numerical results for the canonical MO energies are given in Tables 1–4. The energies of the occupied MOs are also shown in Fig. 1. In the case of the ab initio results we give only the energy levels of the valence electrons. Comparing CNDO and STO-3G results it is easily seen that the general trends are the same for all of these molecules. The innermost MOs are always found at too low energies in the CNDO method. The energy levels of the HOMO and MOs just below are in general quite reasonable, whereas the virtual MOs of CNDO are much too low in energy. It is immediately seen that these systematic errors of CNDO energy levels in the inner valence region are corrected by applying the improved methods *A* and *B*. The shifts of the HOMO and the MOs just below the HOMO are relatively weak even if the energetic sequence of MOs with different symmetry is not always maintained. The energetic up-shift of the most low-lying MO is more pronounced, whereas all virtual MOs

Table 1. Canonical MO energies of CH_4 obtained by different methods described in the text. All energies are given in eV. The virtual levels are marked by an asterisk

	CNDO	*A*	*B*	STO-3G
a_1^*	5.75	49.48	46.67	20.26
t_2^*	6.26	22.04	21.44	19.30
t_2	−14.83	−13.99	−12.90	−14.05
a_1	−29.64	−22.03	−20.98	−24.66

Table 2. Canonical MO energies of C_2H_2 obtained by different methods described in the text. All energies are given in eV. The virtual levels are marked by an asterisk

	CNDO	*A*	*B*	STO-3G
σ_u^{-*}	9.89	220.62	208.36	39.99
σ_g^{+*}	5.17	36.05	35.16	20.00
σ_u^{-*}	3.11	23.73	24.76	15.13
π_g^*	2.24	4.20	4.39	10.73
π_u	−11.47	−10.22	−10.57	−9.47
σ_g^+	−15.75	−15.08	−13.89	−16.57
σ_u^-	−21.17	−20.08	−16.84	−19.28
σ_g^+	−28.30	−23.83	−21.86	−25.92

Table 3. Canonical MO energies of C_2H_4 obtained by different methods described in the text. All energies are given in eV. The virtual levels are marked by an asterisk

	CNDO	*A*	*B*	STO-3G
b_{3u}^*	9.12	96.70	90.22	26.53
b_{1g}^*	5.98	37.85	35.89	25.78
b_{3u}^*	4.07	29.43	29.08	18.74
a_g^*	5.25	33.02	31.62	18.35
b_{2u}^*	6.68	21.30	21.71	17.45
b_{2g}^*	1.07	2.45	2.20	8.66
b_{1u}	−10.52	−9.32	−9.89	−8.78
b_{1g}	−12.59	−14.74	−12.24	−12.66
a_g	−14.39	−13.40	−13.15	−14.20
b_{2u}	−18.58	−15.65	−14.36	−16.49
b_{3u}	−22.25	−19.53	−17.53	−20.14
a_g	−32.20	−23.60	−22.52	−26.58

Table 4. Canonical MO energies of C_2H_6 obtained by different methods described in the text. All energies are given in eV. The virtual levels are marked by an asterisk

	CNDO	*A*	*B*	STO-3G
e_g^*	5.42	24.54	23.58	21.38
a_{2u}^*	7.31	62.83	57.51	21.11
a_{1g}^*	5.78	43.70	40.93	19.54
a_{2u}^*	4.66	28.65	27.41	18.60
e_u^*	6.65	20.86	21.16	17.91
e_g	−12.80	−14.27	−12.30	−12.50
a_{1g}	−12.96	−11.57	−11.81	−12.63
e_u	−17.38	−15.00	−13.93	−15.61
a_{2u}	−24.48	−20.08	−18.45	−21.92
a_{1g}	−34.81	−23.73	−22.76	−26.70

except those with π symmetry are strongly up-shifted. The energetic up-shifts of the occupied levels resulting from the improved MO methods are somewhat too strong but the general trend is reasonable. A more refined parametrization could lead to a better agreement with ab initio results whereas the deviations of the CNDO levels in the inner valence region and for the virtual MOs are a direct consequence of the ZDO approximation. A physically reliable parametrization is hardly possible in this case.

If the up-shifts of the MO energies in the improved MO methods are somewhat too strong for the low-lying MOs they are completely unreasonable for the highest virtual MO, especially in the case of acetylene where the energy of this MO is pushed up to more than 200 eV. It is interesting to note that there is a relationship between the up-shift of the highest unoccupied MO in our method and the lowest eigenvalue of the overlap matrix, i.e., the lower the latter the higher the former. In the case of acetylene, the lowest eigenvalue of the overlap matrix is getting as small as 0.05. If it were exactly zero the AOs would be linearly dependent, the dimension

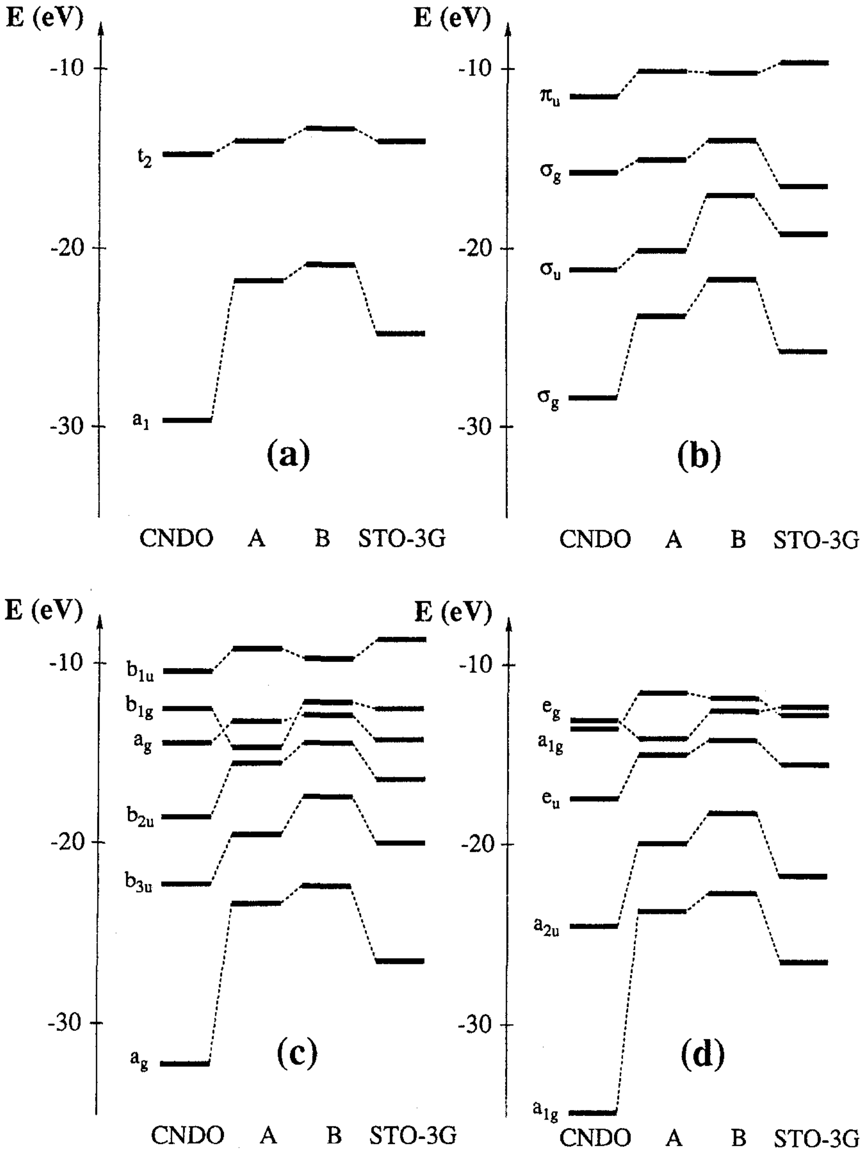

Fig. 1. Energies of the occupied canonical MOs for CH_4 (a), C_2H_2 (b), C_2H_4 (c) and C_2H_6 (d), see legends to Tables 1–4

of the basis set thus being reduced by one. Consequently, one of the MOs would be redundant and this is probably just the one with the unreasonably high energy. If one eigenvalue of the overlap matrix were exactly zero it would be impossible to determine the energy eigenvalue of the redundant MO [54]. If the lowest eigenvalue of the overlap matrix is not zero but rather small one might suspect that the energy eigenvalue of the "quasi-redundant" MO is particularly sensitive to deficiencies in the parametrization. We have seen above that the parametrization of our methods A and B is still far from optimum because it exaggerates the up-shifts of the inner valence and virtual MOs although the general trend of the shifts is reasonable.

The MO shifts shown in Fig. 1 and Tables 1–4 are mainly due to the difference between the core Hamiltonian matrices ${}^{\lambda}\boldsymbol{h}$ and ${}^{\mathrm{ZDO}}\boldsymbol{h}$. The two-electron matrices ${}^{\lambda}\boldsymbol{G}$ and ${}^{\mathrm{ZDO}}\boldsymbol{G}$ also differ but this difference is much less important as far as MO energies are concerned. To illustrate our point we present the matrices ${}^{\lambda}\boldsymbol{h}$ and ${}^{\mathrm{ZDO}}\boldsymbol{h}$ for acetylene in Table 5. The molecular axis is oriented along the x direction so that the p_y and p_z orbitals of the two carbons have π symmetry. From Table 5 we recognize that the corresponding π submatrices consist of matrix elements which are at least comparable in magnitude so that the equation ${}^{\lambda}\boldsymbol{h} \approx {}^{\mathrm{ZDO}}\boldsymbol{h}$ holds approximately for the π submatrices even if the relatively short distance between the two carbons in acetylene leads to a large overlap integral of $S = 0.46$ between the π orbitals. However, the matrix elements of the σ submatrix differ strongly. The difference exceeding 2 a.u. ($\sim$ 55 eV) in some cases can be seen from Table 5. Thus, it is quite remarkable that among the occupied MOs only the most bonding one experiences a considerable energy shift. In any case, it is impossible to base a justification of ZDO methods on the equation ${}^{\lambda}\boldsymbol{h} \approx {}^{\mathrm{ZDO}}\boldsymbol{h}$ in all-valence-electron methods.

The electron charges on carbon and hydrogen in the series C_2H_{2k} with $k = 1, 2, 3$ for the different methods are presented in Table 6. It is interesting to note that the values of CNDO and method A are very close to each other in all cases, whereas the absolute magnitude of the charges is reduced in method B. The correct charge reorganization as a function of k, i.e., an increasing electron density on hydrogen with increasing k is observed for all methods.

We already mentioned that penetration integrals should be included in the core Hamiltonian if the transition from the ZDO to AO parameters is made. This would also diminish the energetic up-shift of the MO energy levels which turned out to be too strong in our test calculations (Tables 1–4, Fig. 1). However, application of the empirical formula suggested for the inclusion of penetration effects in semiempirical MO methods [50, 51] did not result in significant down-shifts of the MO energy levels. In our calculations this shift never exceeded 0.5 eV. Numerical calculations of penetration integrals are known to give much larger effects [21] so that the empirical formula accounts only for a fraction of the penetration effect.

4 Discussion and conclusions

We have seen that a clearcut analysis of the ZDO approximation can only be given for π electron methods. This is due to the fact that in this case a function of the overlap matrix like, e.g., $S^{-1/2}$ can be expanded in a rather rapidly converging power series. Thus, the different integrals and matrix elements in the Löwdin basis can be analyzed in terms of varying order of diatomic overlap densities of the AOs. Combination of such a power series expansion with the Mulliken approximation for the two-electron integrals shows that the notion "zero differential overlap" approximation is misleading because this technique is correct up to first order overlap densities of the AOs. It should be noted that the integrals and matrix elements of ZDO methods must be assumed to refer to a Löwdin basis for which the significance of the term "overlap density" is much less clear than for an AO basis where it can be interpreted as a density in the bond region between two atoms. We reemphasize that, in contrast to a widely accepted argument, there is no inconsistency in neglecting diatomic overlap densities (now referred to Löwdin

Table 5. Core Hamiltonian matrices $^{\mathrm{ZDO}}\boldsymbol{h}$ (top) and $^{\lambda}\boldsymbol{h}$ (bottom) for acetylene. The energies are given in atomic units. H(1) and H(2) are bonded to, respectively, C(1) and C(2)

	C(1)				C(2)				H(1)	H(2)
	$2s$	$2p_x$	$2p_y$	$2p_z$	$2s$	$2p_x$	$2p_y$	$2p_z$	$1s$	$1s$
$2s$	−3.641	0	0	0	−0.232	0.213	0	0	−0.241	−0.059
$2p_x$	0	−3.262	0	0	−0.213	0.182	0	0	0.190	−0.080
$2p_y$	0	0	−3.262	0	0	0	−0.108	0	0	0
$2p_z$	0	0	0	−3.262	0	0	0	−0.108	0	0
$2s$	−0.232	−0.213	0	0	−3.641	0	0	0	−0.059	−0.241
$2p_x$	0.213	0.182	0	0	0	−3.262	0	0	0.080	−0.190
$2p_y$	0	0	−0.108	0	0	0	−3.262	0	0	0
$2p_z$	0	0	0	−0.108	0	0	0	−3.262	0	0
$1s$	−0.241	0.190	0	0	−0.059	0.080	0	0	−2.908	−0.005
$1s$	−0.059	−0.080	0	0	−0.241	−0.190	0	0	−0.005	−2.908
$2s$	−1.602	1.719	0	0	−1.914	2.096	0	0	0.011	−0.633
$2p_x$	1.719	−0.989	0	0	−2.096	2.074	0	0	1.124	−0.520
$2p_y$	0	0	−3.199	0	0	0	−0.137	0	0	0
$2p_z$	0	0	0	−3.199	0	0	0	−0.137	0	0
$2s$	−1.914	−2.096	0	0	−1.602	−1.719	0	0	−0.633	0.011
$2p_x$	2.096	2.074	0	0	−1.719	−0.989	0	0	0.520	−1.124
$2p_y$	0	0	−0.137	0	0	0	−3.199	0	0	0
$2p_z$	0	0	0	−0.137	0	0	0	−3.199	0	0
$1s$	0.011	1.124	0	0	−0.633	0.520	0	0	−2.005	−0.107
$1s$	−0.633	−0.520	0	0	0.011	−1.124	0	0	−0.107	−2.005

Table 6. Changes on carbon and hydrogen atoms for C_2H_{2k} ($k = 1,2,3$) obtained by different methods described in the text

		CNDO	*A*	*B*	STO-3G
C_2H_2	q_C	−0.126	−0.126	−0.086	−0.109
	q_H	0.126	0.126	0.086	0.109
C_2H_4	q_C	−0.107	−0.117	−0.056	−0.125
	q_H	0.054	0.058	0.028	0.063
C_2H_6	q_C	−0.096	−0.093	−0.055	−0.171
	q_H	0.032	0.031	0.018	0.057

orbitals) in the two-electron integrals but retaining them in the resonance integrals.

In the case of all-valence-electron methods a clear theoretical justification of the ZDO approximation is not evident because there is no guarantee that a power series expansion of $S^{-1/2}$ converges. In particular, the assumption ${}^{ZDO}F \approx {}^{\lambda}F$, i.e., identity of the ZDO Fock matrix with the Fock matrix obtained from the Löwdin transformation completely breaks down. We have seen that this is mainly due to differences between the corresponding core Hamiltonian matrices. The fact that rather large overlap integrals can occur in all-valence-electron methods may also lead to approximate linear dependencies of the basis vectors indicated by eigenvalues of the overlap matrix which are close to zero. We have seen in the previous section that a rather small eigenvalue of 0.05 has been obtained for acetylene. If the basis set is linearly dependent the eigenvalue equation (1) has no unique solution [54] and even sufficiently small eigenvalues of the overlap matrix might lead to numerical problems which can be resolved by reducing the dimension of the basis properly [54]. It is clear that the ZDO eigenvalue equation (7) is insensitive to such redundancies of the basis set because the overlap matrix does not appear explicitly in this equation.

In our analysis the emphasis was on systematic errors in the canonical MO energy spectrum obtained by semiempirical MO methods as a result of the ZDO approximation. We have seen that the very low-lying occupied and the virtual MOs are systematically placed at too low energies in ZDO-based schemes. It turned out that an improved method based on explicit performance of the Löwdin transformation can be obtained by very simple manipulations of the ZDO parameters. Of course, we cannot expect that our preliminary calculations based on the two-electron integrals of the CNDO method and completely neglecting penetration effects can reproduce the results of ab initio calculations. But the general trend of our results which give an improved MO energy spectrum in the inner valence region is encouraging. For further improvement it would be necessary to use the two-electron integrals of the NDDO method which take into account the higher multipole moments of the charge distributions and thus also the dependence of the two-electron integrals on the spatial orientation of the orbitals involved. In combination with the inclusion of penetration integrals and perhaps also the effects of core-valence separation [53] such an approach which has been outlined in Sect. 2 should lead to improved results. The use of NDDO integrals would also dispense with the need to account for differences between σ–σ and π–π interactions by rather artificial manipulations of the resonance integrals.

One may wonder how other molecular properties are affected if we follow the procedure described in this paper. At the present stage we are not able to answer this question systematically. In our test calculations for some simple hydrocarbons we have seen that the charge densities obtained by method A are quite close to those of the CNDO version of Ref. 51 and that the correct trend is obtained in the series C_2H_{2k} ($k = 1, 2, 3$). It is highly likely that changes of various molecular properties are in general much less systematic than those of MO energies and more sensitive to the choice of parameters. We have seen in our simple analysis of the Hückel method (Eqs. (50)–(55)) that the eigenvectors and thus the charge densities are the same for both ${}^{ZDO}\boldsymbol{h}$ and ${}^{\lambda}\boldsymbol{h}$ because both matrices commute with the overlap matrix $\boldsymbol{S}$, whereas the eigenvalues, i.e., the MO energies, differ in a systematic manner. From this example one might suspect that the quality of the ZDO approximation has something to do with the difference between the eigenvectors of the Fock matrix $\boldsymbol{F}$ and those of the overlap matrix $\boldsymbol{S}$. If we assume that the Hamiltonian matrix and the overlap matrix commute which is of course in general unrealistic except for the simple Hückel model just mentioned another interesting consequence arises. It can be verified that in this case the bond order matrix (96) is exactly identical to the Löwdin bond order matrix (81). Since the diagonal elements of Eq. (96) represent the gross populations introduced by Mulliken [44], the Löwdin and the Mulliken population analysis give then the same results. However, the diagonal elements of the Löwdin bond order matrix and thus the corresponding orbital populations are necessarily positive. The Mulliken population analysis, on the other hand, can result in negative orbital populations, a phenomenon closely related to counterintuitive orbital mixing [61]. Thus, if negative orbital populations are obtained by the Mulliken analysis the Fock matrix and the overlap matrix cannot commute and one might suspect that the difference between the eigenvectors of the two matrices is particularly large in this case. It would be subject of a separate investigation to examine how this influences the charge distributions obtained by ZDO-based methods but it seems rather likely that ZDO results are particularly unreliable for systems where the Mulliken population analysis gives negative orbital populations.

We already mentioned that semiempirical MO methods are getting out of fashion because modern computers enable ab initio calculations for larger and larger molecules. But there will always be systems large enough to be tractable only by semiempirical methods (e.g. crystalline solids). We would also like to emphasize that semiempirical MO techniques are superior to ab initio methods in the evaluation of electronic transition energies. Thus, improvements of these formalisms should always be welcome. The first CNDO and INDO versions developed by Pople and coworkers tried to mimic the results of minimal basis set ab initio calculations [1]. Later a completely different school of thought (initiated by the group around M.J.S. Dewar) dominated the development of semiempirical methods [2]. It is based on the idea to have a simple formalism the accuracy of which is continuously upgraded by a more and more refined parametrization designed to fit some experimentally observed quantities as closely as possible. It has often been criticized that the disposable parameters in such an approach are void of physical meaning because they are fitted to experimental results and that the accuracy of the results does not tell us anything about the quality of the underlying model even if such a method has some predictive power. Thus, in contrast to ab initio methods which can be improved systematically on the Hartree–Fock level by extending the basis set, there seems to be no systematic and rigorous way to improve parameter-based methods. But why should it not be possible to improve the underlying formalism of a semiempirical approach and then find a new parametrization which should be able to reproduce certain molecular properties for a broader range of molecules? E.g., if the failure of MINDO/3 to reproduce the heats of formation of small strained hydrocarbon rings is a consequence of the ZDO approximation as has been argued by de Bruijn [14], an improved method not employing the ZDO approximation should be able to reproduce the heats of formation of strained and unstrained hydrocarbons equally well with the same parameter set if it is chosen properly. In other words, there might be systematic errors in the results of semiempirical methods which can be ascribed to approximations in the underlying formalism. By focussing on the ZDO approximation we tried to show how one of the most drastic approximations commonly used in semiempirical methods could be overcome. More work remains to be done if such an effort should finally result in an improved semiempirical method.

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