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Orthogonalization corrections for semiempirical methods

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Abstract. Based on a general discussion of orthogonalization effects, two new one-electron orthogonalization corrections are derived to improve existing semiempirical models at the neglect of diatomic differential overlap level. The first one accounts for valence-shell orthogonalization effects on the resonance integrals, while the second one includes the dominant repulsive core–valence interactions through an effective core potential. The corrections for the resonance integrals consist of three-center terms which incorporate stereodiscriminating properties into the two-center matrix elements of the core Hamiltonian. They provide a better description of conformational properties, which is rationalized qualitatively and demonstrated through numerical calculations on small model systems. The proposed corrections are part of a new general-purpose semiempirical method which will be described elsewhere.

Key words: Semiempirical methods – Orthogonalization – Effective core potentials

1 Introduction

Semiempirical methods are widely used in theoretical studies of molecular structure and reactivity [1–4]. Neglect of diatomic differential overlap (NDDO) is the most accurate of the three traditional integral approximations complete neglect of differential overlap (CNDO), intermediate neglect of differential overlap (INDO), and NDDO [5, 6], and consequently the NDDO-based methods modified neglect of differential overlap (MNDO) [7], Austin model 1 (AM1) [8], and parameterized model 3 (PM3) [9] have generally replaced older methods in practical calculations.

A vast body of literature documents the performance of these and other semiempirical methods [1–4]. It has become standard to judge their accuracies primarily from their ability to reproduce the heats of formation for large sets of reference molecules. Considering the difficulties of ab initio methods to predict accurate atomization energies, the errors in semiempirical heats of formation are often surprisingly small [10]; however, these errors tend to be unsystematic so that relative energies are often calculated less reliably by semiempirical methods, and significant problems are indeed encountered in several chemically important areas, for example, with regard to energy differences between conformational and constitutional isomers, intermolecular interaction energies, or reaction barriers [11–15].

A prominent example is the rotational barrier in ethane, which is underestimated by more than a factor of 2 in MNDO, AM1, and PM3, whereas even minimal basis set ab initio self-consistent-field (SCF) calculations reproduce the experimental value well. Although different views have been expressed on the origin of such rotational barriers [16–22], it is generally accepted that proper orthogonality of the orbitals is essential to account for the dominant contributions to the barriers that arise from Pauli exchange repulsion. Due to the approximation of zero differential overlap (ZDO), these orthogonalization effects are neglected in the established semiempirical methods, which can therefore not be expected to treat conformational properties well.

To overcome such qualitative shortcomings, it seems necessary to improve the underlying semiempirical model by introducing orthogonalization corrections. In previous work, orthogonalization corrections have already been proposed at all three levels of integral approximation (CNDO – S^2 [23], SINDO [24], SINDO1 [25, 26], and NDDO [27]). The present development goes beyond these previous attempts, which include corrections only for the one-center core Hamiltonian matrix elements.

Based on a general discussion of orthogonalization effects (Sect. 2), we derive two new orthogonalization

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corrections which are suitable for any semiempirical model. The first one applies to the two-center core Hamiltonian matrix elements, commonly known as resonance integrals (Sect. 3.1). This correction includes three-center terms so that these matrix elements become dependent on the molecular environment, similar to the properly orthogonalized ab initio integrals (Sect. 3.2). As will be demonstrated for several model systems, the three-center terms incorporate stereodiscriminating properties into the semiempirical description of a chemical bond (Sect. 3).

The second correction addresses the orthogonalization effects between core and valence electrons. Ab initio effective core potentials (ECPs) account both for the orthogonalization effects and for the exchange and polarization interactions between core and valence electrons, but the former are known to be dominant [28, 29]. In a semiempirical context, it seems justified to focus on these dominant terms. A corresponding semiempirical ECP has previously been suggested [30] and incorporated at the CNDO [31] and INDO [25] levels. We derive an alternative ECP to account for core–valence orthogonalization (Sect. 4.1) which is conceptually similar, but contains an additional term and offers more flexibility for subsequent parametrization (Sect. 4.2). Compared with the use of scaled ab initio ECPs in NDDO [27] our new approach is less expensive and more versatile.

In semiempirical quantum chemistry, the practical value of a new model can only be judged after its implementation and parameterization. The proposed orthogonalization corrections are central features of a new semiempirical NDDO method called orthogonalization model 2 (OM2), which has been implemented and parameterized for the elements H, C, N, and O [32] and which will be published in detail elsewhere, with a comprehensive and critical examination of its performance.

2 Theoretical background

2.1 General considerations

Ab initio SCF methods solve the Roothaan–Hall pseudoeigenvalue problem

$$\mathbf{FC} = \mathbf{SCE} \ , \tag{1}$$

where **F**, **C**, and **S** denote the Fock, eigenvector, and overlap matrices, respectively, and **E** is the diagonal matrix of orbital energies. Orthogonalization of the basis leads to a standard eigenvalue problem

$$^{\lambda}\mathbf{F}^{\lambda}\mathbf{C} = {}^{\lambda}\mathbf{CE} \ , \tag{2}$$

where the superscript λ denotes a quantity expressed in an orthogonalized basis. The corresponding transformation can be achieved through a symmetric Löwdin orthogonalization [33, 34]

$$^{\lambda}\mathbf{F} = \mathbf{S}^{-1/2}\mathbf{F}\mathbf{S}^{-1/2} \tag{3}$$

$$^{\lambda}\mathbf{C} = \mathbf{S}^{1/2}\mathbf{C} \tag{4}$$

$$^{\lambda}\mathbf{S} = \mathbf{1} \ . \tag{5}$$

By contrast, semiempirical methods solve a secular equation,

$$^{\mathrm{NDDO}}\mathbf{F}^{\mathrm{NDDO}}\mathbf{C} = {}^{\mathrm{NDDO}}\mathbf{CE} \ , \tag{6}$$

where the transformation $\mathbf{F} \rightarrow {}^{\lambda}\mathbf{F}$ is not explicitly performed. This suggests that the semiempirical Fock matrix implicitly refers to an orthogonal basis:

$$^{\mathrm{NDDO}}\mathbf{F} \approx {}^{\lambda}\mathbf{F} \ . \tag{7}$$

The neglect of all three-center and four-center two-electron integrals in the NDDO approximation [5, 6] is consistent with this interpretation because these integrals are vanishingly small only in an orthogonalized basis [35–37].

The Fock matrix contains both one-electron (**H**) and two-electron (**G**) terms, which can be handled separately during Löwdin orthogonalization:

$$^{\lambda}\mathbf{F} = {}^{\lambda}\mathbf{H} + {}^{\lambda}\mathbf{G} \tag{8}$$

$$^{\lambda}\mathbf{H} = \mathbf{S}^{-1/2}\mathbf{H}\mathbf{S}^{-1/2} \tag{9}$$

$$^{\lambda}\mathbf{G} = \mathbf{S}^{-1/2}\mathbf{G}\mathbf{S}^{-1/2} \ . \tag{10}$$

To account for the orthogonalization effects arising from these transformations, different strategies may be followed in a semiempirical context. The direct use of Eq. (10) is not feasible since it requires the prior calculation of all two-electron integrals and would thus sacrifice the computational efficiency of the NDDO approach. On the other hand, the exact orthogonalization of the one-electron part according to Eq. (9) would be feasible computationally; however, using Eq. (9) without Eq. (10) introduces an imbalance between the one- and two-electron parts of the Fock matrix and is therefore problematic. In the literature, several variants of this approach have been studied, where different parts of the Fock matrix are subjected to the exact Löwdin transformation while the ZDO approximation is applied to the remainder [15, 38–41]. To our knowledge, none of these attempts have been successfully incorporated into a general-purpose semiempirical method. Therefore, we shall adopt the alternative strategy of representing the dominant orthogonalization corrections by suitable parametric functions. These corrections can then be adjusted during the parameterization process, as in previous approaches at the CNDO, INDO, and NDDO levels [23–27].

2.2 Orthogonalization effects on basis orbitals

Symmetric orthogonalization transforms a basis $\{\varphi\}$ of nonorthogonal atomic orbitals (AO) into a set of orthogonalized AOs (OAOs)

$$^{\lambda}\varphi = \varphi\mathbf{S}^{-1/2} \ . \tag{11}$$

In the special case of a diatomic molecule with two AOs (μ at atom A, λ at atom B), the $\mathbf{S}^{-1/2}$ matrix, and hence also the orthogonal AOs, can be given in analytical form:

$$
{}^{\lambda}\mu = \left(\frac{\sqrt{1-S_{\mu\lambda}}+\sqrt{1+S_{\mu\lambda}}}{2\sqrt{1-S^{2}_{\mu\lambda}}}\right)\mu + \left(\frac{\sqrt{1-S_{\mu\lambda}}-\sqrt{1+S_{\mu\lambda}}}{2\sqrt{1-S^{2}_{\mu\lambda}}}\right)\lambda \ , \qquad (12)
$$

where $S_{\mu\lambda}$ is the overlap integral between the AOs. In the general case, the $\mathbf{S}^{-1/2}$ matrix is not known analytically, but can be expanded in a Taylor series in terms of the matrix $\mathbf{S}'$, which contains the off-diagonal elements of the overlap matrix and zero diagonal elements,

$$
\begin{aligned}
\mathbf{S}^{-1/2} &= (\mathbf{1}+\mathbf{S}')^{-1/2} \\
&= \mathbf{1} - \frac{1}{2}\mathbf{S}' + \frac{3}{8}\mathbf{S}'^{2} - \frac{5}{16}\mathbf{S}'^{3} + \frac{35}{128}\mathbf{S}'^{4} - \dots \ . \qquad (13)
\end{aligned}
$$

For the special two-orbital case, one obtains

$$
\begin{aligned}
{}^{\lambda}\mu &= \left(1 + \frac{3}{8}S^{2}_{\mu\lambda} + \frac{35}{128}S^{4}_{\mu\lambda} + \dots\right)\mu \\
&\quad - \left(\frac{1}{2}S_{\mu\lambda} + \frac{5}{16}S^{3}_{\mu\lambda} + \dots\right)\lambda \ . \qquad (14)
\end{aligned}
$$

Thus, the convergence depends on the magnitude of the overlap integral: it is fast for small overlap and slow for large overlap. The expansion (Eq. 13) fails to converge if the spectrum of the matrix $\mathbf{S}'$ (its largest eigenvalue) is larger than 1 [42]. However, there are methods to force this expansion to converge [43, 44], by writing the expansion coefficients in Eq. (13) as functions of the spectrum of the overlap matrix, for example, by using suitable Legendre coefficients [44]. Normally, the differences between the fixed and the spectrum-dependent coefficients are very small.

As can be seen from Eqs. (12) and (14), orthogonalization implies delocalization: the OAOs have so-called "orthogonalization tails", i.e. contributions from the AOs at all other centers which are nonorthogonal to the original AO. This mixing depends on the geometry of the molecular environment as reflected in the overlap matrix. Since overlap integrals decrease exponentially with increasing distance, orthogonalization effects are of short range.

In addition, orthogonalization also leads to a contraction. Equations (12) and (14) show that the coefficient of the original AO in its OAO is larger than 1. The resulting increase in density close to the center of the original AO is compensated by a reduction in density in and around the nodal regions of the OAO. The orthogonalization accounts for the Pauli repulsion of the electrons at other centers [35] and prevents penetration into these regions, thus effectively reducing the volume for an electron in the OAO and increasing its kinetic energy. Therefore, the energy of an OAO is higher than that of the corresponding AO (Fig. 1, $H_{\mu\mu} \rightarrow {}^{\lambda}H_{\mu\mu}$).

In a full-overlap treatment based on Eq. (1), the interaction between two nonorthogonal AOs leads to an unsymmetric split of the energy levels to yield the orthogonal molecular orbitals (MOs), such that the antibonding MO is destabilized more than the bonding MO is stabilized. The same MO energy levels are obtained by a symmetric split of the OAO energy levels, which have already been raised by the orthogonalization. Standard semiempirical ZDO methods, on the other hand, do not account for the destabilization due to orthogonalization and therefore yield a symmetric splitting relative to the original AO level (Fig. 1). This results in some of the most severe deficiencies of ZDO-based semiempirical methods [32]:

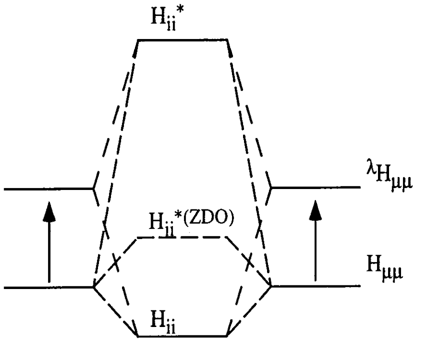

Fig. 1. Molecular orbital (*MO*) scheme for atomic orbitals (*AOs*) and orthogonalized AOs (*OAOs*). The energy levels are given by the one-electron matrix elements: $H_{\mu\mu}$ and ${}^{\lambda}H_{\mu\mu}$ denote the AO and OAO, respectively, while H_{ii} and H_{ii}^{*} refer to the bonding and antibonding MOs, respectively. Without accounting for orthogonalization zero differential overlap (*ZDO*) methods predict a symmetric splitting of the MOs relative to the original AOs, resulting in too low antibonding MOs $H_{ii}^{*(\mathrm{ZDO})}$

1. The gaps between bonding and antibonding MOs, as well as the corresponding excitation energies, are significantly underestimated.
2. The correct pairing properties for the electronic states of conjugated hydrocarbons are not reproduced [15].
3. Barriers to internal rotation as in ethane are severely underestimated, with implications for other conformational properties (for a detailed discussion see Ref. [32]).
4. The closed-shell repulsion of four-electron two-orbital interactions is not recovered, causing for example, the incorrect prediction of a stable He_2 dimer and a stable H_2 triplet state in CNDO [11], a lack of destabilization in antiaromatic systems (Sect. 3.3), and qualitatively wrong intermolecular interaction potentials [12] and transition structures [13, 14].

2.3 Orthogonalization effects on integrals and matrix elements

The ZDO approximation leads to a dramatic reduction in the number of two-electron integrals that are considered, since it neglects all three- and four-center two-electron integrals. It has been justified by theoretical considerations [45, 46] and explicit calculations [35–37] which have shown that three- and four-center two-electron integrals are indeed very small in an OAO basis. Integrals of the type $\langle \mu^{A}\nu^{A} | \lambda^{B}\sigma^{C} \rangle$ are different and have therefore been studied specifically [43, 47, 48]. A recent overview can be found in Ref. [49].

Different approaches are conceivable for calculating the surviving NDDO two-electron integrals in an OAO basis. An exact calculation according to Eq. (10) would defeat the purpose of the NDDO approximation because it requires the prior computation of all two-electron integrals, including the three- and four-center integrals. As a remedy, these latter integrals could be expanded in terms of two-center two-electron AO integrals according to the so-called "Ruedenberg approximation" [37, 47, 50]; however, this scheme is only approximate, computationally expensive, and therefore not recommendable from our experience. Another approach applies the expansion (Eq. 13) to Eq. (10): expanding only to $O(S)$ yields integrals that are identical in the AO and OAO bases, while expanding to $O(S^2)$ provides correction terms containing two-center A—C and B—C integrals [47]. We have reexamined these issues [32] and confirmed previous findings that the exact orthogonalization corrections from Eq. (10) are relatively small for typical NDDO-type two-electron integrals, especially when compared with those for the one-electron integrals. As in previous semiempirical methods, we have therefore decided to neglect these two-electron corrections, with the understanding that their average effect may partly be absorbed through the semiempirical parameterization of the one-electron corrections (see later). Hence, we represent the NDDO two-electron integrals in an OAO basis by

$$ {}^{\lambda}(\mu^{A}\nu^{B}|\lambda^{C}\sigma^{D}) = (\mu^{A}\nu^{B}|\lambda^{C}\sigma^{D})\delta_{AB}\delta_{CD} \ . \tag{15} $$

The orthogonalization effects for the one-electron integrals are most transparent in the homonuclear two-orbital case (μ and λ are AOs of the same type at two centers A and B, respectively). Employing Eq. (9) the two relevant core Hamiltonian matrix elements in the orthogonal basis are given by

$$ {}^{\lambda}H_{\mu\mu} = H_{\mu\mu} - \frac{S_{\mu\lambda}M_{\mu\lambda}}{1 - S_{\mu\lambda}^{2}} \tag{16} $$

$$ {}^{\lambda}H_{\mu\lambda} = \frac{M_{\mu\lambda}}{1 - S_{\mu\lambda}^{2}} \ , \tag{17} $$

where we have introduced the so-called Mulliken function, $M_{\mu\lambda}$, which vanishes identically if the Mulliken approximation (Eq. 19) is applied,

$$ M_{\mu\lambda} = H_{\mu\lambda} - \frac{S_{\mu\lambda}}{2}(H_{\mu\mu} + H_{\lambda\lambda}) \tag{18} $$

$$ \mu\lambda \overset{\text{Mulliken}}{=} \frac{S_{\mu\lambda}}{2}(\mu^{2} + \lambda^{2}) \ . \tag{19} $$

The one-electron Hamiltonian consists of a differential operator for the kinetic energy ($\hat{T}$) and a multiplicative operator for the potential energy ($\hat{V}$). The Mulliken approximation (Eq. 19) can be applied only to the latter yielding

$$ {}^{\lambda}V_{\mu\mu} \overset{\text{Mulliken}}{=} V_{\mu\mu} \tag{20} $$

$$ {}^{\lambda}H_{\mu\mu} = {}^{\lambda}T_{\mu\mu} + {}^{\lambda}V_{\mu\mu} = {}^{\lambda}T_{\mu\mu} + V_{\mu\mu} \tag{21} $$

$$ {}^{\lambda}V_{\mu\lambda} \overset{\text{Mulliken}}{=} 0 \tag{22} $$

$$ {}^{\lambda}H_{\mu\lambda} = {}^{\lambda}T_{\mu\lambda} + {}^{\lambda}V_{\mu\lambda} = {}^{\lambda}T_{\mu\lambda} \ . \tag{23} $$

Obviously, orthogonalization affects the diagonal ${}^{\lambda}H_{\mu\mu}$ one-center terms much less than the off-diagonal ${}^{\lambda}H_{\mu\lambda}$ two-center terms where the potential-energy contribution vanishes. These qualitative conclusions have been confirmed by numerical computation of the exact orthogonalization corrections [51].

The matrix elements ${}^{\lambda}H_{\mu\lambda}$ and $H_{\mu\lambda}$ differ not only in magnitude, but also in their distance dependence. Since both kinetic-energy and potential-energy integrals over AOs generally decrease with increasing distance in a manner similar to the corresponding overlap integrals (e.g. Ref. [52]), it is reasonable to assume the following proportionality in the AO basis:

$$ H_{\mu\lambda} \propto S_{\mu\lambda} \ . \tag{24} $$

In the limit of large internuclear distances, R_{AB}, the relation ${}^{\lambda}H_{\mu\lambda} \propto S_{\mu\lambda}$ should also hold (see Eqs. 17, 18). For intermediate distances, the first-order correction $H_{\mu\lambda} \rightarrow M_{\mu\lambda}$ leads to new minima or maxima, because $M_{\mu\lambda} = 0$ for both $R_{AB} = 0$ and $R_{AB} = \infty$. For short distances, the higher-order corrections from $(1 - S_{\mu\lambda}^{2})^{-1}$ become important and cause more pronounced extrema that are shifted towards shorter distances. Hence, in general,

$$ {}^{\lambda}H_{\mu\lambda} \not\propto S_{\mu\lambda} \ . \tag{25} $$

Graphical presentations of ${}^{\lambda}H_{\mu\lambda}$, $M_{\mu\lambda}$, $H_{\mu\lambda}$, and $S_{\mu\lambda}$ can be found in Refs. [11, 41].

The existing semiempirical methods approximate the two-center one-electron matrix element ${}^{\lambda}H_{\mu\lambda}$ by an empirical resonance integral $\beta_{\mu\lambda}$, which is a local function of the type

$$ {}^{\lambda}H_{\mu\lambda} = \beta_{\mu\lambda} = f(\mu^{A}, \lambda^{B}, R_{AB}) \ . \tag{26} $$

The established MNDO-type methods set the resonance integrals proportional to the overlap integrals, although this is not justified in an OAO basis (see earlier). Functional expressions consistent with Eq. (25) have been suggested, either as theoretically derived formulas such as Eq. (17) [24, 53], or as purely empirical functions tailored to mimic ${}^{\lambda}H_{\mu\lambda}$ in a local A—B system [27],

$$ \beta_{\mu\lambda} = \tfrac{1}{2}(\beta_{\mu}^{A} + \beta_{\lambda}^{B})\sqrt{R_{AB}}\exp\left[-(\alpha_{\mu}^{A} + \alpha_{\lambda}^{B})R_{AB}^{2}\right] \ , \tag{27} $$

where α_{μ} and β_{μ} are adjustable parameters that are specific for a given AO type, and a suitable phase factor is implied [27]. Such expressions can effectively contain higher-order orthogonalization corrections.

Generalizing our discussion from diatomic to polyatomic molecules, the exact orthogonalization according to Eq. (9) will produce one-electron matrix elements ${}^{\lambda}H_{\mu\lambda}$ in the OAO basis which have contributions from all AOs in the molecule and can therefore not be represented by a purely local function such as the resonance integral $\beta_{\mu\lambda}$, Eq. (26). In order to account for these orthogonalization effects in polyatomic molecules, corrections with three-center contributions are needed. These three-center terms emerge naturally when applying the expansion (Eq. 13) to the matrix elements $H_{\mu\lambda}$. This approach has been suggested before [11, 41], but in neither case were the approximations and derivations discussed, nor were the suggested terms tested numerically for their usefulness in practical semiempirical calculations.

3 Orthogonalization corrections to the resonance integrals

3.1 Derivation

We begin the derivation of possible correction terms by applying the $\mathbf{S}^{-1/2}$ expansion (Eq. 13) to the orthogonalization of the core Hamiltonian,

$$
\begin{aligned}
{}^{\lambda}\mathbf{H} &= \mathbf{S}^{-1/2}\mathbf{H}\mathbf{S}^{-1/2} \\
&= \left(\mathbf{1} - \frac{1}{2}\mathbf{S}' + \frac{3}{8}\mathbf{S}'^2 - \dots\right)\mathbf{H}\left(\mathbf{1} - \frac{1}{2}\mathbf{S}' + \frac{3}{8}\mathbf{S}'^2 - \dots\right) \\
&= \mathbf{H} - \tfrac{1}{2}(\mathbf{S}'\mathbf{H} + \mathbf{H}\mathbf{S}') + \tfrac{3}{8}(\mathbf{S}'^2\mathbf{H} + \mathbf{H}\mathbf{S}'^2) \\
&\quad + \tfrac{1}{4}\mathbf{S}'\mathbf{H}\mathbf{S}' + \mathbf{O}(\mathbf{S}'^3) \ .
\end{aligned}
\tag{28}
$$

Only terms up to the second power in $\mathbf{S}'$ have been included. By proper indexing we now focus on the two-center matrix elements,

$$
\begin{aligned}
{}^{\lambda}H_{\mu\lambda} &= H_{\mu\lambda} - \frac{1}{2}\sum_{\rho}\left(S'_{\mu\rho}H_{\rho\lambda} + H_{\mu\rho}S'_{\rho\lambda}\right) \\
&\quad + \frac{1}{8}\sum_{\rho}\sum_{\sigma}\Big(3S'_{\mu\rho}S'_{\rho\sigma}H_{\sigma\lambda} + 3H_{\mu\rho}S'_{\rho\sigma}S'_{\sigma\lambda} \\
&\qquad\qquad + 2S'_{\mu\rho}H_{\rho\sigma}S'_{\sigma\lambda}\Big) \ .
\end{aligned}
\tag{29}
$$

Expanding the first sum and separating the cases where $\rho = \mu$ and $\rho = \lambda$ we obtain

$$
\begin{aligned}
{}^{\lambda}H_{\mu\lambda} &= H_{\mu\lambda} - \frac{1}{2}S_{\mu\lambda}H_{\lambda\lambda} - \frac{1}{2}H_{\mu\mu}S_{\mu\lambda} \\
&\quad - \frac{1}{2}\sum_{\rho\neq\mu,\lambda}\left(S_{\mu\rho}H_{\rho\lambda} + H_{\mu\rho}S_{\rho\lambda}\right) \\
&\quad + \frac{1}{8}\sum_{\rho}\sum_{\sigma}\big(3S_{\mu\rho}S_{\rho\sigma}H_{\sigma\lambda} + 3H_{\mu\rho}S_{\rho\sigma}S_{\sigma\lambda} \\
&\qquad\qquad + 2S_{\mu\rho}H_{\rho\sigma}S_{\sigma\lambda}\big) \ ,
\end{aligned}
\tag{30}
$$

where we have used $S'_{\mu\mu} = 0$ and dropped the primes since $S'_{\mu\lambda} = S_{\mu\lambda}$ for $\mu \neq \lambda$. The first three local terms define the Mulliken function, Eq. (18). Using the reverse relation,

$$
H_{\mu\lambda} = M_{\mu\lambda} + \tfrac{1}{2}S_{\mu\lambda}(H_{\mu\mu} + H_{\lambda\lambda}) \ , \tag{31}
$$

we rewrite the single sum in Eq. (30),

$$
\begin{aligned}
{}^{\lambda}H_{\mu\lambda} &= M_{\mu\lambda} - \frac{1}{2}\sum_{\rho\neq\mu,\lambda}\left\{S_{\mu\rho}\left[M_{\rho\lambda} + \frac{1}{2}S_{\rho\lambda}\big(H_{\rho\rho} + H_{\lambda\lambda}\big)\right]\right. \\
&\qquad \left. + S_{\rho\lambda}\left[M_{\mu\rho} + \frac{1}{2}S_{\mu\rho}\big(H_{\mu\mu} + H_{\rho\rho}\big)\right]\right\} \\
&\quad + \frac{1}{8}\sum_{\rho}\sum_{\sigma}\big(3S_{\mu\rho}S_{\rho\sigma}H_{\sigma\lambda} + 3H_{\mu\rho}S_{\rho\sigma}S_{\sigma\lambda} \\
&\qquad\qquad + 2S_{\mu\rho}H_{\rho\sigma}S_{\sigma\lambda}\big)
\end{aligned}
\tag{32}
$$

$$
\begin{aligned}
&= M_{\mu\lambda} - \frac{1}{2}\sum_{\rho\neq\mu,\lambda}\big(S_{\mu\rho}M_{\rho\lambda} + M_{\mu\rho}S_{\rho\lambda}\big) \\
&\quad - \frac{1}{4}\sum_{\rho\neq\mu,\lambda}S_{\mu\rho}S_{\rho\lambda}\big(H_{\mu\mu} + H_{\lambda\lambda} + 2H_{\rho\rho}\big) \\
&\quad + \frac{1}{8}\sum_{\rho}\sum_{\sigma}\big(3S_{\mu\rho}S_{\rho\sigma}H_{\sigma\lambda} + 3H_{\mu\rho}S_{\rho\sigma}S_{\sigma\lambda} \\
&\qquad\qquad + 2S_{\mu\rho}H_{\rho\sigma}S_{\sigma\lambda}\big) \ .
\end{aligned}
\tag{33}
$$

Up to this point, the derivation was exact – apart from truncating the power expansion of $\mathbf{S}^{-1/2}$ beyond $O(S^2)$, Eq. (28). We now wish to find an orthogonalization correction which approximates the exact difference ${}^{\lambda}H_{\mu\lambda} - H_{\mu\lambda}$ and is at the same time as simple as possible and flexible enough to fit into a semiempirical scheme.

The double sum in Eq. (33) contains four-center contributions of the form $S_{\mu^{\mathrm{A}}\rho^{\mathrm{C}}}S_{\rho^{\mathrm{C}}\sigma^{\mathrm{D}}}H_{\sigma^{\mathrm{D}}\lambda^{\mathrm{B}}}$. Since the $H_{\sigma^{\mathrm{D}}\lambda^{\mathrm{B}}}$ matrix element behaves like the $S_{\sigma^{\mathrm{D}}\lambda^{\mathrm{B}}}$ overlap integral in the present context, this four-center contribution is formally of third order in $\mathbf{S}$. Since the correction terms should be at most of second order in $\mathbf{S}$, we can neglect all terms in the double sum which contain two-center matrix elements of $\mathbf{H}$. Since semiempirical methods usually employ a minimal valence basis, all AOs at the same center will be orthogonal, and two-center contributions in Eq. (33) such as $S_{\mu^{\mathrm{A}}\rho^{\mathrm{B}}}S_{\rho^{\mathrm{B}}\sigma^{\mathrm{B}}}H_{\sigma^{\mathrm{B}}\lambda^{\mathrm{B}}}$ will vanish. Finally, the terms of the second sum in Eq. (33) can be combined with the corresponding terms of the double sum (interchanging indices, if necessary). Introducing all these simplifications leads to

$$
\begin{aligned}
{}^{\lambda}H_{\mu\lambda} &= M_{\mu\lambda} - \frac{1}{2}\sum_{\rho\neq\mu,\lambda}\big(S_{\mu\rho}M_{\rho\lambda} + M_{\mu\rho}S_{\rho\lambda}\big) \\
&\quad + \frac{1}{8}\sum_{\rho}^{\mathrm{C}}S_{\mu\rho}S_{\rho\lambda}\big(H_{\mu\mu} + H_{\lambda\lambda} - 2H_{\rho\rho}\big) \\
&\quad + \frac{1}{8}\sum_{\rho}^{\mathrm{C}}\left(3\sum_{\sigma\neq\lambda}^{\mathrm{B}}S_{\mu\rho}S_{\rho\sigma}H_{\sigma\lambda} + 3\sum_{\sigma\neq\mu}^{\mathrm{A}}S_{\sigma\rho}S_{\rho\lambda}H_{\mu\sigma}\right. \\
&\qquad\qquad \left. + 2\sum_{\sigma\neq\rho}^{\mathrm{C}}S_{\mu\rho}S_{\sigma\lambda}H_{\rho\sigma}\right) \ .
\end{aligned}
\tag{34}
$$

Note that the last two sums contain only three-center contributions, which is indicated by appropriate atomic labels at the summation symbols. In the specific case of a diatomic molecule A—B, this equation thus reduces to

$$
{}^{\lambda}H_{\mu\lambda}^{\mathrm{AB}} = M_{\mu\lambda} - \frac{1}{2}\sum_{\rho\neq\mu,\lambda}\big(S_{\mu\rho}M_{\rho\lambda} + M_{\mu\rho}S_{\rho\lambda}\big) \ . \tag{35}
$$

The sum can be expanded and reformulated using $S_{\mu^{\mathrm{A}}\nu^{\mathrm{A}}} = 0$ and $M_{\mu^{\mathrm{A}}\nu^{\mathrm{A}}} = H_{\mu^{\mathrm{A}}\nu^{\mathrm{A}}}$. Remembering the expansion character of this approach until $O(S^2)$ we write

$$
{}^{\lambda}H_{\mu\lambda}^{\mathrm{AB}} = M_{\mu\lambda} - \frac{1}{2}\sum_{\nu\neq\mu}^{\mathrm{A}}H_{\mu\nu}S_{\nu\lambda} - \frac{1}{2}\sum_{\kappa\neq\lambda}^{\mathrm{B}}S_{\mu\kappa}H_{\kappa\lambda} + O(S^3) \tag{36}
$$

$$
\overset{\mathrm{def}}{\equiv} \beta_{\mu\lambda} \ . \tag{37}
$$

As emphasized in Eq. (37), we suggest representing this local matrix element by an empirical resonance integral, $\beta_{\mu\lambda}$, for example, of the form of Eq. (27) [27]. Conceptually, this resonance integral includes *per definitionem* all local orthogonalization corrections (of second and higher order). Inserting $\beta_{\mu\lambda}$, Eq. (37), into Eq. (34) we can limit the summations to AOs which are centered at neither A nor B,

$$\begin{aligned}{}^{\lambda}H_{\mu\lambda} = \beta_{\mu\lambda} &- \frac{1}{2}\sum_{\rho}^{\mathrm{C}}(S_{\mu\rho}M_{\rho\lambda} + M_{\mu\rho}S_{\rho\lambda}) \\ &+ \frac{1}{8}\sum_{\rho}^{\mathrm{C}} S_{\mu\rho}S_{\rho\lambda}(H_{\mu\mu} + H_{\lambda\lambda} - 2H_{\rho\rho}) \\ &+ \frac{1}{8}\sum_{\rho}^{\mathrm{C}}\left(3\sum_{\sigma\neq\lambda}^{\mathrm{B}} S_{\mu\rho}S_{\rho\sigma}H_{\sigma\lambda} + 3\sum_{\sigma\neq\mu}^{\mathrm{A}} S_{\sigma\rho}S_{\rho\lambda}H_{\mu\sigma}\right. \\ &\qquad \left. +2\sum_{\sigma\neq\rho}^{\mathrm{C}} S_{\mu\rho}S_{\sigma\lambda}H_{\rho\sigma}\right) \ . \end{aligned} \tag{38}$$

At this point, we have achieved a separation of ${}^{\lambda}H_{\mu\lambda}$ into a two-center resonance integral (which may effectively contain local higher-order corrections) and three-center second-order orthogonalization corrections. We now rearrange the latter terms,

$$\begin{aligned}{}^{\lambda}H_{\mu\lambda} = \beta_{\mu\lambda} &- \frac{1}{2}\sum_{\rho}^{\mathrm{C}} \\ &\left\{ S_{\mu\rho}\left[M_{\rho\lambda} - \frac{1}{2}\sum_{\sigma\neq\lambda}^{\mathrm{B}} S_{\rho\sigma}H_{\sigma\lambda} - \frac{1}{2}\sum_{\sigma\neq\rho}^{\mathrm{C}} S_{\sigma\lambda}H_{\rho\sigma}\right.\right. \\ &\qquad \left. - \frac{1}{4}\sum_{\sigma\neq\lambda}^{\mathrm{B}} S_{\rho\sigma}H_{\sigma\lambda} + \frac{1}{4}\sum_{\sigma\neq\rho}^{\mathrm{C}} S_{\sigma\lambda}H_{\rho\sigma}\right] \\ &\quad + S_{\rho\lambda}\left[M_{\mu\rho} - \frac{1}{2}\sum_{\sigma\neq\mu}^{\mathrm{A}} S_{\sigma\rho}H_{\mu\sigma} - \frac{1}{2}\sum_{\sigma\neq\rho}^{\mathrm{C}} S_{\mu\sigma}H_{\rho\sigma}\right. \\ &\qquad \left.\left. - \frac{1}{4}\sum_{\sigma\neq\mu}^{\mathrm{A}} S_{\sigma\rho}H_{\mu\sigma} + \frac{1}{4}\sum_{\sigma\neq\rho}^{\mathrm{C}} S_{\mu\sigma}H_{\rho\sigma}\right]\right\} \\ &+ \frac{1}{8}\sum_{\rho}^{\mathrm{C}} S_{\mu\rho}S_{\rho\lambda}(H_{\mu\mu} + H_{\lambda\lambda} - 2H_{\rho\rho}) \ . \end{aligned} \tag{39}$$

The two expressions in square brackets represent local two-center quantities: the first one for B—C, the second one for A—C. The last two terms in each of these expressions tend to cancel each other and may therefore be neglected. The remaining terms can then be identified with the corresponding resonance integrals $\beta_{\rho\lambda}$ and $\beta_{\mu\rho}$, see Eqs. (36) and (37). Introducing these simplifications into Eq. (39) yields

$$\begin{aligned}{}^{\lambda}H_{\mu\lambda} = \beta_{\mu\lambda} &- \frac{1}{2}\sum_{\rho}^{\mathrm{C}}(S_{\mu\rho}\beta_{\rho\lambda} + \beta_{\mu\rho}S_{\rho\lambda}) \\ &+ \frac{1}{8}\sum_{\rho}^{\mathrm{C}} S_{\mu\rho}S_{\rho\lambda}(H_{\mu\mu} + H_{\lambda\lambda} - 2H_{\rho\rho}) \ . \end{aligned} \tag{40}$$

This is our final formula for the two-center one-electron matrix elements. It contains a relatively simple expression for the three-center second-order orthogonalization corrections which may also implicitly account for some higher-order corrections if these are included in the empirical two-center resonance integrals.

For the sake of completeness, we relate the present development to previous work [11, 47]. The former derivation is terminated at Eq. (30) [47], while the latter arrives at an expression like Eq. (34), but without the last sum of terms [11]. To our knowledge, neither of these corrections have ever been used in actual MO calculations.

3.2 Discussion and qualitative interpretation

The proposed orthogonalization corrections to the resonance integral between AOs μ at A and λ at B act like a pseudopotential which can be decomposed into contributions $V_{\mu\lambda,\mathrm{C}}(\mathrm{ORT})$ from the other atoms, C,

$${}^{\lambda}H_{\mu\lambda} = \beta_{\mu\lambda} + \sum_{\mathrm{C}} V_{\mu\lambda,\mathrm{C}}(\mathrm{ORT}) \tag{41}$$

$$\begin{aligned}V_{\mu\lambda,\mathrm{C}}(\mathrm{ORT}) = &- \frac{1}{2}\sum_{\rho\epsilon\mathrm{C}}(S_{\mu\rho}\beta_{\rho\lambda} + \beta_{\mu\rho}S_{\rho\lambda}) \\ &+ \frac{1}{8}\sum_{\rho\epsilon\mathrm{C}} S_{\mu\rho}S_{\rho\lambda}(H_{\mu\mu} + H_{\lambda\lambda} - 2H_{\rho\rho}) \ . \end{aligned} \tag{42}$$

As in the case of the properly orthogonalized ab initio integrals, the ${}^{\lambda}H_{\mu\lambda}$ matrix elements depend on the type and location of all other AOs, ρ, which are not already orthogonal to the original AOs μ and λ. In our suggested formalism, the three-center pseudopotential terms introduce a sensitivity towards the molecular environment into the core Hamiltonian, and they will therefore critically affect the relative energies of conformers and stereoisomers.

For a qualitative discussion of this pseudopotential we consider a triatomic model molecule ACB with one AO per atom, such as $1s$ or $2p_{\pi}$ (Fig. 2), as introduced by de Bruijn [11, 54]. In this case, the AOs can simply be denoted by the atomic label (e.g. A instead of μ).

3.2.1 Case 1: strong interactions

The matrix element ${}^{\lambda}H_{\mathrm{AC}}$ describes the interaction along the chemical bond A—C. It is given by

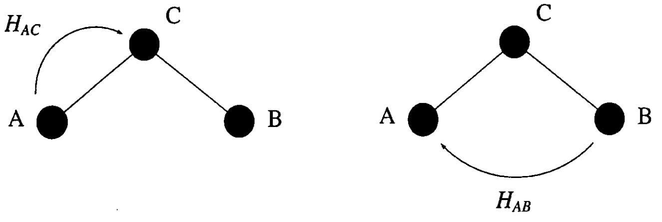

Fig. 2. Two-center matrix elements of the core Hamiltonian in a three-center system; case 1 (*left*) and case 2 (*right*). Each atom carries one single orbital designated by *A*, *B*, and *C*, respectively

$$
\begin{aligned}
{}^{\lambda}H_{AC} &= \beta_{AC} + V_{AC,B}(\mathrm{ORT}) \\
&= \beta_{AC} - \tfrac{1}{2}(S_{AB}\beta_{BC} + \beta_{AB}S_{BC}) \\
&\quad + \tfrac{1}{8}S_{AB}S_{BC}(H_{AA} + H_{CC} - 2H_{BB}) \ . \qquad (43)
\end{aligned}
$$

The two terms of the pseudopotential each contain one small factor involving the nonbonded atoms A and B, either S_{AB} or β_{AB}. The pseudopotential will thus be a small correction to the leading resonance integral β_{AC},

$$|\beta_{AC}| \gg |V_{AC,B}(\mathrm{ORT})| \ . \qquad (44)$$

The first term of the pseudopotential will be repulsive, because overlap and resonance integrals normally have opposite signs. The second term vanishes in the homonuclear case and will gain importance with increasing bond polarity; it may be positive or negative. As long as the bonds are not too polar, the first term is expected to be dominant. The energetic contribution of the pseudopotential is governed by its product with the relevant density matrix element (P_{AC}). Since this is usually positive for case 1 (chemical bond A—C), the overall orthogonalization correction should be repulsive. The closer atoms A and B approach each other, the larger the repulsion.

3.2.2 Case 2: weak or second-neighbor interactions

The matrix element ${}^{\lambda}H_{AB}$ describes the interaction between the nonbonded atoms A and B. It is given by

$$
\begin{aligned}
{}^{\lambda}H_{AB} &= \beta_{AB} + V_{AB,C}(\mathrm{ORT}) \\
&= \beta_{AB} - \tfrac{1}{2}(S_{AC}\beta_{CB} + \beta_{AC}S_{CB}) \\
&\quad + \tfrac{1}{8}S_{AC}S_{CB}(H_{AA} + H_{BB} - 2H_{CC}) \ . \qquad (45)
\end{aligned}
$$

Here, each of the two pseudopotential terms contains two relatively large factors, since the overlap and resonance integrals both refer to the two chemical bonds. In addition, the resonance integral β_{AB} is rather small due to the larger nonbonded distance between A and B, so that we may expect it to be of similar magnitude as the pseudopotential,

$$|\beta_{AB}| \approx |V_{AB,C}(\mathrm{ORT})| \ . \qquad (46)$$

Again, the corrections to the resonance integral will usually be repulsive. The pseudopotential may dominate and so ${}^{\lambda}H_{AB}$ may even become positive. In contrast to case 1, the density matrix elements (P_{AB}) for second-neighbor interactions are usually small and mostly negative, which leads to attractive pseudopotential contributions to the total energy. Neglecting these contributions, the established ZDO methods will tend to overestimate the repulsion of second-neighbor interactions. As long as the number of (too attractive) one-center and direct-neighbor interactions on the one side and (too repulsive) second-neighbor interactions on the other side are in balance, the errors may largely cancel each other; however, when one of them dominates, this balance is lost. For example, the latter dominate in highly branched systems whose stability is underestimated (e.g. neopentane, too unstable by 15.7 kcal/mol in MNDO). In symmetrical clusters [54] one can no longer differentiate between "bonded" and "nonbonded" interactions, and neglect of the orthogonalization corrections may then lead to an underestimation of the steric strain in clusters and small rings (e.g. cubane, too stable by 49.6 kcal/mol in MNDO).

It should be emphasized that the examples discussed in this section are not artefacts of the specific pseudopotential used here. The same effects, such as a positive ${}^{\lambda}H_{AB}$, Eq. (45), are also found at the ab initio level in the corresponding Löwdin orthogonalized core Hamiltonian matrix elements. This has, for example, been shown by effective valence Hamiltonian calculations [55].

3.3 Quantitative analysis of the three-center terms

The total energetic contribution of the three-center pseudopotential terms is given by

$$E_{\mathrm{ORT}} = \sum_{\mu}\sum_{\lambda} P_{\mu\lambda} \sum_{C} V_{\mu\lambda,C}(\mathrm{ORT}) \ . \qquad (47)$$

To gain further insight, it is of interest to evaluate this quantity and to study its specific influence on relative energies, for example, in the case of conformers or constitutional isomers. For this purpose, we have chosen two very small model systems (H_3^- and H_4) where an energy partitioning is still transparent enough to allow meaningful conclusions to be drawn. Since it is well known that the results from energy partitioning can depend critically on the geometry, even in a qualitative sense, we have kept all geometrical parameters fixed except for the one being studied (angle in H_3^- and dihedral angle in H_4). At a given geometry and for a given theoretical approach, the density matrix elements entering Eq. (47) have been determined from an SCF calculation. They vary only very slightly between different calculations (e.g. with or without pseudopotential terms) so that changes in E_{ORT} are generally caused by different pseudopotential terms (and not by different density matrices).

In the OM2 implementation [32] the two terms in Eq. (42) are weighted by prefactors (G_1^{AB}, G_2^{AB}), which are calculated as arithmetic means of atomic parameters. These in turn are adjusted in the semiempirical parameterization,

$$G_1^{AB} = \tfrac{1}{2}(G_1^{A} + G_1^{B}) \qquad (48)$$

$$G_2^{AB} = \tfrac{1}{2}(G_2^{A} + G_2^{B}) \ . \qquad (49)$$

The pseudopotential thus takes the following form,

$$
\begin{aligned}
V_{\mu\lambda,C}(\mathrm{ORT}) = &-\frac{1}{2}G_1^{AB}\sum_{\rho\epsilon C}(S_{\mu\rho}\beta_{\rho\lambda} + \beta_{\mu\rho}S_{\rho\lambda}) \\
&+ \frac{1}{8}G_2^{AB}\sum_{\rho\epsilon C}S_{\mu\rho}S_{\rho\lambda}(H_{\mu\mu} + H_{\lambda\lambda} - 2H_{\rho\rho}) \ . \qquad (50)
\end{aligned}
$$

The optimized OM2 prefactors for hydrogen are $G_1^{H} = 0.652716$ and $G_2^{H} = 0.908437$. For the sake of comparison, results are also reported with full orthogonalization corrections ($G_1^{H} = G_2^{H} = 1$, "OM2*") and without three-center orthogonalization corrections ($G_1^{\mathrm{H}} = G_2^{\mathrm{H}} = 0$, "OM2**"). For the chosen model systems, the second term in Eq. (50) vanishes.

3.3.1 H_3^-: bent versus linear

Qualitative MO schemes show that closed-shell repulsions are smaller in aromatic than in nonaromatic systems [56]. One may expect that they are largest in antiaromatic systems. The smallest antiaromatic system, the cyclic H_3^- ion (D_{3h}), has one bonding MO and two singly-occupied degenerate antibonding MOs. This configuration is unstable, and the system alleviates electronic strain by adopting the linear configuration instead in which the MOs are nondegenerate and the HOMO is nonbonding, so that the system is nonaromatic.

To quantify how far the new correction terms reproduce the closed-shell repulsions, the energy of the H_3^- ion was determined by closed-shell SCF calculations at four different bond angles, with fixed H—H bond lengths of 1.1 Å (Table 1). The minimum angle was chosen to be 90°, since a closed-shell treatment would be inappropriate at 60° (D_{3h} symmetry, degenerate MOs). Ab initio calculations at the restricted Hartree–Fork (RHF)/6-31G** level are used as the reference. They yield an energy difference of 66.6 kcal/mol between the favored linear and the bent 90° configuration. The corresponding MNDO value of 33.6 kcal/mol is much smaller, which is not surprising since MNDO does not account for the orthogonalization effects explicitly. Consistent with this interpretation, OM2 yields a similar value of 36.2 kcal/mol when neglecting the three-center pseudopotential contributions (OM2**), which increases significantly to 58.5 kcal/mol when these contributions are fully included (OM2*). Hence, in the OM2 framework, almost half of the energy increase is caused by closed-shell repulsion.

The orthogonalization energies, Eq. (47), for OM2, OM2*, and OM2** (zero by definition in the latter case) are listed in Table 2. Their relative values reproduce the corresponding differences of relative energies in Table 1 to within 0.3 kcal/mol. This confirms that these differences are caused almost entirely by the three-center orthogonalization corrections (any deviations from additivity being due to very minor changes in the density matrix).

For a more detailed analysis, Table 3 contains the different matrix elements ${}^{\lambda}H_{\mu\lambda}$ and energetic contributions. The orthogonalization effects on the nonbonded interaction A—B are considered first (cf. case 2 in Fig. 2, rows 1–8 in Table 3). Since the distance between the "perturbing atom" C and atoms A and B is constant at 1.1 Å, the overall correction due to the three-center term $V_{\mathrm{AB,C}}$ is independent of the angle. The energy contribution E_{ORT} due to this correction is negative (OM2 −11.6 kcal/mol, OM2* −18.5 kcal/mol) because of the negative bond order and the positive pseudopotential. Note that the matrix element ${}^{\lambda}H_{\mu\lambda}$ (unlike $\beta_{\mu\lambda}$ or $H_{\mu\lambda}$) can be positive, as, for example, in OM2* for bond angles of 150 and 180°.

Angular-dependent contributions to electronic strain appear in the orthogonalization corrections to the in-

Table 1. Relative energies (kcal/mol) of H_3^- at different bond angles

	180°	150°	120°	90°
RHF/6-31G**	0.0	6.0	25.7	66.6
MNDO	0.0	2.5	11.6	33.6
OM2**	0.0	3.1	14.0	36.2
OM2	0.0	4.3	19.2	50.7
OM2*	0.0	4.9	22.0	58.5

Table 2. Absolute and relative orthogonalization energies, E_{ORT}, (kcal/mol) of H_3^- at different bond angles

	E_{ORT}	$E_{\mathrm{ORT}}^{\mathrm{rel}}$			
	180°	180°	150°	120°	90°
OM2**	0.0	0.0	0.0	0.0	0.0
OM2	−4.3	0.0	1.2	5.4	14.8
OM2*	−7.2	0.0	1.8	8.3	22.7

Table 3. Matrix elements in H_3^- at different bond angles (notation as in Fig. 2, bonds A—C and B—C are equivalent due to symmetry, and values are reported only for A—C)

Interaction	Parameters	Matrix element	180°	150°	120°	90°
A—B	OM2	${}^{\lambda}H_{\mathrm{AB}}$ (eV)	−0.100	−0.203	−0.560	−1.261
		β_{AB} (eV)	−0.710	−0.813	−1.170	−1.871
		$V_{\mathrm{AB,C}}$ (eV)	0.610	0.610	0.610	0.610
		$2P_{\mathrm{AB}} \times V_{\mathrm{AB,C}}$ (kcal/mol)	−11.6	−11.6	−11.6	−11.6
	OM2*	${}^{\lambda}H_{\mathrm{AB}}$ (eV)	0.225	0.121	−0.146	−0.936
		β_{AB} (eV)	−0.710	−0.813	−1.170	−1.871
		$V_{\mathrm{AB,C}}$ (eV)	0.935	0.935	0.935	0.935
		$2P_{\mathrm{AB}} \times V_{\mathrm{AB,C}}$ (kcal/mol)	−18.5	−18.5	−18.5	−18.5
A—C	OM2	${}^{\lambda}H_{\mathrm{AC}}$ (eV)	−2.672	−2.654	−2.588	−2.442
		β_{AC} (eV)	−2.786	−2.786	−2.786	−2.786
		$V_{\mathrm{AC,B}}$ (eV)	0.114	0.132	0.198	0.344
		$4P_{\mathrm{AC}} \times V_{\mathrm{AC,B}}$ (kcal/mol)	7.3	8.5	12.7	22.1
	OM2*	${}^{\lambda}H_{\mathrm{AC}}$ (eV)	−2.611	−2.583	−2.483	−2.260
		β_{AC} (eV)	−2.786	−2.786	−2.786	−2.786
		$V_{\mathrm{AC,B}}$ (eV)	0.175	0.203	0.303	0.526
		$4P_{\mathrm{AC}} \times V_{\mathrm{AC,B}}$ (kcal/mol)	11.3	13.1	19.6	34.0

teractions in the bonds A—C and B—C (cf. case 1 in Fig. 2; the bonds A—C and B—C are equivalent due to symmetry; therefore values in Table 3 are reported only for A—C in rows 9—16). Now the resonance integrals remain constant at −2.786 eV, due to the fixed bond lengths A—C and B—C. However, for either interaction, the presence of the third atom induces a repulsive correction to the resonance integral; the correction increases upon lowering the angle from 180 to 90° (OM2 from 0.114 to 0.334 eV, OM2* from 0.175 to 0.526 eV). Multiplying with the corresponding (positive) density matrix elements yields repulsive orthogonalization corrections. Note that the prefactor in these products is not 2 (symmetric matrices) but 4, because there are two equivalent bonds: A—C and B—C. The overall energy contribution due to these angular-dependent orthogonalization corrections to both bonds increase significantly between 180 and 90° (OM2 from 7.3 to 22.1 kcal/mol, OM2* from 11.3 to 34.0 kcal/mol). They are responsible for the correct description of electronic strain in the bent and therefore antiaromatic geometries of the H_3^- ion. They are absent in MNDO and OM2**, which therefore underestimate the antiaromatic destabilization in the bent structures.

3.3.2 H_4: rotational barriers

As a second example we discuss H_4, which has been suggested as a model system to understand the origin of rotational barriers [57, 58]. Two conformations are relevant where the dihedral angle H1—H2 ··· H3—H4 is either 180° (trans, C_{2h}) or 0° (cis, C_{2v}). The H—H and H ··· H distances are fixed at 0.8 and 1.0 Å, respectively, and the two HHH angles at 109.5°. The ab initio RHF/6-31G** reference calculation predicts the cis isomer to be 32.7 kcal/mol higher in energy (Table 4). The established semiempirical methods find differences between 12.9 (PM3) and 15.1 (AM1) kcal/mol, i.e. only about half of the reference value, which invites the assumption that the other half is due to closed-shell repulsions. This is supported by the OM2 results (Table 4): the computed energy differences increase from 14.1 kcal/mol in OM2** (no three-center orthogonalization corrections) to 33.5 kcal/mol in OM2* (full inclusion of the corrections), the latter value being very close to the reference value. Here again, the corrections are approximately additive.

A detailed analysis [32] yields analogous conclusions as in the first example, and is therefore only summarized here (Table 5). The three-center pseudopotential terms do not discriminate between the two conformations with regard to the interactions H1—H4 and H2—H3 because of the fixed bond lengths and angles. Conformation-dependent differences are found for the orthogonalization corrections to the interactions H1—H2 and H1—H3. Because of a very small corresponding density matrix element, the total energy is not changed much by the latter. The correction for the former is due to the pseudopotentials arising from atoms H3 and H4: $V_{12,3}$ is independent of the conformation because of the fixed bond distances and angles, whereas $V_{12,4}$ is the decisive and dihedral-dependent pseudopotential, which causes an additional destabilization of the cis isomer by $\Delta E_{\mathrm{ORT}} = 14.3$ kcal/mol.

Table 4. Relative energies and orthogonalization energies (kcal/mol) of trans H_4 and cis H_4

	ΔE	$E_{\mathrm{ORT}}^{\mathrm{rel}}$
RHF/6-31G**	32.7	
MNDO	14.9	
OM2**	14.1	0.0
OM2	26.5	12.8
OM2*	33.5	20.3

Table 5. OM2 matrix elements in trans H_4 and cis H_4

Interaction	Matrix element	trans H_4	cis H_4	ΔE_{ORT}
H1—H2	${}^{\lambda}H_{12}$ (eV)	−2.603	−2.461	
	β_{12} (eV)	−3.109	−3.109	
	$V_{12,3} + V_{12,4}$ (eV)	0.506	0.648	
	$4P_{12} \times \sum_{\mathrm{C}} V_{12,\mathrm{C}}$ (kcal/mol)	44.7	59.0	14.3
H1—H3	${}^{\lambda}H_{13}$ (eV)	−0.966	−0.655	
	β_{13} (eV)	−2.046	−2.046	
	$V_{13,2} + V_{13,4}$ (eV)	1.080	1.391	
	$4P_{13} \times \sum_{\mathrm{C}} V_{13,\mathrm{C}}$ (kcal/mol)	1.7	0.2	−1.5

The numerical results from both examples indicate that the absolute orthogonalization corrections to first-neighbor interactions (case 1) are larger than those to second-neighbor interactions (case 2). In addition, the latter appear to be rather invariant with respect to structural or conformational changes. By contrast, the corrections to first-neighbor interactions are quite sensitive to small changes in the molecular environment, such as variations in bond angles (e.g. H_3^-) or dihedral angles (e.g. H_4).

4 Orthogonalization corrections for core-valence interactions

4.1 Derivation

Core electrons are not treated explicitly in semiempirical or ab initio pseudopotential calculations. In these approaches, it is commonly assumed that each core electron reduces the effective nuclear charge by 1, to account for the overall screening of the nuclear charge. However, there are additional effects that need to be considered [28, 29]:

1. The orthogonality between core and valence orbitals required by the Pauli principle.
2. The polarization of the core electrons by the valence electrons.
3. The Coulomb and exchange interactions between core and valence electrons, as given by the HF potential.

According to pseudopotential theory, these effects can be simulated by one-electron integrals, commonly referred to as ECPs. The analysis of these interactions at the ab initio level has shown that the orthogonalization effects dominate by far the net Coulomb, exchange, and polarization effects [28, 29]. For semiempirical approaches, it would therefore seem justified to include only the dominant terms due to core–valence orthogonalization, which provide an effective repulsive potential acting on the valence electrons.

For deriving the corresponding corrections, the symmetric Löwdin orthogonalization is not appropriate because the core functions are not part of the actual basis. We therefore use the Schmidt procedure to orthogonalize the valence functions, μ, with respect to the (only hypothetically present) core functions, α. This yields modified AOs, $\tilde{\mu}$,

$$\tilde{\mu} = \mu - \sum_{\alpha} S_{\mu\alpha}\alpha \ , \tag{51}$$

whose overlap with the core functions vanishes,

$$\langle\tilde{\mu}|\alpha\rangle = 0 \quad \text{for all } \alpha \ . \tag{52}$$

The complete Fock matrix is taken into account during core–valence orthogonalization [59]. To develop a pseudopotential for the transformation $F_{\mu\nu} \rightarrow \tilde{F}_{\mu\nu}$, we follow the method of Manne [60] and expand $\tilde{F}_{\mu\nu}$ by using Eq. (51),

$$\begin{aligned}\tilde{F}_{\mu\nu} &= \langle\tilde{\mu}|F|\tilde{\nu}\rangle \\ &= \langle\mu - \sum_{\alpha} S_{\mu\alpha}\alpha|F|\nu - \sum_{\beta} S_{\nu\beta}\beta\rangle \\ &= F_{\mu\nu} - \sum_{\alpha} S_{\mu\alpha}F_{\alpha\nu} - \sum_{\beta} F_{\mu\beta}S_{\beta\nu} + \sum_{\alpha,\beta} S_{\mu\alpha}S_{\beta\nu}F_{\alpha\beta} \\ &= F_{\mu\nu} - \sum_{\alpha}\left[S_{\mu\alpha}(F_{\alpha\nu} - S_{\alpha\nu}F_{\alpha\alpha}) + (F_{\mu\alpha} - S_{\mu\alpha}F_{\alpha\alpha})S_{\alpha\nu}\right] \\ &\qquad - \sum_{\alpha} S_{\mu\alpha}S_{\alpha\nu}F_{\alpha\alpha} + \sum_{\alpha\neq\beta} S_{\mu\alpha}S_{\beta\nu}F_{\alpha\beta} \ ,\end{aligned} \tag{53}$$

where we have rearranged terms in the last step to introduce a quantity

$$G_{\mu\alpha} = F_{\mu\alpha} - S_{\mu\alpha}F_{\alpha\alpha} \ , \tag{54}$$

which formally resembles the Mulliken function (Eq. 18) and approximates the Fock matrix element between a Schmidt orthogonalized valence and a core orbital,

$$\begin{aligned}\langle\tilde{\mu}|F|\alpha\rangle &= \langle\mu - \sum_{\beta} S_{\mu\beta}\beta|F|\alpha\rangle \\ &= F_{\mu\alpha} - S_{\mu\alpha}F_{\alpha\alpha} - \sum_{\beta\neq\alpha} S_{\mu\beta}F_{\alpha\beta} \ .\end{aligned} \tag{55}$$

Neglecting core–core overlap as in ab initio ECP theory [28, 29] yields

$$F_{\alpha\beta} \approx 0 \tag{56}$$

$$\langle\tilde{\mu}|F|\alpha\rangle \simeq G_{\mu\alpha} \ . \tag{57}$$

Introducing Eqs. (54) and (56) into Eq. (53) leads to

$$\tilde{F}_{\mu\nu} = F_{\mu\nu} + \sum_{\mathrm{B}} V_{\mu\nu,\mathrm{B}}(\mathrm{ECP}) \tag{58}$$

$$\begin{aligned}V_{\mu\nu,\mathrm{B}}(\mathrm{ECP}) = &- \sum_{\alpha}^{\mathrm{B}}(S_{\mu\alpha}G_{\alpha\nu} + G_{\mu\alpha}S_{\alpha\nu}) \\ &- \sum_{\alpha}^{\mathrm{B}} S_{\mu\alpha}S_{\alpha\nu}F_{\alpha\alpha} \ ,\end{aligned} \tag{59}$$

where the orthogonalization correction is expressed as the sum of atomic pseudopotentials $V_{\mu\nu,\mathrm{B}}(\mathrm{ECP})$, arising from the core orbitals at a given center B. In the case of first-row elements the core contains only the 1*s* orbital, and Eq. (59) reduces to

$$V_{\mu\nu,\mathrm{B}}(\mathrm{ECP}) = -(S_{\mu\alpha}G_{\alpha\nu} + G_{\mu\alpha}S_{\alpha\nu}) - S_{\mu\alpha}S_{\alpha\nu}F_{\alpha\alpha} \ . \tag{60}$$

To our knowledge, this pseudopotential has never been used before in practical calculations. Zerner [59] has derived a similar potential, which can be obtained from Eq. (60) by assuming

$$G_{\mu\alpha}^{\mathrm{Zerner}} = 0 \tag{61}$$

$$V_{\mu\nu,\mathrm{B}}^{\mathrm{Zerner}}(\mathrm{ECP}) = - S_{\mu\alpha}S_{\alpha\nu}F_{\alpha\alpha} \ . \tag{62}$$

This ECP has been incorporated into two semiempirical methods [25, 31].

4.2 Implementation

In line with the standard semiempirical assumptions for one-electron integrals, we only consider one- and two-center terms in Eq. (58). The one-center contributions (μ and ν at center A, and B = A) need not be computed explicitly since they are part of the one-center energies and thus are implicitly adjusted during the parameterization. We shall therefore focus on the two-center terms, $V_{\mu\nu,\mathrm{B}}(\mathrm{ECP})$ (μ and ν at center A, and B different from A). Their direct evaluation via Eq. (60) would in principle require an a priori all-electron SCF calculation to yield the Fock matrix for the quantities $F_{\alpha\alpha}$ and $G_{\mu\alpha}$. The latter depends on the nature of atoms A and B and on their distance. According to Eq. (54) it contains a core–valence overlap integral, $S_{\mu\alpha}$, which is independent of the remainder of the molecule, and the quantities $F_{\alpha\alpha}$ and $F_{\mu\alpha}$.

We have carried out a number of ab initio SCF calculations with a minimal basis set (STO-3G) to study the behavior of all these matrix elements in different molecules and for different geometries [32]. We draw the following conclusions from these calculations:

1. $F_{\alpha\alpha}$ is generally only weakly sensitive to both molecular environment and geometry and can therefore be treated as an adjustable atomic parameter, as suggested previously [59].
2. $G_{\mu\alpha}$ is surprisingly well transferable between different molecular environments.
3. $G_{\mu\alpha}$ is not negligible; the corresponding first term in the pseudopotential, Eq. (60), is normally smaller than the second one, but may become of similar magnitude or even larger in certain cases.

Plots of $G_{\mu\alpha}$ as a function of the distance A–B [32] indicate that $G_{\mu\alpha}$ indeed resembles a Mulliken function or a resonance integral in OAO basis, with regard to its distance dependence. We have therefore decided to adopt the empirical expression for the resonance integrals, Eq. (27), analogously also for this term,

$$G_{\mu\alpha} = \tfrac{1}{2}(\beta_{\mu}^{\mathrm{A}} + \beta_{\alpha}^{\mathrm{B}})\sqrt{R_{\mathrm{AB}}}\exp\left[-(\alpha_{\mu}^{\mathrm{A}} + \alpha_{\alpha}^{\mathrm{B}})R_{\mathrm{AB}}^{2}\right] \ . \tag{63}$$

This introduces two atomic parameters for each core orbital, for example, β_{1s} und α_{1s} for a 1*s* core orbital. In addition, $F_{\alpha\alpha}$ is needed in Eq. (60), as well as the core orbital exponent (to calculate the core–valence overlap integrals). Hence, the present implementation of the proposed semiempirical ECP requires four adjustable parameters for each first-row element.

Using the optimized OM2 parameters [32], we have plotted the semiempirical ECPs, Eq. (60), as well as the two contributing terms in Eq. (60), and compared them against the corresponding ab initio ECPs, which have been evaluated analytically in the same basis [61] and scaled subsequently according to Klopman–Ohno to be consistent with the treatment of the other two-center terms in OM2. Inspection of the corresponding figures indicates similar qualitative behavior of the semiempirical and the ab initio ECPs [32]. For the C—C pair, the ECPs are negligibly small beyond a distance of 2 Å so that the two-center ECP corrections are important only for chemically bonded atoms; the ECPs are steeply rising repulsive functions around the equilibrium distance and become very large for short (chemically irrelevant) distances below 1 Å. Quantitative agreement between the semiempirical and the ab initio ECPs cannot be expected (due to the parameterization of the former), but it is found that both ECPs are usually of comparable magnitude (not only for the various AO combinations of C—C, but also for O—O). Concerning the separation of the semiempirical ECPs into the two contributing terms, Eq. (60), the first term (involving $G_{\mu\alpha}$) is smaller than the second one for C—C (amounting typically to only 20%), particularly for small distances; it becomes relatively more important for larger distances, and also for O—O [32].

5 Summary

In this paper we have derived and discussed two new one-electron orthogonalization corrections for semiempirical methods. The first one accounts for valence-shell orthogonalization effects on the resonance integrals, while the second one includes the dominant repulsive core–valence interactions through an ECP.

The neglect of valence-shell orthogonalization in established semiempirical methods, such as MNDO, AM1, and PM3, is responsible for some of their most severe deficiencies, for example, with regard to conformational properties or the underestimation of closed-shell repulsions. The proposed orthogonalization corrections for the resonance integrals consist of three-center terms which incorporate stereodiscriminating properties into the two-center matrix elements of the core Hamiltonian. By accounting for the molecular environment, these corrections allow the conformational preferences to be better described; this has been analyzed in some detail for small model systems.

Both corrections have been implemented and parameterized in the framework of a new general-purpose semiempirical method called OM2 [32]. A full description of OM2 with a comprehensive evaluation of the results will be published elsewhere; a brief statistical assessment for heats of formation is already available [10].

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