Neglect of Diatomic Differential Overlap (NDDO) in Non-Empirical Quantum Chemical Orbital Theories

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Z. Naturforsch. **48a,** 819–828 (1993); received March 23, 1993

The possibility of a drastic reduction of electron repulsion and nuclear attraction integral evaluations occurring in non-empirical quantum chemical orbital methods of Hartree-Fock and configuration interaction type is discussed. Simplification schemes are proposed and examined in consideration of useful numerical applications.

Key words: Neglect of diatomic differential overlap; Symmetric Löwdin orthogonalization; Mulliken approximation; Ruedenberg approximation; Slater-type atomic orbital basis sets.

1. Introduction

In order to extend the applicability of non-empirical quantum chemical methods expanding delocalized orbitals of molecules and stereoregular crystals as a linear combination of atomic basis functions, we revive a discussion mainly held in the sixties and seventies about the possibility of neglecting small integral values occurring in numerical calculations of electronic states and their energies with only little loss of accuracy [1].

Within the Born-Oppenheimer picture of fixed nuclear positions any procedure of such kind is based on the evaluation of four different types of integrals over some finite number N_o of *atomic orbitals* $\{\phi_\mu(\boldsymbol{r}-\boldsymbol{R}_M)\,|\,M=1,2,\ldots,N_a;\,\mu\in M\}$ localized at N_a atomic centers [2]. Here, $\boldsymbol{r}$ is the vector of the electronic coordinates (x, y, z), and $\boldsymbol{R}_M$ denotes the position vector of atom M to which all orbitals with index μ belong (notation: $\mu \in M$). For convenience, all these atomic orbitals are taken to be real.

Overlap integrals

$$^{\phi}S_{\mu\nu} = \int \mathrm{d}\boldsymbol{r}\,\phi_\mu(\boldsymbol{r}-\boldsymbol{R}_M)\,\phi_\nu(\boldsymbol{r}-\boldsymbol{R}_N)\,, \qquad (1)$$
$$M, N = 1, 2, \ldots, N_a, \quad \mu\in M, \quad \nu\in N,$$

kinetic energy integrals

$$^{\phi}K_{\mu\nu} = -\tfrac{1}{2}\int \mathrm{d}\boldsymbol{r}\,\phi_\mu(\boldsymbol{r}-\boldsymbol{R}_M)\,[\Delta(\boldsymbol{r})\,\phi_\nu(\boldsymbol{r}-\boldsymbol{R}_N)]\,, \qquad (2)$$
$$M, N = 1, 2, \ldots, N_a, \quad \mu\in M, \quad \nu\in N,$$

with $\Delta(\boldsymbol{r}) = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$, the Laplacian operator in cartesian coordinates, and *nuclear attraction integrals*

$$^{\phi}V_{\mu\nu}(A) = -Z_A\int \mathrm{d}\boldsymbol{r}\,\phi_\mu(\boldsymbol{r}-\boldsymbol{R}_M)\,|\boldsymbol{r}-\boldsymbol{R}_A|^{-1}\,\phi_\nu(\boldsymbol{r}-\boldsymbol{R}_N), \qquad (3)$$
$$M, N, A = 1, 2, \ldots, N_a, \quad \mu\in M, \quad \nu\in N,$$

with Z_A the atomic number of nucleus A, depend on the coordinates of one electron, only.

Using the chemists' (11|22) notation, two-electron *repulsion integrals* read as follows:

$$(\phi_\mu\phi_\nu|\phi_\varrho\phi_\sigma) = \iint \mathrm{d}\boldsymbol{r}_1\,\mathrm{d}\boldsymbol{r}_2\,\phi_\mu(\boldsymbol{r}_1-\boldsymbol{R}_M)\,\phi_\nu(\boldsymbol{r}_1-\boldsymbol{R}_N) \qquad (4)$$
$$\cdot\,|\boldsymbol{r}_1-\boldsymbol{r}_2|^{-1}\,\phi_\varrho(\boldsymbol{r}_2-\boldsymbol{R}_R)\,\phi_\sigma(\boldsymbol{r}_2-\boldsymbol{R}_S),$$
$$M, N, R, S = 1, 2, \ldots, N_a; \quad \mu\in M; \quad \nu\in N; \quad \varrho\in R; \quad \sigma\in S.$$

Like in (1), (2), and (3), the orbital basis is indicated by a left-side superscript throughout in this paper.

2. Neglect of Diatomic Differential Overlap (NDDO)

The most sophisticated *neglect of differential overlap* (NDO) method commonly used is NDDO (*neglect of diatomic differential overlap*) [3], where the differential overlap $\phi_\mu\,\phi_\nu\,\mathrm{d}\boldsymbol{r}$ of two basis functions $\phi_\mu(\boldsymbol{r}-\boldsymbol{R}_M)$ and

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$\phi_\nu(\boldsymbol{r}-\boldsymbol{R}_N)$ centered on different nuclei is taken to be zero. In particular, the number of non-zero two-electron repulsion integrals of order N_o^4 will now be drastically reduced:

$$(\phi_{\mu\in M}\,\phi_{\nu\in N}\,|\,\phi_{\varrho\in R}\,\phi_{\sigma\in S}) := \delta_{MN}\,\delta_{RS}(\phi_{\mu\in M}\,\phi_{\nu\in M}\,|\,\phi_{\varrho\in R}\,\phi_{\sigma\in R}), \quad M, N, R, S = 1, 2, \ldots, N_a\,. \tag{5}$$

Note that repulsive three- and four-center interactions vanish completely. Application of the NDDO scheme on the one-electron attraction integrals of order $N_o^2\,N_a$ will lead (among others) to the neglect of all attractive three-center interactions:

$$^{\phi}V_{\mu\in M\,\nu\in N}(A) := \delta_{MN}\,{}^{\phi}V_{\mu\in M\,\nu\in M}(A), \quad M, N, A = 1, 2, \ldots, N_a\,. \tag{6}$$

In contrast to the CNDO scheme (*complete neglect of differential overlap*) [3], which cannot adequately differentiate between the interactions of two electrons with parallel and antiparallel spins, NDDO is also appropriate for the *unrestricted Hartree-Fock* treatment (UHF) of open-shell systems [2, 3]. Moreover, since the surviving integrals depend only on the nature of the atoms to which the orbitals belong and not on the orbital type, they all are invariant with respect to rotations of the coordinate system [3].

It turns out, however, that the application of NDDO is particularly well suited for symmetrically (Löwdin-)orthogonalized [2] sets of basis functions $\{\lambda_\mu(\boldsymbol{r})\,|\,\mu=1, 2, \ldots, N_o\}$ defined through

$$\lambda_\mu(\boldsymbol{r}) = \sum_{M'}^{N_a} \sum_{\mu'\in M'} {}^{\phi}X_{\mu'\mu}\,\phi_{\mu'}(\boldsymbol{r}-\boldsymbol{R}_{M'})\,, \tag{7}$$

where

$$^{\phi}\mathbf{X} \equiv {}^{\phi}\mathbf{S}^{-\frac{1}{2}} \equiv {}^{\phi}\mathbf{X}^{\dagger} \tag{8}$$

with the property [2]

$$^{\phi}\mathbf{X}^{\dagger}\,{}^{\phi}\mathbf{S}\,{}^{\phi}\mathbf{X} \equiv {}^{\phi}\mathbf{S}^{-\frac{1}{2}}\,{}^{\phi}\mathbf{S}\,{}^{\phi}\mathbf{S}^{-\frac{1}{2}} = {}^{\phi}\mathbf{S}^{-\frac{1}{2}}\,{}^{\phi}\mathbf{S}^{+\frac{1}{2}} = \mathbf{1} \equiv {}^{\lambda}\mathbf{S}\,. \tag{9}$$

Mainly two paths lead to some justification of the NDDO approximation:

- The second order binomial expansion of the symmetrically orthogonalizing (Löwdin) matrix $^{\phi}\mathbf{S}^{-\frac{1}{2}}$ [4] or related approaches [5] and
- the Ruedenberg expansion technique [6] starting from complete basis sets on each atom [7].

A brief survey of all attempts to rationalize the NDDO scheme (together with some critical re-examinations) can be found in Chandler's and Grader's paper [5]. Because of the convergent nature of their expansion method, these authors also claim the formal correctness of their analysis. Assuming an atomic orbital ϕ-basis which is already *locally orthogonalized on each center*, they conclude, similarly to the earlier work of Brown and Roby on this subject [4]:

1. Sums of kinetic energy and all corresponding nuclear attraction energy integrals over atomic orbitals of the original (ϕ-)basis cannot be identified in their entirety with those of the symmetrically orthogonalized (Löwdin) basis. In our notation:

$$^{\lambda}K_{\mu\nu} + \sum_{A}^{N_a} {}^{\lambda}V_{\mu\nu}(A) \not\approx {}^{\phi}K_{\mu\nu} + \sum_{A}^{N_a} {}^{\phi}V_{\mu\nu}(A), \quad M, N = 1, 2, \ldots, N_a, \quad \mu\in M; \quad \nu\in N. \tag{10}$$

2. Concerning the evaluation of electron repulsion integrals, the NDDO approximation has some justification within the λ-basis [8]:

$$(\lambda_{\mu\in M}\,\lambda_{\nu\in N}\,|\,\lambda_{\varrho\in R}\,\lambda_{\sigma\in S}) \approx \delta_{MN}\,\delta_{RS}(\lambda_{\mu\in M}\,\lambda_{\nu\in M}\,|\,\lambda_{\varrho\in R}\,\lambda_{\sigma\in R}), \quad M, N, R, S = 1, 2, \ldots, N_a\,. \tag{11}$$

Exceptions of this statement may arise for three-center integrals involving interactions between a one-center distribution and a two-center distribution.

3. Furthermore, surviving non-zero repulsion integrals over the symmetrically orthogonal λ-basis orbitals can be roughly identified with those of the atomic ϕ-basis:

$$(\lambda_\mu\,\lambda_\nu\,|\,\lambda_\varrho\,\lambda_\sigma) \approx (\phi_\mu\,\phi_\nu\,|\,\phi_\varrho\,\phi_\sigma)\,, \quad \begin{matrix} M, R = 1, 2, \ldots, N_a, \\ \mu, \nu\in M;\ \varrho, \sigma\in R. \end{matrix} \tag{12}$$

Some kinds of one- and two-center repulsion integrals, however, may fail to satisfy (12) to the desired degree of accuracy. Such discrepancies from the general rule gave rise to the introduction of corresponding scaling factors which were expected to the better determined by a careful analysis [5] rather than by comparison with some selected ab-initio results [10].

3. Simplified Integral Evaluation

Referring in parts to the results of the analysis summarized above, we are now in a position to sketch a conceptionally simple integral approximation scheme:

As long as integral evaluations can be performed only for a given set of atomic (ϕ-basis) orbitals but not directly within the λ-basis we cannot profit from result (11) alone, since the full integral transformation of non-zero NDDO-surviving λ-basis repulsion integrals according to

$$(\lambda_\mu \lambda_\nu | \lambda_\varrho \lambda_\sigma) \tag{13}$$
$$= \sum_{M',N',R',S'}^{N_a} \sum_{\substack{\mu' \in M' \\ \nu' \in N' \\ \varrho' \in R' \\ \sigma' \in S'}} {}^\phi X_{\mu'\mu} {}^\phi X_{\nu'\nu} (\phi_{\mu'} \phi_{\nu'} | \phi_{\varrho'} \phi_{\sigma'}) {}^\phi X_{\varrho'\varrho} {}^\phi X_{\sigma'\sigma}, \quad M, R = 1, 2, \ldots, N_a; \quad \mu, \nu \in M; \quad \varrho, \sigma \in R$$

still requires the evaluation of *all* ϕ-basis repulsion integrals.

Using result (12), however, these non-zero NDDO-surviving λ-basis repulsion integrals may be identified directly with those of the ϕ-basis. It is reasonable to assume such an equality to be valid at least for repulsive long-range interactions between two centers M and N with $|\mathbf{R}_M - \mathbf{R}_N| \geq D_r$, specified by a distance parameter D_r.

The simplified repulsion integral set (indicated through a superscript s) over symmetrically orthogonalized orbitals is then obtainable from the corresponding NDDO-surviving ϕ-basis repulsion integral set without performing the full integral transformation (13):

$$(\lambda_\mu \lambda_\nu | \lambda_\varrho \lambda_\sigma)^s := (\phi_\mu \phi_\nu | \phi_\varrho \phi_\sigma), \quad M, R = 1, 2, \ldots, N_a, \quad |\mathbf{R}_M - \mathbf{R}_R| \geq D_r, \quad \mu, \nu \in M; \; \varrho, \sigma \in R. \tag{14}$$

If, however, we assume (12) not to be valid for integrals over orbitals localized at two near-neighbor atoms M and N with $|\mathbf{R}_M - \mathbf{R}_N| < D_r$, an at least approximate integral transformation is unavoidable. The ϕ-basis repulsion integrals of NDDO type then have to be determined implicitly by an approximate expression. Using *Mulliken's approximation* [11] for this purpose in the form

$$\phi_\mu \phi_\nu \, \mathrm{d}\mathbf{r} := \tfrac{1}{2} {}^\phi S_{\mu\nu} (\phi_\mu^2 + \phi_\nu^2) \, \mathrm{d}\mathbf{r}, \quad M, N = 1, 2, \ldots, N_a, \quad M \neq N, \quad \mu \in M; \; \nu \in N \tag{15}$$

we obtain for the simplified short-distance and one-center repulsion integrals

$$\begin{aligned}
(\lambda_\mu \lambda_\nu | \lambda_\varrho \lambda_\sigma)^s := & \sum_{M',R'}^{N_a} \sum_{\substack{\mu',\nu' \in M' \\ \varrho',\sigma' \in R'}} {}^\phi X_{\mu'\mu} {}^\phi X_{\nu'\nu} (\phi_{\mu'} \phi_{\nu'} | \phi_{\varrho'} \phi_{\sigma'}) {}^\phi X_{\varrho'\varrho} {}^\phi X_{\sigma'\sigma} \\
& + \tfrac{1}{2} \sum_{\substack{M',N',R' \\ M' \neq N' \\ |\mathbf{R}_{M'} - \mathbf{R}_{N'}| < D_r}}^{N_a} \sum_{\substack{\mu' \in M' \\ \nu' \in N' \\ \varrho',\sigma' \in R'}} {}^\phi X_{\mu'\mu} {}^\phi X_{\nu'\nu} \{ {}^\phi S_{\mu'\nu'} [(\phi_{\mu'} \phi_{\mu'} | \phi_{\varrho'} \phi_{\sigma'}) + (\phi_{\nu'} \phi_{\nu'} | \phi_{\varrho'} \phi_{\sigma'})] \} {}^\phi X_{\varrho'\varrho} {}^\phi X_{\sigma'\sigma} \\
& + \tfrac{1}{2} \sum_{\substack{M',R',S' \\ R' \neq S' \\ |\mathbf{R}_{R'} - \mathbf{R}_{S'}| < D_r}}^{N_a} \sum_{\substack{\mu',\nu' \in M' \\ \varrho' \in R' \\ \sigma' \in S'}} {}^\phi X_{\mu'\mu} {}^\phi X_{\nu'\nu} \{ {}^\phi S_{\varrho'\sigma'} [(\phi_{\mu'} \phi_{\nu'} | \phi_{\varrho'} \phi_{\varrho'}) + (\phi_{\mu'} \phi_{\nu'} | \phi_{\sigma'} \phi_{\sigma'})] \} {}^\phi X_{\varrho'\varrho} {}^\phi X_{\sigma'\sigma} \\
& + \tfrac{1}{4} \sum_{\substack{M',N',R',S' \\ M' \neq N', R' \neq S' \\ |\mathbf{R}_{M'} - \mathbf{R}_{N'}| < D_r \\ |\mathbf{R}_{R'} - \mathbf{R}_{S'}| < D_r}}^{N_a} \sum_{\substack{\mu' \in M' \\ \nu' \in N' \\ \varrho' \in R' \\ \sigma' \in S'}} {}^\phi X_{\mu'\mu} {}^\phi X_{\nu'\nu} \{ {}^\phi S_{\mu'\nu'} {}^\phi S_{\varrho'\sigma'} [(\phi_{\mu'} \phi_{\mu'} | \phi_{\varrho'} \phi_{\varrho'}) + (\phi_{\nu'} \phi_{\nu'} | \phi_{\varrho'} \phi_{\varrho'}) \\
& \qquad + (\phi_{\mu'} \phi_{\mu'} | \phi_{\sigma'} \phi_{\sigma'}) + (\phi_{\nu'} \phi_{\nu'} | \phi_{\sigma'} \phi_{\sigma'})] \} {}^\phi X_{\varrho'\varrho} {}^\phi X_{\sigma'\sigma}, \\
& M, R = 1, 2, \ldots, N_a, \quad |\mathbf{R}_M - \mathbf{R}_R| < D_r, \quad \mu, \nu \in M; \; \varrho, \sigma \in R.
\end{aligned} \tag{16}$$

An equivalent formula can be developed, using instead of (15) the more expensive *Ruedenberg approximation* [6] in the form

$$\phi_\mu \phi_\nu \, \mathrm{d}\mathbf{r} := \tfrac{1}{2} \left(\sum_{\mu' \in M} {}^\phi S_{\mu'\nu} \phi_{\mu'} \phi_\mu + \sum_{\nu' \in N} {}^\phi S_{\nu'\mu} \phi_{\nu'} \phi_\nu \right) \mathrm{d}\mathbf{r}, \quad M, N = 1, 2, \ldots, N_a, \quad M \neq N, \quad \mu \in M; \; \nu \in N. \tag{17}$$

Similarly to the ideas of Brown, Burdon, and Williams [12] we then get

$$(\lambda_\mu \lambda_\nu | \lambda_\varrho \lambda_\sigma)^s := \sum_{M',R'}^{N_a} \sum_{\substack{\mu',\nu' \in M' \\ \varrho',\sigma' \in R'}} {}^\phi X_{\mu'\mu} {}^\phi X_{\nu'\nu} (\phi_{\mu'} \phi_{\nu'} | \phi_{\varrho'} \phi_{\sigma'}) {}^\phi X_{\varrho'\varrho} {}^\phi X_{\sigma'\sigma}$$

$$
\begin{aligned}
&+\tfrac{1}{2}\sum_{\substack{M',N',R'\\ M'\neq N'\\ |\boldsymbol{R}_{M'}-\boldsymbol{R}_{N'}|<D_r}}^{N_a}\ \sum_{\substack{\mu'\in M'\\ \nu'\in N'\\ \varrho',\sigma'\in R'}} {}^{\phi}X_{\mu'\mu}\,{}^{\phi}X_{\nu'\nu}\Big\{\sum_{\mu''\in M'}{}^{\phi}S_{\mu''\nu'}(\phi_{\mu''}\phi_{\mu''}|\phi_{\varrho'}\phi_{\sigma'})+\sum_{\nu''\in N'}{}^{\phi}S_{\nu''\mu'}(\phi_{\nu''}\phi_{\nu''}|\phi_{\varrho'}\phi_{\sigma'})\Big\}\,{}^{\phi}X_{\varrho'\varrho}\,{}^{\phi}X_{\sigma'\sigma}\\
&+\tfrac{1}{2}\sum_{\substack{M',R',S'\\ R'\neq S'\\ |\boldsymbol{R}_{R'}-\boldsymbol{R}_{S'}|<D_r}}^{N_a}\ \sum_{\substack{\mu',\nu'\in M'\\ \varrho'\in R'\\ \sigma'\in S'}} {}^{\phi}X_{\mu'\mu}\,{}^{\phi}X_{\nu'\nu}\Big\{\sum_{\varrho''\in R'}{}^{\phi}S_{\varrho''\sigma'}(\phi_{\mu'}\phi_{\nu'}|\phi_{\varrho''}\phi_{\varrho''})+\sum_{\sigma''\in S'}{}^{\phi}S_{\sigma''\varrho'}(\phi_{\mu'}\phi_{\nu'}|\phi_{\sigma''}\phi_{\sigma''})\Big\}\,{}^{\phi}X_{\varrho'\varrho}\,{}^{\phi}X_{\sigma'\sigma}\\
&+\tfrac{1}{4}\sum_{\substack{M',N',R',S'\\ M'\neq N',\,R'\neq S'\\ |\boldsymbol{R}_{M'}-\boldsymbol{R}_{N'}|<D_r\\ |\boldsymbol{R}_{R'}-\boldsymbol{R}_{S'}|<D_r}}^{N_a}\ \sum_{\substack{\mu'\in M'\\ \nu'\in N'\\ \varrho'\in R'\\ \sigma'\in S'}} {}^{\phi}X_{\mu'\mu}\,{}^{\phi}X_{\nu'\nu}\Big\{\sum_{\mu''\in M'}{}^{\phi}S_{\mu''\nu'}\Big[\sum_{\varrho''\in R'}{}^{\phi}S_{\varrho''\sigma'}(\phi_{\mu''}\phi_{\mu''}|\phi_{\varrho''}\phi_{\varrho''})+\sum_{\sigma''\in S'}{}^{\phi}S_{\sigma''\varrho'}(\phi_{\mu''}\phi_{\mu''}|\phi_{\sigma''}\phi_{\sigma''})\Big]\\
&\qquad+\sum_{\nu''\in N'}{}^{\phi}S_{\nu''\mu'}\Big[\sum_{\varrho''\in R'}{}^{\phi}S_{\varrho''\sigma'}(\phi_{\nu''}\phi_{\nu''}|\phi_{\varrho''}\phi_{\varrho''})+\sum_{\sigma''\in S'}{}^{\phi}S_{\sigma''\varrho'}(\phi_{\nu''}\phi_{\nu''}|\phi_{\sigma''}\phi_{\sigma''})\Big]\Big\}\,{}^{\phi}X_{\varrho'\varrho}\,{}^{\phi}X_{\sigma'\sigma}\,,\\
&\qquad M,R=1,2,\dots,N_a,\quad |\boldsymbol{R}_M-\boldsymbol{R}_R|<D_r,\quad \mu,\nu\in M;\quad \varrho,\sigma\in R.
\end{aligned}
\tag{18}
$$

The distance parameter D_r in (14), (16) and (18) controls the level of sophistication. A big D_r implies that the simplified transformation includes even small long-range interaction. If, on the other hand, D_r is chosen to be zero, then the simple equality (14) will be applied to repulsive short-range and one-center interactions as well, instead of (16) or (18). A practical choice of D_r will ensure that the transformations (16) or (18) will be performed only for NDDO-surviving integrals over next-neighbor atomic orbitals, thereby taking only next-neighbor interactions with considerable overlap into account.

According to the result (10), on the other hand, the kinetic matrix ${}^{\phi}\mathbf{K}$ as well as the attraction matrices $\{{}^{\phi}\mathbf{V}(A)\,|\,A=1,2,\dots,N_a\}$ have to be transformed accurately into the symmetrically orthogonalized basis

$$
{}^{\lambda}\mathbf{K}={}^{\phi}\mathbf{X}^{\dagger}\,{}^{\phi}\mathbf{K}\,{}^{\phi}\mathbf{X}\,,
\tag{19}
$$

$$
{}^{\lambda}\mathbf{V}(A)={}^{\phi}\mathbf{X}^{\dagger}\,{}^{\phi}\mathbf{V}(A)\,{}^{\phi}\mathbf{X},\quad A=1,2,\dots,N_a\,.
\tag{20}
$$

However, in order to compensate the effect of neglecting repulsive contributions and to get rid of all three-center one-electron integrals too, we introduce equivalent simplifying assumptions (again indicated through a superscript *s*) concerning the evaluation of nuclear attraction integrals. Again using Mulliken's approximation, we obtain

$$
\begin{aligned}
{}^{\lambda}V^{s}_{\mu\nu}(A):=\sum_{M'}^{N_a}\ \sum_{\mu',\nu'\in M'}{}^{\phi}X_{\mu'\mu}\,{}^{\phi}V_{\mu'\nu'}(A)\,{}^{\phi}X_{\nu'\nu}+\tfrac{1}{2}\sum_{\substack{M',N'\\ M'\neq N'\\ |\boldsymbol{R}_{M'}-\boldsymbol{R}_{N'}|<D_a}}^{N_a}\ \sum_{\substack{\mu'\in M'\\ \nu'\in N'}}{}^{\phi}X_{\mu'\mu}\,\{{}^{\phi}S_{\mu'\nu'}\,[{}^{\phi}V_{\mu'\mu'}(A)\;+{}^{\phi}V_{\nu'\nu'}(A)]\}\,{}^{\phi}X_{\nu'\nu}\,,\\
M,A=1,2,\dots,N_a,\quad |\boldsymbol{R}_M-\boldsymbol{R}_A|<D_a,\quad \mu,\nu\in M\,.
\end{aligned}
\tag{21}
$$

Using Ruedenberg's approximation, instead we get

$$
\begin{aligned}
{}^{\lambda}V^{s}_{\mu\nu}(A):=&\sum_{M'}^{N_a}\ \sum_{\mu',\nu'\in M'}{}^{\phi}X_{\mu'\mu}\,{}^{\phi}V_{\mu'\nu'}(A)\,{}^{\phi}X_{\nu'\nu}\\
&+\tfrac{1}{2}\sum_{\substack{M',N'\\ M'\neq N'\\ |\boldsymbol{R}_{M'}-\boldsymbol{R}_{N'}|<D_a}}^{N_a}\ \sum_{\substack{\mu'\in M'\\ \nu'\in N'}}{}^{\phi}X_{\mu'\mu}\Big\{\sum_{\mu''\in M'}{}^{\phi}S_{\mu''\nu'}\,{}^{\phi}V_{\mu''\mu'}(A)+\sum_{\nu''\in N'}{}^{\phi}S_{\nu''\mu'}\,{}^{\phi}V_{\nu''\nu'}(A)\Big\}\,{}^{\phi}X_{\nu'\nu}\,,\\
&M,A=1,2,\dots,N_a,\quad |\boldsymbol{R}_M-\boldsymbol{R}_A|<D_a,\quad \mu,\nu\in M.
\end{aligned}
\tag{22}
$$

Again, the distance parameter D_a for attractive interactions defines the environment in which ϕ-basis orbitals are expected to overlap considerably. In all other cases, the much simpler following equality will be used:

$$
{}^{\lambda}V^{s}_{\mu\nu}(A):={}^{\phi}V_{\mu\nu}(A),\quad M,A=1,2,\dots,N_a,\quad |\boldsymbol{R}_M-\boldsymbol{R}_A|\geq D_a,\quad \mu,\nu\in M.
\tag{23}
$$

4. Atomic Orbital Bases

We consider a *real all-electron minimal basis set of atomic Slater-type orbitals* $\{\phi_j(n, l, |m|, \zeta) \mid j = 1, 2, \dots, N_o\}$ [13] each characterized by the three quantum numbers n, l, and m, and the orbital exponent ζ. Since, according to the equations of the preceding paragraph, only one-center and two-center integrals have to be evaluated, a basis set of atomic Slater-type orbitals (STO) seems to be more adequate than an equivalent contracted set of Gaussian-type orbitals (GTO) (cf. [2]):

- In contrast to Gaussian functions, orbitals of Slater type show a qualitatively correct shape in the vicinity of their atomic centers as well as far away from them.
- We cannot profit by the main advantage of Gaussian functions, namely that evaluations of three- and four-center integrals can be reduced to calculations of one- and two-center integrals only.

An all-electron basis set is considered in order to keep our approach conceptionally simple. In this case, no further assumptions, like the frozen-core approximation, have to be made. In particular, such an approach seems to be justified for the second period elements Li, Be, B, C, N, O, and F, where only one 1s Slater-type orbital per atom has to be handled additionally.

Within an ordinary all-electron minimal basis set of Slater type not all atomic orbitals are orthogonal to one another [13]. Since a contamination of inner shell orbitals by admixtures of valence orbitals "has a disastrous effect on the energy" [10] in simplified quantum chemical calculations a locally orthogonal atomic orbital basis of Slater type may be preferable, such that atomic orbitals of higher principal quantum numbers are successively orthogonalized against their next inner shells by means of the Schmidt procedure [14]. Alternatively, symmetrically orthogonalized atomic orbitals can be used, available through N_a local Löwdin orthogonalizations [2].

By inspection of (14), (16), (18), and (21), (22), (23) it becomes apparent that no approximations at all will be introduced into the evaluation of one-center integrals whenever a locally orthogonalized atomic orbital basis is used. Consequently, the described simplifications then have no effect in any quantum chemical orbital method applied on atoms.

Because the integrals needed in any simplified procedure originally have to be evaluated within a basis of ordinary Slater-type orbitals (χ-basis), the use of an all-electron basis set of orthogonalized atomic Slater-type orbitals (ϕ-basis) requires local transformations of all χ-basis orbitals belonging to the same atom. The square $N_o \times N_o$ transformation matrix ${}^{\chi}\mathbf{L}$ which performs such local orthogonalizations has only few nonzero elements. It attains a block-diagonal form whenever a suitable orbital sequence has been chosen. The overlap integrals ${}^{\phi}S_{\mu\nu}$ of the orthogonalized ϕ-basis then are obtainable from those of the ordinary Slater-type χ-basis through

$$ {}^{\phi}S_{\mu\nu} = \sum_{\substack{\mu' \in M \\ \nu' \in N}} {}^{\chi}L_{\mu'\mu}\, {}^{\chi}S_{\mu'\nu'}\, {}^{\chi}L_{\nu'\nu}, \qquad M, N = 1, 2, \dots N_a, \quad \mu \in M;\ \nu \in N. \tag{24} $$

Equivalent formulas hold for the kinetic energy integrals ${}^{\phi}K_{\mu\nu}$ and the surviving nuclear attraction integrals ${}^{\phi}V_{\mu\nu}(A)$:

$$ {}^{\phi}K_{\mu\nu} = \sum_{\substack{\mu' \in M \\ \nu' \in N}} {}^{\chi}L_{\mu'\mu}\, {}^{\chi}K_{\mu'\nu'}\, {}^{\chi}L_{\nu'\nu}, \qquad M, N = 1, 2, \dots N_a, \quad \mu \in M;\ \nu \in N. \tag{25} $$

$$ {}^{\phi}V_{\mu\nu}(A) = \sum_{\mu', \nu' \in M} {}^{\chi}L_{\mu'\mu}\, {}^{\chi}V_{\mu'\nu'}(A)\, {}^{\chi}L_{\nu'\nu}, \qquad M, A = 1, 2, \dots N_a, \quad \mu, \nu \in M. \tag{26} $$

The surviving repulsion integrals of the ϕ-basis are obtainable through

$$ (\phi_\mu \phi_\nu | \phi_\varrho \phi_\sigma) = \sum_{\substack{\mu', \nu' \in M \\ \varrho', \sigma' \in R}} {}^{\chi}L_{\mu'\mu}\, {}^{\chi}L_{\nu'\nu} (\chi_{\mu'} \chi_{\nu'} | \chi_{\varrho'} \chi_{\sigma'})\, {}^{\chi}L_{\varrho'\varrho}\, {}^{\chi}L_{\sigma'\sigma}, \qquad M, R = 1, 2, \dots, N_a, \quad \mu, \nu \in M;\ \varrho, \sigma \in R. \tag{27} $$

The matrix ${}^{\chi}\mathbf{L}$ is available from ${}^{\chi}\mathbf{S}$ by the standard numerical Schmidt [14] or Löwdin procedure [2], respectively. It should be stressed, that the transformation (27) is only feasible at moderate expense, because the transformation matrix ${}^{\chi}\mathbf{L}$ is sufficiently sparse. Of course, an application of the original (in parts non-orthogonal) Slater-type atomic orbital set does not require any local transformation at all, i.e. ${}^{\chi}\mathbf{L} = \mathbf{1}$ in this case.

5. Practical Considerations

For the determination of integral values over ordinary (χ-basis) atomic orbitals of Slater type needed in our simplified approach we make use of the FORTRAN program DIATOM [15] available at QCPE

[16], which produces all non-redundant one-center and two-center integrals using different local coordinate systems for different pairs of atoms [17]. The transformation of these diatomic integrals into the global coordinate system is described in [18]. Subsequently the χ-basis diatomic integrals have to be locally orthogonalized by means of the Schmidt or Löwdin procedure [14, 2] (cf. (24), (25), (26), and (27)).

The (global) symmetrical (Löwdin) orthogonalization will be performed as follows [2]: Diagonalization of the positive definite overlap matrix ${}^{\phi}\mathbf{S}$ by means of standard numerical algorithms [20]

$$ {}^{\phi}\mathbf{U}^{\dagger}\,{}^{\phi}\mathbf{S}\,{}^{\phi}\mathbf{U} = \mathbf{s} \tag{28} $$

yields an orthogonal (column-)eigenvector matrix ${}^{\phi}\mathbf{U}$ as well as the corresponding diagonal matrix $\mathbf{s}$ of positive eigenvalues. By taking the inverse square root of each eigenvalue in $\mathbf{s}$ we get the diagonal matrix $\mathbf{s}^{-\frac{1}{2}}$ that can be "undiagonalized", whereby we finally obtain the desired ${}^{\phi}\mathbf{S}^{-\frac{1}{2}}$ matrix

$$ {}^{\phi}\mathbf{S}^{-\frac{1}{2}} = {}^{\phi}\mathbf{U}\,\mathbf{s}^{-\frac{1}{2}}\,{}^{\phi}\mathbf{U}^{\dagger}. \tag{29} $$

Local Löwdin orthogonalizations will only include the orbitals of each center separately.

6. Illustrative Examples

In order to gain some insight into the nature of the integral approximations of Section 3, and to illustrate what can be expected from them, we first list all non-redundant ϕ-basis repulsion and attraction integral values occurring in a minimal basis set description of the hydrogen molecule with one 1s atomic orbital ($\zeta = 1.2$) centered on each of both nuclei. The experimental equilibrium bond length used as fixed interatomic distance R is 0.742 Å (1.402 a.u.) [21]. Local orthogonalizations are inapplicable in this case, and there is no difference between Mulliken's and Ruedenberg's approximation. The only overlap integral value then is $S_{12} = S_{21} = 0.674$.

Though an explicit four-index transformation of all ϕ-basis repulsion integrals into the λ-basis according to (13) is self-prohibitory in general, it may be quite instructive to see the effect of symmetrical orthogonalization on the integral values of interest in the special case of our minimal basis H_2 example with only 16 repulsion integrals. Furthermore, a back-transformation of the simplified λ-basis repulsion integrals into the original ϕ-basis through

$$ (\phi_\mu \phi_\nu | \phi_\varrho \phi_\sigma)^s = \sum_{\mu', \nu', \varrho', \sigma'}^{N_o} {}^{\phi}S^{+\frac{1}{2}}_{\mu'\mu}\,{}^{\phi}S^{+\frac{1}{2}}_{\nu'\nu}\,(\lambda_{\mu'} \lambda_{\nu'} | \lambda_{\varrho'} \lambda_{\sigma'})^s\,{}^{\phi}S^{+\frac{1}{2}}_{\varrho'\varrho}\,{}^{\phi}S^{+\frac{1}{2}}_{\sigma'\sigma} \tag{30} $$

$$ \mu, \nu, \varrho, \sigma = 1, 2, \ldots, N_o $$

promises additional information about the validity of (14), (16), and (18)

Table 1 a. Non-redundant ϕ-basis repulsion integrals [22].

μ ν ϱ σ	$(\phi_\mu \phi_\nu \| \phi_\varrho \phi_\sigma)$	$(\phi_\mu \phi_\nu \| \phi_\varrho \phi_\sigma)^s$ $D_r = 0$	$(\phi_\mu \phi_\nu \| \phi_\varrho \phi_\sigma)^s$ $D_r > R$ using (16) or (18)
1 1 1 1	0.750	0.707	0.750
1 1 1 2	0.442	0.441	0.441
1 2 1 2	0.302	0.298	0.298
1 1 2 2	0.560	0.603	0.560

Table 1 b. Non-redundant λ-basis repulsion integrals.

μ ν ϱ σ	$(\lambda_\mu \lambda_\nu \| \lambda_\varrho \lambda_\sigma)$	$(\lambda_\mu \lambda_\nu \| \lambda_\varrho \lambda_\sigma)^s$ $D_r = 0$	$(\lambda_\mu \lambda_\nu \| \lambda_\varrho \lambda_\sigma)^s$ $D_r > R$ using (16) or (18)
1 1 1 1	0.832	0.750	0.829
1 1 1 2	−0.006	0.000	0.000
1 2 1 2	0.011	0.000	0.000
1 1 2 2	0.483	0.560	0.480

From Tables 1a and 1b we can see that in our example all neglected λ-basis repulsion integrals are indeed much smaller than corresponding ϕ-basis integral values. The assumption (11) may be justified here. The inseparably related assumption (12), on the other hand, seems to be less justified if D_r is chosen to be 0, but can be greatly improved by taking any $D_r > R$ instead [22].

Similar observations concerning the validity of equivalent assumption for the attraction integrals can be made from Tables 2a and 2b, where

$$ {}^{\phi}\mathbf{V}^s(A) = {}^{\phi}\mathbf{S}^{+\frac{1}{2}\,\lambda}\mathbf{V}^s(A)\,{}^{\phi}\mathbf{S}^{+\frac{1}{2}}, \quad A = 1, 2, \ldots, N_a. \tag{31} $$

The list of kinetic energy integrals in Table 3, however, shows that there is no way to apply the NDDO approximation scheme here. Fortunately, these few integrals are easy to evaluate, so that their exact transformation according to (19) causes no problems.

Although the full transformation (13) of ϕ-basis repulsion integrals into the λ-basis should be excluded in general, it may be carried out for a few simple cases of diatomic molecules, where all integral values over

Table 2a. Non-redundant ϕ-basis attraction integrals [23].

μ ν A	${}^{\phi}V_{\mu\nu}(A)$	${}^{\phi}V^{s}_{\mu\nu}(A)$ $D_a=0$	${}^{\phi}V^{s}_{\mu\nu}(A)$ $D_a>R$ using (21) or (22)
1 1 1	−1.200	−1.128	−1.200
1 2 1	−0.598	−0.623	−0.623
2 2 1	−0.647	−0.719	−0.647

Table 2b. Non-redundant λ-basis attraction integrals.

μ ν A	${}^{\lambda}V_{\mu\nu}(A)$	${}^{\lambda}V^{s}_{\mu\nu}(A)$ $D_a=0$	${}^{\lambda}V^{s}_{\mu\nu}(A)$ $D_a>R$ using (21) or (22)
1 1 1	−1.328	−1.200	−1.298
1 2 1	−0.044	0.000	0.000
2 2 1	−0.579	−0.647	−0.549

Table 3. Non-redundant kinetic energy integrals.

μ ν	${}^{\phi}K_{\mu\nu}$	${}^{\lambda}K_{\mu\nu}$
1 1	0.720	1.032
1 2	0.233	−0.463

Table 4. Total orbitals numbers N_o and interatomic distances R [21].

Molecule	N_o	R (Å)	R (a.u.)
H_2	2	0.742	1.402
LiH	3	1.595	3.014
HF	6	0.917	1.733
LiF	7	1.510	2.853
BeO	7	1.331	2.515
BN	10	1.281	2.421
CO	10	1.128	2.132
N_2	10	1.094	2.067
O_2	10	1.207	2.281
F_2	10	1.435	2.712

Table 5. Slater orbital exponents [24].

Atom	ζ_{1s}	ζ_{2s}	ζ_{2p}
H	1.20000		
Li	2.69063	0.63961	
Be	3.68478	0.95603	
B	4.67939	1.28808	1.21066
C	5.67263	1.60833	1.56788
N	6.66507	1.92368	1.91703
O	7.65781	2.24588	2.22662
F	8.65007	2.56387	2.54997

Slater-type atomic orbitals are easily obtainable. As a criterion for the validity of our simplifications, in Tables 6a, 6b, 6c and 7a, 7b, 7c we list the quadratic means ${}^{\phi}\sigma_r$, ${}^{\lambda}\sigma_r$, ${}^{\phi}\sigma_a$, and ${}^{\lambda}\sigma_a$ for three sets of simplified repulsion and attraction integral differences from the corresponding true integrals values:

$$ {}^{\phi}\sigma_r = \left[\frac{1}{N_o^4}\sum_{\mu,\nu,\varrho,\sigma}^{N_o}\left((\phi_\mu\phi_\nu|\phi_\varrho\phi_\sigma)^s-(\phi_\mu\phi_\nu|\phi_\varrho\phi_\sigma)\right)^2\right]^{1/2}, \qquad (32) $$

$$ {}^{\lambda}\sigma_r = \left[\frac{1}{N_o^4}\sum_{\mu,\nu,\varrho,\sigma}^{N_o}\left((\lambda_\mu\lambda_\nu|\lambda_\varrho\lambda_\sigma)^s-(\lambda_\mu\lambda_\nu|\lambda_\varrho\lambda_\sigma)\right)^2\right]^{1/2}, \qquad (33) $$

$$ {}^{\phi}\sigma_a = \left[\frac{1}{N_o^2 N_a}\sum_{A}^{N_a}\sum_{\mu,\nu}^{N_o}\left({}^{\phi}V^s_{\mu\nu}(A)-{}^{\phi}V_{\mu\nu}(A)\right)^2\right]^{1/2}, \qquad (34) $$

$$ {}^{\lambda}\sigma_a = \left[\frac{1}{N_o^2 N_a}\sum_{A}^{N_a}\sum_{\mu,\nu}^{N_o}\left({}^{\lambda}V^s_{\mu\nu}(A)-{}^{\lambda}V_{\mu\nu}(A)\right)^2\right]^{1/2}, \qquad (35) $$

Total numbers N_o of atomic basis functions, interatomic distances R in Å and atomic units (a.u.), and Slater orbital exponents ζ can be taken from Tables 4 and 5, respectively.
From inspection of Tables 6a–c and 7a–c we conclude:

- Repulsion integral evaluations in general can be simplified with higher fidelity than nuclear attraction integrals.
- Identical results will be obtained for any locally orthogonalized basis set if $0 \leqq \{D_r, D_a\} \leqq R$.
- With the exception of the H_2 molecule, there are no improvements to be expected from choosing $D_r > 0$ and $D_a > 0$, whenever locally orthogonalized basis sets are used.
- Best results will be obtained with ordinary (in parts non-orthogonal) Slater-type atomic orbitals, choosing $D_r > R$ and $D_a > R$ and using Mulliken's approximation. Only in this case extensions of D_r and D_a yield considerable improvements. Compared to locally orthogonalized basis set results with $D_r = 0$ and $D_a = 0$, however, these improvements may be regarded as negligible (again with the exception of the H_2 molecule).

As a quintessence of our study we state: With the simple distance parameter choice $D_r = D_a = 0$ and locally orthogonalized basis sets we hope to obtain an acceptable agreement between simplied repulsion and attraction integrals and their corresponding true values.

7. Summary

The main features of the proposed simplified integral evaluation procedure are:

Table 6a. Quadratic means (32) and (33) for simplified atomic Slater-basis repulsion integral sets.

Molecule	${}^{\phi}\sigma_r$ $D_r=0$	${}^{\phi}\sigma_r$ $D_r>0$ $D_r\leqq R$	${}^{\phi}\sigma_r$ $D_r>R$ using (16)	${}^{\phi}\sigma_r$ $D_r>R$ using (18)	${}^{\lambda}\sigma_r$ $D_r=0$	${}^{\lambda}\sigma_r$ $D_r>0$ $D_r\leqq R$	${}^{\lambda}\sigma_r$ $D_r>R$ using (16)	${}^{\lambda}\sigma_r$ $D_r>R$ using (18)
H_2	0.022	0.622	0.002	0.002	0.040	0.546	0.007	0.007
LiH	0.043	0.031	0.006	0.013	0.040	0.031	0.006	0.009
HF	0.062	0.053	0.010	0.060	0.056	0.050	0.011	0.050
LiF	0.046	0.009	0.004	0.008	0.041	0.009	0.005	0.007
BeO	0.042	0.017	0.005	0.020	0.038	0.016	0.006	0.016
BN	0.020	0.121	0.031	0.141	0.020	0.101	0.022	0.110
CO	0.025	0.113	0.031	0.132	0.024	0.096	0.022	0.106
N_2	0.025	0.178	0.050	0.208	0.024	0.145	0.032	0.157
O_2	0.028	0.033	0.009	0.046	0.025	0.029	0.008	0.039
F_2	0.032	0.008	0.002	0.007	0.028	0.007	0.002	0.007

Table 6b. Quadratic means (32) and (33) for simplified atomic Schmidt-basis repulsion integral sets.

Molecule	${}^{\phi}\sigma_r$ $D_r=0$	${}^{\phi}\sigma_r$ $D_r>0$ $D_r\leqq R$	${}^{\phi}\sigma_r$ $D_r>R$ using (16)	${}^{\phi}\sigma_r$ $D_r>R$ using (18)	${}^{\lambda}\sigma_r$ $D_r=0$	${}^{\lambda}\sigma_r$ $D_r>0$ $D_r\leqq R$	${}^{\lambda}\sigma_r$ $D_r>R$ using (16)	${}^{\lambda}\sigma_r$ $D_r>R$ using (18)
H_2	0.022	0.622	0.002	0.002	0.040	0.546	0.007	0.007
LiH	0.009	0.027	0.008	0.015	0.010	0.029	0.008	0.012
HF	0.012	0.051	0.013	0.063	0.014	0.050	0.014	0.056
LiF	0.005	0.006	0.005	0.009	0.006	0.007	0.006	0.008
BeO	0.007	0.013	0.007	0.022	0.008	0.015	0.008	0.019
BN	0.006	0.117	0.031	0.163	0.009	0.101	0.022	0.126
CO	0.007	0.110	0.031	0.150	0.010	0.096	0.023	0.120
N_2	0.007	0.174	0.050	0.247	0.011	0.145	0.032	0.184
O_2	0.005	0.031	0.010	0.049	0.007	0.029	0.009	0.043
F_2	0.003	0.005	0.003	0.007	0.003	0.004	0.003	0.007

Table 6c. Quadratic means (32) and (33) for simplified atomic Löwdin-basis repulsion integral sets.

Molecule	${}^{\phi}\sigma_r$ $D_r=0$	${}^{\phi}\sigma_r$ $D_r>0$ $D_r\leqq R$	${}^{\phi}\sigma_r$ $D_r>R$ using (16)	${}^{\phi}\sigma_r$ $D_r>R$ using (18)	${}^{\lambda}\sigma_r$ $D_r=0$	${}^{\lambda}\sigma_r$ $D_r>0$ $D_r\leqq R$	${}^{\lambda}\sigma_r$ $D_r>R$ using (16)	${}^{\lambda}\sigma_r$ $D_r>R$ using (18)
H_2	0.022	0.622	0.002	0.002	0.040	0.546	0.007	0.007
LiH	0.009	0.027	0.007	0.011	0.010	0.029	0.008	0.009
HF	0.012	0.051	0.012	0.049	0.014	0.050	0.014	0.043
LiF	0.005	0.006	0.005	0.007	0.006	0.007	0.006	0.007
BeO	0.007	0.013	0.007	0.016	0.008	0.015	0.008	0.014
BN	0.006	0.117	0.031	0.122	0.009	0.101	0.023	0.097
CO	0.007	0.110	0.031	0.115	0.010	0.096	0.023	0.094
N_2	0.007	0.174	0.050	0.179	0.011	0.145	0.033	0.139
O_2	0.005	0.031	0.009	0.040	0.007	0.029	0.009	0.036
F_2	0.003	0.005	0.003	0.006	0.003	0.004	0.003	0.006

- The approximation scheme is completely non-empirical, retaining the rotational invariance property.
- Application of the NDDO approximation is considered for the evaluation of repulsion and attraction integrals only.
- All complicated three-center and four-center integrals vanish completely. The number of integrals to be calculated and stored is drastically reduced.
- Non-vanishing long-range repulsion and attraction integrals over symmetrically orthogonalized Löwdin orbitals are identified directly with those of the original basis.
- For the evaluation of non-vanishing repulsion and attraction integrals between near neighbors a greatly simplified transformation may be considered, using Mulliken's or alternatively Rueden-

Table 7 a. Quadratic means (34) and (35) for simplified atomic Slater-basis attraction integral sets.

Molecule	${}^{\phi}\sigma_a$ $D_a=0$	${}^{\phi}\sigma_a$ $D_a>0$ $D_a\leqq R$	${}^{\phi}\sigma_a$ $D_a>R$ using (21)	${}^{\phi}\sigma_a$ $D_a>R$ using (22)	${}^{\lambda}\sigma_a$ $D_a=0$	${}^{\lambda}\sigma_a$ $D_a>0$ $D_a\leqq R$	${}^{\lambda}\sigma_a$ $D_a>R$ using (21)	${}^{\lambda}\sigma_a$ $D_a>R$ using (22)
H_2	0.054	0.418	0.017	0.017	0.079	0.373	0.038	0.038
LiH	0.242	0.064	0.021	0.026	0.248	0.062	0.021	0.023
HF	1.751	0.554	0.284	0.359	1.902	0.544	0.283	0.308
LiF	1.523	0.154	0.127	0.134	1.560	0.156	0.120	0.122
BeO	1.188	0.229	0.154	0.178	1.255	0.237	0.149	0.156
BN	0.643	1.017	0.274	0.369	0.821	0.974	0.266	0.285
CO	0.900	1.168	0.327	0.438	1.104	1.106	0.314	0.349
N_2	0.836	1.501	0.366	0.453	1.030	1.402	0.331	0.367
O_2	1.161	0.523	0.207	0.254	1.258	0.478	0.211	0.232
F_2	1.515	0.176	0.102	0.107	1.536	0.169	0.111	0.112

Table 7 b. Quadratic means (34) and (35) for simplified atomic Schmidt-basis attraction integral sets.

Molecule	${}^{\phi}\sigma_a$ $D_a=0$	${}^{\phi}\sigma_a$ $D_a>0$ $D_a\leqq R$	${}^{\phi}\sigma_a$ $D_a>R$ using (21)	${}^{\phi}\sigma_a$ $D_a>R$ using (22)	${}^{\lambda}\sigma_a$ $D_a=0$	${}^{\lambda}\sigma_a$ $D_a>0$ $D_a\leqq R$	${}^{\lambda}\sigma_a$ $D_a>R$ using (21)	${}^{\lambda}\sigma_a$ $D_a>R$ using (22)
H_2	0.054	0.418	0.017	0.017	0.079	0.373	0.038	0.038
LiH	0.036	0.063	0.039	0.033	0.039	0.068	0.037	0.037
HF	0.410	0.671	0.474	0.405	0.515	0.661	0.481	0.494
LiF	0.200	0.208	0.206	0.200	0.210	0.216	0.206	0.208
BeO	0.237	0.281	0.256	0.235	0.266	0.300	0.255	0.260
BN	0.228	1.022	0.357	0.220	0.409	1.013	0.356	0.397
CO	0.295	1.185	0.441	0.288	0.507	1.158	0.443	0.489
N_2	0.263	1.493	0.424	0.250	0.492	1.444	0.426	0.482
O_2	0.265	0.567	0.317	0.263	0.359	0.526	0.325	0.342
F_2	0.158	0.185	0.161	0.157	0.169	0.176	0.165	0.166

Table 7 c. Quadratic means (34) and (35) for simplified atomic Löwdin-basis attraction integral sets.

Molecule	${}^{\phi}\sigma_a$ $D_a=0$	${}^{\phi}\sigma_a$ $D_a>0$ $D_a\leqq R$	${}^{\phi}\sigma_a$ $D_a>R$ using (21)	${}^{\phi}\sigma_a$ $D_a>R$ using (22)	${}^{\lambda}\sigma_a$ $D_a=0$	${}^{\lambda}\sigma_a$ $D_a>0$ $D_a\leqq R$	${}^{\lambda}\sigma_a$ $D_a>R$ using (21)	${}^{\lambda}\sigma_a$ $D_a>R$ using (22)
H_2	0.054	0.418	0.017	0.017	0.079	0.373	0.038	0.038
LiH	0.036	0.063	0.034	0.033	0.039	0.068	0.037	0.037
HF	0.410	0.671	0.419	0.405	0.515	0.661	0.484	0.494
LiF	0.200	0.208	0.201	0.200	0.210	0.216	0.207	0.208
BeO	0.237	0.281	0.238	0.235	0.266	0.300	0.258	0.260
BN	0.228	1.022	0.297	0.220	0.409	1.013	0.390	0.397
CO	0.295	1.185	0.370	0.288	0.507	1.158	0.475	0.489
N_2	0.263	1.493	0.381	0.250	0.492	1.444	0.472	0.482
O_2	0.265	0.567	0.284	0.263	0.359	0.526	0.331	0.342
F_2	0.158	0.185	0.158	0.157	0.169	0.176	0.165	0.166

berg's approximation to represent all those integral values which have not been evaluated explicitly. It turns out, however, that for these integrals a direct identification of λ- with ϕ-basis values is quite justifiable.

- All remaining one- and two-center one-electron and two-electron integrals can be easily evaluated within an all-electron basis set of ordinary Slater-type atomic orbitals, possibly followed by local orthogonalizations.
- Using different orbitals for different spins (DODS), the simplified integral evaluation scheme is also appropriate for the treatment of open shells.

Acknowledgement

The author is grateful to his colleagues Dr. D. Hoffmann, K. Neymeyr, and K. Strecker for many discussions and much help as well as to Prof. F. F. Seelig for his kind support.

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[17] Actually, since the DIATOM program produces integrals over complex STO which for some repulsion integrals may be different from equivalent ones over real STO [18], we immediately form appropriate linear combinations of the repulsion integrals over complex STO in order to get equivalent integral values for real STO [19]. Furthermore, since DIATOM avoids a multiple evaluation of symmetry-related integrals, a couple of symmetry equivalences of repulsion integrals [18] have to be taken into account within the diatomic coordinate system.

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[23] Note the coincidenc of ${}^{\phi}V_{11}^{s}(1)$ with ${}^{\phi}V_{11}(1)$ and of ${}^{\phi}V_{22}^{s}(1)$ with ${}^{\phi}V_{22}(1)$ for $D_a > R$ in our simple minimal basis H_2 example.

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