"Neglect of Diatomic Differential Overlap" in Nonempirical Quantum Chemical Orbital Theories. I. On the Justification of the Neglect of Diatomic Differential Overlap Approximation

KLAUS NEYMEYR AND FRIEDRICH FRANZ SEELIG

Institut für Physikalische und Theoretische Chemie der Universität Tübingen, Auf der Morgenstelle 8, D-72076 Tübingen, Germany

Received March 18, 1994; revised manuscript received June 23, 1994; accepted July 6, 1994

ABSTRACT

A short review of the different approaches to the justification of the Neglect of Diatomic Differential Overlap in the basis of symmetrically orthogonalized basis functions is given. Brown and Roby employed the binomial expansion for the approximation of the inverse square root of the overlap matrix. For some overlap matrices, this expansion does not converge. The always-convergent power series given by Chandler and Grader provides a worse second-order approximation in comparison with the second-order binomial expansion. © 1995 John Wiley & Sons, Inc.

Introduction

The often-cited so-called "computational bottleneck" in quantum chemistry describes the problem of calculation, storing, and processing the $O(N^4)$ electron repulsion integrals that arise in ab initio quantum chemical calculations with N basis functions.

There are basically two strategies of solution of this problem: Recently discussed developments, which are implemented in the direct-SCF method, make use of the fact that the number of "important" integrals, which exceed a small threshold, is proportional to $N^2 \ln N$ [1,2]. Such an upper bound is given, for instance, by the Cauchy–Schwarz inequality by interpreting the two-electron integral as a scalar product on the linear space of charge distributions. These approximative methods can be characterized by an *adaptive* algorithm, i.e., integrals will not be neglected a priori but in the course of the computation depending on the absolute value of these integrals or on an upper bound, respectively.

International Journal of Quantum Chemistry, Vol. 53, 515–518 (1995)

CCC 0020-7608/95/050515-04

In contrast to that, a great number of approaches for neglecting a specific part of a priori-specified two-electron integrals have been given in quantum chemistry. These algorithms must be distinguished from the first stream because they are based upon a *structural* criterion. All types of neglected integrals are a priori-fixed. Most of these proposals are applied in semiempirical calculation methods. Exact upper bounds for the error introduced by the neglect of repulsion integrals are often unavailable; consequently, the reliability of these methods is only restricted.

In this series of articles, it will be investigated whether the Neglect of Diatomic Differential Overlap (NDDO) method belonging to the second class of algorithms neglects only unimportant integrals. Several attempts have been made to justify the Neglect of Differential Overlap (NDO) approximation in a basis of symmetrically (Löwdin) orthogonalized functions [3–7]. The most favorable case of this class is that of NDDO, which can be described by assuming disjoint supports for functions that are localized at different centers:

$$\mu_A(\mathbf{r})\nu_B(\mathbf{r}) \approx 0 \qquad \text{for } A \neq B .$$

The basis function (orbital) μ_A is localized at atom A and ν_B is localized at atom B. The NDDO approximation is usually applied to two-electron integrals:

$$(\mu_A\nu_B \mid \kappa_C\sigma_D) \approx 0 \qquad \text{for } A \neq B \text{ or } C \neq D ,$$

where the integral is given by

$$\begin{aligned}(\mu_A\nu_B \mid \kappa_C\sigma_D) = \iint d\mathbf{r}_1 d\mathbf{r}_2 \mu^*(\mathbf{r}_1 - \mathbf{R}_A) \\ \times \nu(\mathbf{r}_1 - \mathbf{R}_B)\,|\mathbf{r}_1 - \mathbf{r}_2|^{-1} \\ \times \kappa^*(\mathbf{r}_2 - \mathbf{R}_C)\sigma(\mathbf{r}_2 - \mathbf{R}_D) .\end{aligned}$$

In the past, it was shown that the symmetrically orthogonalized (Löwdin) basis is appropriate for the application of NDDO.

THE LÖWDIN BASIS

Let $(\phi_1, \ldots, \phi_N)$ be the row vector of a normalized, linearly independent set of N localized real basis functions (atomic orbitals) and define the overlap matrix Δ:

$$\Delta = \int d\mathbf{r}\,(\phi_1, \ldots, \phi_N)^t(\phi_1, \ldots, \phi_N)$$

(t denotes the transpose) with matrix elements

$$\begin{aligned}\Delta_{\mu\nu} &:= (\phi_{\mu_A} \mid \phi_{\nu_B}) \\ &= \int d\mathbf{r}\,\phi_\mu(\mathbf{r} - \mathbf{R}_A)\phi_\nu(\mathbf{r} - \mathbf{R}_B) ,\end{aligned}$$

where $\mathbf{R}_A$ is the position vector of atom A and μ_A is localized at atom A. Δ is a positive definite and symmetric matrix. We will assume later that this set of functions is locally orthogonalized, i.e., local orthogonality is assumed at each atomic center, confer [4]. For the present, we make no use of this property.

This set of functions can be transformed to the symmetrically orthogonalized basis by

$$(\lambda_1, \ldots, \lambda_N) = (\phi_1, \ldots, \phi_N)\Delta^{-1/2} .$$

These functions are orthonormal because

$$\begin{aligned}(\lambda_i \mid \lambda_j) &= \sum_{k=1}^{N}\sum_{l=1}^{N}(\Delta^{-1/2})_{ik}(\phi_k \mid \phi_l)(\Delta^{-1/2})_{lj} \\ &= (\Delta^{-1/2}\Delta\Delta^{-1/2})_{ij} = \delta_{ij} .\end{aligned}$$

The matrix representation of a one-electron operator over the Löwdin basis reads

$$^{\lambda}\mathbf{M} = \Delta^{-1/2}\,{}^{\phi}\mathbf{M}\Delta^{-1/2} . \tag{1}$$

The left superscript λ denotes the Löwdin basis; analogously, ϕ indicates that the matrix elements are calculated in the ϕ-basis.

The charge density matrix Ω in the ϕ-basis $(\phi_i)_{i=1,\ldots,N}$,

$$\Omega := (\phi_1, \ldots, \phi_N)^t(\phi_1, \ldots, \phi_N) , \tag{2}$$

transforms like one-electron operators into the Löwdin basis:

$$^{\lambda}\Omega = \Delta^{-1/2}\Omega\Delta^{-1/2} . \tag{3}$$

Thus, the repulsion integrals are given by

$$\begin{aligned}{}^{\lambda}(\mu\nu \mid \kappa\sigma) &= ({}^{\lambda}\Omega_{\mu\nu}(1) \mid {}^{\lambda}\Omega_{\kappa\sigma}(2)) \\ &= \iint d\mathbf{r}_1 d\mathbf{r}_2\, {}^{\lambda}\Omega_{\mu\nu}(1) \\ &\quad \times |\mathbf{r}_1 - \mathbf{r}_2|^{-1}\, {}^{\lambda}\Omega_{\kappa\sigma}(2) .\end{aligned} \tag{4}$$

Justification of NDDO by Polynomial Expansions of $\Delta^{-1/2}$

In the following articles, only justifications of NDDO employing a polynomial expansion for the

approximation of $\Delta^{-1/2}$ will be investigated. An expansion in $\mathbf{S} = \Delta - \mathbf{I}$ ($\mathbf{I}$ is the identity matrix) was given by Brown and Roby [3]. This expansion was revised by Chandler and Grader [4]. There, they also briefly reviewed the different approaches to the justification of NDDO. Here, Roby's approach [8] using a complete set of basis functions on each atom will not be treated further, because the assumption of completeness is an extremely crude approximation, especially for the justification of minimal basis-set calculations.

THE S-EXPANSION TECHNIQUE

For an analytical study of the transformation of one-electron operators (1) and of the repulsion integrals (4), Brown and Roby [3] represented the matrix function $\Delta^{-1/2}$ by the binomial expansion, truncated to the first or to the second order:

$$\Delta^{-1/2} = (\mathbf{I} + \mathbf{S})^{-1/2} = \sum_{i=0}^{\infty} \frac{(-1)^i (2i)!}{2^{2i}(i!)^2} \mathbf{S}^i$$

$$= \underbrace{\mathbf{I} - \frac{1}{2}\mathbf{S} + \frac{3}{8}\mathbf{S}^2}_{\Delta_{BR}^{-1/2}} + O(\mathbf{S}^3). \qquad (5)$$

This power series converges under the precondition

$$\sigma(\mathbf{S}) \subset]-1, 1[$$

to the spectrum of S. Brown and Roby disregarded this precondition. This was criticized by Gray and Stone [9], who gave the example of the overlap matrix of the methane molecule with S having an eigenvalue of about 1.38417. The results of Brown and Roby concerning the justification of NDDO were revised by Chandler and Grader, [4] who gave a formally convergent power series expansion.

THE P-EXPANSION TECHNIQUE

For the matrix P given by Chandler and Grader,

$$\mathbf{P} = \frac{1}{1 + x}(\mathbf{S} - x\mathbf{I}),$$

with

$$x = \frac{\max|\sigma(\mathbf{S})| + \min \sigma(\mathbf{S})}{2}.$$

$\sigma(\mathbf{P}) \subset]-1, 1[$ holds and thus the binomial expansion in P converges:

$$\Delta^{-1/2} = \left(\frac{1}{1 + x}\right)^{1/2} (\mathbf{I} + \mathbf{P})^{-1/2}$$

$$= \left(\frac{1}{1 + x}\right)^{1/2} \left[\mathbf{I} - \frac{1}{2}\mathbf{P} + \frac{3}{8}\mathbf{P}^2 + O(\mathbf{P}^3)\right].$$

By transformation of one-electron integrals following (1) and electron repulsion integrals according to (4) to the second order in P, Chandler and Grader showed that

- Matrix elements of one-electron operators (core integrals) cannot be neglected.
- NDDO can only be justified for selected types of the repulsion integrals (cf. [4]).

But Chandler and Grader's approach can also be criticized: In the second article of this series, it will be shown that a polynomial expansion in P to the second degree,

$$\Delta_{CG}^{-1/2} := \left(\frac{1}{1 + x}\right)^{1/2} \left[\mathbf{I} - \frac{1}{2}\mathbf{P} + \frac{3}{8}\mathbf{P}^2\right],$$

often shows greater errors than the expansion

$$\Delta_{BR}^{-1/2} := \mathbf{I} - \frac{1}{2}\mathbf{S} + \frac{3}{8}\mathbf{S}^2$$

according to Brown and Roby. (A second-order expansion of $\Delta^{-1/2}$ is the best, which can be used for the transformation of one- and two-electron integrals to the symmetrically orthogonalized basis. Third-order expansions result in much too complicated formulas and the errors introduced by several integral approximations become too great. These aspects will be discussed in Parts IV and V.)

Guide for a New Approach to the Justification of NDDO

It is the purpose of this series of articles to introduce a new technique, the Γ-expansion, for an optimal approximation of $\Delta^{-1/2}$ using orthogonal polynomials. The starting point of this approach was the insufficient convergence of the second-order expansion in P. The Γ-expansion will be introduced in Part II. In the third article, a spectral property of the overlap matrix of diatomic molecules assuming local orthogonality of the basis

functions will be proved. Using these properties, one can see that different expansion techniques become identical. Moreover, they will be useful for the following study of the integral transformations.

The fourth article is a reexamination of the justification of NDDO using the optimized expansion techniques. The argumentation follows the ideas both of Brown and Roby and of Chandler and Grader.

In the last article of this series, an attempt to eliminate a central weakness of all formerly proposed justifications of NDO methods will be implemented for the given approach: Several types of approximations have been used, but control over the introduced error is only insufficient. For all types of approximations, rigorously analytic formulas for the caused error will be given. Numerical evaluations in the simple case of diatomic molecules allow critical judgment on the value of the general approximation method and on the proposed concept of a nonempirical quantum chemical computation method founded upon the Neglect of Diatomic Differential Overlap approximation.

References

1. R. Ahlrichs, Theor. Chim. Acta **33**, 157 (1974).
2. J. Cioslowski, *Reviews in Computational Chemistry*, K.B. Lipkowitz and D.B. Boyd, Eds. (VCH, New York, 1993), Vol. 4, pp. 1–33.
3. R.D. Brown and K.R. Roby, Theor. Chim. Acta **16**, 175 (1970).
4. G.S. Chandler and F.E. Grader, Theor. Chim. Acta **54**, 131 (1980).
5. I. Fischer-Hjalmars, Adv. Quantum Chem. **2**, 25 (1965).
6. K. Jug, Theor. Chim. Acta **14**, 91 (1969).
7. K.R. Roby, Chem. Phys. Lett. **11**, 6 (1971).
8. K.R. Roby, Chem. Phys. Lett. **12**, 579 (1972).
9. N.A.B. Gray and A.J. Stone, Theor. Chim. Acta **18**, 389 (1970).

"Neglect of Diatomic Differential Overlap" in Nonempirical Quantum Chemical Orbital Theories. II. A Polynomial Expansion for $\Delta^{-1/2}$ in Terms of Legendre and Chebyshev Polynomials

KLAUS NEYMEYR AND FRIEDRICH FRANZ SEELIG

Institut für Physikalische und Theoretische Chemie der Universität Tübingen, Auf der Morgenstelle 8, D-72076 Tübingen, Germany

Received March 18, 1994; revised manuscript received June 23, 1994; accepted July 6, 1994

ABSTRACT

Several attempts to justify the Neglect of Diatomic Differential Overlap (NDDO) approximation in terms of a power series expansion for $\Delta^{-1/2}$ (Δ is the overlap matrix) have been made (cf. Part I). The new approach for attaining an optimal approximation of $\Delta^{-1/2}$ represented here transfers the problem of finding an optimal matrix polynomial to an approximation problem of real functions within the spectrum of Δ. Best approximations are derived by use of Legendre and Chebyshev polynomials.

Introduction

The Neglect of Diatomic Differential Overlap (NDDO) approximation can be justified partially by techniques based upon power series expansions for $\Delta^{-1/2}$, where Δ is the overlap matrix. This argumentation relies on an approximative transformation of the one-electron integrals and the electron repulsion integrals into the symmetrically orthogonalized basis (Löwdin basis) [1]. The fundamentals of these expansion techniques have been represented in the first paper of this series. Let us summarize the S-expansion technique of Brown and Roby [2] and the P-expansion of Chandler and Grader. Brown and Roby expand the matrix function $\Delta^{-1/2}$ by a binomial expansion in $\mathbf{S} = \Delta - \mathbf{I}$:

$$\Delta^{-1/2} = (\mathbf{I} + \mathbf{S})^{-1/2} = \sum_{i=0}^{\infty} \frac{(-1)^i (2i)!}{2^{2i}(i!)^2} \mathbf{S}^i$$

$$= \underbrace{\mathbf{I} - \frac{1}{2}\mathbf{S} + \frac{3}{8}\mathbf{S}^2}_{\Delta_{BR}^{-1/2}} + O(\mathbf{S}^3). \qquad (1)$$

International Journal of Quantum Chemistry, Vol. 53, 519–535 (1995)

CCC 0020-7608/95/050519-17

Brown and Roby only made use of the polynomial expansion $\mathbf{\Delta}_{BR}^{-1/2}$ to the second degree. They disregarded the radius of convergence of binomial expansion. By the spectral mapping theorem [3], this power series converges for $\sigma(\mathbf{\Delta}) \subset]0,2[$ or, equivalently, $\sigma(\mathbf{S}) \subset]-1,1[$. $\sigma(\mathbf{A})$ denotes the spectrum of the matrix $\mathbf{A}$. This imperfection was criticized by Gray and Stone [4] in the discussion of the overlap matrix of methane molecule. Chandler and Grader [5] developed a formally convergent expansion in $\mathbf{P}$:

$$\mathbf{P} = \frac{1}{1+x}(\mathbf{S} - \mathbf{X}),$$

with

$$x = \frac{\max|\sigma(\mathbf{S})| + \min \sigma(\mathbf{S})}{2}.$$

For this $\mathbf{P}$, it holds that $\sigma(\mathbf{P}) \subset]-1,1[$ and, thus, the binomial expansion in $\mathbf{P}$ converges:

$$\mathbf{\Delta}^{-1/2} = \left(\frac{1}{1+x}\right)^{1/2}(\mathbf{I} + \mathbf{P})^{-1/2}$$
$$= \left(\frac{1}{1+x}\right)^{1/2}\left[\mathbf{I} - \frac{1}{2}\mathbf{P} + \frac{3}{8}\mathbf{P}^2 + O(\mathbf{P}^3)\right].$$

But the polynomial expansion to second degree,

$$\mathbf{\Delta}_{CG}^{-1/2} := \left(\frac{1}{1+x}\right)^{1/2}\left[\mathbf{I} - \frac{1}{2}\mathbf{P} + \frac{3}{8}\mathbf{P}^2\right],$$

converges often worse than does the binomial expansion to the second degree:

$$\mathbf{\Delta}_{BR}^{-1/2} := \mathbf{I} - \frac{1}{2}\mathbf{S} + \frac{3}{8}\mathbf{S}^2.$$

Numerical results are tabulated in the section Numerical Study.

In this article, we describe a new technique, the Γ-expansion, for an optimal approximation of $\mathbf{\Delta}^{-1/2}$ to the second order within the spectral interval $\mathrm{conv}(\sigma(\mathbf{\Delta}))$, i.e., the convex hull of the spectrum of the overlap matrix $\mathbf{\Delta}$. Instead of fixed binomial expansion coefficients, optimized polynomial expansions are derived in terms of Legendre and Chebyshev polynomials.

The Γ Expansion Technique

MOTIVATION

The proceeding is motivated by the spectral mapping theorem that can be simply formulated for the positive definite symmetric matrix $\mathbf{\Delta}$. Under the given assumptions, we have an orthogonal matrix $\mathbf{U}$ that diagonalizes $\mathbf{\Delta}$:

$$\mathbf{U}^t\mathbf{\Delta}\mathbf{U} = \begin{pmatrix} \lambda_1 & & 0 \\ & \ddots & \\ 0 & & \lambda_N \end{pmatrix} \quad \lambda_i \in \sigma(\mathbf{\Delta}).$$

All eigenvalues are strictly positive, so that we can formulate the matrix function $\mathbf{\Delta}^{-1/2}$ by

$$\mathbf{\Delta}^{-1/2} = \mathbf{U}\begin{pmatrix} \lambda_1^{-1/2} & & 0 \\ & \ddots & \\ 0 & & \lambda_N^{-1/2} \end{pmatrix}\mathbf{U}^t.$$

Now, we look for a polynomial approximation $p(x) = \sum_{i=0}^{n} a_i x^i$ of degree n for $\mathbf{\Delta}^{-1/2}$:

$$\mathbf{\Delta}^{-1/2} = \underbrace{\sum_{i=0}^{n} a_i \mathbf{\Delta}^i}_{=: \mathbf{\Delta}_{approx}^{-1/2}} + O(\mathbf{\Delta}^{n+1}).$$

The error d of this approximation can be measured in an appropriate norm:

$$d = \|\mathbf{\Delta}^{-1/2} - \mathbf{\Delta}_{approx}^{-1/2}\|$$
$$= \left\|\mathbf{U}\begin{pmatrix} \lambda_1^{-1/2} - p(\lambda_1) & & 0 \\ & \ddots & \\ 0 & & \lambda_N^{-1/2} - p(\lambda_N) \end{pmatrix}\mathbf{U}^t\right\|.$$

If one chooses unitarily invariant norms, one has

$$\|\mathbf{\Delta}^{-1/2} - p(\mathbf{\Delta})\|_q \begin{cases} = \max\limits_{\lambda\in\sigma(\mathbf{\Delta})} |\lambda^{-1/2} - p(\lambda)| & \text{for } q = 2 \\ \leq \max\limits_{x\in\mathrm{conv}(\sigma(\mathbf{\Delta}))} |x^{-1/2} - p(x)| & \text{for } q = F. \end{cases}$$

Proofs are given by Golub and van Loan [6]. Herein, $q = 2$ denotes the spectral norm that reads for a Hermitian matrix $\mathbf{B}$:

$$\|\mathbf{B}\|_2 = \max_{\lambda\in\sigma(\mathbf{B})} |\lambda|,$$

and $q = F$ denotes the Frobenius norm of a matrix $\mathbf{B} \in \mathbf{R}^{NN}$:

$$\|B\|_F = \left(\sum_{i=1}^{N}\sum_{j=1}^{N}(b_{ij})^2\right)^{1/2}.$$

The convex hull of the spectrum of $\mathbf{\Delta}$ is given by $\mathrm{conv}(\sigma(\mathbf{\Delta}))$. Therewith, optimal approximations of the matrix function can be found by the solution of the real approximation problem, i.e., by minimizing the deviation of the polynomial p from the function $f(x) = x^{-1/2}$ on the specified set.

INDUCTIVE APPROACH

The given approximation problem should first be solved for a polynomial of second degree; only such a polynomial is used for the integral transformations in Part IV.

Let $f(x) = x^{-1/2}$ be defined on the convex hull of the spectrum of the overlap matrix

$$\text{conv } \sigma(\Delta) = [s,t] \quad \text{with } 0 < s = \min \sigma(\Delta) \leq t = \max \sigma(\Delta), \quad (2)$$

and $p(x) = \tilde{a} + \tilde{b}x + \tilde{c}x^2$, a polynomial of second degree. Suppose for the following that $s \neq t$ and, therefore, $\Delta \neq \mathbf{I}$. The distance of both functions in $L_2[s,t]$ with the $\|\cdot\|_2$ norm [3] is given by

$$I(\tilde{a},\tilde{b},\tilde{c}) = \|x^{-1/2} - p(x)\|_2^2 = \int_s^t (x^{-1/2} - (\tilde{a} + \tilde{b}x + \tilde{c}x^2))^2\,dx.$$

The $\|\cdot\|_2$ norm on the function space $L_2[s,t]$ should not be confused with the equally denoted spectral norm of the space of matrices. Developing $\Delta^{-1/2}$ in

$$\Delta_\kappa = \Delta - \kappa\mathbf{I},$$

instead of an expansion in Δ, we can also minimize a truncation error that results from expanding one-electron operators over the symmetrically orthogonalized basis to the second degree. This can be done by an optimization of the real parameter κ. Thus, it holds that

$$\begin{aligned} I(\tilde{a},\tilde{b},\tilde{c}) &= \int_s^t (x^{-1/2} - (\tilde{a} + \tilde{b}x + \tilde{c}x^2))^2\,dx \\ &= \int_{s-\kappa}^{t-\kappa} ((z+\kappa)^{-1/2} - (\tilde{a} + \tilde{b}(z+\kappa) + \tilde{c}(z+\kappa)^2))^2\,dz \\ &= \int_{s-\kappa}^{t-\kappa} \Bigg((z+\kappa)^{-1/2} - (\underbrace{(\tilde{a} + \tilde{b}\kappa + \tilde{c}\kappa^2)}_{a_\kappa} \\ &\qquad + \underbrace{(\tilde{b} + 2\tilde{c}\kappa)}_{b_\kappa} z + \underbrace{\tilde{c}}_{c_\kappa} z^2) \Bigg)^2 dz \\ &=: J(a_\kappa, b_\kappa, c_\kappa). \end{aligned} \quad (3)$$

The solution of the minimization problem can be determined elementarily by integration of (3). The partial derivatives of J after a_κ, b_κ, and c_κ lead to a system of linear equations with the symmetric Hessian A of $J(a_\kappa, b_\kappa, c_\kappa)$. $\mathbf{A}$ is regular, because $\det(\mathbf{A}) = (1/270)(t-s)^9 > 0$. All other principal minors are also greater than zero. Thus, $\mathbf{A}$ is positive definite and the minimization problem has a unique solution (regularity), which is a minimum (positive definiteness). The coefficients read

$$\begin{aligned} a_\kappa &= 2(s-t)^{-5}[-3t^{9/2} + 9s^{1/2}t^4 \\ &\quad + t^{7/2}(-12s + 8\kappa) + t^3(24s^{3/2} - 36s^{1/2}\kappa) \\ &\quad + t^{5/2}(-48s^2 + 68s\kappa - 6\kappa^2) \\ &\quad + t^2(48s^{5/2} - 80s^{3/2}\kappa + 30s^{1/2}\kappa^2) \\ &\quad + t^{3/2}(-24s^3 + 80s^2\kappa - 60s\kappa^2) \\ &\quad + t(12s^{7/2} - 68s^{5/2}\kappa + 60s^{3/2}\kappa^2) \\ &\quad + t^{1/2}(-9s^4 + 36s^3\kappa - 30s^2\kappa^2) \\ &\quad + 3s^{9/2} - 8s^{7/2}\kappa + 6s^{5/2}\kappa^2]; \end{aligned} \quad (4)$$

$$\begin{aligned} b_\kappa &= 8(s-t)^{-5}[2t^{7/2} - 9s^{1/2}t^3 + t^{5/2}(17s - 3\kappa) \\ &\quad + t^2(-20s^{3/2} + 15s^{1/2}\kappa) + t^{3/2}(20s^2 - 30s\kappa) \\ &\quad + t(-17s^{5/2} + 30s^{3/2}\kappa) + t^{1/2}(9s^3 - 15s^2\kappa) \\ &\quad - 2s^{7/2} + 3s^{5/2}\kappa]; \end{aligned} \quad (5)$$

$$c_\kappa = 12(t^{1/2} + s^{1/2})^{-5}. \quad (6)$$

The optimal approximation (in the sense of the L_2 norm) is now

$$\Delta^{-1/2} = \underbrace{a_\kappa\mathbf{I} + b_\kappa\Delta_\kappa + c_\kappa(\Delta_\kappa)^2}_{\Delta^{-1/2}_{approx}} + O((\Delta_\kappa)^3).$$

We call the second-order approximation $\Delta^{-1/2}_{approx}$. It can be seen that this second-order approximation is independent of κ (a_κ, b_κ, and c_κ have to be calculated for each κ).

Now, the influence of κ on the transformation of integrals should be studied. Let $\mathbf{M}$ be the matrix representation of a one-electron operator that is now to be transformed into the symmetrically orthogonalized basis. We choose a second-order expansion, too:

$$\begin{aligned} {}^\lambda\mathbf{M} &= \Delta^{-1/2}\mathbf{M}\Delta^{-1/2} \\ &= (a_\kappa\mathbf{I} + b_\kappa\Delta_\kappa + c_\kappa(\Delta_\kappa)^2) \\ &\quad \times \mathbf{M}(a_\kappa\mathbf{I} + b_\kappa\Delta_\kappa + c_\kappa(\Delta_\kappa)^2) + O((\Delta_\kappa)^3) \\ &= a_\kappa^2\mathbf{M} + a_\kappa b_\kappa(\mathbf{M}\Delta_\kappa + \Delta_\kappa\mathbf{M}) \\ &\quad + a_\kappa c_\kappa(\mathbf{M}\Delta_\kappa^2 + \Delta_\kappa^2\mathbf{M}) + b_\kappa^2\Delta_\kappa\mathbf{M}\Delta_\kappa \\ &\quad + \underbrace{b_\kappa c_\kappa(\Delta_\kappa\mathbf{M}\Delta_\kappa^2 + \Delta_\kappa^2\mathbf{M}\Delta_\kappa) + c_\kappa^2\Delta_\kappa^2\mathbf{M}\Delta_\kappa^2}_{\equiv \mathbf{D}(\kappa)} \\ &\quad + O((\Delta_\kappa)^3) \\ &= a_\kappa^2\mathbf{M} + a_\kappa b_\kappa(\mathbf{M}\Delta_\kappa + \Delta_\kappa\mathbf{M}) \\ &\quad + a_\kappa c_\kappa(\mathbf{M}\Delta_\kappa^2 + \Delta_\kappa^2\mathbf{M}) + b_\kappa^2\Delta_\kappa\mathbf{M}\Delta_\kappa \\ &\quad + O((\Delta_\kappa)^3). \end{aligned}$$

All terms of third- and fourth-order are collected in $\mathbf{D}(\kappa)$, which is the additional truncation error, if we start from a second-order approximation for $\mathbf{\Delta}^{-1/2}$ and even develop ${}^{\lambda}\mathbf{M}$ to second order.

This error can now be studied in a suitable norm: We choose the spectral norm, which has been given above for a Hermitian square matrix $\mathbf{B}$:

$$\|\mathbf{B}\|_2 = \max(|\sigma(\mathbf{B})|) = r(\mathbf{B}),$$

with the spectral radius r of $\mathbf{B}$.

All studied matrices are Hermitian. By the continuity of matrix operators and by the triangle inequality, it follows that

$$\begin{aligned}\|\mathbf{D}(\kappa)\|_2 &= \|b_\kappa c_\kappa(\mathbf{\Delta}_\kappa\mathbf{M}(\mathbf{\Delta}_\kappa)^2 + (\mathbf{\Delta}_\kappa)^2\mathbf{M}\mathbf{\Delta}_\kappa) \\ &\quad + (c_\kappa)^2(\mathbf{\Delta}_\kappa)^2\mathbf{M}(\mathbf{\Delta}_\kappa)^2\|_2 \\ &\le 2|b_\kappa c_\kappa|\,\|\mathbf{\Delta}_\kappa\|_2^3\|\mathbf{M}\|_2 \\ &\quad + (c_\kappa)^2\|\mathbf{\Delta}_\kappa\|_2^4\|\mathbf{M}\|_2 \\ &= \|\mathbf{M}\|_2(2|b_\kappa c_\kappa|\,\|\mathbf{\Delta}_\kappa\|_2^3 \\ &\quad + (c_\kappa)^2\|\mathbf{\Delta}_\kappa\|_2^4) =: \tilde{d}. \end{aligned} \tag{7}$$

The upper limit $\tilde{d}$ can now be lowered by minimizing the spectral norm of $\mathbf{\Delta}_\kappa$. The coefficient c_κ and $\|\mathbf{M}\|_2$ are independent of κ and observe the third and fourth power for $\|\mathbf{\Delta}_\kappa\|_2$ in $\tilde{d}$. Thus, minimizing $\|\mathbf{\Delta}_\kappa\|$, is a good approximation to reduce $\tilde{d}$. Starting from a second-order expansion for $\mathbf{\Delta}_\kappa$, one has to neglect terms of third to eighth order while calculating a second-order representation of two-electron integrals in the symmetrically orthogonalized basis.

By definition of $\mathbf{\Delta}_\kappa$, we have

$$\begin{aligned}\|\mathbf{\Delta}_\kappa\|_2 &:= \max(|\sigma(\mathbf{\Delta} - \kappa\mathbf{I})|) \\ &= \max(|s - \kappa|, |t - \kappa|),\end{aligned}$$

which is minimized in κ_{min}:

$$\kappa_{min} := \frac{t + s}{2}.$$

The matrix $\mathbf{\Delta}_{\kappa_{min}}$ is of special importance in the following:

$$\mathbf{\Gamma} := \mathbf{\Delta}_{\kappa_{min}} = \mathbf{\Delta} - \frac{t + s}{2}\mathbf{I}.$$

Its spectral norm reads

$$\|\mathbf{\Gamma}\|_2 = r(\mathbf{\Gamma}) = \frac{t - s}{2} (> 0). \tag{8}$$

This inductive approach yields that

- $\mathbf{\Delta}^{-1/2}$ is to be expanded in

$$\mathbf{\Gamma} = \mathbf{\Delta} - \frac{s + t}{2}\mathbf{I}.$$

$\mathbf{\Gamma}$ has the smallest spectral norm concerning the considered variation.

- The expansion coefficients for a second order-polynomial,

$$\mathbf{\Delta}^{-1/2} = a\mathbf{I} + b\mathbf{\Gamma} + c\mathbf{\Gamma}^2 + O(\mathbf{\Gamma}^3), \tag{9}$$

are given by [from Eqs. (4)–(6)]

$$a = \frac{1}{t^{1/2} + s^{1/2}}\left[2 - \left(\frac{t^{1/2} - s^{1/2}}{t^{1/2} + s^{1/2}}\right)^2\right] \tag{10}$$

$$b = -4(t^{1/2} + s^{1/2})^{-3} \tag{11}$$

$$c = 12(t^{1/2} + s^{1/2})^{-5}. \tag{12}$$

DEDUCTIVE APPROACH

A general solution of the approximation problem using Legendre and Chebyshev orthogonal polynomials can now be developed. This leads to a compact description of the coefficients for polynomials of any degree. We make use of the results of the last section and formulate an expansion in $\mathbf{\Gamma}$ directly.

Legendre Approximation

Legendre polynomials P_n are a set of orthogonal functions in $C[-1, 1]$:

$$\forall\, n \in \mathbf{N} \quad P_n(x) = \frac{1}{2^n n!}\frac{d^n}{dx^n}((x^2 - 1)^n), \tag{13}$$

which fulfill the orthogonality relation

$$(P_n \mid P_m) = \int_{-1}^{1} P_n(x)P_m(x)\,dx = \frac{2}{2n + 1}\delta_{nm}.$$

We like to use orthonormalized Legendre polynomials

$$\hat{P}_n(x) = \sqrt{\frac{2n + 1}{2}}P_n(x).$$

Legendre approximation is a generalization of the inductive approach in the last section, because the polynomials result from a Schmidt-orthogonalization procedure of the monomials x^i in $C[-1, 1]$ by the represented scalar product. Thus, we have

$$\langle\langle x^0, x^1, \ldots, x^k\rangle\rangle = \langle\langle P_0, P_1, \ldots, P_k\rangle\rangle.$$

$\langle\langle\cdot\rangle\rangle$ denotes the generated linear space. For an approximation of second degree, we expect the same result as given in (10)–(12).

Starting now with the linear mapping τ (a bijection for $\sigma \neq 0$),

$$\tau\colon [-1,1] \longrightarrow [s,t]\colon x \mapsto x\sigma + \kappa_{min},$$

with $\kappa_{min} = (t+s)/2$ and $\sigma = (t-s)/2$ succeeds a representation of the approximation problem of $f(x) = x^{-1/2}$ on $C[-1,1]$, because it is

$$f \circ \tau\colon [-1,1] \longrightarrow \mathbf{R}\colon x \mapsto f \circ \tau(x),$$

with

$$f \circ \tau(x) = \sqrt{2}\,(x(t-s) + (t+s))^{-1/2}.$$

The condition $s \neq t$, i.e., $\mathbf{\Delta} \neq \mathbf{I}$, must be always fulfilled.

For the expansion coefficients of the orthogonal Legendre expansion, it holds that $\forall\, n \in \mathbf{N} \cup \{0\}$:

$$\begin{aligned} a_n &= (f \circ \tau \mid \hat{P}_n(x)) \\ &= \sqrt{2n+1}\int_{-1}^{1} (x(t-s) + (t+s))^{-1/2} P_n(x)\,dx \\ &= \frac{2^{3/2}}{(2n+1)^{1/2}}(-1)^n \frac{(t^{1/2} - s^{1/2})^{2n+1}}{(t-s)^{n+1}}. \end{aligned} \tag{14}$$

For the proof of the last identity, see Appendix A.

The approximation S_k of degree k for $f \circ \tau$ on $C[-1,1]$ reads

$$S_k\colon [-1,1] \longrightarrow \mathbf{R}\colon x \mapsto \sum_{n=0}^{k} a_n \hat{P}_n(x)$$

$$\forall\, x \in [-1,1] \quad f \circ \tau(x) = S_k(x) + O(x^{k+1}). \tag{15}$$

For an expansion of $\mathbf{\Delta}^{-1/2}$ in $\mathbf{\Gamma}$ over the convex hull of the spectrum $\sigma(\mathbf{\Delta})$,

$$\mathrm{conv}(\sigma(\mathbf{\Gamma})) = [-\sigma, \sigma],$$

a composition of S_k with the linear mapping η is needed:

$$\eta\colon [-\sigma,\sigma] \longrightarrow [-1,1]\colon x \mapsto \frac{x}{\sigma} \tag{16}$$

$$S_k \circ \eta\colon [-\sigma,\sigma] \longrightarrow \mathbf{R}\colon x \mapsto \sum_{n=0}^{k} a_n \hat{P}_n\left(\frac{x}{\sigma}\right). \tag{17}$$

For all $x \in [-\sigma,\sigma]$, it holds that

$$\begin{aligned} f \circ \tau \circ \eta(x) &= S_k \circ \eta(x) + O(x^{k+1}) \\ &= \sum_{n=0}^{k} a_n \hat{P}_n\left(\frac{x}{\sigma}\right) + O(x^{k+1}). \end{aligned}$$

The expansion for $\mathbf{\Delta}^{-1/2}$ in Legendre polynomials in $\mathbf{\Gamma}$ reads

$$\mathbf{\Delta}^{-1/2} = \sum_{n=0}^{k} a_n \hat{P}_n\left(\frac{\mathbf{\Gamma}}{\sigma}\right) + O(\mathbf{\Gamma}^{k+1}).$$

Substitution of the explicit form of Legendre polynomials [9],

$$P_n(x) = 2^{-n} \sum_{j=0}^{[n/2]} (-1)^j \binom{n}{j} \binom{2n-2j}{n} x^{n-2j},$$

in (17) leads to

$$\begin{aligned} S_k \circ \eta(x) = \sum_{n=0}^{k} a_n \sqrt{\frac{2n+1}{2}}\, 2^{-n} \\ \times \sum_{l=0}^{[n/2]} (-1)^l \binom{n}{l} \binom{2n-2l}{n} \left(\frac{x}{\sigma}\right)^{n-2l}. \end{aligned}$$

We like to calculate now the coefficients $c_m(k)$ of $S_k \circ \eta(x)$,

$$S_k \circ \eta(x) = \sum_{m=0}^{k} c_m(k) x^m, \tag{18}$$

by permutation of the sums. As shown in Appendix A for the coefficients $c_0(k), \ldots, c_k(k)$ of a polynomial of degree k, it holds that

$$\begin{aligned} c_m(k) = \frac{2}{(t-s)^m (t^{1/2} + s^{1/2})} \sum_{n=0}^{[(k-m)/2]} (-1)^{m+n} \\ \times \left(\frac{t^{1/2} - s^{1/2}}{t^{1/2} + s^{1/2}}\right)^{2n+m} 4^{-n} \binom{2n+2m}{n} \binom{n+2m}{n+m}. \end{aligned} \tag{19}$$

These coefficients are used for the transformation of quantum chemical integrals. For a $\mathbf{\Gamma}$ expansion of the k-th degree for $\mathbf{\Delta}^{-1/2}$, this yields

$$\mathbf{\Delta}^{-1/2} = \sum_{m=0}^{k} c_m \mathbf{\Gamma}^m + O(\mathbf{\Gamma}^{k+1}). \tag{20}$$

The coefficients $c_m(k)$ for $k = 0, \ldots, 3$ read explicitly as follows:

$\underline{k = 0}$:

$$c_0(0) = 2(t^{1/2} + s^{1/2})^{-1}.$$

This result for an expansion of degree zero is interesting, because the integral transformation changes to an integral-scaling as proposed by Chandrasekhar et al. [7]. As we will see in Part V, an expansion of zeroth degree is of no practical importance.

$\underline{k = 1}$:

$$c_0(1) = 2(t^{1/2} + s^{1/2})^{-1}$$
$$c_1(1) = -4(t^{1/2} + s^{1/2})^{-3}.$$

$\underline{k = 2}$:

$$c_0(2) = (t^{1/2} + s^{1/2})^{-1}\left[2 - \left(\frac{t^{1/2} - s^{1/2}}{t^{1/2} + s^{1/2}}\right)^2\right] \quad (21)$$
$$c_1(2) = -4(t^{1/2} + s^{1/2})^{-3} \quad (22)$$
$$c_2(2) = 12(t^{1/2} + s^{1/2})^{-5}. \quad (23)$$

This result is equivalent to Eqs. (10)–(12).

$\underline{k = 3}$:

$$c_0(3) = (t^{1/2} + s^{1/2})^{-1}\left[2 - \left(\frac{t^{1/2} - s^{1/2}}{t^{1/2} + s^{1/2}}\right)^2\right]$$
$$c_1(3) = \frac{1}{(t - s)(t^{1/2} + s^{1/2})} \times \left[-4\left(\frac{t^{1/2} - s^{1/2}}{t^{1/2} + s^{1/2}}\right) + 6\left(\frac{t^{1/2} - s^{1/2}}{t^{1/2} + s^{1/2}}\right)^3\right]$$
$$c_2(3) = 12(t^{1/2} + s^{1/2})^{-5}$$
$$c_3(3) = -40(t^{1/2} + s^{1/2})^{-7}.$$

Note that the coefficient formula $c_m(k)$ has two interesting properties:

- $c_m(k)$ is invariant under permutation of s and t:

$$c_m(k)(s,t) = c_m(k)(t,s).$$

- The coefficients fulfill the following identity, $\forall\, i, m \in \mathbf{N} \cup \{0\}$:

$$c_m(m + 2i) = c_m(m + 2i + 1).$$

This relation can be illustrated by

	0	1	2	3	4	$\underline{k}$
0	$c_0(0) = c_0(1)$		$c_0(2) = c_0(3)$		$c_0(4)$	
1		$c_1(1) = c_1(2)$		$c_1(3) = c_1(4)$		
2			$c_2(2) = c_2(3)$		$c_2(4)$	
3				$c_3(3) = c_3(4)$		
$\downarrow m$						

Chebyshev Approximation

An approximation in the Chebyshev polynomials allows a larger error in the quadratic mean, i.e., the Legendre expansion, but reduces the extreme error.

For a $f \in C[a,b]$, the polynomial that fulfills

$$\inf_{\substack{p \in \mathbf{R}[x] \\ \deg p = k}} \max_{x \in [a,b]} |f(x) - p(x)|$$

is called the minimax-polynomial (L_∞ approximation). It has the smallest maximal deviation from the function $f(x)$ among all polynomials of degree k. This minimax-polynomial is difficult to find; an approximation in Chebyshev polynomials is almost identical and is easy to compute [8].

Especially at the boundaries of the interval $[a,b]$, the approximation is somewhat better than in the case of Legendre approximation; compare Figures 1 and 2.

The Chebyshev polynomials of type I T_n represent an orthogonal set on $C[-1,1]$ with respect to the weighted scalar product:

$$f, g \in C[-1,1]$$
$$(f \mid g) = \int_{-1}^{1} f(t)g(t)(1 - t^2)^{-1/2}\, dt.$$

They are defined by

$$n \in \mathbf{N} \cup \{0\} \quad T_n(x) := \cos(n \arccos x)$$

and fulfill [9]

$$\int_{-1}^{1} T_m(x)T_n(x)(1 - x^2)^{-1/2}\, dx = \begin{cases} 0 & : m \neq n \\ \pi/2 & : m = n \neq 0 \\ \pi & : m = n = 0. \end{cases}$$

For a function $g \in C[-1,1]$, the expansion coefficients are determined by

$$a_n = \frac{2}{\pi(1 + \delta_{0n})} \int_{-1}^{1} g(x)T_n(x)(1 - x^2)^{-1/2}\, dx.$$

By $\deg T_n = n$, we obtain the Chebyshev approximation as a polynomial of degree k by

$$q(x) = \sum_{n=0}^{k} a_n T_n(x).$$

Similar to the Legendre approximation, we transform the approximation of $f(x) = x^{-1/2}$ on $C[-1,1]$ by the linear mapping

$$\tau\colon [-1,1] \longrightarrow [s,t]\colon x \mapsto x\sigma + \frac{t + s}{2},$$

with $\sigma = (t - s)/2$ and the assumption $s \neq t$. It follows then that

$$f \circ \tau(x) = \left(x\sigma + \frac{t + s}{2}\right)^{-1/2} = \sqrt{2}[x(t - s) + t + s]^{-1/2},$$

which can be expanded in Chebyshev polynomials.

$$a_n = \frac{2^{3/2}}{\pi(1+\delta_{0n})}\int_{-1}^{1}(x(t-s)+t+s)^{-1/2}T_n(x) \times (1-x^2)^{-1/2}\,dx$$
$$= \frac{2^{3/2}}{\pi(1+\delta_{0n})\sqrt{t+s}}\sum_{i=0}^{\infty}(-1)^i\frac{(2i-1)!!}{(2i)!!} \times \left(\frac{t-s}{t+s}\right)^i\int_0^{\pi}(\cos y)^i\cos(ny)\,dy. \quad (24)$$

The last identity is proved in Appendix A.

For the transformation of one- and two-electron integrals in Part IV, we need only a polynomial approximation of second degree; hence, we restrict our discussion for the a_n on the cases $n = 0, 1, 2$:

$\underline{n = 0:}$

Integration by parts leads to

$$\int_0^{\pi}(\cos y)^i\cos(ny)\,dy = \int_0^{\pi}(\cos y)^i\,dy = \frac{(i-1)!!}{i!!}\pi((i+1) \bmod 2), \quad (25)$$

using the definition

$$i!! = \begin{cases} i(i-2)\ldots 3\cdot 1 & : \text{for uneven } i \in \mathbf{N} \\ i(i-2)\ldots 2 & : \text{for even } i \in \mathbf{N} \end{cases}$$

and convention $(-1)!! = 0!! = 1$.

From substitution of (25) in (24) it follows that

$$a_0 = \frac{\sqrt{2}}{\sqrt{t+s}}\sum_{i=0}^{\infty}\frac{(4i-1)!!}{(4i)!!}\frac{(2i-1)!!}{(2i)!!}\left(\frac{t-s}{t+s}\right)^{2i}. \quad (26)$$

$\underline{n = 1:}$

Using (25), we have

$$\int_0^{\pi}(\cos y)^i\cos(ny)\,dy = \frac{i!!}{(i+1)!!}\pi(i \bmod 2)$$

and

$$a_1 = -\frac{2^{3/2}}{\sqrt{t+s}}\sum_{i=0}^{\infty}\frac{(4i+1)!!}{(4i+2)!!}\frac{(2i+1)!!}{(2i+2)!!} \times \left(\frac{t-s}{t+s}\right)^{2i+1}. \quad (27)$$

$\underline{n = 2:}$

Analogously, it follows that

$$\int_0^{\pi}(\cos y)^i\cos(2y)\,dy = i\frac{(i-1)!!}{(i+2)!!} \times \pi((i+1) \bmod 2);$$

hence, we have

$$a_2 = -\frac{4\sqrt{2}}{\sqrt{t+s}}\sum_{i=0}^{\infty}\frac{(4i-1)!!}{(4i)!!}\frac{(2i-1)!!}{(2i+2)!!}i\left(\frac{t-s}{t+s}\right)^{2i}. \quad (28)$$

For the approximation of second-degree S_2 for $f \circ \tau$, it follows that

$$S_2\colon [-1,1] \longrightarrow \mathbf{R}\colon x \mapsto a_0T_0 + a_1T_1 + a_2T_2.$$

Composition with η leads to

$$S_2 \circ \eta\colon [-\sigma,\sigma] \longrightarrow \mathbf{R}\colon x \mapsto a_0T_0\left(\frac{x}{\sigma}\right) + a_1T_1\left(\frac{x}{\sigma}\right) + a_2T_2\left(\frac{x}{\sigma}\right)$$

and $\forall\, x \in [-\sigma,\sigma]$:

$$f \circ \tau \circ \eta(x) = S_2 \circ \eta(x) + O(x^3)$$
$$= a_0 + a_1\left(\frac{x}{\sigma}\right) + a_2\left(2\left(\frac{x}{\sigma}\right)^2 - 1\right) + O(x^3)$$
$$= \underbrace{a_0 - a_2}_{a} + \underbrace{\frac{a_1}{\sigma}}_{b}x + \underbrace{\frac{2a_2}{\sigma^2}}_{c}x^2 + O(x^3).$$

The coefficients for a second-order expansion in $\mathbf{\Gamma}$ have the form

$$a = a_0 - a_2 \quad (29)$$
$$b = a_1/\sigma = \frac{2a_1}{(t-s)} \quad (30)$$
$$c = 2a_2/\sigma = \frac{8a_2}{(t-s)^2}, \quad (31)$$

and the approximation reads

$$\mathbf{\Delta}^{-1/2} = a\mathbf{I} + b\mathbf{\Gamma} + c\mathbf{\Gamma}^2 + O(\mathbf{\Gamma}^3).$$

For a numerical evaluation of the series (26)–(28), we like to given some error estimations. For

$$a_0 = \frac{\sqrt{2}}{\sqrt{t+s}}\sum_{i=0}^{\infty}\underbrace{\frac{(4i-1)!!}{(4i)!!}\frac{(2i-1)!!}{(2i)!!}}_{q_i}\left(\frac{t-s}{t+s}\right)^{2i},$$

it holds that $0 < q_i \leq 1$. As shown in Appendix A for $\alpha = [(t-s)/(t+s)]$, we have $0 < \alpha < 1$. Further,

$$\frac{q_i}{q_{i+1}} = \frac{(1+1/i)^2}{\left(1+\frac{3}{4i}\right)\left(1+\frac{1}{4i}\right)} \xrightarrow{i\to\infty} 1;$$

hence, for an expansion of M-th order ($M \in \mathbf{N}$),

$$a_{0,approx} := \frac{\sqrt{2}}{\sqrt{t+s}} \sum_{i=0}^{M} q_i \alpha^{2i},$$

and an error $r_0 = |a_0 - a_{0,approx.}|$, the series is limited by a geometric series:

$$\begin{aligned} r_0 &= \left| \frac{\sqrt{2}}{\sqrt{t+s}} \sum_{i=M+1}^{\infty} q_i (\alpha^2)^i \right| \leq \frac{\sqrt{2}}{\sqrt{t+s}} \sum_{i=M+1}^{\infty} \alpha^{2i} \\ &= \frac{\sqrt{2}}{\sqrt{t+s}} \left(\sum_{i=0}^{\infty} \alpha^{2i} - \sum_{i=0}^{M} \alpha^{2i} \right) \\ &= \frac{\sqrt{2}}{\sqrt{t+s}} \left(\frac{1}{1-\alpha^2} - \frac{1-\alpha^{2(M+1)}}{1-\alpha^2} \right) \\ &= \frac{\sqrt{2}}{\sqrt{t+s}} \frac{\alpha^{2(M+1)}}{1-\alpha^2} \leq \epsilon . \end{aligned}$$

With ϵ as an upper limit for the error the expansion order $M_0 \in \mathbf{N}$, it follows that

$$M_0 \geq \frac{1}{2 \ln \alpha} \left[\ln \epsilon + \ln\left((1-\alpha^2) \frac{\sqrt{t+s}}{\sqrt{2}} \right) \right] - 1 .$$

Analogously, the error estimation for a_1 yields

$$M_1 \geq \frac{1}{2 \ln \alpha} \left[\ln \epsilon + \ln\left((1-\alpha^2) \frac{\sqrt{t+s}}{2^{3/2}(t-s)} \right) \right] - 1 ,$$

and for a_2,

$$M_2 \geq \frac{1}{2 \ln \alpha} \left[\ln \epsilon + \ln\left((1-\alpha^2) \frac{\sqrt{t+s}}{2^{5/2}} \right) \right] - 1 .$$

As an example, we take the methane molecule as discussed in the Section on Numerical Study with $\epsilon = 10^{-7}$, $s \approx 0.2068$ and $t \approx 2.3842$, which yields

$$M_0 = 47 \quad M_1 = 50 \quad M_2 = 46 .$$

Hence, the series converge sufficiently.

Numerical Approximation of the Minimax Polynomial

Now let us consider a numerical approximation of the minimax polynomial q of second degree, that is defined (on the finite set $\sigma(\mathbf{\Delta})$) by

$$\inf_{\substack{p \in \mathbf{R}[x] \\ \deg p = 2}} \max_{\lambda \in \sigma(\mathbf{\Delta})} |f(\lambda) - p(\lambda)| \geq \max_{\lambda \in \sigma(\mathbf{\Delta})} |f(\lambda) - q(\lambda)| .$$

All results are reported in the section Numerical Study; for the calculations, a routine of the Numerical Algorithm Group (NAG) [10] was used. The algorithm was described by Stiefel [11].

Numerical Study

The expansion techniques of Brown and Roby, Chandler and Grader, and the here-developed methods should be compared. For this purpose, we provide four different examples of overlap matrices listed in Appendix B.

1. Methane:

   This example was used by Gray and Stone [4] to criticize the S-expansion of Brown and Roby [2]. The greatest eigenvalue of this overlap matrix of valence orbitals reads $t \approx 2.3842$. The binomial expansion is nonconvergent.

2. Nitrogen:

   Chandler and Grader [5] gave this example (only valence orbitals). For this diatomic molecule, we have $s + t = 2$ and $\sigma(\mathbf{\Delta}) \subset]0,2[$. These relations will be proved generally for diatomic molecules under the assumption of locally orthogonalized basis functions in Part III of this series. By $\sigma(\mathbf{\Delta}) \subset]0,2[$, the binomial expansion converges formally, but the speed of convergence is insufficient. The Legendre and Chebyshev expansions provide more accurate results.

3. Hydrogen fluoride:

   This example is given by Pople and Beveridge [12]. Additionally, the orbitals at the fluorine atom are locally orthogonalized.

4. Formaldehyde:

   The overlap matrix is given by Cook [13]. The greatest eigenvalue reads $t \approx 2.1068$.

APPROXIMATIONS TO $\mathbf{\Delta}^{-1/2}$

The graph of the function $f(x) = x^{-1/2}$ and the different approximations on the convex hull of the spectrum $[s,t] = \text{conv}\ \sigma(\mathbf{\Delta})$ of the overlap matrix are shown in Figures 1 and 2. In Figure 1, it can be seen that the binomial expansion truncated to the second degree is a poor approximation to $x^{-1/2}$ in the interval $[s,t]$. The Legendre approximation yields a more accurate result. The Legendre and

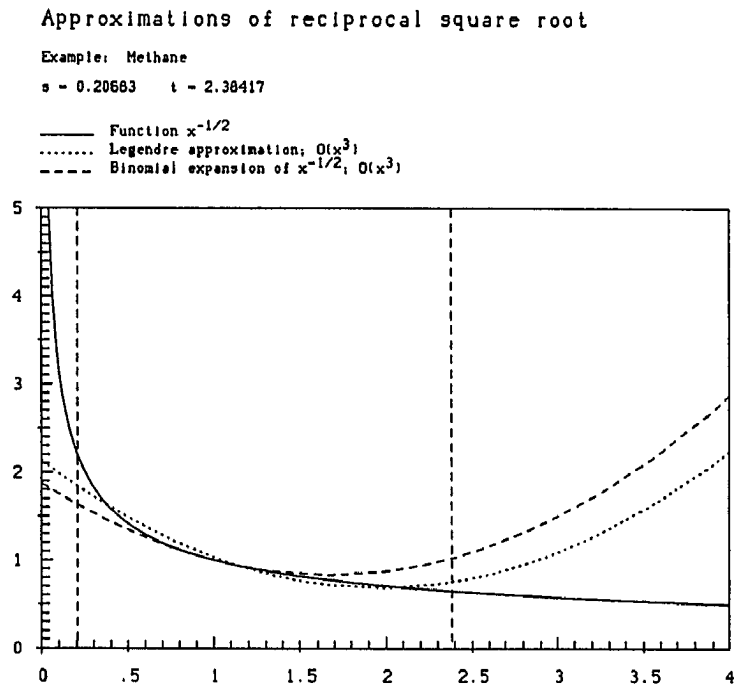

FIGURE 1. Graphs of the functions $x^{-1/2}$ (solid line), of binomial expansion (broken line), and of Legendre approximation (dotted line) for the overlap matrix of methane (cf. Numerical Study) with the smallest eigennvalue $s \approx 0.20683$ and the greatest eigenvalue $t \approx 2.38417$ (vertical broken lines).

Chebyshev approximation and the minimax polynomial are compared in Figure 2. The Chebyshev approximation and the minimax polynomial provide and improved approximation, especially in the boundary points of the interval, whereas the Legendre expansion yields best results in the middle of the interval.

For a comparison of the approximations to the matrix function $\Delta^{-1/2}$, we consider matrix polynomials of second degree, which are formally

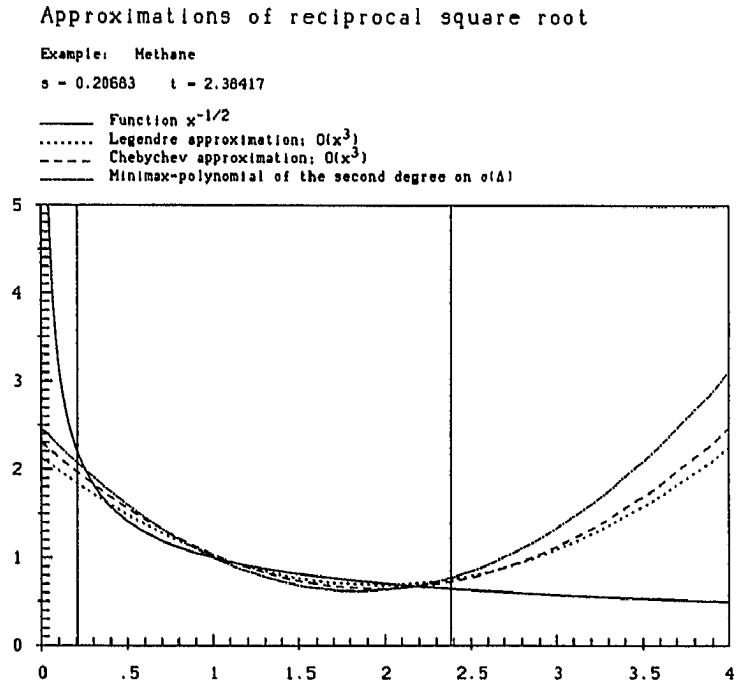

FIGURE 2. Comparison of different approximations.

given by

$$\mathbf{B} = a\mathbf{I} + b\mathbf{A} + c\mathbf{A}^2 + O(\mathbf{A}^3), \qquad (32)$$

with the already defined quantities

$$\mathbf{S} = \mathbf{\Delta} - \mathbf{I}$$

$$\mathbf{P} = (1 + x)^{-1}(\mathbf{S} - x\mathbf{I})$$

with $x = [\max|\sigma(\mathbf{S})| + \min \sigma(\mathbf{S})]/2$

$$\mathbf{\Gamma} = \mathbf{\Delta} - \frac{s + t}{2}\mathbf{I}$$

with $s = \min \sigma(\mathbf{\Delta}), \quad t = \max \sigma(\mathbf{\Delta})$.

Let us now define the following matrices:

1. Truncated binomial expansion of Brown and Roby:

$$\mathbf{\Delta}_{\mathrm{BR}}^{-1/2} := \mathbf{I} - \frac{1}{2}\mathbf{S} + \frac{3}{8}\mathbf{S}^2.$$

2. Modified truncated binomial expansion of Chandler and Grader:

$$\mathbf{\Delta}_{\mathrm{CG}}^{-1/2} := \left(\frac{1}{1 + x}\right)^{1/2}\left[\mathbf{I} - \frac{1}{2}\mathbf{P} + \frac{3}{8}\mathbf{P}^2\right].$$

3. $\mathbf{\Delta}$-expansion with Legendre coefficients according to (4)–(6) for $\kappa_{min} = 0$:

$$\mathbf{\Delta}_{Legendre,\Delta}^{-1/2} := a\mathbf{I} + b\mathbf{\Delta} + c\mathbf{\Delta}^2.$$

4. S-expansion with Legendre coefficients according to (4)–(6) for $\kappa_{min} = 1$:

$$\mathbf{\Delta}_{Legendre,S}^{-1/2} := a\mathbf{I} + b\mathbf{S} + c\mathbf{S}^2.$$

5. $\mathbf{\Gamma}$-expansion with Legendre coefficients according to (21)–(23):

$$\mathbf{\Delta}_{Legendre,\Gamma}^{-1/2} := a\mathbf{I} + b\mathbf{\Gamma} + c\mathbf{\Gamma}^2.$$

6. $\mathbf{\Gamma}$-expansion with Chebyshev coefficients according to (29)–(31):

$$\mathbf{\Delta}_{Chebychev,\Gamma}^{-1/2} := a\mathbf{I} + b\mathbf{\Gamma} + c\mathbf{\Gamma}^2.$$

7. $\mathbf{\Gamma}$-expansion using minimax polynomial of the section Numerical Approximation of the Minimax Polynomial:

$$\mathbf{\Delta}_{Minimax,\Gamma}^{-1/2} := a\mathbf{I} + b\mathbf{\Gamma} + c\mathbf{\Gamma}^2.$$

In definitions 4–7, we employ the same symbols a, b, and c for the expansion coefficients. They have to be calculated by the specified formula in each case. The quality of the different approximations will be rated in the Frobenius norm given above:

$$d := \|\mathbf{\Delta}^{-1/2} - \mathbf{\Delta}_{approx}^{-1/2}\|_F = \left(\sum_{i,j=1}^{N}((\mathbf{\Delta}^{-1/2})_{ij} - (\mathbf{\Delta}_{approx}^{-1/2})_{ij})^2\right)^{1/2}.$$

A ratio of norms is defined as follows:

$$q = d/\|\mathbf{\Delta}^{-1/2}\|_F.$$

(For $q = 0$, one has the best possible approximation $\mathbf{\Delta}^{-1/2} = \mathbf{\Delta}_{approx}^{-1/2}$, whereas for $q = 1$, the approximation is useless; e.g., $\mathbf{\Delta}^{-1/2} = \mathbf{0}$.) Table I shows a comparison of the different approximations for $\mathbf{\Delta}^{-1/2}$.

It can be seen that for diatomic molecules the expansion techniques 1 and 2 give the same result. For a proof, confer Part III (Corollary 3) of this series. For methane and formaldehyde, the P-expansion gets less accurate results than does the expansion of Brown and Roby, whereas the Legendre expansion in $\mathbf{\Delta}$, S, and $\mathbf{\Gamma}$ produces identical results. But comparing this with the approximation of Brown and Roby, we obtain norms, which are smaller by a factor of 2–3. The Chebyshev expansion and the minimax polynomial provide the best approximations of $\mathbf{\Delta}^{-1/2}$.

APPROXIMATIONS TO $\mathbf{\Delta}^{-1}$

In the section Inductive Approach, the expansion in $\mathbf{\Gamma}$ was justified by minimizing an additional truncation error while developing ${}^{\lambda}\mathbf{M}$. Both $\mathbf{\Delta}^{-1/2}$ and ${}^{\lambda}\mathbf{M}$ are expanded to the second order. For a numerical illustration, let us select $\mathbf{M} = \mathbf{I}$:

$${}^{\lambda}\mathbf{I} = \mathbf{\Delta}^{-1/2}\mathbf{I}\mathbf{\Delta}^{-1/2} = \mathbf{\Delta}^{-1}.$$

Using the formal expansion (32), this leads to

$$\mathbf{B}^2 = a^2\mathbf{I} + 2ab\mathbf{A} + (2ac + b^2)\mathbf{A}^2 + O(\mathbf{A}^3). \qquad (33)$$

Hence, we have the following:

1. Truncated binomial expansion of Brown and Roby:

$$\mathbf{\Delta}_{\mathrm{BR}}^{-1} := \mathbf{I} - \mathbf{S} + \mathbf{S}^2.$$

TABLE I
Comparison of different polynomial approximations to $\Delta^{-1/2}$.

	CH_4	HF (local orthogonalization)	N_2 (local orthogonalization)	CH_2O
Brown and Roby				
d	0.7896	0.1172	0.7017	0.7459
q	0.1959	$4.4569 \cdot 10^{-2}$	0.1989	0.1681
Chandler and Grader				
d	0.9361	0.1172	0.7017	0.8473
q	0.2322	$4.4568 \cdot 10^{-2}$	0.1989	0.1909
Legendre, Δ				
d	0.3892	$5.0009 \cdot 10^{-2}$	0.3681	0.3665
q	$9.655 \cdot 10^{-2}$	$1.9009 \cdot 10^{-2}$	0.1043	$8.2587 \cdot 10^{-2}$
Legendre, **S**				
d	0.3892	$5.0009 \cdot 10^{-2}$	0.3681	0.3665
q	$9.655 \cdot 10^{-2}$	$1.9009 \cdot 10^{-2}$	0.1043	$8.2587 \cdot 10^{-2}$
Legendre, Γ				
d	0.3892	$5.0009 \cdot 10^{-2}$	0.3681	0.3665
q	$9.655 \cdot 10^{-2}$	$1.9009 \cdot 10^{-2}$	0.1043	$8.2587 \cdot 10^{-2}$
Chebyshev, Γ				
d	0.2935	$3.2892 \cdot 10^{-2}$	0.2856	0.2623
q	$7.2806 \cdot 10^{-2}$	$1.2502 \cdot 10^{-2}$	$8.0943 \cdot 10^{-2}$	$5.9101 \cdot 10^{-2}$
Minimax, Γ				
d	0.3584	$7.8364 \cdot 10^{-16}$	0.2414	0.2547
q	$8.892 \cdot 10^{-2}$	$2.9787 \cdot 10^{-16}$	$6.8418 \cdot 10^{-2}$	$5.7395 \cdot 10^{-2}$

2. Modified truncated binomial expansion of Chandler and Grader:

$$\Delta_{CG}^{-1} := \frac{1}{1+x}[\mathbf{I} - \mathbf{P} + \mathbf{P}^2].$$

3. Δ-expansion (Legendre):

$$\Delta_{Legendre,\Delta}^{-1} := a^2\mathbf{I} + 2ab\Delta + (2ac + b^2)\Delta^2.$$

4. S-expansion (Legendre):

$$\Delta_{Legendre,S}^{-1} := a^2\mathbf{I} + 2ab\mathbf{S} + (2ac + b^2)\mathbf{S}^2.$$

5. Γ-expansion (Legendre):

$$\Delta_{Legendre,\Gamma}^{-1} := a^2\mathbf{I} + 2ab\Gamma + (2ac + b^2)\Gamma^2.$$

6. Γ-expansion (Chebyshev):

$$\Delta_{Chebyshev,\Gamma}^{-1} := a^2\mathbf{I} + 2ab\Gamma + (2ac + b^2)\Gamma^2.$$

7. Γ-expansion (minimax-polynomial on $\sigma(\Gamma)$):

$$\Delta_{Minimax,\Gamma}^{-1} := a^2\mathbf{I} + 2ab\Gamma + (2ac + b^2)\Gamma^2.$$

Numerical results are shown in Table II. As discussed in the section Inductive Approach, the Legendre expansion in Δ is a poor approximation. The best one is that in the minimax polynomial of second degree.

APPROXIMATIONS OF $r_{ij,kl}$

Using the charge density matrix, one can expand the electron repulsion integrals to the second order. Starting with a second-order expansion for $\Delta^{-1/2}$, truncation errors from third- to eighth-order arise.

The charge density matrix Ω in the basis $\phi_{i=1,\ldots,N}$ is represented by (for a detailed description see Part IV)

$$\Omega = \begin{pmatrix} \phi_1\phi_1 & \cdots & \phi_1\phi_N \\ \vdots & & \vdots \\ \phi_N\phi_1 & \cdots & \phi_N\phi_N \end{pmatrix}$$

$$^{\lambda}\Omega = \Delta^{-1/2}\Omega\Delta^{-1/2}$$

$$^{\lambda}(\phi_i\phi_j \mid \phi_k\phi_l) = \int {}^{\lambda}\Omega_{ij}(1)\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}{}^{\lambda}\Omega_{kl}(2) \times d\mathbf{r}_1\, d\mathbf{r}_2 .$$

A formally analogous, real quantity $r_{ij,kl}$ can be defined by (assuming constant functions ϕ_i with pairwise disjoint supports)

$$\Omega = \mathbf{I}$$

$$^{\lambda}\Omega = \Delta^{-1/2}\Omega\Delta^{-1/2} = \Delta^{-1}$$

and

$$r_{ij,kl} := {}^{\lambda}\Omega_{ij}{}^{\lambda}\Omega_{kl} = (\Delta^{-1})_{ij}(\Delta^{-1})_{kl} .$$

TABLE II
Comparison of approximations to Δ^{-1}.

	CH_4	HF (local orthogonalization)	N_2 (local orthogonalization)	CH_2O
Brown and Roby				
d	3.0629	0.4194	3.0753	3.0055
q	0.4261	0.1353	0.4974	0.4074
Chandler and Grader				
d	3.5679	0.4194	3.0753	3.3425
q	0.4964	0.1353	0.4974	0.4531
Legendre, Δ				
d	11.7414	4.7759	14.4240	13.2015
q	1.6336	1.5405	2.3331	1.7690
Legendre, **S**				
d	2.1522	0.2717	2.2774	2.053
q	0.2994	$8.7632 \cdot 10^{-2}$	0.3684	0.2784
Legendre, Γ				
d	2.4192	0.2717	2.2774	2.2752
q	0.3366	$8.7632 \cdot 10^{-2}$	0.3684	0.3084
Chebyshev, Γ				
d	2.0633	0.2338	2.0265	1.9432
q	0.2871	$7.5408 \cdot 10^{-2}$	0.3278	0.2634
Minimax, Γ				
d	2.0035	0.1595	1.7772	1.6905
q	0.2787	$5.1456 \cdot 10^{-2}$	0.2875	0.2292

With Eq. (33), it follows that

$$(\Delta^{-1})_{ij} = a^2\delta_{ij} + 2abA_{ij} + (2ac + b^2)\sum_{\beta=1}^{N} A_{i\beta}A_{\beta j} + O(\mathbf{A}^3)$$

and $r_{ij,kl}$ reads

$$\begin{aligned} r_{ij,kl} = a^2\Bigg[& a^2\delta_{ij}\delta_{kl} + \delta_{ij} \\ & \times \left(2abA_{kl} + (2ac + b^2)\sum_{\gamma=1}^{N} A_{k\gamma}A_{\gamma l}\right) \\ & + 4b^2A_{ij}A_{kl} + \delta_{kl} \\ & \times \left(2abA_{ij} + (2ac + b^2)\sum_{\gamma=1}^{N} A_{i\gamma}A_{\gamma j}\right)\Bigg] \\ & + O(\mathbf{A}^3). \end{aligned}$$

The approximations to the second degree can now be computed:

1. Truncated binomial expansion of Brown and Roby:
   $\mathbf{A} = \mathbf{S}$ and $a = 1$, $b = -1/2$, $c = 3/8$.
2. Modified truncated binomial expansion of Chandler and Grader:
   $\mathbf{A} = \mathbf{P}$ and $a = 1$, $b = -1/2$, $c = 3/8$. Additional coefficient $[1/(1 + x)^2]$.
3. Γ-expansion (Legendre):
   $\mathbf{A} = \Gamma$ and a, b, and c are the Legendre coefficients for a Γ-expansion.
4. Γ-expansion (Chebyshev):
   $\mathbf{A} = \Gamma$ and a, b, and c are the Chebyshev coefficients for a Γ-expansion.
5. Γ-expansion (minimax-polynomial on $\sigma(\Gamma)$):
   $\mathbf{A} = \Gamma$ and a, b, and c are the coefficients of the minimax polynomial for a Γ-expansion on $\sigma(\Gamma)$.

Numerical results are shown in Table III. For this "real analog" of repulsion integrals, let us quantify the quality of approximation by an analog to the Frobenius norm:

$$\begin{aligned} d &:= \|r - r_{approx.}\|_F \\ &= \left(\sum_{i,j,k,l=1}^{N} (r_{ij,kl} - r_{ij,kl}^{approx.})^2\right)^{1/2}. \end{aligned}$$

The quotient of norms reads

$$q = d/\|r\|_F.$$

TABLE III
Comparison of approximations to $r_{ij,kl}$.

	CH_4	HF (local orthogonalization)	N_2 (local orthogonalization)	CH_2O
Brown and Roby				
d	36.0702	2.4835	28.9068	36.7080
q	0.6982	0.2584	0.7563	0.6746
Chandler and Grader				
d	40.7779	2.4835	28.9068	39.6786
q	0.7893	0.2584	0.7563	0.7292
Legendre, Γ				
d	36.1400	1.9828	26.0439	34.6996
q	0.6995	0.2063	0.6814	0.6377
Chebyshev, Γ				
d	34.7807	1.8637	25.2896	33.3098
q	0.6732	0.1939	0.6617	0.6122
Minimax, Γ				
d	35.8321	1.5789	24.1084	32.2317
q	0.6936	0.1643	0.6308	0.5924

Summary

Various expansions have been developed for an optimal approximation of $\mathbf{\Delta}^{-1/2}$ to the second degree in L_2 and L_∞ norm. The coefficients of the polynomials depend on the quantum chemical problem by the spectrum of the overlap matrix. In comparison with binomial expansion, we have detected considerable improvement. The numerical realization is easy, because the "optimized coefficients" have to be calculated only once. They are used instead of fixed binomial coefficients. The $\mathbf{\Gamma}$-expansion technique represents a new solution of the convergence problem of the S-expansion technique [4,5]; the last one was used for the justification of NDO methods in the symmetrically orthogonalized basis.

A summary of the expansion to the second degree reads

$$\mathbf{\Delta}^{-1/2}_{approx.} = a\mathbf{I} + b\mathbf{\Gamma} + c\mathbf{\Gamma}^2$$

$$\mathbf{\Gamma} = \mathbf{\Delta} - \frac{s+t}{2}\mathbf{I} \quad \text{with} \quad s = \min \sigma(\mathbf{\Delta}),$$
$$t = \max \sigma(\mathbf{\Delta}).$$

Legendre approximation yields

$$a = (t^{1/2} + s^{1/2})^{-1}\left[2 - \left(\frac{t^{1/2} - s^{1/2}}{t^{1/2} + s^{1/2}}\right)^2\right]$$
$$b = -4(t^{1/2} + s^{1/2})^{-3}$$
$$c = 12(t^{1/2} + s^{1/2})^{-5}.$$

Using the Chebyshev approximation leads to

$$a = a_0 - a_2$$
$$b = \frac{2a_1}{(t-s)}$$
$$c = \frac{8a_2}{(t-s)^2},$$

with

$$a_0 = \frac{\sqrt{2}}{\sqrt{t+s}} \sum_{i=0}^{\infty} \frac{(4i-1)!!}{(4i)!!} \frac{(2i-1)!!}{(2i)!!} \left(\frac{t-s}{t+s}\right)^{2i}$$

$$a_1 = -\frac{2^{3/2}}{\sqrt{t+s}} \sum_{i=0}^{\infty} \frac{(4i+1)!!}{(4i+2)!!} \frac{(2i+1)!!}{(2i+2)!!} \left(\frac{t-s}{t+s}\right)^{2i+1}$$

$$a_2 = -\frac{4\sqrt{2}}{\sqrt{t+s}} \sum_{i=0}^{\infty} \frac{(4i-1)!!}{(4i)!!} \frac{(2i-1)!!}{(2i+2)!!} i \left(\frac{t-s}{t+s}\right)^{2i}$$

We further see that the P-expansion of Chandler and Grader does not bring any improvement in the examples discussed. In the following articles, we make use only of polynomial approximations of the second degree without specifying with which method the coefficients *a*, *b*, and *c* are to be computed. For some analytical studies in Part IV, we prefer Legendre coefficients because of their concise representation. For numerical computations (see Part V), we utilize the Chebyshev coefficients.

ACKNOWLEDGMENTS

The authors are very grateful to Dr. W. Koch for fruitful discussions of this work and to Dr. K. Engel for his help. K.N. was supported by the "Studienstiftung des deutschen Volkes."

Appendix A: Approximation by Orthogonal Polynomials

Some assertions that we have made for the derivation of the Legendre and the Chebyshev expansions, are to be proved here.

Lemma: In Eq. (14), it was assumed that

$$a_n = \frac{2^{3/2}}{(2n+1)^{1/2}}(-1)^n \frac{(t^{1/2}-s^{1/2})^{2n+1}}{(t-s)^{n+1}}.$$

Proof: The Legendre polynomials may be defined by the generating function [14]

$$(1-2xr+r^2)^{-1/2} = \sum_{k=0}^{\infty} P_k(x) r^k \quad \text{for} \quad |r|<1.$$

Then, from the orthogonality of Legendre functions,

$$\int_{-1}^{1} (1-2xr+r^2)^{-1/2} P_n(x)\,dx = \sum_{k=0}^{\infty} (P_k \mid P_n) r^k = \frac{2}{2n+1} r^n$$

$$= \frac{1}{(1+r^2)^{1/2}} \int_{-1}^{1} \frac{1}{\left(1-\frac{2xr}{1+r^2}\right)^{1/2}} P_n(x)\,dx$$

$$= \frac{1}{(1+r^2)^{1/2}} \int_{-1}^{1} \frac{1}{\left(1+\frac{2yr}{1+r^2}\right)^{1/2}} P_n(-y)\,dy$$

$$= \frac{(-1)^n}{(1+r^2)^{1/2}} \int_{-1}^{1} \frac{1}{\left(1+\frac{2xr}{1+r^2}\right)^{1/2}} P_n(x)\,dx.$$

The last step is valid with regard to the symmetry property of Legendre polynomials:

$$\forall\, n \in \mathbf{N} \quad P_n(-x) = (-1)^n P_n(x).$$

Hence, we have

$$\int_{-1}^{1} \frac{P_n(x)}{\left(1+\frac{2rx}{1+r^2}\right)^{1/2}} dx = \frac{2^{3/2}}{2n+1}(-1)^n r^{n+1/2} \times \left(\frac{1+r^2}{2r}\right)^{1/2}. \quad (34)$$

Using the definition of a_n, it follows that

$$a_n = \sqrt{2n+1} \int_{-1}^{1} \frac{P_n(x)}{(t+s+(t-s)x)^{1/2}} dx$$

$$= \frac{\sqrt{2n+1}}{\sqrt{t+s}} \int_{-1}^{1} \frac{P_n(x)}{\left(1+\frac{t-s}{t+s}x\right)^{1/2}} dx.$$

Now let $\alpha = (t-s)/(t+s)$ and determine an appropriate r that fulfills

$$\frac{2r}{1+r^2} = \frac{t-s}{t+s} = \alpha > 0$$

$$\Longleftrightarrow r = \frac{1 \pm \sqrt{1-\alpha^2}}{\alpha}.$$

We have then by $t > s > 0$

$$\frac{t-s}{t+s} = \alpha \in]0,1[. \quad (35)$$

With respect to the condition $r < 1$, one obtains

$$r = \frac{1-\sqrt{1-\alpha^2}}{\alpha},$$

and with

$$r = \frac{(t^{1/2}-s^{1/2})^2}{(t-s)} > 0$$

it follows for even $|r| < 1$. For the expansion coefficients results with (34),

$$a_n = \frac{\sqrt{2n+1}}{\sqrt{t+s}} \frac{2^{3/2}}{2n+1}(-1)^n \frac{(t^{1/2}-s^{1/2})^{2n+1}}{(t-s)^{n+1/2}} \times \left(\frac{t+s}{t-s}\right)^{1/2}$$

$$= \frac{2^{3/2}}{(2n+1)^{1/2}}(-1)^n \frac{(t^{1/2}-s^{1/2})^{2n+1}}{(t-s)^{n+1}}. \quad \blacksquare$$

In the section Legendre Approximation, we claim for the coefficients $c_m(k)$ of the monomials the following:

Lemma:

$$S_k \circ \eta(x) = \sum_{n=0}^{k} a_n \sqrt{\frac{2n+1}{2}} 2^{-n} \sum_{l=0}^{[n/2]} (-1)^l \binom{n}{l} \times \binom{2n-2l}{n} \left(\frac{x}{\sigma}\right)^{n-2l} = \sum_{m=0}^{k} c_m(k) x^m,$$

with the coefficients

$$c_m(k) = \frac{2}{(t-s)^m (t^{1/2}+s^{1/2})} \sum_{n=0}^{[(k-m)/2]} (-1)^{m+n} \times \left(\frac{t^{1/2}-s^{1/2}}{t^{1/2}+s^{1/2}}\right)^{2n+m} 4^{-n} \times \binom{2n+2m}{n} \binom{n+2m}{n+m}.$$

Proof: The proof succeeds by permutation of the sums. First, the exponent of x, a function of the summation indices n and l, should be simplified by introducing a third summation:

$$x^{n-2l} = \sum_{m=0}^{n-2l} x^m \delta_{n-2l,m}.$$

Hence, we have

$$S_k \circ \eta(x) = \sum_{n=0}^{k} a_n \sqrt{\frac{2n+1}{2}} 2^{-n} \sum_{l=0}^{[n/2]} (-1)^l \binom{n}{l} \times \binom{2n-2l}{n} \sigma^{2l-n} \sum_{m=0}^{n-2l} x^m \delta_{n-2l,m},$$

with the following sequence of sums:

$$\sum_{n=0}^{k} \sum_{l=0}^{[n/2]} \sum_{m=0}^{n-2l} \omega_{n,l,m}.$$

The bounds of the inner sums are functions of the outer indices of summation. The sum over m shall become the outer sum. This succeeds by introducing characteristic functions $\chi_{[a,b]}$ with $a \leq b \in \mathbf{R}$:

$$\chi_{[a,b]}: \mathbf{R} \longrightarrow \{0,1\}: x \mapsto \begin{cases} 1 & : \ x \in [a,b] \\ 0 & : \ else \end{cases}.$$

After transforming the summation array into a cube in $\mathbf{N}^3$,

$$\sum_{n=0}^{k} \sum_{l=0}^{[n/2]} \sum_{m=0}^{n-2l} \omega_{n,l,m} = \sum_{n=0}^{k} \sum_{l=0}^{k} \chi_{[0,[n/2]]}(l) \times \sum_{m=0}^{k} \chi_{[0,n-2l]}(m) \omega_{n,l,m},$$

we can permute the sums. In the last step, we eliminate the characteristic functions by changing the bounds of the summation:

$$\begin{aligned} &\sum_{n=0}^{k} \sum_{l=0}^{k} \chi_{[0,[n/2]]}(l) \sum_{m=0}^{k} \chi_{[0,n-2l]}(m) \omega_{n,l,m} \\ &\quad = \sum_{n=0}^{k} \sum_{l=0}^{k} \sum_{m=0}^{k} \chi_{[0,[n/2]]}(l) \chi_{[0,n-2l]}(m) \omega_{n,l,m} \\ &\quad = \sum_{m=0}^{k} \sum_{n=0}^{k} \sum_{l=0}^{k} \chi_{[0,[n/2]]}(l) \chi_{[0,n-2l]}(m) \omega_{n,l,m} \\ &\quad = \sum_{m=0}^{k} \sum_{n=0}^{k} \sum_{l=0}^{[n/2]} \chi_{[0,n-2l]}(m) \omega_{n,l,m} \\ &\quad \vdots \\ &\quad = \sum_{m=0}^{k} \sum_{n=m}^{k} \sum_{l=0}^{[(n-m)/2]} \omega_{n,l,m}. \end{aligned}$$

Hence, we have

$$S_k \circ \eta(x) = \sum_{m=0}^{k} x^m \sum_{n=m}^{k} \sum_{l=0}^{[(n-m)/2]} a_n \sqrt{\frac{2n+1}{2}} 2^{-n} (-1)^l \times \binom{n}{l} \binom{2n-2l}{n} \sigma^{2l-n} \delta_{n-2l,m}.$$

The Kronecker function and summation over l can now be eliminated. For fixed m, $m \in [0,k] \cap \mathbf{N}$, we have $n \in [m,k] \cap \mathbf{N}$. By

$$\delta_{n-2l,m} = 1 \Longleftrightarrow l = \frac{n-m}{2}$$

and by running l through the set $[0,[(n-m)/2]] \cap \mathbf{N}$, it follows that

$$\begin{aligned} &((n-m+1) \bmod 2) = 1 \\ &\qquad \longrightarrow \text{summation over } l \text{ only for } l = \frac{n-m}{2} \\ &((n-m+1) \bmod 2) = 0 \quad \longrightarrow \text{no } l\text{-summation} \end{aligned}$$

$$\begin{aligned} S_k \circ \eta(x) &= \sum_{m=0}^{k} x^m \left(\frac{t-s}{2}\right)^{-m} \sum_{n=m}^{k} \times ((n-m+1) \bmod 2) a_n (n+1/2)^{1/2} \\ &\quad \times 2^{-n} (-1)^{[(n-m)/2]} \binom{n}{\left[\frac{n-m}{2}\right]} \binom{n+m}{n} \\ &=: \sum_{m=0}^{k} c_m(k) x^m. \end{aligned}$$

$c_m(k)$ are the coefficients of monomials x^m for an expansion of degree k. Substitution of a_n leads to

$$\begin{aligned} c_m(k) &= \frac{2^{m+1}}{(t-s)^m} (t^{1/2} + s^{1/2})^{-1} \sum_{n=m}^{k} \times ((n-m+1) \bmod 2) (-1)^{n+[(n-m)/2]} \\ &\quad \times \left(\frac{t^{1/2} - s^{1/2}}{t^{1/2} + s^{1/2}}\right)^n 2^{-n} \binom{n}{\left[\frac{n-m}{2}\right]} \\ &\quad \times \binom{n+m}{n}. \end{aligned}$$

By substitution $\tilde{n} = n - m$, the sum can be simplified further:

$$\sum_{\tilde{n}=0}^{k-m} ((\tilde{n}+1) \bmod 2) g(\tilde{n}) = \sum_{n=0}^{[(k-m)/2]} g(2n)$$

$$c_m(k) = \frac{2^{m+1}}{(t-s)^m (t^{1/2} + s^{1/2})} \sum_{n=0}^{[(k-m)/2]} (-1)^{m+n} \times \left(\frac{t^{1/2} - s^{1/2}}{t^{1/2} + s^{1/2}}\right)^{2n+m} 2^{-m-2n} \binom{2n+m}{n} \binom{2n+2m}{2n+m}.$$

Using the identity

$$\binom{2n+2m}{2n+m}\binom{2n+m}{n} = \binom{2n+2m}{n}\binom{n+2m}{n+m},$$

we obtain

$$c_m(k) = \frac{2}{(t-s)^m(t^{1/2}+s^{1/2})} \sum_{n=0}^{[(k-m)/2]} (-1)^{m+n} \times \left(\frac{t^{1/2}-s^{1/2}}{t^{1/2}+s^{1/2}}\right)^{2n+m} 4^{-n}\binom{2n+2m}{n} \times \binom{n+2m}{n+m}, \quad \blacksquare$$

Finally, we have to prove an identity for the Chebyshev coefficients as claimed in the section Chebyshev Approximation:

Lemma:

$$a_n = \frac{2^{3/2}}{\pi(1+\delta_{0n})} \int_{-1}^{1} (x(t-s)+t+s)^{-1/2} T_n(x) \times (1-x^2)^{-1/2}\,dx = \frac{2^{3/2}}{\pi(1+\delta_{0n})\sqrt{t+s}} \sum_{i=0}^{\infty} (-1)^i \frac{(2i-1)!!}{(2i)!!} \times \left(\frac{t-s}{t+s}\right)^i \int_0^{\pi} (\cos y)^i \cos(ny)\,dy.$$

Proof: By substitution $x = \cos(y)$, we transform the first line of the assertion in

$$a_n = \frac{2^{3/2}}{\pi(1+\delta_{0n})} \int_{\pi}^{0} (\cos y(t-s)+t+s)^{-1/2} \times T_n(\cos y)(1-(\cos y)^2)^{-1/2}(-\sin y)\,dy$$

Using the definition of Chebyshev polynomials $T_n(\cos y) = \cos(n \arccos(\cos(y))) = \cos(ny)$, it holds that

$$a_n = \frac{2^{3/2}}{\pi(1+\delta_{0n})} \times \int_0^{\pi} (\cos y(t-s)+t+s)^{-1/2} \cos(ny)\,dy = \frac{2^{3/2}}{\pi(1+\delta_{0n})\sqrt{t+s}} \times \int_0^{\pi} \frac{1}{(\alpha \cos y+1)^{1/2}} \cos(ny)\,dy, \qquad (36)$$

with $\alpha = (t-s)/(t+s)$. By Eq. (35), one has $\alpha \in]0,1[$. The reciprocal square root can now be represented by the binomial expansion, which converges because $\alpha \cos y \in]-1,1[$:

$$(\alpha \cos y+1)^{-1/2} = \sum_{i=0}^{\infty} (-1)^i \frac{(2i-1)!!}{(2i)!!} (\alpha \cos(y))^i.$$

Substituting this in (36) completes the proof. $\blacksquare$

Appendix B: Overlap Matrices

The overlap matrices, as used for numerical calculations in the section Numerical Study, read explicitly

1. Methane:

$$\Delta \approx \begin{pmatrix} 1.0000 & 0.0000 & 0.0000 & 0.0000 & 0.5239 & 0.5239 & 0.5239 & 0.5239 \\ 0.0000 & 1.0000 & 0.0000 & 0.0000 & -0.2789 & -0.2789 & 0.2789 & 0.2789 \\ 0.0000 & 0.0000 & 1.0000 & 0.0000 & 0.3944 & -0.3944 & 0.0000 & 0.0000 \\ 0.0000 & 0.0000 & 0.0000 & 1.0000 & 0.0000 & 0.0000 & -0.3944 & 0.3944 \\ 0.5239 & -0.2789 & 0.3944 & 0.0000 & 1.0000 & 0.1970 & 0.1970 & 0.1970 \\ 0.5239 & -0.2789 & -0.3944 & 0.0000 & 0.1970 & 1.0000 & 0.1970 & 0.1970 \\ 0.5239 & 0.2789 & 0.0000 & -0.3944 & 0.1970 & 0.1970 & 1.0000 & 0.1970 \\ 0.5239 & 0.2789 & 0.0000 & 0.3944 & 0.1970 & 0.1970 & 0.1970 & 1.0000 \end{pmatrix}.$$

2. Nitrogen:

$$\Delta \approx \begin{pmatrix} 1.0000 & 0.0000 & 0.0000 & 0.0000 & 0.4500 & 0.4300 & 0.0000 & 0.0000 \\ 0.0000 & 1.0000 & 0.0000 & 0.0000 & -0.4300 & -0.3200 & 0.0000 & 0.0000 \\ 0.0000 & 0.0000 & 1.0000 & 0.0000 & 0.0000 & 0.0000 & 0.2800 & 0.0000 \\ 0.0000 & 0.0000 & 0.0000 & 1.0000 & 0.0000 & 0.0000 & 0.0000 & 0.2800 \\ 0.4500 & -0.4300 & 0.0000 & 0.0000 & 1.0000 & 0.0000 & 0.0000 & 0.0000 \\ 0.4300 & -0.3200 & 0.0000 & 0.0000 & 0.0000 & 1.0000 & 0.0000 & 0.0000 \\ 0.0000 & 0.0000 & 0.2800 & 0.0000 & 0.0000 & 0.0000 & 1.0000 & 0.0000 \\ 0.0000 & 0.0000 & 0.0000 & 0.2800 & 0.0000 & 0.0000 & 0.0000 & 1.0000 \end{pmatrix}.$$

3. Hydrogen fluoride:

$$\Delta \approx \begin{pmatrix} 1.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0000 & -0.0590 \\ 0.0000 & 1.0000 & 0.0000 & 0.0000 & 0.0000 & 0.4717 \\ 0.0000 & 0.0000 & 1.0000 & 0.0000 & 0.0000 & 0.2989 \\ 0.0000 & 0.0000 & 0.0000 & 1.0000 & 0.0000 & 0.0000 \\ 0.0000 & 0.0000 & 0.0000 & 0.0000 & 1.0000 & 0.0000 \\ -0.0590 & 0.4717 & 0.2989 & 0.0000 & 0.0000 & 1.0000 \end{pmatrix}.$$

4. Formaldehyde:

$$\Delta \approx \begin{pmatrix} 1.0000 & 0.2203 & 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0353 & 0.0000 & -0.0595 & 0.0000 & 0.0707 & 0.0707 \\ 0.2203 & 1.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0400 & 0.3749 & 0.0000 & -0.3078 & 0.0000 & 0.5367 & 0.5367 \\ 0.0000 & 0.0000 & 1.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.2159 & 0.0000 & 0.0000 & 0.0000 & 0.0000 \\ 0.0000 & 0.0000 & 0.0000 & 1.0000 & 0.0000 & 0.0683 & 0.4594 & 0.0000 & -0.3056 & 0.0000 & -0.2489 & -0.2489 \\ 0.0000 & 0.0000 & 0.0000 & 0.0000 & 1.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.2159 & 0.4311 & -0.4311 \\ 0.0000 & 0.0400 & 0.0000 & 0.0683 & 0.0000 & 1.0000 & 0.2333 & 0.0000 & 0.0000 & 0.0000 & 0.0058 & 0.0058 \\ 0.0353 & 0.3749 & 0.0000 & 0.4594 & 0.0000 & 0.2333 & 1.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0874 & 0.0874 \\ 0.0000 & 0.0000 & 0.2159 & 0.0000 & 0.0000 & 0.0000 & 0.0000 & 1.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0000 \\ -0.0595 & -0.3078 & 0.0000 & -0.3056 & 0.0000 & 0.0000 & 0.0000 & 0.0000 & 1.0000 & 0.0000 & -0.0785 & -0.0785 \\ 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.2159 & 0.0000 & 0.0000 & 0.0000 & 0.0000 & 1.0000 & 0.0412 & -0.0412 \\ 0.0707 & 0.5367 & 0.0000 & -0.2489 & 0.4311 & 0.0058 & 0.0874 & 0.0000 & -0.0785 & 0.0412 & 1.0000 & 0.1709 \\ 0.0707 & 0.5367 & 0.0000 & -0.2489 & -0.4311 & 0.0058 & 0.0874 & 0.0000 & -0.0785 & -0.0412 & 0.1709 & 1.0000 \end{pmatrix}.$$

References

1. P.-O. Löwdin, J. Chem. Phys. **18**, 365 (1950).
2. R.D. Brown and K.R. Roby, Theor. Chim. Acta **16**, 175 (1970).
3. Kiyosi Ito, Ed., Encyclopedic Dictionary of Mathematics, 2nd ed. (MIT Press, Cambridge, MA, 1987).
4. N.A.B. Gray and A.J. Stone, Theor. Chim. Acta **18**, 389 (1970).
5. G.S. Chandler and F.E. Grader, Theor. Chim. Acta **54**, 131 (1980).
6. G.H. Golub and C.F. van Loan, *Matrix Computations* (John Hopkins University Press, Baltimore MD, 1983), Chap. 11.2.
7. J. Chandrasekhar, P.K. Mehrota, S. Subramanian, and P.T. Manoharan, Theor. Chim. Acta **41**, 243 (1976).
8. W.H. Press, B.P. Flannery, S.A. Teukolsky, and W.T. Vetterling, *Numerical Recipes* (Cambridge University Press, Cambridge, 1986), p. 149.
9. G. Arfken, *Mathematical Methods for Physicists* (Academic Press, San Diego, 1985).
10. The Numerical Algorithm Group Limited, NAG, Mark 14 Fortran 77 Library (Wilkinson House, Jordan Hill Road, Oxford UK, 1990), Routine E02ACF.
11. E. Stiefel, in *On Numerical Approximation*, R.E. Langer, Ed. (University of Wisconsin Press, Madison, 1959), pp. 217–232.
12. J.A. Pople and D.L. Beveridge, *Approximate Molecular Orbital Theory* (McGraw-Hill, New York, 1970).
13. D.B. Cook, *Structures and Approximations for Electrons in Molecules* (Ellis Horwood, Chichester, 1978).
14. I.N. Bronstein and K.A. Semendjajew, *Taschenbuch der Mathematik* (Verlag Harri Deutsch, Thun, 1984).

"Neglect of Diatomic Differential Overlap" in Nonempirical Quantum Chemical Orbital Theories. III. On the Spectrum of the Overlap Matrix for Diatomic Molecules over Locally Orthogonalized Basis Functions

KLAUS NEYMEYR

Institut für Physikalische und Theoretische Chemie der Universität Tübingen, Auf der Morgenstelle 8, D-72076 Tübingen, Germany

KLAUS ENGEL

Mathematisches Institut der Universität Tübingen, Auf der Morgenstelle 10, D-72076 Tübingen, Germany

Received March 18, 1994; revised manuscript received June 23, 1994; accepted July 6, 1994

ABSTRACT

The sum of the smallest and the greatest eigenvalue of the overlap matrix of diatomic molecules in a basis of locally orthogonalized linearly independent functions is equal to 2. Therewith, polynomial expansion techniques for the justification of the NDDO approximation become identical for diatomic molecules. © 1995 John Wiley & Sons, Inc.

Introduction

In the second article of this series, the Γ-expansion technique for an approximate polynomial expansion of $\Delta^{-1/2}$ (Δ is the overlap matrix) was developed. This expansion revises the S-expansion for the justification of the Neglect of Differential Overlap (NDO) methods [1,2].

The coefficients of this polynomial are determined by Legendre and Chebyshev approximation, i.e., the best approximation has been calculated under the L_2 and L_∞ norms. For the following integral transformations in Part IV (core integrals and repulsion integrals), one requires only a second-order expansion for $\Delta^{-1/2}$. In contrast to former expansions, these coefficients are functions of the smallest (s) and the greatest (t) eigenvalue of the

International Journal of Quantum Chemistry, Vol. 53, 537–540 (1995)

CCC 0020-7608/95/050537-04

Hermitian and positive definite overlap matrix, which has been calculated from a finite set of linearly independent localized and normalized basis functions.

Here, we show some properties of the spectrum of the overlap matrix for diatomic molecules. The localized basis functions, for instance, Slater orbitals, are assumed to be orthogonalized at both atomic centers. This local orthogonalization is also demanded from Chandler and Grader [2]. By the corollaries of the following theorem, we derive some identities between the expansion techniques, as discussed in part II. Therefore, we would like to give a short summary of the expansion techniques:

1. The binomial expansion as proposed by Brown and Roby [1] in $\mathbf{S} := \mathbf{\Delta} - \mathbf{I}$ converges only for $\sigma(\mathbf{\Delta}) \subset]0,2[$. The second-order approximation reads

$$\mathbf{\Delta}_{\mathrm{BR}}^{-1/2} := \mathbf{I} - \frac{1}{2}\mathbf{S} + \frac{3}{8}\mathbf{S}^2.$$

The numbers 1, 1/2, and 3/8 are the first coefficients of binomial expansion of $f(x) = x^{-1/2}$.

2. The formally convergent expansion of Chandler and Grader also uses the binomial expansion:

$$\mathbf{P} = \frac{1}{1+x}(\mathbf{S} - \mathbf{X}), \qquad (1)$$

with $\mathbf{X} = x\mathbf{I}$ and

$$x = \frac{\max|\sigma(\mathbf{S})| + \min \sigma(\mathbf{S})}{2}. \qquad (2)$$

$\mathbf{P}$ fulfills the condition $\sigma(\mathbf{P}) \subset]-1,1[$; hence, we have a convergent binomial expansion and a second-order approximation:

$$\mathbf{\Delta}_{\mathrm{CG}}^{-1/2} := \left(\frac{1}{1+x}\right)^{1/2}\left[\mathbf{I} - \frac{1}{2}\mathbf{P} + \frac{3}{8}\mathbf{P}^2\right].$$

3. As represented in Part II, one can calculate expansion coefficients a, b, and c by Legendre and Chebyshev approximations. With $s = \min \sigma(\mathbf{\Delta})$ and $t = \max \sigma(\mathbf{\Delta})$ and definition

$$\mathbf{\Gamma} = \mathbf{\Delta} - \frac{s+t}{2}\mathbf{I} \qquad \kappa_{min} := \frac{t+s}{2},$$

the approximation for $\mathbf{\Delta}^{-1/2}$ reads

$$\mathbf{\Delta}_{approx}^{-1/2} = a\mathbf{I} + b\mathbf{\Gamma} + c\mathbf{\Gamma}^2.$$

Spectral Properties of the Overlap Matrix for Diatomic Molecules

Two finite sets of real functions, each set orthonormalized, are given by

$$\phi_n^\alpha \qquad 1 \le n \le n_\alpha$$
$$\phi_n^\beta \qquad 1 \le n \le n_\beta,$$

with

$$(\phi_i^\alpha \mid \phi_j^\alpha) = \delta_{ij} \quad \text{and} \quad (\phi_i^\beta \mid \phi_j^\beta) = \delta_{ij}.$$

All functions $\phi_1^\alpha, \ldots, \phi_{n_\alpha}^\alpha, \phi_1^\beta, \ldots, \phi_{n_\beta}^\beta$ are linearly independent. (One possible interpretation is a diatomic molecule with locally orthogonalized Slater functions: ϕ_i^α at one atom and ϕ_i^β at the other atom.) Under these presumptions, the following theorem holds:

Theorem 1: The given overlap matrix $\mathbf{\Delta}$ with $\Delta_{ij} = (\phi_i \mid \phi_j)$ has the following properties:

1. $\lambda \in \sigma(\mathbf{\Delta}) \Rightarrow 2 - \lambda \in \sigma(\mathbf{\Delta})$
2. $\sigma(\mathbf{\Delta}) \subset]0,2[$

Thereby, a symmetry of the spectrum to 1 is stated. For the proof, we need a theorem about the invertibility of an operator matrix [3].

Theorem (Schur) 2: Let $n, m \in \mathbf{N}$ and let $\mathbf{A} \in \mathbf{R}^{nn}, \mathbf{B} \in \mathbf{R}^{nm}, \mathbf{C} \in \mathbf{R}^{mn}, \mathbf{D} \in \mathbf{R}^{mm}$. For invertible $\mathbf{A}$ ($\det \mathbf{A} \neq 0$), the following equivalence holds:

$$\mathcal{A} = \begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{C} & \mathbf{D} \end{pmatrix} \text{ invertible in } \mathbf{R}^{(n+m)(n+m)}$$
$$\Longleftrightarrow \mathbf{D} - \mathbf{C}\mathbf{A}^{-1}\mathbf{B} \text{ invertible in } \mathbf{R}^{mm}.$$

Herein, $\mathbf{D} - \mathbf{C}\mathbf{A}^{-1}\mathbf{B}$ is called the Schur complement of $\mathcal{A}$ in $\mathbf{A}$.

Proof of 2: We have to verify the equation

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{C} & \mathbf{D} \end{pmatrix} = \underbrace{\begin{pmatrix} \mathbf{I} & \mathbf{0} \\ \mathbf{C}\mathbf{A}^{-1} & \mathbf{I} \end{pmatrix}}_{C_1} \begin{pmatrix} \mathbf{A} & \mathbf{0} \\ \mathbf{0} & \mathbf{D} - \mathbf{C}\mathbf{A}^{-1}\mathbf{B} \end{pmatrix} \times \underbrace{\begin{pmatrix} \mathbf{I} & \mathbf{A}^{-1}\mathbf{B} \\ \mathbf{0} & \mathbf{I} \end{pmatrix}}_{C_2}.$$

The right side of the equation is invertible, if the Schur complement is invertible, because the inverse

of C_1 and C_2 are easy to find:

$$\begin{pmatrix} 1 & x \\ 0 & 1 \end{pmatrix}$$

is the inverse of

$$\begin{pmatrix} 1 & -x \\ 0 & 1 \end{pmatrix},$$

and likewise for block matrices. ■

Now Theorem 1 can be proved.

Proof of 1: The considered overlap matrix has the form

$$\mathbf{\Delta} = \begin{pmatrix} \mathbf{I}_{n_\alpha} & \mathbf{B} \\ \mathbf{C} & \mathbf{I}_{n_\beta} \end{pmatrix}.$$

By symmetry of $\mathbf{\Delta}$ we have $\mathbf{C} = \mathbf{B}^t$.

First, we can assume that $\lambda \neq 1$, because for $\lambda = 1 \in \sigma(\mathbf{\Delta})$ it already holds that $2 - \lambda = 1 \in \sigma(\mathbf{\Delta})$. Then, we have for the elements of the resolvent set $\rho(\mathbf{\Delta}) = \mathbb{C}\backslash\sigma(\mathbf{\Delta})$ ($\mathbb{C}$ are the complex numbers):

$$\lambda \in \rho(\mathbf{\Delta}) \iff \lambda\mathbf{I} - \mathbf{\Delta} \text{ invertible}, \qquad (3)$$

with

$$\lambda\mathbf{I} - \mathbf{\Delta} = \begin{pmatrix} (\lambda - 1)\mathbf{I}_{n_\alpha} & -\mathbf{B} \\ -\mathbf{B}^t & (\lambda - 1)\mathbf{I}_{n_\beta} \end{pmatrix}.$$

Let us make use of Schur's theorem: $\mathbf{A} := (\lambda - 1)\mathbf{I}_{n_\alpha}$ is invertible with $\mathbf{A}^{-1} = (\lambda - 1)^{-1}\mathbf{I}_{n_\alpha}$. Thus, it follows that

$$\begin{aligned} \lambda \in \rho(\mathbf{\Delta}) &\overset{(3)}{\iff} \lambda\mathbf{I} - \mathbf{\Delta} \text{ invertible} \\ &\overset{\text{Schur}}{\iff} (\lambda - 1)\mathbf{I}_{n_\beta} - \mathbf{B}^t \\ &\qquad \times (\lambda - 1)^{-1}\mathbf{I}_{n_\alpha}\mathbf{B} \text{ invertible} \\ &\overset{\lambda \neq 1}{\iff} (\lambda - 1)^2\mathbf{I}_{n_\beta} - \mathbf{B}^t\mathbf{B} \text{ invertible}. \end{aligned} \qquad (4)$$

With $\lambda \in \rho(\mathbf{\Delta})$ then for $\lambda' = 2 - \lambda$, the matrix

$$(\lambda' - 1)^2\mathbf{I}_{n_\beta} - \mathbf{B}^t\mathbf{B} = (1 - \lambda)^2\mathbf{I}_{n_\beta} - \mathbf{B}^t\mathbf{B}$$

is invertible, too. Using (4), we have $\lambda' = 2 - \lambda \in \rho(\mathbf{\Delta})$.

For the complement in $\mathbb{C}$, $\sigma(\mathbf{\Delta}) = \mathbb{C}\backslash\rho(\mathbf{\Delta})$, we have the analogous statement

$$\lambda \in \sigma(\mathbf{\Delta}) \implies 2 - \lambda \in \sigma(\mathbf{\Delta}),$$

[because, suppose that $2 - \lambda \in \rho(\mathbf{\Delta})$, so $2 - (2 - \lambda) = \lambda \in \rho(\mathbf{\Delta})$, in contradiction to the disjointness of $\sigma(\mathbf{\Delta})$ and $\rho(\mathbf{\Delta})$].

Statement (2) follows from the positive definiteness of $\mathbf{\Delta}$, i.e., $\sigma(\mathbf{\Delta}) \subset]0, \infty[$. If we further suppose that $\lambda \in \sigma(\mathbf{\Delta})$ with $\lambda \geq 2$, one has $\lambda' = 2 - \lambda \in \sigma(\mathbf{\Delta})$, with $\lambda' \leq 0$, in contradiction to positive definiteness. Thus, we see that $\sigma(\mathbf{\Delta}) \subset]0, 2[$. ■

Under the presuppositions of Theorem 1, especially for diatomic molecules, we can draw some conclusions:

Corollary 1: For the given overlap matrix of diatomic molecules with $s = \min \sigma(\mathbf{\Delta})$ and $t = \max \sigma(\mathbf{\Delta})$, it holds that

$$s + t = 2.$$

Proof: By statement (1) of Theorem 1, the assumption $\tilde{t} = 2 - s \neq t$ leads to a contradiction. ■

Corollary 2: For diatomic molecules, it holds that $\mathbf{\Gamma} = \mathbf{S}$.

Proof: $\mathbf{\Gamma} = \mathbf{\Delta} - \frac{1}{2}(s + t)\mathbf{I}$. ■

Observe that the expansion of Brown and Roby and the $\mathbf{\Gamma}$-expansion technique (cf. Part II of this series) are expansions in the same matrix. The expansion coefficients are different. For the case $s, t \to 1$, the limes for the Legendre coefficients reads ($s = t = 1$, i.e., $\mathbf{\Delta} = \mathbf{I}$ or a globally orthogonalized basis, was excluded in Part II):

$$a = c_0(2) = 1, \quad b = c_1(2) = -\frac{1}{2},$$

$$c = c_2(2) = \frac{3}{8}.$$

Corollary 3: For diatomic molecules, the expansion technique of Chandler and Grader becomes identical to the binomial expansion of Brown and Roby. Thus,

$$\mathbf{P} = \mathbf{S}$$
$$x = \frac{\lambda_{|max|} + \lambda_{min}}{2} = 0.$$

Proof: Referring to the definition [2] of λ_{min} and $\lambda_{|max|}$, we have

$$\begin{aligned} \lambda_{min} &= \min \sigma(\mathbf{\Delta} - \mathbf{I}) \\ &= (\min \sigma(\mathbf{\Delta})) - 1 = s - 1 \\ \lambda_{|max|} &= \max |\sigma(\mathbf{\Delta} - \mathbf{I})| \\ &= \max |\sigma(\mathbf{\Delta}) - 1| = \max\{|t - 1|, |s - 1|\} \\ &\overset{s+t=2}{=} \max\{|t - 1|, |1 - t|\} = t - 1. \end{aligned}$$

(Notice that $t > s > 0$ and $2 = s + t$ implies $t - 1 > 0$.) With Eq. (2) and Corollary 1, it follows that

$$x = \frac{\lambda_{|max|} + \lambda_{min}}{2} = \frac{s - 1 + t - 1}{2} = 0.$$

For $\mathbf{P}$ defined by (1), it follows that

$$\mathbf{P} = \frac{1}{1 + x}(\mathbf{S} - \mathbf{X}) = \mathbf{S},$$

so we have

$$\Delta^{-1/2} = \left(\frac{1}{1 + x}\right)^{1/2}(\mathbf{I} + \mathbf{P})^{-1/2}$$
$$= (\mathbf{I} + \mathbf{S})^{-1/2} = \mathbf{I} - \frac{1}{2}\mathbf{S} + \frac{3}{8}\mathbf{S}^2 + O(\mathbf{S}^3).$$

■

Hence, the binomial expansion is convergent for diatomic molecules. Thus, for diatomic molecules (Chandler and Grader discussed the example of the N_2 and HF molecules explicitly), Chandler and Grader's revision of the former work of Brown and Roby does not yield any improvement.

Conclusions

Diatomic molecules are often the first objects of study when developing a quantum chemical computation method. For this class of molecules, it has been shown that the binomial expansion and the **P**-expansion of Chandler and Grader give identical results. By Corollary 2, it can be seen that the Γ-expansion, as proposed in part II of this series, also becomes an expansion in **S** for diatomic molecules. However, because of its dependance on the expansion coefficients from the spectrum of Δ, the numerical study in Part II shows that such a Legendre or Chebyshev expansion in **S** yields the best approximations under the discussed norms.

The proved theorem is of importance for the discussion of the reexamination of justification of the NDDO approximation in Part IV, where the diatomic case is most favorable. Furthermore, it plays a central role in the numerical study of some diatomic molecules while accomplishing a calculus of error of integral transformations (see Part V).

A generalization of the theorem for the case of n-atomic molecules ($n > 2$) is formulated in the following weak theorem:

Lemma: For the overlap matrix of a set of N linearly independent normalized basis functions, the following relations hold:

$$\left(\kappa_{min} = \frac{s + t}{2}\right)$$
$$1/2 < \kappa_{min} < (N + 1)/2.$$

The proof follows easily from positive definiteness of Δ and by regarding the trace of Δ: $\mathrm{tr}(\Delta) = N$. So, we have an estimation for Γ:

$$\Gamma = \Delta - \frac{s + t}{2}\mathbf{I},$$

which is the matrix for the Γ-expansion technique. A stronger formulation of these inequalities should make use of local orthogonality of the basis functions, i.e., the block structure of the overlap matrix.

ACKNOWLEDGMENTS

K.N. is very grateful to Prof. Dr. F.F. Seelig for the continuous discussions of this work. K.N. was supported by the "Studienstiftung des deutschen Volkes."

References

1. R.D. Brown and K.R. Roby, Theor. Chim. Acta **16**, 175 (1970).
2. G.S. Chandler and F.E. Grader, Theor. Chim. Acta **54**, 131 (1980).
3. D. Carlson, Lin. Alg. Appl. 74, 257 (1986).

"Neglect of Diatomic Differential Overlap" in Nonempirical Quantum Chemical Orbital Theories. IV. An Examination of the Justification of the Neglect of Diatomic Differential Overlap (NDDO) Approximation

KLAUS NEYMEYR

Institut für Physikalische und Theoretische Chemie der Universität Tübingen, Auf der Morgenstelle 8, D-72076 Tübingen, Germany

Received March 18, 1994; revised manuscript received June 23, 1994; accepted July 6, 1994

ABSTRACT

The Neglect of Diatomic Differential Overlap approximation is examined in terms of a polynomial expansion in Γ. The expansion is based upon the Legendre or Chebyshev approximation as developed in Part II. Analogous to the theorems of Chandler and Grader, NDDO cannot be justified for one-electron integrals and only partially for the two-electron repulsion integrals. © 1995 John Wiley & Sons, Inc.

Introduction

In this part of the series, the justification of the Neglect of Diatomic Differential Overlap (NDDO) approximation will be examined. The approximation can be summarized by

$$\mu_A \nu_B \approx \delta_{AB} \mu_A \nu_A ,$$

where δ_{AB} is the Kronecker delta and μ_A is a basis function (orbital) localized at atom A and ν_B is localized at atom B. Thus, the NDDO approximation assumes disjoint supports for the functions localized at different centers.

For the two-center matrix element of a one-electron operator, the NDDO approximation leads to

$$M_{\mu\nu} \approx 0 .$$

(μ is localized at atom A, and ν, at atom B; $A \neq B$.) As will be developed in the following, no justification for this approximation can be given.

International Journal of Quantum Chemistry, Vol. 53, 541–552 (1995)

CCC 0020-7608/95/050541-12

The NDDO approximation is more favorable for electron repulsion integrals (two-electron integrals):

$$(\mu_A \nu_B \,|\, \kappa_C \sigma_D) \approx \delta_{AB}\delta_{CD}(\mu_A \nu_A \,|\, \kappa_C \sigma_C). \quad (1)$$

The two-electron integral reads

$$(\mu_A \nu_B \,|\, \kappa_C \sigma_D) = \iint d\mathbf{r}_1 d\mathbf{r}_2 \mu(\mathbf{r}_1 - \mathbf{R}_A) \times \nu(\mathbf{r}_1 - \mathbf{R}_B)\,|\mathbf{r}_1 - \mathbf{r}_2|^{-1} \times \kappa(\mathbf{r}_2 - \mathbf{R}_C)\sigma(\mathbf{r}_2 - \mathbf{R}_D).$$

(μ_A is localized at atom A, and ν_B, localized at atom B, and so on. Real basis functions are assumed.)

The $\mathbf{\Gamma}$-expansion technique for $\mathbf{\Delta}^{-1/2}$ ($\mathbf{\Delta}$ is the overlap matrix) in terms of Legendre and Chebyshev polynomials as developed in Part II will now be applied to the justification of the NDDO approximation. As can be seen in the following, NDDO cannot be justified in the general form (1).

Under the different methods of justification of general ZDO approximations, the **S**-expansion technique developed by Fischer–Hjalmars [1] for π-electron systems is of central importance. The **S**-expansion technique works in a basis of symmetrically orthogonalized functions, often called the Löwdin-basis. Some other methods are summarized by Chandler and Grader [2]. The presuppositions of some methods for the theoretical foundation of the NDDO approximation seem to be of more theoretical interest. For instance, in Roby's approach [3, 4], the discussion starts from a complete basis set on each atom. The minimal basis ansatz of valence orbitals for the calculation of methane molecule (cf. Gray and Stone in their criticism of **S**-expansion technique [5]) is remote from a complete basis. The one-dimensional space of a $1s$ Slater orbital at one hydrogen atom is not suitable for generating the four-dimensional space at the carbon atom.

The $\mathbf{\Gamma}$-expansion technique of Part II is a generalization of the **S**-expansion technique. A second-order expansion in $\mathbf{\Gamma}$ reads

$$\mathbf{\Delta}^{-1/2} = a\mathbf{I} + b\mathbf{\Gamma} + c\mathbf{\Gamma}^2 + O(\mathbf{\Gamma}^3), \quad (2)$$

with $\mathbf{\Gamma} = \mathbf{\Delta} - [(s + t)/2]\mathbf{I}$ and $s = \min \sigma(\mathbf{\Delta})$, $t = \max \sigma(\mathbf{\Delta})$. Legendre approximation yields for the expansion coefficients

$$a = (t^{1/2} + s^{1/2})^{-1}\left[2 - \left(\frac{t^{1/2} - s^{1/2}}{t^{1/2} + s^{1/2}}\right)^2\right], \quad (3)$$

$$b = -4(t^{1/2} + s^{1/2})^{-3}, \quad (4)$$

$$c = 12(t^{1/2} + s^{1/2})^{-5}. \quad (5)$$

Using Chebyshev approximation, one obtains

$$a = a_0 - a_2,$$

$$b = \frac{2a_1}{(t - s)},$$

$$c = \frac{8a_2}{(t - s)^2},$$

with

$$a_0 = \frac{\sqrt{2}}{\sqrt{t + s}} \sum_{i=0}^{\infty} \frac{(4i - 1)!!}{(4i)!!} \frac{(2i - 1)!!}{(2i)!!} \left(\frac{t - s}{t + s}\right)^{2i},$$

$$a_1 = -\frac{2^{3/2}}{\sqrt{t + s}} \sum_{i=0}^{\infty} \frac{(4i + 1)!!}{(4i + 2)!!} \frac{(2i + 1)!!}{(2i + 2)!!} \left(\frac{t - s}{t + s}\right)^{2i+1},$$

$$a_2 = -\frac{4\sqrt{2}}{\sqrt{t + s}} \sum_{i=0}^{\infty} \frac{(4i - 1)!!}{(4i)!!} \frac{(2i - 1)!!}{(2i + 2)!!} i\left(\frac{t - s}{t + s}\right)^{2i}.$$

In this article, an examination of the justification of NDDO approximation is given. Therefore, we use a $\mathbf{\Gamma}$-expansion. The dependence of the expansion coefficients a, b, and c on the spectrum of the overlap matrix of the discussed quantum chemical problem gives insight into the relation between quality of NDDO and the spectrum of the overlap matrix. Interesting results for diatomic molecules are obtained by utilizing the spectral properties of the overlap matrix (see Part III).

DEFINITIONS

It is advantageous to index the sums in a transparent manner for the following integral transformations. Thus, let S be a finite set of N localized and linearly independent atomic orbitals. Moreover, the elements of S are normalized and locally orthogonalized, i.e., the orthogonality is required for orbitals that are localized at the same atomic center. The orbitals are labeled by small Greek letter:

$$S = \{\mu, \nu, \lambda, \sigma, \kappa \ldots\}; \qquad N := |S|.$$

The equivalence relation $\sim$ "localized at the same center,"

$$\mu \sim \nu \iff \mu \text{ and } \nu \text{ are orbitals at the same atom},$$

decomposes S in disjoint subsets $A, B, C, \ldots$, which corresponds to an indexation of the atoms. Let C

(Cores) be the set of the N_a atoms:

$$S/_{\sim} \simeq C = \{A, B, C, \ldots\}, \qquad N_a := |C|.$$

(The algebraic notation $S/_{\sim}$ denotes the set of equivalence classes of S with respect to $\sim$ and is called the quotient set of S with respect to $\sim$ [6].)

Sometimes it may be useful to index the orbitals of S with $1, \ldots, N$. In this case, let $(\phi_i)_{i=1,\ldots,N}$ be the orbitals of the locally orthogonalized set S of basis functions (ϕ-basis), and $(\lambda_i)_{i=1,\ldots,N}$, the same basis after a symmetrical orthogonalization (λ-basis). Furthermore, let $\mathbf{\Delta}$ be the overlap matrix in the ϕ-basis and $\mathbf{S} := \mathbf{\Delta} - \mathbf{I}$.

Integral Representation in the Löwdin Basis by the Γ-expansion Technique: Transformation of One-electron Operators

With the vector of locally orthogonalized functions $(\phi_1, \ldots, \phi_N)$ and the overlap matrix

$$\mathbf{\Delta} = \int d\mathbf{r}(\phi_1, \ldots, \phi_N)^t(\phi_1, \ldots, \phi_N),$$

one gets the vector of symmetrically orthogonalized functions $(\lambda_1, \ldots, \lambda_N)$:

$$(\lambda_1, \ldots, \lambda_N) = (\phi_1, \ldots, \phi_N)\mathbf{\Delta}^{-1/2}.$$

The local orthogonality of the functions of S can be expressed by $\forall A \in C$, $\forall \mu, \nu \in A$:

$$\Delta_{\mu\nu} = \delta_{\mu\nu} \Rightarrow S_{\mu\nu} = 0 \quad \text{and}$$
$$\Gamma_{\mu\nu} = \delta_{\mu\nu}\left(1 - \frac{s+t}{2}\right).$$

The transformation of the matrix representation of a one-electron operator into the locally orthogonalized basis is as follows:

$${}^{\lambda}\mathbf{M} = \mathbf{\Delta}^{-1/2}\mathbf{M}\mathbf{\Delta}^{-1/2}.$$

With the Γ-expansion (2) to the second order, one obtains

$${}^{\lambda}\mathbf{M} = a^2\mathbf{M} + ab(\mathbf{M\Gamma} + \mathbf{\Gamma M}) + ac(\mathbf{M\Gamma}^2 + \mathbf{\Gamma}^2\mathbf{M}) + b^2\mathbf{\Gamma M\Gamma} + O(\mathbf{\Gamma}^3). \tag{6}$$

Now let us calculate the matrix elements of ${}^{\lambda}\mathbf{M}$; therefore, we utilize the Mulliken approximation [7] in the ϕ-basis $\forall A, B \in C, A \neq B, \mu \in A, \nu \in B$:

$$M_{\mu\nu} \approx \frac{\Delta_{\mu\nu}}{2}[M_{\mu\mu} + M_{\nu\nu}] = \frac{\Gamma_{\mu\nu}}{2}[M_{\mu\mu} + M_{\nu\nu}]. \tag{7}$$

The Mulliken approximation is only applied to those two-center elements $M_{\mu\nu}^{AB}$ that have a leading coefficient of the second order in Γ. [For those nondiagonal elements of Δ, it holds that $\mu, \nu \in S$, $\mu \neq \nu$, and $\Gamma_{\mu\nu} = S_{\mu\nu}$. Hence, after applying the Mulliken approximation, these terms can be collected in $O(\Gamma^3)$.]

Strictly analogous to Eqs. (26) and (27) of Chandler and Grader [2], the calculation results:

$\forall \mu, \nu \in S; \mu, \nu \in A, \mu \neq \nu$

$$\begin{aligned}
{}^{\lambda}M_{\mu\mu}^{AA} \approx\ & M_{\mu\mu}\left(a^2 + 2ab\Gamma_{\mu\mu} + 2ac\sum_{\sigma\in S}\Gamma_{\mu\sigma}^2\right) \\
& + 2ab\sum_{\sigma\in S\setminus\{\mu\}} M_{\mu\sigma}\Gamma_{\sigma\mu} \\
& + b^2\sum_{\sigma\in S} M_{\sigma\sigma}\Gamma_{\mu\sigma}^2 \\
& + 2ac\sum_{\sigma\in S\setminus\{\mu\}}\sum_{\sigma\in S} M_{\lambda\mu}\Gamma_{\mu\sigma}\Gamma_{\sigma\lambda} \\
& + b^2\sum_{\lambda\in S\setminus\{\sigma\}}\sum_{\sigma\in S} M_{\lambda\sigma}\Gamma_{\mu\lambda}\Gamma_{\sigma\mu} + O(\mathbf{\Gamma}^3)
\end{aligned} \tag{8}$$

$$\begin{aligned}
{}^{\lambda}M_{\mu\nu}^{AA} \approx\ & M_{\mu\nu}(a^2 + 2ab\Gamma_{\mu\mu} + b^2\Gamma_{\mu\mu}^2) \\
& + ab\sum_{\sigma\in S\setminus\{\mu,\nu\}}[M_{\mu\sigma}\Gamma_{\sigma\nu} + M_{\sigma\nu}\Gamma_{\mu\sigma}] \\
& + ac\sum_{\sigma\in S} M_{\mu\nu}[\Gamma_{\mu\sigma}^2 + \Gamma_{\nu\sigma}^2] \\
& + \sum_{\sigma\in S\setminus A} \\
& \times [ac(M_{\mu\mu} + M_{\nu\nu})\Gamma_{\mu\sigma}\Gamma_{\sigma\nu} + b^2 M_{\sigma\sigma}\Gamma_{\mu\sigma}\Gamma_{\sigma\nu}] \\
& + ac\sum_{\rho\in A\setminus\{\nu,\mu\}}\sum_{\sigma\in S} \\
& \times [M_{\rho\nu}\Gamma_{\mu\sigma}\Gamma_{\sigma\rho} + M_{\mu\rho}\Gamma_{\rho\sigma}\Gamma_{\sigma\nu}] \\
& + b^2\sum_{\rho\in S\setminus A}\sum_{\sigma\in S\setminus(A\cup\{\rho\})}[M_{\rho\sigma}\Gamma_{\mu\rho}\Gamma_{\sigma\nu}] + O(\mathbf{\Gamma}^3).
\end{aligned} \tag{9}$$

This and the following equations are written approximatively, using "≈", because the Mulliken approximation has been employed. In Part V of this

series, all approximation errors will be thoroughly analyzed.

For the two-center matrix element, ${}^{\lambda}\mathbf{M}^{AB}_{\mu\nu}$, one obtains by an exhaustive application of the Mulliken approximation:

$$\forall A, B \in C, A \neq B, \forall \mu \in A, \forall \nu \in B$$

$$\begin{aligned}
{}^{\lambda}M^{AB}_{\mu\nu} \approx\ & \Gamma_{\mu\nu}(M_{\mu\mu} + M_{\nu\nu}) \\
& \times [a^2/2 + ab + \Gamma_{\mu\mu}(ab + b^2 + 2ac)] \\
& + ab \sum_{\sigma \in B\setminus\{\nu\}} \Gamma_{\mu\sigma} M_{\sigma\nu} + ab \sum_{\sigma \in A\setminus\{\mu\}} \Gamma_{\sigma\nu} M_{\mu\sigma} \\
& + \frac{ab}{2} \sum_{\sigma \in S\setminus(A\cup B)} \Gamma_{\mu\sigma}\Gamma_{\sigma\nu} \\
& \times [M_{\mu\mu} + 2M_{\sigma\sigma} + M_{\nu\nu}] \\
& + \sum_{\sigma \in S\setminus(A\cup B)} \Gamma_{\mu\sigma}\Gamma_{\sigma\nu} \\
& \times [acM_{\mu\mu} + b^2 M_{\sigma\sigma} + acM_{\nu\nu}] \\
& + b^2 \sum_{E \in C\setminus\{A,B\}} \sum_{\substack{\rho,\sigma \in E \\ \rho \neq \sigma}} \Gamma_{\mu\sigma} M_{\sigma\rho} \Gamma_{\rho\nu} \\
& + (2ac + b^2) \\
& \times \left[\sum_{\sigma \in A\setminus\{\mu\}} \Gamma_{\mu\mu} M_{\mu\sigma} \Gamma_{\sigma\nu} + \sum_{\sigma \in B\setminus\{\nu\}} \Gamma_{\mu\sigma} M_{\sigma\nu} \Gamma_{\mu\mu} \right] \\
& + ac \sum_{\sigma \in S\setminus(A\cup B)} \\
& \times \left[\sum_{\rho \in A\setminus\{\mu\}} \Gamma_{\rho\sigma}\Gamma_{\sigma\nu} M_{\mu\rho} + \sum_{\rho \in B\setminus\{\nu\}} \Gamma_{\mu\sigma}\Gamma_{\sigma\rho} M_{\rho\nu} \right] \\
& + O(\mathbf{\Gamma}^3). \qquad (10)
\end{aligned}$$

Hence, two conclusions can be drawn:

1. No justification for an application of the NDDO approximation on two-center integrals can be seen. It is true that
$$ {}^{\lambda}M^{AB}_{\mu\nu} \approx 0 + O(\mathbf{\Gamma}); $$
however, the terms of the first order cannot be neglected. In accordance with Brown, et al. [8], Brown and Burton [9], and Chandler and Grader, the NDDO approximation is not applicable to one-electron operators.
2. Furthermore, an identification of the integrals in the ϕ- and the λ-basis is not possible. A very rough approximation is an expansion of the zeroth degree, where
$$ {}^{\lambda}M_{\mu\nu} \approx {}^{\phi}M_{\mu\nu} a^2 + O(\mathbf{\Gamma}), $$
with a scaling constant a^2. (The scaling constant has to be calculated for a polynomial expansion of the zeroth degree; cf. Part II.)

Two-electron Integrals

The charge density matrix in the ϕ-basis is defined by

$$ \mathbf{\Omega} := (\phi_1, \ldots, \phi_N)^t (\phi_1, \ldots, \phi_N). \qquad (11) $$

Like one-electron operators, it transforms into the Löwdin basis:

$$ {}^{\lambda}\mathbf{\Omega} = \mathbf{\Delta}^{-1/2} \mathbf{\Omega} \mathbf{\Delta}^{-1/2}. \qquad (12) $$

From this follows the representation of the repulsion integrals by

$$\begin{aligned}
{}^{\lambda}(\mu\nu \mid \kappa\lambda) &= ({}^{\lambda}\Omega_{\mu\nu}(1) \mid {}^{\lambda}\Omega_{\kappa\lambda}(2)) \\
&= \iint d\mathbf{r}_1 d\mathbf{r}_2\, {}^{\lambda}\Omega_{\mu\nu}(1) \\
&\quad \times |\mathbf{r}_1 - \mathbf{r}_2|^{-1}\, {}^{\lambda}\Omega_{\kappa\lambda}(2).
\end{aligned}$$

In agreement with the other works cited above, Chandler and Grader asserted that the NDDO approximation is only partially justifiable for the two-electron integrals. For the justification in the Löwdin basis, one has to transform the integrals by

$$\begin{aligned}
{}^{\lambda}(\mu\nu \mid \kappa\lambda) = & \sum_{u,v,s,t \in S} (\mathbf{\Delta}^{-1/2})_{\mu u} \\
& \times (\mathbf{\Delta}^{-1/2})_{\nu v} (\mathbf{\Delta}^{-1/2})_{\kappa s} \\
& \times (\mathbf{\Delta}^{-1/2})_{\lambda t}\, {}^{\phi}(uv \mid st). \qquad (13)
\end{aligned}$$

However, for this full transformation, one needs all two-electron integrals in the ϕ-basis; such a procedure has no advantages. Hence, we have to restrict the domain of the linear mapping (13) to the NDDO-surviving integrals by substitution of the two-center charge distributions by one-center charge distributions using the Mulliken approximation [7]:

$$\forall \mu \in A, \forall \nu \in B, \forall A, B \in C$$

$$ \Omega_{\mu\nu} \approx \frac{\Gamma_{\mu\nu}}{2} [\Omega_{\mu\mu} + \Omega_{\nu\nu}]. \qquad (14) $$

(For nondiagonal elements of $\mathbf{\Delta}$, it holds that $\Gamma_{\mu\nu} = \Delta_{\mu\nu}$.)

One obtains by Mulliken approximation

$$C \neq D$$

$$\begin{aligned}
{}^{\phi}(\mu_A \nu_A \mid \kappa_C \lambda_D) \approx \frac{\Delta_{\kappa\lambda}}{2} & [{}^{\phi}(\mu_A \nu_A \mid \kappa_C \kappa_C) \\
& + {}^{\phi}(\mu_A \nu_A \mid \lambda_D \lambda_D)],
\end{aligned}$$

and for $A \neq B$ and $C \neq D$,

$$\phi(\mu_A\nu_B \mid \kappa_C\lambda_D) \approx \frac{\Delta_{\mu\nu}\Delta_{\kappa\lambda}}{2} \times [\phi(\mu\mu \mid \kappa\kappa) + \phi(\mu\mu \mid \lambda\lambda) + \phi(\nu\nu \mid \kappa\kappa) + \phi(\nu\nu \mid \lambda\lambda)].$$

Figure 1 summarizes some aspects of the concept. The two-electron integrals in the ϕ-basis can be found on the left side and on the right side those in the λ-basis. The domain of the linear mapping from the ϕ-basis to the λ-basis can be restricted to the NDDO-surviving integrals due to the Mulliken approximation (vertical arrow). For this reason, the lower-left box containing the integrals $\phi(\mu_A\nu_B \mid \kappa_C\lambda_D)$ is not connected to the integrals in the λ-basis. In the section NDDO-surviving Integrals the transformation of the NDDO-surviving integrals is given (horizontal arrow); in the section Integrals with Two-center Charge Distributions follows the discussion of the justification of NDDO by an analysis of the integrals with two-center charge distributions (diagonal arrow).

By Eqs. (8)–(10) and with respect to (14), one can calculate the matrix elements of the charge density matrix in the Löwdin basis, which only depend on one-center matrix elements in the locally orthogonalized basis. By means of a Kronecker delta, (8) and (9) can be treated commonly. The calculation leads to $\forall \mu, \nu \in A \in C$:

$$\begin{aligned}
{}^{\lambda}\Omega_{\mu\nu}^{AA} \approx \Omega_{\mu\nu}\Big[& a^2 + 2ab\Gamma_{\mu\mu} + (2ac + b^2)\Gamma_{\mu\mu}^2 \\
& + (1 - \delta_{\mu\nu})ac \sum_{\sigma\in S\setminus A} (\Gamma_{\mu\sigma}^2 + \Gamma_{\nu\sigma}^2)\Big] \\
& + \sum_{\sigma\in S\setminus A} \Gamma_{\mu\sigma}\Gamma_{\nu\sigma} \\
& \times \left(\left(\frac{ab}{2} + ac\right)(\Omega_{\mu\mu} + \Omega_{\nu\nu}) + (ab + b^2)\Omega_{\sigma\sigma}\right) \\
& + ac \sum_{\rho\in A\setminus\{\mu,\nu\}} \sum_{\sigma\in S\setminus A} \\
& \times \{\Gamma_{\mu\sigma}\Gamma_{\sigma\rho}\Omega_{\rho\nu} + \Gamma_{\nu\sigma}\Gamma_{\sigma\rho}\Omega_{\rho\mu}\} \\
& + b^2 \sum_{C\in C\setminus\{A\}} \sum_{\substack{\sigma,\rho\in C \\ \rho\neq\sigma}} \Gamma_{\mu\rho}\Gamma_{\sigma\nu}\Omega_{\rho\sigma} + O(\Gamma^3), \qquad (15)
\end{aligned}$$

and $\forall A, B \in C, A \neq B, \mu \in A, \nu \in B$:

$$\begin{aligned}
{}^{\lambda}\Omega_{\mu\nu}^{AB} \approx & \Gamma_{\mu\nu}(\Omega_{\mu\mu} + \Omega_{\nu\nu}) \\
& \times [a^2/2 + ab + \Gamma_{\mu\mu}(ab + b^2 + 2ac)] \\
& + ab \sum_{\sigma\in B\setminus\{\nu\}} \Gamma_{\mu\sigma}\Omega_{\sigma\nu} + ab \sum_{\sigma\in A\setminus\{\mu\}} \Gamma_{\sigma\nu}\Omega_{\mu\sigma} \\
& + \frac{ab}{2} \sum_{\sigma\in S\setminus(A\cup B)} \Gamma_{\mu\sigma}\Gamma_{\sigma\nu} \\
& \times [\Omega_{\mu\mu} + 2\Omega_{\sigma\sigma} + \Omega_{\nu\nu}] \\
& + \sum_{\sigma\in S\setminus(A\cup B)} \Gamma_{\mu\sigma}\Gamma_{\sigma\nu} \\
& \times [ac\Omega_{\mu\mu} + b^2\Omega_{\sigma\sigma} + ac\Omega_{\nu\nu}] + O(\Gamma^3). \qquad (16)
\end{aligned}$$

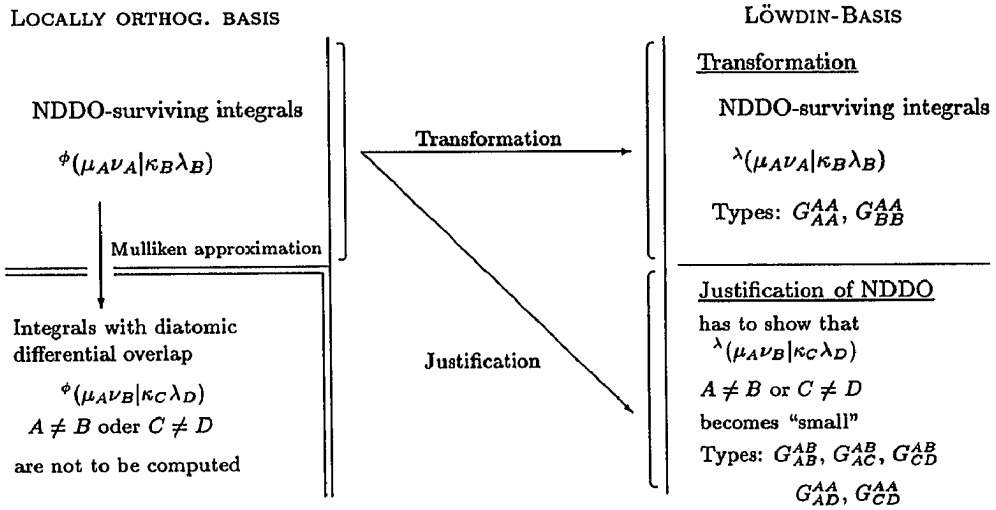

FIGURE 1. The two-electron integrals in the locally orthogonalized basis (ϕ-basis) can be found on the left side and on the right side those in the Löwdin basis (λ-basis). The transformation of the NDDO-surviving integrals are analyzed in the section NDDO-Surviving Integrals (horizontal arrow). The section Integrals with Two-center Charge Distributions is a discussion on the justification of NDDO (diagonal arrow).

The last formula follows from employing a further approximation as introduced by Chandler and Grader [2]. In our notation, it reads

$$(\mu_A \nu_A \mid \kappa\kappa) \approx O(\mathbf{\Gamma})\,(\mu\mu \mid \kappa\kappa) \quad \text{for} \quad \mu \neq \nu\,.$$

This approximation neglects one-center nondiagonal elements of $\mathbf{\Omega}$, if they have a leading coefficient of the second order in $\mathbf{\Gamma}$, since after application of this approximation, the term vanishes in $O(\mathbf{\Gamma}^3)$:

$$\Gamma_{ab}\Gamma_{cd}(\mu_A \nu_A \mid \kappa\kappa) \approx O(\Gamma^3)\,. \tag{17}$$

Thus, from the terms of the second order in $\mathbf{\Gamma}$, only diagonal elements of $\mathbf{\Omega}$ are preserved. Therefore, let us call this approximation the "diagonal-approximation."

The diagonal-approximation is applied for the transformation from (10) to (16). After calculating the representation of the two-electron-integrals, one can employ the diagonal-approximation exhaustively.

The discussed proceeding follows the argumentation of Chandler and Grader; analogously, we obtain some results that partially justify the NDDO approximation. The effects of the various integral approximations (truncated binomial expansion of $\mathbf{\Delta}^{-1/2}$, Mulliken approximation, and the diagonal-approximation) will be studied critically in Part V.

Let us proceed in developing the two-electron integrals in the symmetrically orthogonalized basis:

$$^{\lambda}(\mu\nu \mid \kappa\lambda) = (^{\lambda}\Omega_{\mu\nu}(1) \mid {}^{\lambda}\Omega_{\kappa\lambda}(2))\,. \tag{18}$$

The integrals can be classified from the manner in which they are derived. Let G be the *set* of all (N^4) repulsion integrals. This set can be decomposed into seven disjoint subsets (compare with the slightly different definition by Chandler and Grader):

$$G = \underbrace{G^{AA}_{AA}}_{\text{one center}} \cup \underbrace{G^{AA}_{BB} \cup G^{AA}_{AD} \cup G^{AB}_{AB}}_{\text{two centers}} \cup \underbrace{G^{AA}_{CD} \cup G^{AB}_{AC}}_{\text{three centers}} \cup \underbrace{G^{AB}_{CD}}_{\text{four centers}} \tag{19}$$

For instance, G^{AB}_{CD} consists of all four-center integrals:

$$G^{AB}_{CD} = \{(\mu_A \nu_B \mid \kappa_C \lambda_D);\ A, B, C, D \text{ pairwise different}\}\,.$$

The different combinations of (15) and (16) lead to a classification into three types:

(i) The sets G^{AA}_{AA} and G^{AA}_{BB} consist only of one-center charge distributions. They describe the NDDO-surviving integrals.

(ii) G^{AB}_{AB}, G^{AB}_{AC}, G^{AB}_{CD}. These two-, three-, and four-center integrals contain in their (generalized) "bra" and "ket" only two-center charge distributions. They have to be calculated from (16). The generalized "bra" of (18) is $^{\lambda}\Omega_{\mu\nu}(1)$, and the "ket" $^{\lambda}\Omega_{\kappa\lambda}(2)$.

(iii) G^{AA}_{AD}, G^{AA}_{CD}. These integrals can be calculated from a one-center and two-center charge distribution: (15) and (16). The two-center term can be found in the "bra" or in the "ket."

The transformation of the integrals of type (i) provides an approximative description of the NDDO-surviving integrals in the Löwdin basis. The other types are needed for the justification of NDDO approximation.

NDDO-SURVIVING INTEGRALS

With the one-center charge density $^{\lambda}\Omega^{AA}_{\mu\nu}$ (15) and (18), one obtains the integral representation of type (i):

$$\forall A, B \in C, A = B \quad \text{or} \quad A \neq B, \forall \mu, \nu \in A, \forall \kappa, \lambda \in B$$

$$\begin{aligned}
\frac{1}{a^2}\,^{\lambda}(\mu\nu \mid \kappa\lambda) \approx\ & (\mu\nu \mid \kappa\lambda) \\
& \times (a^2 + 4ab\Gamma_{\mu\mu} + (6b^2 + 4ac)\Gamma^2_{\mu\mu}) \\
& + \sum_{\sigma \in S\setminus B} \Big\{ a\Big(\frac{b}{2} + c\Big)\Gamma_{\kappa\sigma}\Gamma_{\sigma\lambda}((\mu\nu \mid \kappa\kappa) \\
& \quad + (\mu\nu \mid \lambda\lambda)) + b(a + b) \\
& \quad \times \Gamma_{\kappa\sigma}\Gamma_{\sigma\lambda}(\mu\nu \mid \sigma\sigma) \Big\} \\
& + \sum_{\sigma \in S\setminus A} \Big\{ a\Big(\frac{b}{2} + c\Big)\Gamma_{\mu\sigma}\Gamma_{\sigma\nu}((\mu\mu \mid \kappa\lambda) \\
& \quad + (\nu\nu \mid \kappa\,\lambda)) \\
& \quad + b(a + b)\Gamma_{\mu\sigma}\Gamma_{\sigma\nu}(\sigma\sigma \mid \kappa\lambda) \Big\} \\
& + ac(\mu\nu \mid \kappa\lambda) \\
& \times \Big\{ (1 - \delta_{\kappa\lambda}) \sum_{\sigma \in S\setminus B}
\end{aligned}$$

$$\times (\Gamma_{\lambda\sigma}^2 + \Gamma_{\kappa\sigma}^2)$$

$$+ (1 - \delta_{\mu\nu}) \sum_{\sigma \in S\setminus A} (\Gamma_{\nu\sigma}^2 + \Gamma_{\mu\sigma}^2) \Big\}$$

$$+ ac \sum_{\rho \in B\setminus\{\kappa,\lambda\}} \sum_{\sigma \in S\setminus B}$$

$$\times [(\mu\nu \mid \rho\lambda)\Gamma_{\kappa\sigma}$$

$$\times \Gamma_{\sigma\rho} + (\mu\nu \mid \kappa\rho)\Gamma_{\rho\sigma}\Gamma_{\sigma\lambda}]$$

$$+ ac \sum_{\rho \in A\setminus\{\mu,\nu\}} \sum_{\sigma \in S\setminus A}$$

$$\times [(\rho\nu \mid \kappa\lambda)\Gamma_{\mu\sigma}\Gamma_{\sigma\rho}$$

$$+ (\mu\rho \mid \kappa\lambda)\Gamma_{\rho\sigma}\Gamma_{\sigma\nu}]$$

$$+ b^2 \sum_{C \in C\setminus\{B\}} \sum_{\substack{\sigma,\rho \in C \\ \rho \neq \sigma}} (\mu\nu \mid \sigma\rho)\Gamma_{\kappa\rho}\Gamma_{\sigma\lambda}$$

$$+ b^2 \sum_{C \in C\setminus\{A\}} \sum_{\substack{\sigma,\rho \in C \\ \rho \neq \sigma}} (\rho\sigma \mid \kappa\lambda)\Gamma_{\mu\rho}\Gamma_{\sigma\nu}$$

$$+ O(\Gamma^3). \tag{20}$$

The integral ${}^{\lambda}(\mu\nu \mid \kappa\lambda)$ can only be written approximatively due to the Mulliken approximation.

By identification of the atoms A and B and/or identification of the functions μ, ν, κ, and λ (observe the Kronecker delta), one obtains linear transformations for all NDDO-surviving integrals. Equation (20) correspond to Eqs. (42)–(45) from Chandler and Grader but in a more generalized form. Chandler and Grader [2] proposed an identification of the integrals in the local orthogonalized basis with that in the Löwdin basis:

$$\forall A, B \in C, \mu, \nu \in A, \kappa, \lambda \in B$$

$${}^{\lambda}(\mu_A\nu_A \mid \kappa_B\lambda_B) \approx {}^{\phi}(\mu_A\nu_A \mid \kappa_B\lambda_B).$$

By regarding (20), one cannot agree to this proposal. Only an expansion of the zeroth degree leads to an integral scaling

$${}^{\lambda}(\mu_A\nu_A \mid \kappa_B\lambda_B) \approx {}^{\phi}(\mu_A\nu_A \mid \kappa_B\lambda_B)a^4 + O(\Gamma).$$

For this approximation, the Legendre coefficient reads $a = c_0(0) = 2(t^{1/2} + s^{1/2})^{-1}$ (cf. Part II). Therewith, we have established a scaling constant analytically; compare Chandrasekhar et al. [10]. Nevertheless, the proposed identification of integrals will find some justification by study of the approximation errors in Part V.

INTEGRALS WITH TWO-CENTER CHARGE DISTRIBUTIONS

For the calculation of these integrals of the types (ii) and (iii), the diagonal-approximation (17) is utilized. As mentioned above, a subsequent check must be made to determine whether the wish to have simple equations for justifying NDDO was causal for the introduction of the above approximation. For the integral types (ii), i.e., G_{AB}^{AB}, G_{AC}^{AB}, and G_{CD}^{AB}, one obtains

$$\forall \mu \in A, \forall \nu \in B, \forall \kappa \in C, \forall \lambda \in D, A \neq B \quad \text{and} \quad C \neq D$$

$${}^{\lambda}(\mu\nu \mid \kappa\lambda) \approx (a^2/2 + ab)^2\Gamma_{\mu\nu}\Gamma_{\kappa\lambda}$$

$$\times [(\mu\mu \mid \kappa\kappa) + (\mu\mu \mid \lambda\lambda) + (\nu\nu \mid \kappa\kappa)$$

$$+ (\nu\nu \mid \lambda\lambda)] + O(\Gamma^3). \tag{21}$$

Conclusions will be discussed in the next section.

In the remaining case (iii), i.e., the integrals G_{AD}^{AA} and G_{CD}^{AA}, we have to make a further distinction. Only G_{CD}^{AA} has to be investigated, because the identification $C = A$ leads to the two-center integrals.

Let $\mu, \nu \in A, \kappa \in C, \lambda \in D, C \neq D$, then

(1) $\underline{\mu \neq \nu}$

$${}^{\lambda}(\mu\nu \mid \kappa\lambda) \approx a^2(a^2/2 + ab)\Gamma_{\kappa\lambda}$$

$$\times [(\mu\nu \mid \kappa\kappa) + (\mu\nu \mid \lambda\lambda)] + O(\Gamma^3). \tag{22}$$

(2) $\underline{\mu = \nu}$

$$\frac{1}{a^2}{}^{\lambda}(\mu\mu \mid \kappa\lambda) = \frac{1}{a^2}({}^{\lambda}\Omega_{\mu\mu}^{AA} \mid {}^{\lambda}\Omega_{\kappa\lambda}^{CD})$$

$$\approx (a^2/2 + ab + \Gamma_{\mu\mu}(2ab + 2ac + 3b^2))$$

$$\times \Gamma_{\kappa\lambda}[(\mu\mu \mid \kappa\kappa) + (\mu\mu \mid \lambda\lambda)]$$

$$+ (ab + 2b^2\Gamma_{\mu\mu})$$

$$\times \Bigg[\sum_{\sigma \in D\setminus\{\lambda\}} \Gamma_{\kappa\sigma}(\mu\mu \mid \sigma\lambda)$$

$$+ \sum_{\sigma \in C\setminus\{\kappa\}} \Gamma_{\sigma\lambda}(\mu\mu \mid \kappa\sigma) \Bigg]$$

$$+ \sum_{\sigma \in S\setminus(C\cup D)} \Gamma_{\kappa\sigma}\Gamma_{\sigma\lambda}$$

$$\times \Bigg[\left(ac + \frac{ab}{2}\right)\{(\mu\mu \mid \kappa\kappa) + (\mu\mu \mid \lambda\lambda)\}$$

$$+ (ab + b^2)(\mu\mu \mid \sigma\sigma) \Bigg]$$

$$+ O(\Gamma^3). \tag{23}$$

TO THE JUSTIFICATION NDDO

The approximation of NDDO applied to two-electron integrals leads to a reliable nonempirical quantum chemical computation method, if the inspected integrals in the last section "become sufficiently small." Let us first analyze Eqs. (21)–(23) for the instructive diatomic case:

(a) Diatomic molecules:

Chandler and Grader showed in Eq. (36) of [2] for the integral type G_{CD}^{AB} (for the diatomic case only G_{AB}^{AB}) that

$$\begin{aligned}(1+x)^2\,{}^{\lambda}(\mu\nu\,|\,\lambda\sigma) \approx \frac{1}{4}[&S_{\mu\nu}S_{\lambda\sigma} - S_{\mu\nu}P_{\lambda\sigma} \\ &- P_{\mu\nu}S_{\lambda\sigma} + P_{\mu\nu}P_{\lambda\sigma}] \\ &\times [(\mu\mu\,|\,\lambda\lambda) + (\nu\nu\,|\,\lambda\lambda) \\ &+ (\mu\mu\,|\,\sigma\sigma) + (\nu\nu\,|\,\sigma\sigma)] \\ &+ O(\mathbf{P}^3)\,.\end{aligned}$$

This equation stands in close analogy to Eq. (21). Using Corollary 3 of the theorem in Part III of this series, which says $\mathbf{P} = \mathbf{S}$ for diatomic molecules, one derives

$$\begin{aligned}[S_{\mu\nu}S_{\lambda\sigma} - S_{\mu\nu}P_{\lambda\sigma} - P_{\mu\nu}S_{\lambda\sigma} + P_{\mu\nu}P_{\lambda\sigma}] &= 0 \\ {}^{\lambda}(\mu\nu\,|\,\lambda\sigma) &\approx 0 + O(\mathbf{P}^3)\,.\end{aligned}$$

The corresponding factor q^2 of the sum of the second order in Γ of (21) reads

$$q^2 = \left(\frac{a^2}{2} + ab\right)^2. \tag{24}$$

Employing the Γ-expansion technique, the relation between the spectrum of the overlap matrix and the quality of NDDO approximation can be studied. Because of their closed representation, let us use the Legendre coefficients (3)–(5) and use the proved property, $s = 2 - t$, found in Part III:

$$\begin{aligned}q = \frac{a^2}{2} + ab = -6 \\ \times \frac{(4t^{1/2} - t^{3/2})(2-t)^{1/2} - t^{1/2}(2-t)^{3/2} + 3t^2 - 6t + 1}{(t^{1/2} + (2-t)^{1/2})^6}.\end{aligned} \tag{25}$$

Figure 2 shows the function for $t \in]1,2[$ that is the possible interval for the greatest eigenvalue of the overlap matrix of a diatomic molecule. By the symmetry under permutation of s and t of the general coefficient formula (cf. Part II), let us continue the function to $t \in]0,1[\cup]1,2[$. For $s = t \to 1$, the limes reads (the choice $s = t = 1$ was excluded)

$$a = 1, \qquad b = -1/2, \qquad c = 3/8.$$

These are the first coefficients of the binomial expansion. In this case, one obtains

$$q = \frac{a^2}{2} + ab \longrightarrow 0.$$

The limes $s = t = 1$ is equivalent to $\sigma(\mathbf{\Delta}) = \{1\}$ and $\mathbf{\Delta} = \mathbf{I}$. Thus, for a globally orthogonalized ϕ-basis, one has the best possible justification of the NDDO approximation for the integral G_{CD}^{AB} (here only G_{AB}^{AB}) of diatomic molecules:

$$s = t = 1: \quad {}^{\lambda}(\mu\nu\,|\,\kappa\lambda) \approx 0 + O(\mathbf{\Gamma}^3).$$

Moreover, q is bounded (see Fig. 2). For $t \to 2$ ($s \to 0$), it holds that

$$q^2 = \left(\frac{a^2}{2} + ab\right)^2 \longrightarrow (-0.75)^2 = 0.5625.$$

One has for G_{CD}^{AB} generally

$${}^{\lambda}(\mu\nu\,|\,\kappa\lambda) \approx 0 + O(\mathbf{\Gamma}^2);$$

therefore, the NDDO approximation seems to be sufficiently justified in agreement with Chandler and Grader.

The judgment for the remaining integrals G_{AD}^{AA} is unfavorable, because Eqs. (22) and (23) contain terms of the first order in Γ. However, in case (1) for $\mu \neq \nu$, the leading coefficient q (to the power of one) provides some restricted justification, especially for $t \to 1 (q \to 0)$. In case (2) for $\mu = \nu$, no justification of the NDDO approximation can be seen. Also, the substitution $\Gamma_{\mu\mu} = 0$ (valid for diatomic molecules under local orthogonality) does not simplify (23) sufficiently.

(b) n-atomic molecules:

The coefficient (24) reads for Legendre coefficients as a function of s and t:

$$q = \frac{-8(t+s) + t^2 + s^2 + s^{1/2}(12t^{3/2} - 48t^{1/2}) + 38ts + 12t^{1/2}s^{3/2}}{2(t^{1/2} + s^{1/2})^6}.$$

Figure 3 shows $q(s,t)$ for $(s,t) \in]0,8]^2$; by the invariance of q under permutation of s and t, the function can be continued. The limes $s = t \to 1$,

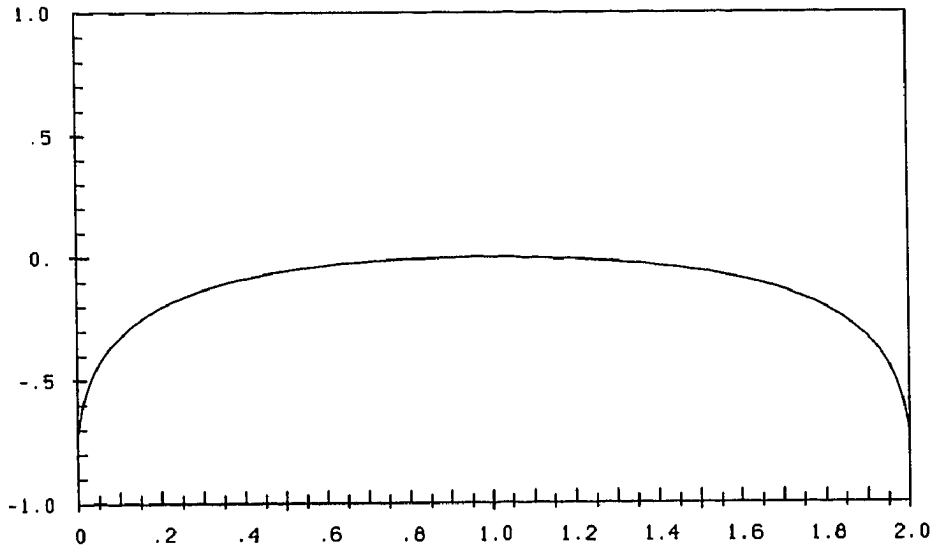

FIGURE 2. Coefficient $q(t)$ for diatomic molecules. Abscissa: t; ordinate: $q(t)$.

which implies a globally orthogonalized basis, leads also to $q = 0$. From the normalization of the basis follows $s < 1$ (by the discussion of the trace of the overlap matrix). One can conclude by inspection of Figure 3 that the greater s is the better the NDDO approximation is fulfilled.

With (21), we conclude analogously that for G_{CD}^{AB} (G_{AC}^{AB}, G_{AB}^{AB}), the approximation is sufficiently justified. For the two- and three-center integrals G_{AD}^{AA} and G_{CD}^{AA}, especially for $\mu = \nu$, the validity is restricted to the zeroth degree only.

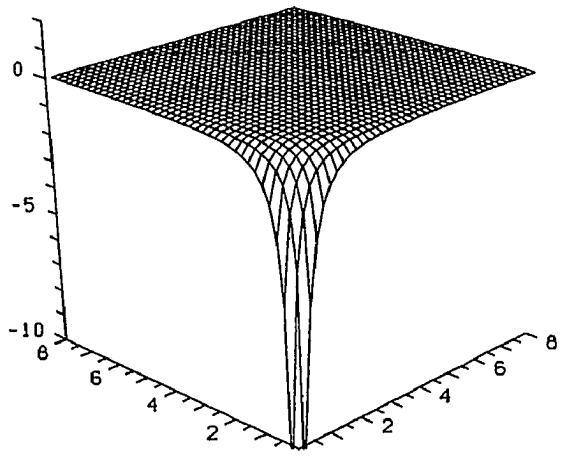

FIGURE 3. Coefficient $q(s,t)$. Abscissa: s,t; ordinate: $q(s,t) = q(t,s)$.

Numerical Illustration: Boron Nitride (BN)

Let us discuss the isolated boron nitride (BN) molecule to represent the order of magnitude of the involved integrals exemplarily. An all-electron minimal Slater basis of 10 Slater orbitals has been used: bond distance, $d_{BN} = 1.281$ Å; single-zeta exponents are given by Clementi and Roetti [11].

Figures 4 and 5 allow a comparison of the frequency distributions of the values of repulsion integrals in the locally orthogonalized basis with that in the Löwdin basis. The calculation was performed without integral approximations following Eq. (13) using the program DIATOM available at QCPE [12]. DIATOM is embedded in a program package UHF2 by Koch [13], from which only the integral part was used. On the ordinate, the frequency of repulsion integrals within the abscissa interval $[(i)/(1000), (i + 1)/(1000)]$ for $i \in [-1000, 1000] \cap \mathbf{Z}$ can be found. Except for the integrals of value zero, most of the integrals are plotted in the selected window. Integrals of value zero lie outside this window. From the 2500 NDDO-surviving integrals, 1712 have the value zero. In Figure 4(a) and (b), one can compare the integrals with differential two-center overlap; these integrals are neglected by NDDO approximation.

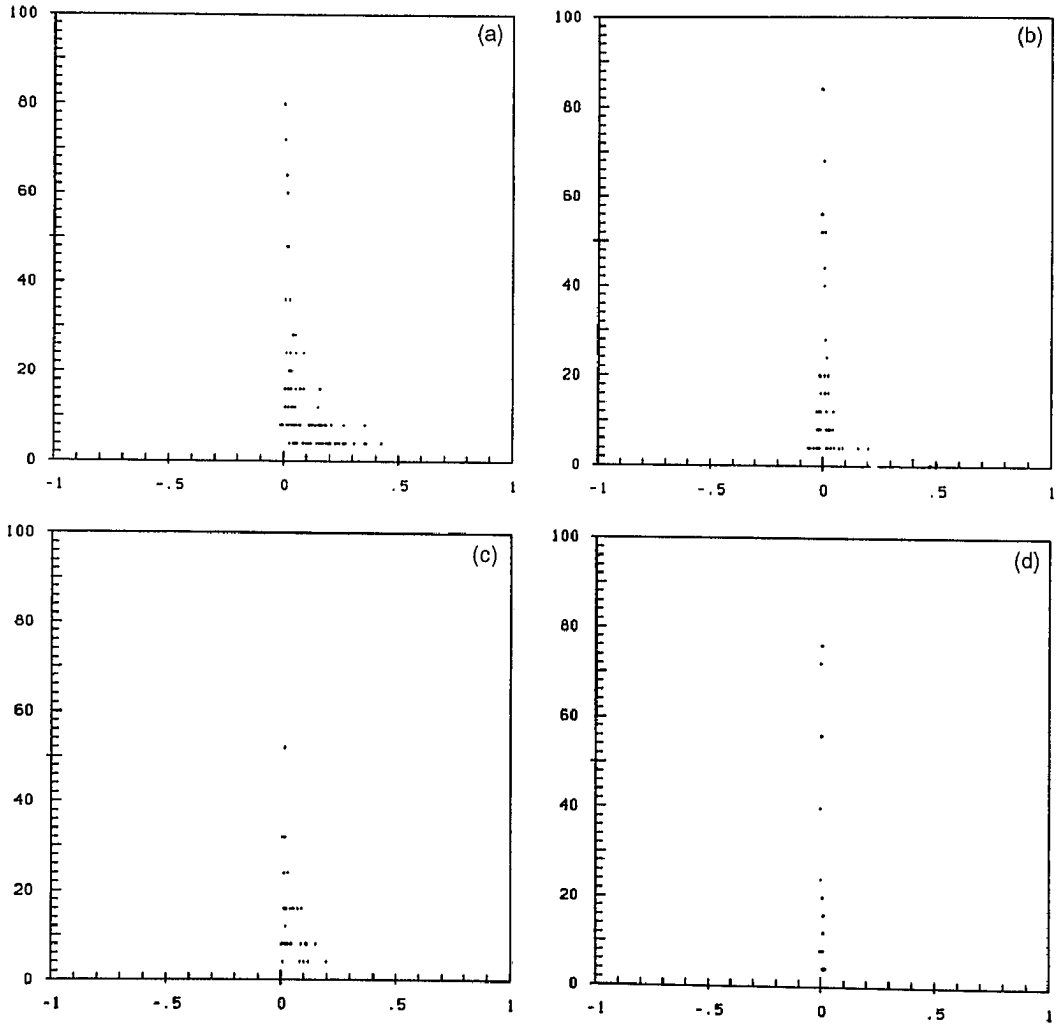

FIGURE 4. Frequency distribution of repulsion integrals of boron nitride (BN); Abscissa: value of integrals; ordinate: frequency within abscissa interval 1/1000. The notation (x,y) stands for x integrals of value zero from a total of y integrals. (a, b) Repulsion integrals with two-center charge distribution: (a) locally orthogonalized basis (5136, 7500); (b) Löwdin basis (5136, 7500). (c, d) Repulsion integrals of types G_{CD}^{AB} (G_{AC}^{AB}, G_{AB}^{AB}); (c) locally orthogonalized basis (1712,2500); (d) Löwdin basis (1712,2500).

The NDDO approximation is only poorly fulfilled in the locally orthogonalized basis because of the wide flank in the abscissa interval [0, 0.5]. It is much better justified in the symmetrically orthogonalized basis due to the peak that is centered at zero and sharper than in the other basis. (This empirical finding motivates the theoretical investigations of the symmetrically orthogonalized basis.) Local orthogonalization was performed using a Schmidt procedure.

Figure 4(c) and (d) show an analogous behavior for the integrals of the type G_{CD}^{AB} (G_{AC}^{AB}, G_{AB}^{AB}) for which the approximation is best justified. The frequency distribution of these integrals is characterized by a sharp peak at zero.

The remaining integrals with differential two-center overlap of types G_{CD}^{AA} and G_{AD}^{AA} are investigated in Figure 5. For these integrals, the NDDO approximation is badly fulfilled, especially for the case of identical functions $\mu, \nu \in A$ with $\mu = \nu$, which is shown in Figure 5(c) and (d).

The symmetrically orthogonalized basis is for NDDO approximation more appropriate: This orthogonalization "centers" and "sharpens" the in-

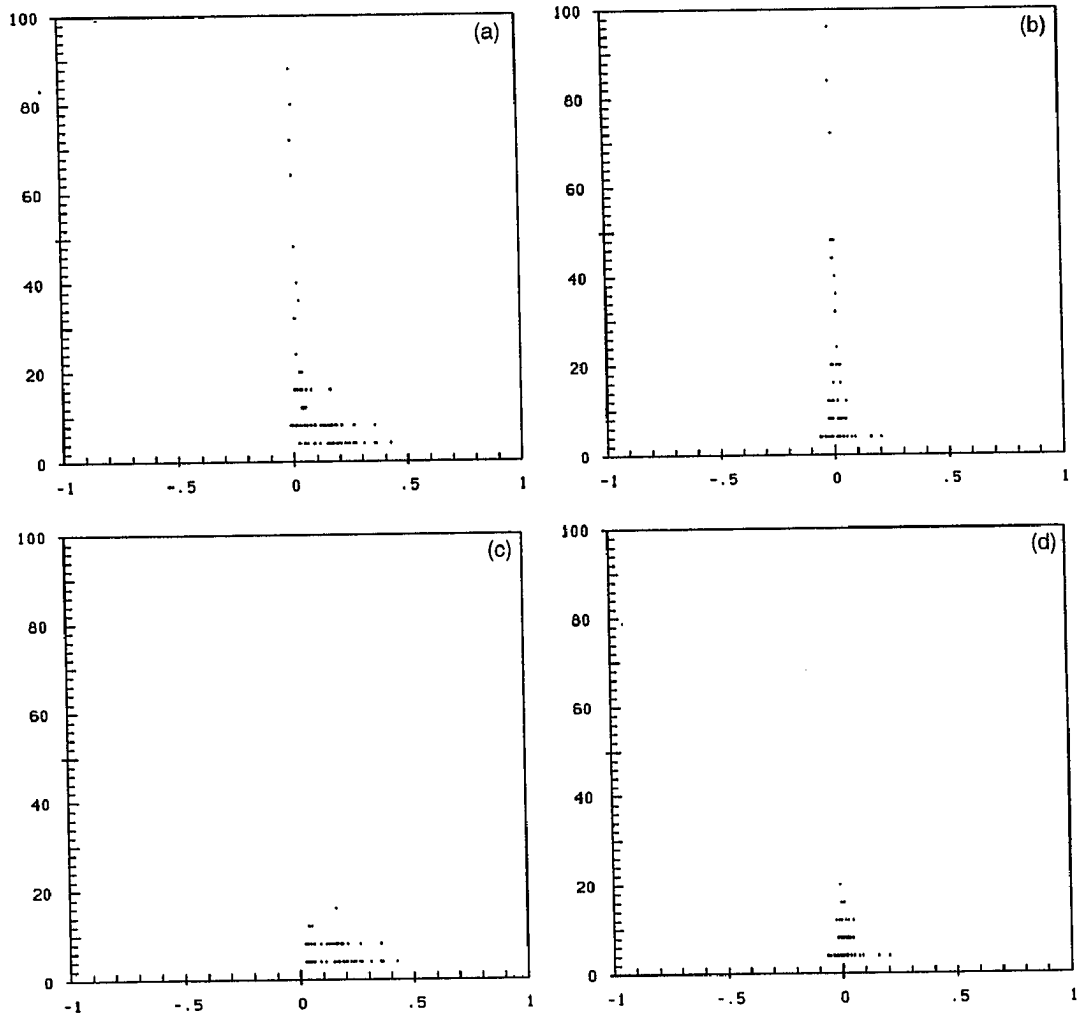

FIGURE 5. Frequency distribution of repulsion integrals of boron nitride (BN); Abscissa: value of integral; ordinate: frequency of within abscissa interval 1/1000. The notation (x, y) stands for x integrals of value zero from a total of y integrals. (a, b) Repulsion integrals of type G_{CD}^{AA} (G_{AD}^{AA}): (a) locally orthogonalized basis (3424, 5000); (b) Löwdin basis (3424, 5000). (c, d) Repulsion integrals of type G_{CD}^{AA} (G_{AD}^{AA}) with $\mu = \nu$: (c) locally orthogonalized basis (560, 1000); (d) Löwdin basis (560, 1000).

tegral distribution. The results of the theoretical investigation are in agreement with this numerical example.

Summary and Conclusions

The discussion of the one- and two-electron integrals in the symmetrically orthogonalized basis lead to the following results:

- The application of the NDDO approximation on one-electron operators is only justifiable for an expansion of the zeroth degree in Γ. An identification of the matrix elements of one-electron operators of the locally and the symmetrically orthogonalized basis is a crude approximation. The expansion of the zeroth degree leads to an integral scaling constant a^2.

  Already for an expansion of the first degree, no justification of the NDDO approximation can be found. All one-electron integrals have to be calculated and transformed.

- The neglect of two-electron integrals with two-center charge distributions in the generalized "bra" and "ket" finds the best justification.

  For repulsion integrals with only one two-center charge distribution, we have a limited justification, if the one-center charge distribution consists of different functions. A neglect of integrals $(\mu\mu \mid \kappa\lambda)$ with $\kappa \in B \neq C \ni \lambda$ is only possible for an expansion of the zeroth degree. This is too crude for the concept of a nonempirical quantum chemical computation method using the NDDO approximation as formerly proposed [8, 9, 14, 15].

  By neglecting integrals of the type G_{AD}^{AA}, one has to expect uncontrolled errors even for diatomic molecules. Brown and Burton [9] called the integrals of G_{AD}^{AA} and G_{CD}^{AA} the "essential structural elements of the ab initio SCF–LCAO F matrix." Their proposal of a nonempirical (ab initio) computation method works in the locally orthogonalized basis.
- For all NDDO-surviving integrals, approximative transformations into the Löwdin basis are given. An identification of the integrals in both bases corresponds to a polynomial expansion of the zeroth degree with a fixed scaling constant $a^4 = 1$.

CRITIQUE OF PROCEDURE

- All employed arguments relate to the polynomial expansion in Γ. However, the errors introduced by the Mulliken and diagonal approximation remain uncontrolled. Furthermore, the error that is caused by the second-order polynomial in Γ cannot be estimated. This situation is unsatisfactory and not helpful for the development of a simplified nonempirical quantum chemical computation method.

  Therefore, all integral transformations in this article are written approximatively ("≈"), what has been uncustomary up to now. A complete calculus of error for all different types of approximations that have been made in the course of the derivation of the transformations of two-electron integrals can be found in Part V.

ACKNOWLEDGMENTS

The author is very grateful to Prof. Dr. F. F. Seelig as well as to Dr. W. Koch for the continuous support and fruitful discussions of this work. This work was supported by the "Studienstiftung des deutschen Volkes."

References

1. I. Fischer-Hjalmars, J. Chem. Phys. **42**, 1962 (1965).
2. G. S. Chandler and F. E. Grader, Theor. Chim. Acta **54**, 131 (1980).
3. K. R. Roby, Chem. Phys. Lett. **11**, 6 (1971).
4. K. R. Roby, Chem. Phys. Lett. **12**, 579 (1972).
5. N. A. B. Gray and A. J. Stone, Theor. Chim. Acta **18**, 389 (1970).
6. Kiyosi Ito, Ed., *Encyclopedic Dictionary of Mathematics*, 2nd ed. (MIT Press, Cambridge, MA, 1987).
7. R. S. Mulliken, J. Chim. Phys. **46**, 497 (1949).
8. R. D. Brown, F. R. Burden, and G. R. Williams, Theor. Chim. Acta **18**, 98 (1970).
9. R. D. Brown and P. G. Burton, Chem. Phys. Lett. **20**, 45 (1973).
10. J. Chandrasekhar, P. K. Mehrota, S. Subramanian, and P. T. Manoharan, Theor. Chim. Acta **41**, 243 (1976).
11. E. Clementi and C. Roetti, Atom. Data Nucl. Data Tab. **14**, 177 (1974).
12. DIATOM–Diatomic Molecular Integral Program, Program Number 138 (Quantum Chemistry Program Exchange, Indiana University, Chemistry Department, Bloomington, IN.
13. W. Koch, Z. Naturforsch. **48a**, 819 (1993).
14. R. D. Brown, F. R. Burden, and G. R. Williams, Theor. Chim. Acta **21**, 205 (1971).
15. D. B. Cook, *Structures and Approximations for Electrons in Molecules* (Ellis Horwood, Chichester, 1978).

"Neglect of Diatomic Differential Overlap" in Nonempirical Quantum Chemical Orbital Theories. V. A Calculus of Error Concerning the Justification of the Neglect of Diatomic Differential Overlap (NDDO) Approximation

KLAUS NEYMEYR

Institut für Physikalische und Theoretische Chemie der Universität Tübingen, Auf der Morgenstelle 8, D-72076 Tübingen, Germany

Received March 18, 1994; revised manuscript received June 23, 1994; accepted July 6, 1994

ABSTRACT

Several types of approximations have been used for the justification of the Neglect of Diatomic Differential Overlap (NDDO) in Part IV but control of the introduced error remains insufficient. Analytic formulas describing the induced error for all types of approximations are given. Numerically lower bounds for these errors can be derived from the discussion on diatomic molecules. Far-reaching consequences on the applicability of NDDO will be discussed. © 1995 John Wiley & Sons, Inc.

Introduction

In the preceding articles of this five-part series, a new approach to the justification of the Neglect of Diatomic Differential Overlap (NDDO) approximation was developed. First, a polynomial expansion for $\Delta^{-1/2}$ (Δ is the overlap matrix) in terms of Legendre and Chebyshev polynomials was given. This expansion technique is a new solution of the convergence problem [1] of the S-expansion of Brown and Roby [2]. This technique was called the Γ-expansion; herein, $\Gamma = \Delta - [(s + t)/2]\mathbf{I}$, with $s = \min \sigma(\Delta)$ and $t = \max \sigma(\Delta)$. It has been shown in Part II that this technique achieves more accurate results than does the formally convergent P-expansion of Chandler and Grader [3]. The techniques are developed for the transformation of the one- and two-electron integrals into the symmetrically orthogonalized basis. In Part IV, the Γ-expansion was used for an examination of the justification of the NDDO approximation in the

International Journal of Quantum Chemistry, Vol. 53, 553–568 (1995)

CCC 0020-7608/95/050553-16

symmetrically orthogonalized basis. NDDO was not justified for one-electron operators and only partially for the two-center repulsion integrals (cf. Part IV).

All the integral transformations were deduced with use of the following three approximations (Mulliken approximation, diagonal-approximation, and the polynomial expansion to the second degree). But control over the introduced error is insufficient. Taking into account this problem, the integral transformation in Part IV are written approximatively, using "≈", a practice that has been uncustomary up to now.

Moreover, the insufficient control of error seems to be an essential weakness in former proposed justifications of approximative quantum chemical computation methods. Primarily, the truncated expansions of $\mathbf{\Delta}^{-1/2}$, the Mulliken approximation, and the incompleteness of bases that are used for Rüdenberg expansions are to be listed while justifying Neglect of Differential Overlap (NDO) methods. Here, a complete calculus of error and analytic formulas is given for the caused error for each approximation that was employed. The numerical evaluation of these formulas shows that the representation of a two-electron integral containing two-center charge densities in the Löwdin basis is of the same magnitude as the error that belongs to the considered integral transformation.

DEFINITIONS

Let us summarize the definitions of Part IV that are used here:

S is the set of N localized and linear independent orbitals that describe a locally orthogonalized basis:

$$S = \{\mu, \nu, \lambda, \sigma, \kappa \ldots\} \qquad N := |S|;$$

$\mathbf{\Delta}$ is the overlap matrix of these orbitals; $\mathbf{S} := \mathbf{\Delta} - \mathbf{I}$. The quotient set under the equivalence relation "localized at the same center" is used to label the atoms:

$$C = \{A, B, C, \ldots\} \qquad N_a := |C|.$$

The basis of the functions of S is called the ϕ-basis; after symmetrical orthogonalization, it is called the λ-basis.

The $\mathbf{\Gamma}$-expansion for $\mathbf{\Delta}^{-1/2}$ reads

$$\mathbf{\Delta}^{-1/2} = a\mathbf{I} + b\mathbf{\Gamma} + c\mathbf{\Gamma}^2 + O(\mathbf{\Gamma}^3), \qquad (1)$$

with $\mathbf{\Gamma} = \mathbf{\Delta} - [(s + t)/2]\mathbf{I}$ and $s = \min \sigma(\mathbf{\Delta})$, $t = \max \sigma(\mathbf{\Delta})$. The expansion coefficients a, b, and c are to be computed by Legendre or Chebyshev expansion (cf. Part II).

Calculus of Error for the Integral Transformations

USED APPROXIMATIONS

In the course of the derivation of integral transformations in part IV, the following integral approximations were utilized:

1. Polynomial expansion for $\mathbf{\Delta}^{-1/2}$ to the second degree in $\mathbf{\Gamma}$.
2. Mulliken approximation used for one-electron operators in the ϕ-basis:

$$\mu \in A \neq B \ni \nu$$

$$^{\phi}M^{AB}_{\mu\nu} \approx \frac{\Delta_{\mu\nu}}{2}[^{\phi}M_{\mu\mu} + {}^{\phi}M_{\nu\nu}].$$

The analogous formulation for the charge densities $\phi_\mu \phi_\nu dr$ reads

$$\phi^A_\mu \phi^B_\nu \approx \frac{\Delta_{\mu\nu}}{2}[\phi_\mu \phi_\mu + \phi_\nu \phi_\nu].$$

3. Diagonal-approximation neglects by

$$(\mu_A \nu_A \,|\, \kappa\kappa) \approx O(\mathbf{\Gamma})\,(\mu\mu \,|\, \kappa\kappa) \quad \text{for} \quad \mu \neq \nu$$

one-center non-diagonal elements of $\mathbf{\Omega}$ if the considered integral has a leading factor of the second degree in $\mathbf{\Gamma}$. After application of this approximation, the term vanishes in $O(\mathbf{\Gamma}^3)$.

A formulation of the diagonal-approximation for one-electron operators that is compatible with the definition above reads

$$M_{\omega\rho} \approx O(\mathbf{\Gamma})M_{\omega\omega} \quad \text{for} \quad \omega \neq \rho.$$

This approximation is only applied if $M_{\omega\rho}$ has a leading factor of the second degree in $\mathbf{\Gamma}$. Then, the considered term vanishes under this approximation to $O(\mathbf{\Gamma}^3)$. An exhaustive application of diagonal-approximation to repulsion integrals cannot be represented by applying the approximation to the charge density matrix; one has to regard this for the calculation of integral transformations.

THE APPROXIMATION ERRORS OF ONE-ELECTRON OPERATORS

In the following, analytical formulas describing the approximation errors shall be developed. On the one hand, these equations shall allow estimations of maximum error; on the other hand, they shall be appropriate for a numerical evaluation by a nonapproximative method. Some new notation has to be defined for the realization of this scheme.

For two-center matrix elements of a one-electron operator $M_{\mu\nu}$ the approximation by means of one-center matrix elements reads by Mulliken [4]

$$\mu \in A \neq B \ni \nu \qquad M_{\mu\nu} \approx \frac{\Delta_{\mu\nu}}{2}(M_{\mu\mu} + M_{\nu\nu}).$$

For the nondiagonal elements, one has $\mu \neq \nu$: $\Delta_{\mu\nu} = \Gamma_{\mu\nu}$. Let $m_{\mu\nu}$ be the error of Mulliken approximation, then, the following equation results:

$$\mu \in A \neq B \ni \nu$$
$$M_{\mu\nu} = \frac{\Gamma_{\mu\nu}}{2}(M_{\mu\mu} + M_{\nu\nu}) + m_{\mu\nu}. \qquad (2)$$

Now the representation of the matrix-elements of one-electron operators in the Löwdin basis can be calculated as in Part IV, but all errors due to the Mulliken approximation will be collected in ${}_{Mull}^{\lambda}\mathbf{M}$.

The treatment of the diagonal-approximation is easy: Let ${}_{diag}^{\lambda}\mathbf{M}$ be the sum of all terms that are to be neglected by diagonal-approximation. As mentioned above, these are nondiagonal elements of one-electron operators with a leading coefficient of the second order in Γ:

$$\Gamma_{ab}\Gamma_{cd}M_{\omega\rho} \approx O(\Gamma^3) \qquad \text{with} \qquad \omega \neq \rho.$$

Therefore, the matrix representation of a one-electron operator in the Löwdin basis decomposes to

$${}^{\lambda}\mathbf{M} = {}_{tr}^{\lambda}\mathbf{M} + {}_{diag}^{\lambda}\mathbf{M} + {}_{Mull}^{\lambda}\mathbf{M} + O(\Gamma^3). \qquad (3)$$

The matrix ${}_{tr}^{\lambda}\mathbf{M}$ describes the contribution of integral transformation after applying the approximations; it is identical to the representation as developed in Part IV. Equation (3) is exact in the limes of the O-function.

The nonapproximative transformation into the symmetrically orthogonalized basis reads

$${}^{\lambda}\mathbf{M} = \mathbf{\Delta}^{-1/2}\mathbf{M}\mathbf{\Delta}^{-1/2}.$$

Now, the error ${}^{\lambda}O$ that is caused by the expansion of $\mathbf{\Delta}^{-1/2}$ to the second order can be estimated. One has to calculate ${}^{\lambda}\mathbf{M}$, ${}_{tr}^{\lambda}\mathbf{M}$, ${}_{diag}^{\lambda}\mathbf{M}$, and ${}_{Mull}^{\lambda}\mathbf{M}$ by a nonapproximative method "exactly":

$${}^{\lambda}\mathbf{O} := {}^{\lambda}\mathbf{M} - ({}_{tr}^{\lambda}\mathbf{M} + {}_{diag}^{\lambda}\mathbf{M} + {}_{Mull}^{\lambda}\mathbf{M}). \qquad (4)$$

With a Γ-expansion of the second degree, one obtains

$${}^{\lambda}\mathbf{M} = a^2\mathbf{M} + ab(\mathbf{M}\mathbf{\Gamma} + \mathbf{\Gamma}\mathbf{M}) + ac(\mathbf{M}\mathbf{\Gamma}^2 + \mathbf{\Gamma}^2\mathbf{M}) + b^2\mathbf{\Gamma}\mathbf{M}\mathbf{\Gamma} + O(\mathbf{\Gamma}^3).$$

Therewith, analogously to Paper IV for the one-center matrix elements, follows

$${}^{\lambda}M_{\mu\nu}^{AA} = {}_{tr}^{\lambda}M_{\mu\nu}^{AA} + {}_{diag}^{\lambda}M_{\mu\nu}^{AA} + {}_{Mull}^{\lambda}M_{\mu\nu}^{AA} + O(\mathbf{\Gamma}^3). \qquad (5)$$

They read explicitly (free of restriction $\mu = \nu$ or $\mu \neq \nu$) $\forall A \in C, \forall \mu, \nu \in A$:

$$\begin{aligned} {}_{tr}^{\lambda}M_{\mu\nu} = {} & M_{\mu\nu}[a^2 + 2ab\Gamma_{\mu\mu} + (2ac + b^2)\Gamma_{\mu\mu}^2] \\ & + \sum_{\sigma \in S\setminus A} \Gamma_{\mu\sigma}\Gamma_{\nu\sigma} \\ & \times \left(\left(\frac{ab}{2} + ac\right)(M_{\mu\mu} + M_{\nu\nu}) \right. \\ & \left. + (ab + b^2)M_{\sigma\sigma}\right) + O(\mathbf{\Gamma}^3), \end{aligned} \qquad (6)$$

and for ${}_{diag}^{\lambda}M_{\mu\nu}$,

$$\begin{aligned} {}_{diag}^{\lambda}M_{\mu\nu} = {} & M_{\mu\nu}(1 - \delta_{\mu\nu})ac \sum_{\sigma \in S\setminus A} (\Gamma_{\mu\sigma}^2 + \Gamma_{\nu\sigma}^2) \\ & + ac \sum_{\rho \in A\setminus\{\mu,\nu\}} \sum_{\sigma \in S\setminus A} (\Gamma_{\mu\sigma}\Gamma_{\sigma\rho}M_{\rho\nu} \\ & + \Gamma_{\nu\sigma}\Gamma_{\sigma\rho}M_{\rho\mu}) \\ & + b^2 \sum_{C \in C\setminus\{A\}} \sum_{\substack{\sigma,\rho \in C \\ \rho \neq \sigma}} \Gamma_{\mu\rho}\Gamma_{\sigma\nu}M_{\rho\sigma} \\ & + O(\mathbf{\Gamma}^3). \end{aligned} \qquad (7)$$

and for the error introduced by the Mulliken approximation ${}_{Mull}^{\lambda}M_{\mu\nu}^{AA}$,

$$\begin{aligned} {}_{Mull}^{\lambda}M_{\mu\nu} = {} & ab \sum_{\sigma \in S\setminus A} (\Gamma_{\mu\sigma}m_{\sigma\nu} + \Gamma_{\sigma\nu}m_{\mu\sigma}) \\ & + b^2 \sum_{\substack{C,D \in C\setminus\{A\} \\ C \neq D}} \sum_{\substack{\rho \in C \\ \sigma \in D}} \Gamma_{\mu\rho}\Gamma_{\sigma\nu}m_{\rho\sigma} \\ & + (2ac + b^2) \sum_{\sigma \in S\setminus A} \Gamma_{\mu\mu} \\ & \times (\Gamma_{\sigma\nu}m_{\mu\sigma} + \Gamma_{\sigma\mu}m_{\nu\sigma}) \\ & + ac \sum_{\substack{C,D \in C\setminus\{A\} \\ C \neq D}} \sum_{\substack{\rho \in C \\ \sigma \in D}} \Gamma_{\rho\sigma} \\ & \times (\Gamma_{\mu\sigma}m_{\rho\nu} + \Gamma_{\nu\sigma}m_{\sigma\mu}) + O(\mathbf{\Gamma}^3). \end{aligned} \qquad (8)$$

The summand $M_{\mu\nu}(2ac + b^2)\Gamma_{\mu\mu}^2$ remains in ${}^{\lambda}_{tr}M_{\mu\nu}$ to meet the requirement of the case $\mu = \nu$. A similar summand in ${}^{\lambda}_{diag}M_{\mu\nu}$ causes no difficulties because of the Kronecker function.

The representation of two-center matrix elements in the Löwdin basis decomposes to three sums, also:

$$ {}^{\lambda}M^{AB}_{\mu\nu} = {}^{\lambda}_{tr}M^{AB}_{\mu\nu} + {}^{\lambda}_{diag}M^{AB}_{\mu\nu} + {}^{\lambda}_{Mull}M^{AB}_{\mu\nu} + O(\mathbf{\Gamma}^3). \tag{9} $$

For $A,B \in C, A \neq B, \mu \in A, \nu \in B$, holds that

$$ \begin{aligned} {}^{\lambda}_{tr}M^{AB}_{\mu\nu} &= \Gamma_{\mu\nu}(M_{\mu\mu} + M_{\nu\nu}) \\ &\quad \times [a^2/2 + ab + \Gamma_{\mu\mu}(ab + b^2 + 2ac)] \\ &\quad + ab \sum_{\sigma\in B\setminus\{\nu\}} \Gamma_{\mu\sigma}M_{\sigma\nu} \\ &\quad + ab \sum_{\sigma\in A\setminus\{\mu\}} \Gamma_{\sigma\nu}M_{\mu\sigma} \\ &\quad + \frac{ab}{2} \sum_{\sigma\in S\setminus(A\cup B)} \Gamma_{\mu\sigma}\Gamma_{\sigma\nu} \\ &\quad \times [M_{\mu\mu} + 2M_{\sigma\sigma} + M_{\nu\nu}] \\ &\quad + \sum_{\sigma\in S\setminus(A\cup B)} \Gamma_{\mu\sigma}\Gamma_{\sigma\nu} \\ &\quad \times [acM_{\mu\mu} + b^2M_{\sigma\sigma} + acM_{\nu\nu}] \\ &\quad + O(\mathbf{\Gamma}^3), \end{aligned} \tag{10} $$

$$ \begin{aligned} {}^{\lambda}_{diag}M^{AB}_{\mu\nu} &= b^2 \sum_{E\in C\setminus\{A,B\}} \sum_{\substack{\rho,\sigma\in E \\ \rho\neq\sigma}} \Gamma_{\mu\sigma}M_{\sigma\rho}\Gamma_{\rho\nu} \\ &\quad + (2ac + b^2) \\ &\quad \times \Bigg[\sum_{\sigma\in A\setminus\{\mu\}} \Gamma_{\mu\mu}M_{\mu\sigma}\Gamma_{\sigma\nu} \\ &\quad\quad + \sum_{\sigma\in B\setminus\{\nu\}} \Gamma_{\mu\sigma}M_{\sigma\nu}\Gamma_{\mu\mu} \Bigg] \\ &\quad + ac \sum_{\sigma\in S\setminus(A\cup B)} \\ &\quad \times \Bigg[\sum_{\rho\in A\setminus\{\mu\}} \Gamma_{\rho\sigma}\Gamma_{\sigma\nu}M_{\mu\rho} \\ &\quad\quad + \sum_{\rho\in B\setminus\{\nu\}} \Gamma_{\mu\sigma}\Gamma_{\sigma\rho}M_{\rho\nu} \Bigg] \\ &\quad + O(\mathbf{\Gamma}^3), \end{aligned} \tag{11} $$

$$ \begin{aligned} {}^{\lambda}_{Mull}M^{AB}_{\mu\nu} &= [a^2 + 2ab\Gamma_{\mu\mu} + (b^2 + 2ac)\Gamma_{\mu\mu}^2]m_{\mu\nu} \\ &\quad + ab \sum_{\sigma\in S\setminus(A\cup B)} \Gamma_{\mu\sigma}m_{\sigma\nu} + \Gamma_{\sigma\nu}m_{\mu\sigma} \\ &\quad + b^2 \sum_{\sigma\in E\in C\setminus\{A\}} \sum_{\rho\in F\in C\setminus\{B,E\}} \Gamma_{\mu\sigma}m_{\sigma\rho}\Gamma_{\rho\nu} \\ &\quad + (ac + b^2) \sum_{\sigma\in S\setminus(A\cup B)} \\ &\quad \times [\Gamma_{\mu\mu}\Gamma_{\mu\sigma}m_{\sigma\nu} + \Gamma_{\mu\mu}\Gamma_{\sigma\nu}m_{\mu\sigma}] \\ &\quad + ac \sum_{\sigma\in E\in C\setminus\{A\}} \sum_{\rho\in S\setminus(B\cup E)} \Gamma_{\mu\sigma}\Gamma_{\sigma\rho}m_{\rho\nu} \\ &\quad + ac \sum_{\sigma\in E\in C\setminus\{B\}} \sum_{\rho\in S\setminus(A\cup E)} \Gamma_{\rho\sigma}\Gamma_{\sigma\nu}m_{\mu\rho} \\ &\quad + ac \sum_{\sigma\in S\setminus A} \Gamma_{\mu\mu}\Gamma_{\mu\sigma}m_{\sigma\nu} \\ &\quad + ac \sum_{\sigma\in S\setminus B} \Gamma_{\mu\mu}\Gamma_{\sigma\nu}m_{\mu\sigma} + O(\mathbf{\Gamma}^3). \end{aligned} \tag{12} $$

THE APPROXIMATION ERRORS OF THE REPULSION INTEGRALS

The charge density matrix Ω in the ϕ-basis $(\phi_i)_{i=1,\ldots,N}$,

$$ \Omega := (\phi_1,\ldots,\phi_N)^t\,(\phi_1,\ldots,\phi_N), $$

transforms like one-electron operators into the Löwdin basis:

$$ {}^{\lambda}\mathbf{\Omega} = \mathbf{\Delta}^{-1/2}\mathbf{\Omega}\mathbf{\Delta}^{-1/2}. $$

Therefore, the one-center matrix elements of Ω are given by Eqs. (6)–(8) and the two-center elements by (10)–(12).

The Mulliken approximation for a two-center matrix element ${}^{\phi}\Omega^{AB}_{\mu\nu}$ in the locally orthogonalized basis with the term of error $\omega_{\mu\nu}$ (residual charge density) reads

$$ A \neq B \qquad {}^{\phi}\Omega^{AB}_{\mu\nu} = \frac{\Gamma_{\mu\nu}}{2}[{}^{\phi}\Omega^{AA}_{\mu\mu} + {}^{\phi}\Omega^{BB}_{\nu\nu}] + \omega_{\mu\nu}. \tag{13} $$

Therewith, the charge density matrix in the symmetrically orthogonalized basis decomposes to

$$ {}^{\lambda}\mathbf{\Omega} = {}^{\lambda}_{tr}\mathbf{\Omega} + {}^{\lambda}_{diag}\mathbf{\Omega} + {}^{\lambda}_{Mull}\mathbf{\Omega} + O(\mathbf{\Gamma}^3). \tag{14} $$

The two-electron integrals are to be calculated by

$$ {}^{\lambda}(\mu\nu \mid \kappa\lambda) = ({}^{\lambda}\Omega_{\mu\nu}(1) \mid {}^{\lambda}\Omega_{\kappa\lambda}(2)). $$

Therefore, all integrals containing the residual charge density $\omega_{\mu\nu}$ can be calculated by employing a nonapproximative (complete) method. It holds

that

$$^{\phi}(\mu\nu \mid \omega_{\kappa\lambda}) = {}^{\phi}(\mu\nu \mid \kappa\lambda) - \frac{\Gamma_{\kappa\lambda}}{2}[{}^{\phi}(\mu\nu \mid \kappa\kappa) + {}^{\phi}(\mu\nu \mid \lambda\lambda)] \tag{15}$$

and

$$\begin{aligned}{}^{\phi}(\omega_{\mu\nu} \mid \omega_{\kappa\lambda}) = {}&{}^{\phi}(\mu\nu \mid \kappa\lambda) \\ &- \frac{\Gamma_{\mu\nu}}{2}[{}^{\phi}(\mu\mu \mid \kappa\lambda) + {}^{\phi}(\nu\nu \mid \kappa\lambda)] \\ &- \frac{\Gamma_{\kappa\lambda}}{2}[{}^{\phi}(\mu\nu \mid \kappa\kappa) + {}^{\phi}(\mu\nu \mid \lambda\lambda)] \\ &+ \frac{\Gamma_{\mu\nu}\Gamma_{\kappa\lambda}}{4}[{}^{\phi}(\mu\mu \mid \kappa\kappa) \\ &\quad + {}^{\phi}(\nu\nu \mid \kappa\kappa) + {}^{\phi}(\mu\mu \mid \lambda\lambda) \\ &\quad + {}^{\phi}(\nu\nu \mid \lambda\lambda).\end{aligned} \tag{16}$$

Let us adopt the notation for the integrals sets and for the classification from Part IV. A summary of the classification in three types read as follows:

(i) G^{AA}_{AA}, G^{AA}_{BB}: NDDO-surviving integrals.
(ii) $G^{AB}_{AB}, G^{AB}_{AC}, G^{AB}_{CD}$: These integrals contain only two-center charge distributions.
(iii) G^{AA}_{AD}, G^{AA}_{CD}. These integrals can be calculated from a one-center and a two-center charge distribution.

The NDDO-surviving Integrals

The one- and two-center integrals of the types G^{AA}_{AA} or G^{AA}_{BB} were deduced without applying the diagonal-approximation in Part IV. Let us, therefore, combine Eqs. (6) and (7):

$$_{tr*}^{\lambda}M^{AA}_{\mu\nu} := {}_{tr}^{\lambda}M^{AA}_{\mu\nu} + {}_{diag}^{\lambda}M^{AA}_{\mu\nu}.$$

Hence, the NDDO-surviving integrals are given by

The integral $_{approx}^{\lambda}(\mu\nu \mid \kappa\lambda)$ was already given in Part IV:

$$\forall A, B \in C, A = B \quad \text{or} \quad A \neq B, \forall \mu, \nu \in A, \forall \kappa, \lambda \in B$$

$$\begin{aligned}\frac{1}{a^2}{}_{approx}^{\lambda}(\mu\nu \mid \kappa\lambda) = {}&(\mu\nu \mid \kappa\lambda) \\ &\times (a^2 + 4ab\Gamma_{\mu\mu} + (6b^2 + 4ac)\Gamma^2_{\mu\mu}) \\ &+ \sum_{\sigma\in S\setminus B} \\ &\times \left\{a\left(\frac{b}{2} + c\right)\Gamma_{\kappa\sigma}\Gamma_{\sigma\lambda}((\mu\nu \mid \kappa\kappa) + (\mu\nu \mid \lambda\lambda)) + b(a+b)\Gamma_{\kappa\sigma}\Gamma_{\sigma\lambda}(\mu\nu \mid \sigma\sigma)\right\} \\ &+ \sum_{\sigma\in S\setminus A} \\ &\times \left\{a\left(\frac{b}{2} + c\right)\Gamma_{\mu\sigma}\Gamma_{\sigma\nu} \times ((\mu\mu \mid \kappa\lambda) + (\nu\nu \mid \kappa\lambda)) + b(a+b) \times \Gamma_{\mu\sigma}\Gamma_{\sigma\nu}(\sigma\sigma \mid \kappa\lambda)\right\} \\ &+ ac(\mu\nu \mid \kappa\lambda) \\ &\times \left\{(1-\delta_{\kappa\lambda})\sum_{\sigma\in S\setminus B}(\Gamma^2_{\lambda\sigma} + \Gamma^2_{\kappa\sigma}) + (1-\delta_{\mu\nu})\sum_{\sigma\in S\setminus A}(\Gamma^2_{\nu\sigma} + \Gamma^2_{\mu\sigma})\right\} \\ &+ ac\sum_{\rho\in B\setminus\{\kappa,\lambda\}}\sum_{\sigma\in S\setminus B} \\ &\times [(\mu\nu \mid \rho\lambda)\Gamma_{\kappa\sigma}\Gamma_{\sigma\rho} + (\mu\nu \mid \kappa\rho)\Gamma_{\rho\sigma}\Gamma_{\sigma\lambda}] \\ &+ ac\sum_{\rho\in A\setminus\{\mu,\nu\}}\sum_{\sigma\in S\setminus A}\end{aligned}$$

$$\begin{aligned}{}^{\lambda}(\mu\nu \mid \kappa\lambda) &= ({}^{\lambda}\Omega_{\mu\nu}(1) \mid {}^{\lambda}\Omega_{\kappa\lambda}(2)) = ({}_{tr*}^{\lambda}\Omega_{\mu\nu} + {}_{Mull}^{\lambda}\Omega_{\mu\nu} \mid {}_{tr*}^{\lambda}\Omega_{\kappa\lambda} + {}_{Mull}^{\lambda}\Omega_{\kappa\lambda}) \\ &= \underbrace{({}_{tr*}^{\lambda}\Omega_{\mu\nu} \mid {}_{tr*}^{\lambda}\Omega_{\kappa\lambda})}_{=:{}_{approx}^{\lambda}(\mu\nu \mid \kappa\lambda)} \\ &\quad + \underbrace{({}_{tr*}^{\lambda}\Omega_{\mu\nu} \mid {}_{Mull}^{\lambda}\Omega_{\kappa\lambda}) + ({}_{Mull}^{\lambda}\Omega_{\mu\nu} \mid {}_{tr*}^{\lambda}\Omega_{\kappa\lambda}) + ({}_{Mull}^{\lambda}\Omega_{\mu\nu} \mid {}_{Mull}^{\lambda}\Omega_{\kappa\lambda})}_{=:{}_{Mull}^{\lambda}(\mu\nu \mid \kappa\lambda)} \\ &= : {}_{approx}^{\lambda}(\mu\nu \mid \kappa\lambda) + {}_{Mull}^{\lambda}(\mu\nu \mid \kappa\lambda).\end{aligned}$$

$$\times [(\rho\nu \mid \kappa\lambda)\Gamma_{\mu\sigma}\Gamma_{\sigma\rho} + (\mu\rho \mid \kappa\lambda)\Gamma_{\rho\sigma}\Gamma_{\sigma\nu}] + b^2 \sum_{C\in C\setminus\{B\}} \sum_{\substack{\sigma,\rho\in C\\ \rho\neq\sigma}} (\mu\nu \mid \rho\sigma)\Gamma_{\kappa\rho}\Gamma_{\sigma\lambda} + b^2 \sum_{C\in C\setminus\{A\}} \sum_{\substack{\sigma,\rho\in C\\ \rho\neq\sigma}} (\rho\sigma \mid \kappa\lambda)\Gamma_{\mu\rho}\Gamma_{\sigma\nu} + O(\mathbf{\Gamma}^3). \quad (17)$$

For the error of Mulliken approximation it holds that

$$\forall A, B \in C,\ A = B \quad \text{or} \quad A \neq B, \forall \mu, \nu \in A, \forall \kappa, \lambda \in B: \quad (18)$$

$$\frac{1}{a^2}\,{}^{\lambda}_{Mull}(\mu\nu \mid \kappa\lambda) = (ab + \Gamma_{\mu\mu}(3b^2 + 2ac)) \times \Big[\sum_{\sigma\in S\setminus A} \Gamma_{\mu\sigma}(\omega_{\sigma\nu} \mid \kappa\lambda) + \Gamma_{\sigma\nu}(\omega_{\mu\sigma} \mid \kappa\lambda) + \sum_{\sigma\in S\setminus B} \Gamma_{\kappa\sigma}(\mu\nu \mid \omega_{\sigma\lambda}) + \Gamma_{\sigma\lambda}(\mu\nu \mid \omega_{\kappa\sigma}) \Big]$$
$$+ b^2 \Big[\sum_{\substack{C,D\in C\setminus\{A\}\\ C\neq D}} \sum_{\substack{\sigma\in C\\ \rho\in D}} \Gamma_{\mu\rho}\Gamma_{\sigma\nu} \times (\omega_{\rho\sigma} \mid \kappa\lambda) + \sum_{\substack{C,D\in C\setminus\{B\}\\ C\neq D}} \sum_{\substack{\sigma\in C\\ \rho\in D}} \Gamma_{\kappa\rho}\Gamma_{\sigma\lambda} \times (\mu\nu \mid \omega_{\rho\sigma}) \Big]$$
$$+ ac \Big[\sum_{\substack{C,D\in C\setminus\{A\}\\ C\neq D}} \sum_{\substack{\sigma\in C\\ \rho\in D}} \Gamma_{\mu\rho}\Gamma_{\rho\sigma} \times (\omega_{\sigma\nu} \mid \kappa\lambda) + \Gamma_{\nu\rho}\Gamma_{\rho\sigma}(\omega_{\sigma\mu} \mid \kappa\lambda) + \sum_{\substack{C,D\in C\setminus\{B\}\\ C\neq D}} \sum_{\substack{\sigma\in C\\ \rho\in D}} \Gamma_{\kappa\rho}\Gamma_{\rho\sigma} \times (\mu\nu \mid \omega_{\sigma\lambda}) + \Gamma_{\lambda\rho}\Gamma_{\rho\sigma}(\mu\nu \mid \omega_{\sigma\kappa}) \Big]$$
$$+ b^2 \sum_{\sigma\in S\setminus A} \sum_{\rho\in S\setminus B} \times [\Gamma_{\mu\sigma}\Gamma_{\kappa\rho}(\omega_{\sigma\nu} \mid \omega_{\rho\lambda}) + \Gamma_{\sigma\nu}\Gamma_{\kappa\rho}(\omega_{\mu\sigma} \mid \omega_{\rho\lambda}) + \Gamma_{\mu\sigma}\Gamma_{\rho\lambda}(\omega_{\sigma\nu} \mid \omega_{\kappa\rho}) + \Gamma_{\sigma\nu}\Gamma_{\rho\lambda}(\omega_{\mu\sigma} \mid \omega_{\kappa\rho})] + O(\mathbf{\Gamma}^3). \quad (18)$$

Integrals with Two-center Charge Distribution

Let us first discuss the integrals with two-center charge distributions in the generalized "bra" and "ket," which are G^{AB}_{CD}, G^{AB}_{AC}, and G^{AB}_{AB}. The two-center elements of charge density matrix partition into

$${}^{\lambda}\Omega^{AB}_{\mu\nu} = {}^{\lambda}_{tr}\Omega^{AB}_{\mu\nu} + {}^{\lambda}_{diag}\Omega^{AB}_{\mu\nu} + {}^{\lambda}_{Mull}\Omega^{AB}_{\mu\nu} + O(\mathbf{\Gamma}^3).$$

Thus, the repulsion integrals in the Löwdin basis read

$${}^{\lambda}(\mu\nu \mid \kappa\lambda) = ({}^{\lambda}_{tr}\Omega^{AB}_{\mu\nu} + {}^{\lambda}_{diag}\Omega^{AB}_{\mu\nu} + {}^{\lambda}_{Mull}\Omega^{AB}_{\mu\nu} \mid {}^{\lambda}_{tr}\Omega^{CD}_{\kappa\lambda} + {}^{\lambda}_{diag}\Omega^{CD}_{\kappa\lambda} + {}^{\lambda}_{Mull}\Omega^{CD}_{\kappa\lambda}) + O(\mathbf{\Gamma}^3).$$

Nine different products arise; they can be further classified. The integral type G^{AB}_{AC} results from identifying D and A; for G^{AB}_{AB}, let $C = B$:

(a) Part of transformation (before applying the diagonal-approximation exhaustively):

$$({}^{\lambda}_{tr}\Omega^{AB}_{\mu\nu} \mid {}^{\lambda}_{tr}\Omega^{CD}_{\kappa\lambda}).$$

(b) Diagonal-approximation:

$$({}^{\lambda}_{diag}\Omega^{AB}_{\mu\nu} \mid {}^{\lambda}_{diag}\Omega^{CD}_{\kappa\lambda}), ({}^{\lambda}_{tr}\Omega^{AB}_{\mu\nu} \mid {}^{\lambda}_{diag}\Omega^{CD}_{\kappa\lambda}), ({}^{\lambda}_{diag}\Omega^{AB}_{\mu\nu} \mid {}^{\lambda}_{tr}\Omega^{CD}_{\kappa\lambda}).$$

(c) Mulliken approximation:

$$({}^{\lambda}_{Mull}\Omega^{AB}_{\mu\nu} \mid {}^{\lambda}_{Mull}\Omega^{CD}_{\kappa\lambda}), ({}^{\lambda}_{tr}\Omega^{AB}_{\mu\nu} \mid {}^{\lambda}_{Mull}\Omega^{CD}_{\kappa\lambda}), ({}^{\lambda}_{Mull}\Omega^{AB}_{\mu\nu} \mid {}^{\lambda}_{tr}\Omega^{CD}_{\kappa\lambda}).$$

(d) Mixed terms:

$$({}^{\lambda}_{diag}\Omega^{AB}_{\mu\nu} \mid {}^{\lambda}_{Mull}\Omega^{CD}_{\kappa\lambda}), ({}^{\lambda}_{Mull}\Omega^{AB}_{\mu\nu} \mid {}^{\lambda}_{diag}\Omega^{CD}_{\kappa\lambda}).$$

The part of transformation (a) partitions by an exhaustive application of diagonal-approximation further:

$$({}^{\lambda}_{tr}\Omega^{AB}_{\mu\nu} \mid {}^{\lambda}_{tr}\Omega^{CD}_{\kappa\lambda}) = {}^{\lambda}_{approx}(\mu\nu \mid \kappa\lambda) + r_{diag}.$$

The integrals read

$${}^{\lambda}_{approx}(\mu\nu \mid \kappa\lambda) = (a^2/2 + ab)^2\Gamma_{\mu\nu}\Gamma_{\kappa\lambda} \times [(\mu\mu \mid \kappa\kappa) + (\mu\mu \mid \lambda\lambda) + (\nu\nu \mid \kappa\kappa) + (\nu\nu \mid \lambda\lambda)] + O(\mathbf{\Gamma}^3). \quad (19)$$

The error r_{diag} is given by

$$
\begin{aligned}
r_{diag} = {} & \Gamma_{\kappa\lambda}\left(\frac{a^2}{2} + ab\right)ab \\
& \times \left[\sum_{\sigma\in B\setminus\{\nu\}} \Gamma_{\mu\sigma}((\sigma\nu \mid \kappa\kappa) + (\sigma\nu \mid \lambda\lambda)) \right. \\
& \quad \left. + \sum_{\sigma\in A\setminus\{\mu\}} \Gamma_{\sigma\nu}((\mu\sigma \mid \kappa\kappa) + (\mu\sigma \mid \lambda\lambda))\right] \\
& + \Gamma_{\mu\nu}\left(\frac{a^2}{2} + ab\right)ab \\
& \times \left[\sum_{\sigma\in D\setminus\{\lambda\}} \Gamma_{\kappa\sigma}((\mu\mu \mid \sigma\lambda) + (\nu\nu \mid \sigma\lambda)) \right. \\
& \quad \left. + \sum_{\sigma\in C\setminus\{\kappa\}} \Gamma_{\sigma\lambda}((\mu\mu \mid \kappa\sigma) + (\nu\nu \mid \kappa\sigma))\right] \\
& + (ab)^2 \sum_{\sigma\in B\setminus\{\nu\}} \Gamma_{\mu\sigma} \\
& \times \left[\sum_{\rho\in D\setminus\{\lambda\}} \Gamma_{\kappa\rho}(\sigma\nu \mid \rho\lambda) \right. \\
& \quad \left. + \sum_{\rho\in C\setminus\{\kappa\}} \Gamma_{\rho\lambda}(\sigma\nu \mid \kappa\rho)\right] \\
& + (ab)^2 \sum_{\sigma\in A\setminus\{\mu\}} \Gamma_{\sigma\nu} \\
& \times \left[\sum_{\rho\in D\setminus\{\lambda\}} \Gamma_{\kappa\rho}(\mu\sigma \mid \rho\lambda) \right. \\
& \quad \left. + \sum_{\rho\in C\setminus\{\kappa\}} \Gamma_{\rho\lambda}(\mu\sigma \mid \kappa\rho)\right] + O(\Gamma^3). \qquad (20)
\end{aligned}
$$

All terms of error of the diagonal-approximation cancel to the third order because

$$
\begin{aligned}
{}^{\lambda}_{tr}\Omega^{AB}_{\mu\nu} &= 0 + O(\Gamma), \\
{}^{\lambda}_{diag}\Omega^{AB}_{\mu\nu} &= 0 + O(\Gamma^2);
\end{aligned}
$$

thus,

$$
\begin{aligned}
({}^{\lambda}_{diag}\Omega^{AB}_{\mu\nu} \mid {}^{\lambda}_{diag}\Omega^{CD}_{\kappa\lambda}) &= 0 + O(\Gamma^3), \\
({}^{\lambda}_{tr}\Omega^{AB}_{\mu\nu} \mid {}^{\lambda}_{diag}\Omega^{CD}_{\kappa\lambda}) &= 0 + O(\Gamma^3), \\
({}^{\lambda}_{diag}\Omega^{AB}_{\mu\nu} \mid {}^{\lambda}_{tr}\Omega^{CD}_{\kappa\lambda}) &= 0 + O(\Gamma^3).
\end{aligned}
$$

The error terms that are caused by Mulliken approximation read

$$
\begin{aligned}
\frac{1}{a^2}({}^{\lambda}_{Mull}\Omega^{AB}_{\mu\nu} \mid {}^{\lambda}_{Mull}\Omega^{CD}_{\kappa\lambda}) = {} & (a^2 + 4ab\Gamma_{\mu\mu} \\
& + (4ac + 6b^2)\Gamma^2_{\mu\mu}) \\
& \times (\omega_{\mu\nu} \mid \omega_{\kappa\lambda}) \\
& + (ab + (ac + 3b^2)\Gamma_{\mu\mu}) \\
& \times \left[\sum_{\sigma\in S\setminus(A\cup B)} \{\Gamma_{\mu\sigma}(\omega_{\sigma\nu} \mid \omega_{\kappa\lambda}) \right. \\
& \quad + \Gamma_{\sigma\nu}(\omega_{\mu\sigma} \mid \omega_{\kappa\lambda})\} \\
& \quad + \sum_{\sigma\in S\setminus(C\cup D)} \{\Gamma_{\kappa\sigma}(\omega_{\mu\nu} \mid \omega_{\sigma\lambda}) \\
& \quad \left. + \Gamma_{\sigma\lambda}(\omega_{\mu\nu} \mid \omega_{\kappa\sigma})\}\right] \\
& + b^2 \sum_{\sigma\in E\in C\setminus\{A\}} \sum_{\rho\in F\in C\setminus\{B,E\}} \\
& \times \Gamma_{\mu\sigma}\Gamma_{\rho\nu}(\omega_{\sigma\rho} \mid \omega_{\kappa\lambda}) \\
& + b^2 \sum_{\sigma\in E\in C\setminus\{C\}} \sum_{\rho\in F\in C\setminus\{D,E\}} \\
& \times \Gamma_{\kappa\sigma}\Gamma_{\rho\lambda}(\omega_{\mu\nu} \mid \omega_{\sigma\rho}) \\
& + ac \sum_{\sigma\in E\in C\setminus\{A\}} \sum_{\rho\in S\setminus(B\cup E)} \\
& \times \Gamma_{\mu\sigma}\Gamma_{\sigma\rho}(\omega_{\rho\nu} \mid \omega_{\kappa\lambda}) \\
& + ac \sum_{\sigma\in E\in C\setminus\{B\}} \sum_{\rho\in S\setminus(A\cup E)} \\
& \times \Gamma_{\rho\sigma}\Gamma_{\sigma\nu}(\omega_{\mu\rho} \mid \omega_{\kappa\lambda}) \\
& + ac \sum_{\sigma\in E\in C\setminus\{C\}} \sum_{\rho\in S\setminus(D\cup E)} \\
& \times \Gamma_{\kappa\sigma}\Gamma_{\sigma\rho}(\omega_{\mu\nu} \mid \omega_{\rho\lambda}) \\
& + ac \sum_{\sigma\in E\in C\setminus\{D\}} \sum_{\rho\in S\setminus(C\cup E)} \\
& \times \Gamma_{\rho\sigma}\Gamma_{\sigma\lambda}(\omega_{\mu\nu} \mid \omega_{\kappa\rho}) \\
& + ac\Gamma_{\mu\mu}\left[\sum_{\sigma\in S\setminus A} \Gamma_{\mu\sigma}(\omega_{\sigma\nu} \mid \omega_{\kappa\lambda}) \right. \\
& \quad + \sum_{\sigma\in S\setminus B} \Gamma_{\sigma\nu}(\omega_{\mu\sigma} \mid \omega_{\kappa\lambda}) \\
& \quad + \sum_{\sigma\in S\setminus C} \Gamma_{\kappa\sigma}(\omega_{\mu\nu} \mid \omega_{\sigma\lambda}) \\
& \quad \left. + \sum_{\sigma\in S\setminus D} \Gamma_{\sigma\lambda}(\omega_{\mu\nu} \mid \omega_{\kappa\sigma})\right] \\
& + b^2\left[\sum_{\sigma\in S\setminus(A\cup B)} \sum_{\rho\in S\setminus(C\cup D)} \right. \\
& \quad \times \Gamma_{\mu\sigma}\Gamma_{\kappa\rho}(\omega_{\sigma\nu} \mid \omega_{\rho\lambda}) \\
& \quad + \Gamma_{\sigma\nu}\Gamma_{\kappa\rho}(\omega_{\mu\sigma} \mid \omega_{\rho\lambda}) \\
& \quad + \Gamma_{\mu\sigma}\Gamma_{\rho\lambda}(\omega_{\sigma\nu} \mid \omega_{\kappa\rho}) \\
& \quad + \Gamma_{\sigma\nu}\Gamma_{\rho\lambda} \\
& \quad \left. \times (\omega_{\mu\sigma} \mid \omega_{\kappa\rho})\right] \\
& + O(\Gamma^3), \qquad (21)
\end{aligned}
$$

$$\frac{1}{a^2}\left({}^{\lambda}_{tr}\Omega^{AB}_{\mu\nu}\,|\,{}^{\lambda}_{Mull}\Omega^{CD}_{\kappa\lambda}\right) = \Gamma_{\mu\nu}[(\mu\mu\,|\,\omega_{\kappa\lambda}) + (\nu\nu\,|\,\omega_{\kappa\lambda})] \times \left[\frac{a^2}{2} + ab + \Gamma_{\mu\mu}(2ab + 2ac + 3b^2)\right] + (ab + \Gamma_{\mu\mu}2b^2) \times \left[\sum_{\sigma\in B\setminus\{\nu\}} \Gamma_{\mu\sigma}(\sigma\nu\,|\,\omega_{\kappa\lambda}) + \sum_{\sigma\in A\setminus\{\mu\}} \Gamma_{\sigma\nu}(\mu\sigma\,|\,\omega_{\kappa\lambda})\right] + \sum_{\sigma\in S\setminus(A\cup B)} \Gamma_{\mu\sigma}\Gamma_{\sigma\nu} \times \left[\left(\frac{ab}{2} + ac\right) \times \{(\mu\mu\,|\,\omega_{\kappa\lambda}) + (\nu\nu\,|\,\omega_{\kappa\lambda})\} + (ab + b^2)(\sigma\sigma\,|\,\omega_{\kappa\lambda})\right] + \left(\frac{ab}{2} + b^2\right)\Gamma_{\mu\nu} \sum_{\sigma\in S\setminus(C\cup D)} \times [\Gamma_{\kappa\sigma}\{(\mu\mu\,|\,\omega_{\sigma\lambda}) + (\nu\nu\,|\,\omega_{\sigma\lambda})\} + \Gamma_{\sigma\lambda} \times \{(\mu\mu\,|\,\omega_{\kappa\sigma}) + (\nu\nu\,|\,\omega_{\kappa\sigma})\}] + b^2 \sum_{\eta\in S\setminus(C\cup D)} \times \left[\sum_{\sigma\in B\setminus\{\nu\}} \{\Gamma_{\kappa\eta}\Gamma_{\mu\sigma}(\sigma\nu\,|\,\omega_{\eta\lambda}) + \Gamma_{\eta\lambda}\Gamma_{\mu\sigma}(\sigma\nu\,|\,\omega_{\kappa\eta})\} + \sum_{\sigma\in A\setminus\{\mu\}} \{\Gamma_{\kappa\eta}\Gamma_{\sigma\nu} \times (\mu\sigma\,|\,\omega_{\eta\lambda}) + \Gamma_{\eta\lambda}\Gamma_{\sigma\nu}(\mu\sigma\,|\,\omega_{\kappa\eta})\}\right] + O(\mathbf{\Gamma}^3), \tag{22}$$

$$\frac{1}{a^2}\left({}^{\lambda}_{Mull}\Omega^{AB}_{\mu\nu}\,|\,{}^{\lambda}_{tr}\Omega^{CD}_{\kappa\lambda}\right) = \Gamma_{\kappa\lambda}[(\omega_{\mu\nu}\,|\,\kappa\kappa) + (\omega_{\mu\nu}\,|\,\lambda\lambda)] \times \left[\frac{a^2}{2} + ab + \Gamma_{\mu\mu}(2ab + 2ac + 3b^2)\right] + (ab + \Gamma_{\mu\mu}2b^2) \times \left[\sum_{\sigma\in D\setminus\{\lambda\}} \Gamma_{\kappa\sigma}(\omega_{\mu\sigma}\,|\,\sigma\lambda) + \sum_{\sigma\in C\setminus\{\kappa\}} \Gamma_{\sigma\lambda}(\omega_{\sigma\nu}\,|\,\kappa\sigma)\right] + \sum_{\sigma\in S\setminus(C\cup D)} \Gamma_{\kappa\sigma}\Gamma_{\sigma\lambda} \times \left[\left(\frac{ab}{2} + ac\right)\{(\omega_{\mu\sigma}\,|\,\kappa\kappa) + (\omega_{\mu\sigma}\,|\,\lambda\lambda)\} + (ab + b^2)(\omega_{\mu\sigma}\,|\,\sigma\sigma)\right] + \left(\frac{ab}{2} + b^2\right)\Gamma_{\kappa\lambda} \sum_{\sigma\in S\setminus(A\cup B)} \times [\Gamma_{\mu\sigma}\{(\omega_{\sigma\nu}\,|\,\kappa\kappa) + (\omega_{\sigma\nu}\,|\,\lambda\lambda)\} + \Gamma_{\sigma\nu} \times \{(\omega_{\mu\sigma}\,|\,\kappa\kappa) + (\tilde{\omega}_{\mu\sigma}\,|\,\lambda\lambda)\}] + b^2 \sum_{\sigma\in S\setminus(A\cup B)} \times \left[\sum_{\eta\in D\setminus\{\lambda\}} \Gamma_{\mu\sigma}\Gamma_{\kappa\eta}(\omega_{\sigma\nu}\,|\,\eta\lambda) + \Gamma_{\sigma\nu}\Gamma_{\kappa\eta}(\omega_{\mu\sigma}\,|\,\eta\lambda) + \sum_{\eta\in C\setminus\{\kappa\}} \Gamma_{\mu\sigma}\Gamma_{\eta\lambda}(\omega_{\sigma\nu}\,|\,\kappa\eta) + \Gamma_{\sigma\nu}\Gamma_{\eta\lambda}(\omega_{\mu\sigma}\,|\,\kappa\eta)\right] + O(\mathbf{\Gamma}^3). \tag{23}$$

Finally, one obtains for the mixed products

$$\frac{1}{a^2}\left({}^{\lambda}_{diag}\Omega^{AB}_{\mu\nu}\,|\,{}^{\lambda}_{Mull}\Omega^{CD}_{\kappa\lambda}\right) = b^2 \sum_{E\in C\setminus\{A,B\}} \times \sum_{\substack{\rho,\sigma\in E\\ \rho\neq\sigma}} \Gamma_{\mu\sigma}\Gamma_{\rho\nu} \times (\sigma\rho\,|\,\omega_{\kappa\lambda}) + (2ac + b^2)\Gamma_{\mu\mu} \times \left[\sum_{\sigma\in B\setminus\{\nu\}} \Gamma_{\mu\sigma}(\sigma\nu\,|\,\omega_{\kappa\lambda}) + \sum_{\sigma\in A\setminus\{\mu\}} \Gamma_{\sigma\nu}(\mu\sigma\,|\,\omega_{\kappa\lambda})\right] + ac \sum_{\sigma\in S\setminus(A\cup B)} \times \left[\sum_{\sigma\in B\setminus\{\nu\}} \Gamma_{\mu\sigma}\Gamma_{\sigma\rho}(\rho\nu\,|\,\omega_{\kappa\lambda}) + \sum_{\sigma\in A\setminus\{\mu\}} \Gamma_{\rho\sigma}\Gamma_{\sigma\nu}(\mu\rho\,|\,\omega_{\kappa\lambda})\right] + O(\mathbf{\Gamma}^3), \tag{24}$$

$$\frac{1}{a^2}({}_{Mull}{}^{\lambda}\Omega_{\mu\nu}^{AB} \mid {}_{diag}{}^{\lambda}\Omega_{\kappa\lambda}^{CD}) = b^2 \sum_{E\in C\setminus\{C,D\}} \times \sum_{\substack{\rho,\sigma\in E \\ \rho\neq\sigma}} \Gamma_{\kappa\sigma}\Gamma_{\rho\lambda} \times (\omega_{\mu\nu} \mid \sigma\rho) + (2ac + b^2)\Gamma_{\mu\mu} \times \Big[\sum_{\sigma\in D\setminus\{\lambda\}} \Gamma_{\kappa\sigma}(\omega_{\mu\nu} \mid \sigma\lambda) + \sum_{\sigma\in C\setminus\{\kappa\}} \Gamma_{\sigma\lambda}(\omega_{\mu\nu} \mid \kappa\sigma) \Big] + ac \sum_{\sigma\in S\setminus(C\cup D)} \times \Big[\sum_{\rho\in D\setminus\{\lambda\}} \Gamma_{\kappa\sigma}\Gamma_{\sigma\rho}(\omega_{\mu\nu} \mid \rho\lambda) + \sum_{\rho\in C\setminus\{\kappa\}} \Gamma_{\rho\sigma}\Gamma_{\sigma\lambda}(\omega_{\mu\nu} \mid \kappa\rho) \Big] + O(\mathbf{\Gamma}^3). \quad (25)$$

Now, the two- and three-center integrals of type (iii), G_{CD}^{AA} and G_{AD}^{AA}, remain for discussion. The repulsion integrals are represented by

$${}^{\lambda}(\mu\nu \mid \kappa\lambda) = ({}_{tr}{}^{\lambda}\Omega_{\mu\nu}^{AA} + {}_{diag}{}^{\lambda}\Omega_{\mu\nu}^{AA} + {}_{Mull}{}^{\lambda}\Omega_{\mu\nu}^{AA} \mid {}_{tr}{}^{\lambda}\Omega_{\kappa\lambda}^{CD} + {}_{diag}{}^{\lambda}\Omega_{\kappa\lambda}^{CD} + {}_{Mull}{}^{\lambda}\Omega_{\kappa\lambda}^{CD}) + O(\mathbf{\Gamma}^3).$$

Nine products arise; they are classified analogously to the argumentation above:

(a) Part of transformation (before applying diagonal-approximation exhaustively):

$$({}_{tr}{}^{\lambda}\Omega_{\mu\nu}^{AA} \mid {}_{tr}{}^{\lambda}\Omega_{\kappa\lambda}^{CD}).$$

(b) Diagonal-approximation:

$$({}_{diag}{}^{\lambda}\Omega_{\mu\nu}^{AA} \mid {}_{diag}{}^{\lambda}\Omega_{\kappa\lambda}^{CD}), ({}_{tr}{}^{\lambda}\Omega_{\mu\nu}^{AA} \mid {}_{diag}{}^{\lambda}\Omega_{\kappa\lambda}^{CD}), ({}_{diag}{}^{\lambda}\Omega_{\mu\nu}^{AA} \mid {}_{tr}{}^{\lambda}\Omega_{\kappa\lambda}^{CD}).$$

(c) Mulliken approximation:

$$({}_{Mull}{}^{\lambda}\Omega_{\mu\nu}^{AA} \mid {}_{Mull}{}^{\lambda}\Omega_{\kappa\lambda}^{CD}), ({}_{tr}{}^{\lambda}\Omega_{\mu\nu}^{AA} \mid {}_{Mull}{}^{\lambda}\Omega_{\kappa\lambda}^{CD}), ({}_{Mull}{}^{\lambda}\Omega_{\mu\nu}^{AA} \mid {}_{tr}{}^{\lambda}\Omega_{\kappa\lambda}^{CD}).$$

(d) Mixed terms

$$({}_{diag}{}^{\lambda}\Omega_{\mu\nu}^{AA} \mid {}_{Mull}{}^{\lambda}\Omega_{\kappa\lambda}^{CD}), ({}_{Mull}{}^{\lambda}\Omega_{\mu\nu}^{AA} \mid {}_{diag}{}^{\lambda}\Omega_{\kappa\lambda}^{CD}).$$

(The integrals of the type G_{AA}^{CD} can be obtained from G_{CD}^{AA} because of the permutation symmetry of repulsion integrals.)

Let us first investigate the part of transformation. For the functions μ and ν localized at atom A, the cases $\mu \neq \nu$ and $\mu = \nu$ for class (a) have to be treated differently because of the different application of the diagonal-approximation. In the case $\mu = \nu$, the justification of the NDDO approximation in Part IV was not successful. In both cases, the following partition holds:

$$({}_{tr}{}^{\lambda}\Omega_{\mu\nu}^{AA} \mid {}_{tr}{}^{\lambda}\Omega_{\kappa\lambda}^{CD}) = {}_{approx}{}^{\lambda}(\mu\nu \mid \kappa\lambda) + r_{diag}.$$

The approximative representation of this integral ${}_{approx}{}^{\lambda}(\mu\nu \mid \kappa\lambda)$ is known from Part IV:

1. $\mu \neq \nu$

$${}_{approx}{}^{\lambda}(\mu\nu \mid \kappa\lambda) = a^2(a^2/2 + ab)\Gamma_{\kappa\lambda} \times [(\mu\nu \mid \kappa\kappa) + (\mu\nu \mid \lambda\lambda)] + O(\mathbf{\Gamma}^3). \quad (26)$$

Exhaustive application of diagonal-approximation on $({}_{tr}{}^{\lambda}\Omega_{\mu\nu}^{AA} \mid {}_{tr}{}^{\lambda}\Omega_{\kappa\lambda}^{CD})$ results in the error r_{diag}:

$$r_{diag}/a^2 = \Gamma_{\mu\mu}\Gamma_{\kappa\lambda} \times [(\mu\nu \mid \kappa\kappa) + (\mu\nu \mid \lambda\lambda)] \times (2ab + 2ac + 3b^2) + (ab + 2b^2\Gamma_{\mu\mu}) \times \Big[\sum_{\sigma\in D\setminus\{\lambda\}} \Gamma_{\kappa\sigma}(\mu\nu \mid \sigma\lambda) + \sum_{\sigma\in C\setminus\{\kappa\}} \Gamma_{\sigma\lambda}(\mu\nu \mid \kappa\sigma) \Big] + \sum_{\sigma\in S\setminus(C\cup D)} \Gamma_{\kappa\sigma}\Gamma_{\sigma\lambda} \times \Big[\Big(ac + \frac{ab}{2}\Big)\{(\mu\nu \mid \kappa\kappa) + (\mu\nu \mid \lambda\lambda)\} + (ab + b^2)((\mu\nu \mid \sigma\sigma) \Big] + O(\mathbf{\Gamma}^3). \quad (27)$$

2. $\mu = \nu$:

$$\frac{1}{a^2}{}_{approx}{}^{\lambda}(\mu\mu \mid \kappa\lambda) = \frac{1}{a^2}({}_{tr}{}^{\lambda}\Omega_{\mu\mu}^{AA} \mid {}_{tr}{}^{\lambda}\Omega_{\kappa\lambda}^{CD}) = (a^2/2 + ab + \Gamma_{\mu\mu}(2ab + 2ac + 3b^2)) \times \Gamma_{\kappa\lambda}[(\mu\mu \mid \kappa\kappa) + (\mu\mu \mid \lambda\lambda)] + (ab + 2b^2\Gamma_{\mu\mu})$$

$$\times \Bigg[\sum_{\sigma \in D \setminus \{\lambda\}} \Gamma_{\kappa\sigma}(\mu\mu \mid \sigma\lambda) + \sum_{\sigma \in C \setminus \{\kappa\}} \Gamma_{\sigma\lambda}(\mu\mu \mid \kappa\sigma) \Bigg]$$
$$+ \sum_{\sigma \in S \setminus (C \cup D)} \Gamma_{\kappa\sigma}\Gamma_{\sigma\lambda} \times \Bigg[\left(ac + \frac{ab}{2}\right)\{(\mu\mu \mid \kappa\kappa) + (\mu\mu \mid \lambda\lambda)\} + (ab + b^2)(\mu\mu \mid \sigma\sigma) \Bigg] + O(\Gamma^3). \quad (28)$$

For this case, one has $r_{diag} = 0 + O(\Gamma^3)$. The errors introduced by diagonal-approximation are given by

$$\frac{1}{a^2}({}^{\lambda}_{tr}\Omega^{AA}_{\mu\nu} \mid {}^{\lambda}_{diag}\Omega^{CD}_{\kappa\lambda}) = b^2 \sum_{G \in C \setminus \{C,D\}} \times \sum_{\substack{\sigma,\rho \in G \\ \sigma \neq \rho}} \Gamma_{\kappa\sigma}\Gamma_{\rho\lambda}(\mu\nu \mid \sigma\rho) + (b^2 + 2ac)\Gamma_{\mu\mu} \times \Bigg[\sum_{\sigma \in D \setminus \{\lambda\}} \Gamma_{\kappa\sigma}(\mu\nu \mid \sigma\lambda) + \sum_{\sigma \in C \setminus \{\kappa\}} \Gamma_{\sigma\lambda}(\mu\nu \mid \kappa\sigma) \Bigg] + ac \sum_{\sigma \in S \setminus (C \cup D)} \times \Bigg[\sum_{\rho \in D \setminus \{\lambda\}} \Gamma_{\kappa\sigma}\Gamma_{\sigma\rho}(\mu\nu \mid \rho\lambda) + \sum_{\rho \in C \setminus \{\kappa\}} \Gamma_{\rho\sigma}\Gamma_{\sigma\lambda}(\mu\nu \mid \kappa\rho) \Bigg] + O(\Gamma^3), \quad (29)$$

$$({}^{\lambda}_{diag}\Omega^{AA}_{\mu\nu} \mid {}^{\lambda}_{diag}\Omega^{CD}_{\kappa\lambda}) = 0 + O(\Gamma^3), \quad (30)$$

$$({}^{\lambda}_{diag}\Omega^{AA}_{\mu\nu} \mid {}^{\lambda}_{tr}\Omega^{CD}_{\kappa\lambda}) = 0 + O(\Gamma^3). \quad (31)$$

The Mulliken approximation induces

$$\frac{1}{a^2}({}^{\lambda}_{Mull}\Omega^{AA}_{\mu\nu} \mid {}^{\lambda}_{Mull}\Omega^{CD}_{\kappa\lambda}) = (ab + \Gamma_{\mu\mu}(3b^2 + 2ac)) \times \sum_{\sigma \in S \setminus A} \{\Gamma_{\mu\sigma}(\omega_{\sigma\nu} \mid \omega_{\kappa\lambda}) + \Gamma_{\sigma\nu}(\omega_{\mu\sigma} \mid \omega_{\kappa\lambda})\} + b^2 \sum_{\rho \in E \in C \setminus \{A\}} \sum_{\sigma \in F \in C \setminus \{A,E\}} \times \Gamma_{\mu\rho}\Gamma_{\sigma\nu}(\omega_{\rho\sigma} \mid \omega_{\kappa\lambda}) + ac \sum_{\sigma \in S \setminus A} \sum_{\substack{\rho \in S \setminus A \\ \rho \neq \sigma}} \times \{\Gamma_{\mu\rho}\Gamma_{\rho\sigma}(\omega_{\sigma\nu} \mid \omega_{\kappa\lambda}) + \Gamma_{\nu\rho}\Gamma_{\rho\sigma}(\omega_{\sigma\mu} \mid \omega_{\kappa\lambda})\} + b^2 \sum_{\eta \in S \setminus (C \cup D)} \times \Bigg[\Gamma_{\kappa\eta}\Bigg(\sum_{\sigma \in S \setminus A} \Gamma_{\mu\sigma}(\omega_{\sigma\nu} \mid \omega_{\eta\lambda}) + \Gamma_{\sigma\nu}(\omega_{\mu\sigma} \mid \omega_{\eta\lambda}) \Bigg) + \Gamma_{\eta\lambda}\Bigg(\sum_{\sigma \in S \setminus A} \Gamma_{\mu\sigma}(\omega_{\sigma\nu} \mid \omega_{\kappa\eta}) + \Gamma_{\sigma\nu}(\omega_{\mu\sigma} \mid \omega_{\kappa\eta}) \Bigg) \Bigg] + O(\Gamma^3), \quad (32)$$

$$\frac{1}{a^2}({}^{\lambda}_{Mull}\Omega^{AA}_{\mu\nu} \mid {}^{\lambda}_{tr}\Omega^{CD}_{\kappa\lambda}) = \Gamma_{\kappa\lambda}\left(\frac{ab}{2} + b^2\right) \times \Bigg[\sum_{\sigma \in S \setminus A} \Gamma_{\mu\sigma}(\omega_{\sigma\nu} \mid \kappa\kappa) + \Gamma_{\mu\sigma}(\omega_{\sigma\nu} \mid \lambda\lambda) + \Gamma_{\sigma\nu}(\omega_{\mu\sigma} \mid \kappa\kappa) + \Gamma_{\sigma\nu}(\omega_{\mu\sigma} \mid \lambda\lambda) \Bigg] + b^2 \sum_{\rho \in D \setminus \{\lambda\}} \times \Gamma_{\kappa\rho}\Bigg(\sum_{\sigma \in S \setminus A} \Gamma_{\mu\sigma}(\omega_{\sigma\nu} \mid \rho\lambda) + \Gamma_{\sigma\nu}(\omega_{\mu\sigma} \mid \rho\lambda) \Bigg) + b^2 \sum_{\rho \in C \setminus \{\kappa\}} \times \Gamma_{\rho\lambda}\Bigg(\sum_{\sigma \in S \setminus A} \Gamma_{\mu\sigma}(\omega_{\sigma\nu} \mid \kappa\rho) + \Gamma_{\sigma\nu}(\omega_{\mu\sigma} \mid \kappa\rho) \Bigg) + O(\Gamma^3), \quad (33)$$

$$\frac{1}{a^2}({}^{\lambda}_{tr}\Omega^{AA}_{\mu\nu} \mid {}^{\lambda}_{Mull}\Omega^{CD}_{\kappa\lambda}) = (\mu\nu \mid \omega_{\kappa\lambda}) \times [a^2 + 4ab\Gamma_{\mu\mu} + \Gamma^2_{\mu\mu}(4ac + 6b^2)] + \sum_{\sigma \in S \setminus A} \{\Gamma_{\mu\sigma}\Gamma_{\nu\sigma}\left(ac + \frac{ab}{2}\right) \times [(\mu\mu \mid \omega_{\kappa\lambda}) + (\nu\nu \mid \omega_{\kappa\lambda})]$$

$$
\begin{aligned}
&+ (ab + b^2)(\sigma\sigma \mid \omega_{\kappa\lambda})\} \\
&+ (ab + \Gamma_{\mu\mu}(3b^2 + ac)) \\
&\times \sum_{\sigma \in S\setminus(C\cup D)} \{\Gamma_{\kappa\sigma}(\mu\nu \mid \omega_{\sigma\lambda}) \\
&+ \Gamma_{\sigma\lambda}(\mu\nu \mid \omega_{\kappa\sigma})\} \\
&+ ac\Gamma_{\mu\mu}\Big[\sum_{\sigma\in S\setminus C} \Gamma_{\kappa\sigma}(\mu\nu \mid \omega_{\sigma\lambda}) \\
&\qquad + \sum_{\sigma\in S\setminus D} \Gamma_{\sigma\lambda}(\mu\nu \mid \omega_{\kappa\sigma})\Big] \\
&+ \sum_{\sigma\in G\in C\setminus\{C\}} \sum_{\rho\in S\setminus(D\cup G)} \\
&\times [b^2\Gamma_{\kappa\sigma}\Gamma_{\rho\lambda}(\mu\nu \mid \omega_{\sigma\rho}) \\
&\quad + ac\Gamma_{\kappa\sigma}\Gamma_{\sigma\rho}(\mu\nu \mid \omega_{\rho\lambda})] \\
&+ ac \sum_{\sigma\in G\in C\setminus\{D\}} \sum_{\rho\in S\setminus(C\cup G)} \\
&\times \Gamma_{\rho\sigma}\Gamma_{\sigma\lambda}(\mu\nu \mid \omega_{\kappa\rho}) \\
&+ O(\Gamma^3). \qquad (34)
\end{aligned}
$$

One has for the mixed terms

$$
\begin{aligned}
\frac{1}{a^2}({}^{\lambda}_{diag}\Omega^{AA}_{\mu\nu} \mid {}^{\lambda}_{Mull}\Omega^{CD}_{\kappa\lambda}) &= ac(1 - \delta_{\mu\nu}) \\
&\times (\mu\nu \mid \omega_{\kappa\lambda}) \sum_{\sigma\in S\setminus A} \\
&\times (\Gamma^2_{\mu\sigma} + \Gamma^2_{\nu\sigma}) \\
&+ ac \sum_{\rho\in A\setminus\{\mu,\nu\}} \sum_{\sigma\in S\setminus A} \\
&\times \Gamma_{\mu\sigma}\Gamma_{\sigma\rho}(\rho\nu \mid \omega_{\kappa\lambda}) \\
&+ \Gamma_{\nu\sigma}\Gamma_{\sigma\rho}(\rho\mu \mid \omega_{\kappa\lambda}) \\
&+ b^2 \sum_{\substack{\rho,\sigma\in E\in C\setminus\{A\} \\ \rho\neq\sigma}} \Gamma_{\mu\rho}\Gamma_{\sigma\nu} \\
&\times (\rho\sigma \mid \omega_{\kappa\lambda}) \\
&+ O(\Gamma^3), \qquad (35)
\end{aligned}
$$

$$
({}^{\lambda}_{Mull}\Omega^{AA}_{\mu\nu} \mid {}^{\lambda}_{diag}\Omega^{CD}_{\kappa\lambda}) = 0 + O(\Gamma^3). \qquad (36)
$$

Numerical Evaluation of the Error Terms

A numerical evaluation of the "expansive" error functionals on G, the set of all repulsion integrals in the ϕ-basis, as derived in the last section, permits a judgment on the quality of the approximative integral transformations as described in the fourth paper. Especially, the practicability of Eq. (17) for the change of basis for the NDDO-surviving integrals is of interest.

Let us restrict the discussion on the analysis of the repulsion integrals because application of NDDO is not justified for one-electron operators by Part IV. Such integrals have to be calculated completely and transformed correctly.

A CRITERION OF NORM FOR THE QUALITY OF APPROXIMATION

The standard for the quality of a simplified nonempirical quantum chemical computation method is always the result of the complete procedure. Often, the ground-state energy serves as an exclusive standard, but this quantity is not sufficient for a differentiated analysis of an approximative method. Moreover, the ground-state energy seems to be a poor indicator to judge on integral approximations because of the nonlinear nature of the self-consistent field procedure.

Therefore, it is more plausible to require a reproduction of the repulsion integrals of the nonapproximative method as well as possible. Only "small" integrals may be approximated by zero. Let M be a subset of the set of repulsion integrals—maybe, the integrals of the type G^{AB}_{CD}. To each integral $(\mu\nu \mid \kappa\lambda)$ of the set M, an approximation $(\mu\nu \mid \kappa\lambda)'$ is given. Let M' be the set of these approximate integrals. The weighted quadratic mean m (a l^2 norm) provides a notion of distance:

$$
m := \left(\frac{1}{|M|} \sum_{(\mu\nu \mid \kappa\lambda)\in M} ((\mu\nu \mid \kappa\lambda) - (\mu\nu \mid \kappa\lambda)')^2\right)^{1/2}. \qquad (37)
$$

The weighted quadratic mean can also be used to quantify the (mean) magnitude of a set of integrals:

$$
\tilde{m} = \left(\frac{1}{|M|} \sum_{(\mu\nu \mid \kappa\lambda)\in M} (\mu\nu \mid \kappa\lambda)^2\right)^{1/2}. \qquad (38)
$$

CALCULUS OF ERROR FOR SOME DIATOMIC MOLECULES

For some diatomic molecules, the error functionals shall be evaluated numerically to allow an estimation of the magnitude of the various

errors. Therefore, these examples provide a lower numerical limit for the errors. This lower bound allows some far-reaching consequences.

Diatomic molecules are preferred since the error functionals of the section Calculus of Error for the Integral Transformations are simplified drastically:

1. $\forall \mu \in S\ \Gamma_{\mu\mu} = 0$ (by Corollary 2 of the theorem in Part III).
2. All sums like

$$\sum_{\substack{C,D\in C\setminus\{A\}\\ C\neq D}} \sum_{\substack{\sigma\in C\\ \rho\in D}} \cdots$$

vanish if A is an atom of the considered molecule. The first sum operates first for three-atomic molecules. For diatomic molecules AB, the following sums vanish, too:

$$\sum_{E\in C\setminus\{A,B\}} \ldots, \quad \sum_{\sigma\in S\setminus(A\cup B)} \ldots \quad \text{and so on.}$$

Therefore, some of the error functionals of the section The Approximation Errors of the Repulsion Integrals are of the third order. For the integral types G_{CD}^{AB} (here G_{AB}^{AB}), it follows from Eqs. (24) and (25) that

$$({}_{diag}^{\lambda}\Omega_{\mu\nu}^{AB} \mid {}_{Mull}^{\lambda}\Omega_{\kappa\lambda}^{AB}) = 0 + O(\Gamma^3),$$
$$({}_{Mull}^{\lambda}\Omega_{\mu\nu}^{AB} \mid {}_{diag}^{\lambda}\Omega_{\kappa\lambda}^{AB}) = 0 + O(\Gamma^3),$$

and further for G_{CD}^{AA} (here G_{AB}^{AA}) by (29), that

$$({}_{tr}^{\lambda}\Omega_{\mu\nu}^{AA} \mid {}_{diag}^{\lambda}\Omega_{\kappa\lambda}^{AB}) = 0 + O(\Gamma^3).$$

The remaining equations are reduced; e.g., Eq. (23) for diatomic molecules ($C = A, D = B$) becomes

$$\frac{1}{a^2}({}_{Mull}^{\lambda}\Omega_{\mu\nu}^{AB} \mid {}_{tr}^{\lambda}\Omega_{\kappa\lambda}^{CD}) = \Gamma_{\kappa\lambda}[(\omega_{\mu\nu} \mid \kappa\kappa) + (\omega_{\mu\nu} \mid \lambda\lambda)]\left(\frac{a^2}{2} + ab\right) + ab\left[\sum_{\sigma\in D\setminus\{\lambda\}} \Gamma_{\kappa\sigma}(\omega_{\mu\sigma} \mid \sigma\lambda) + \sum_{\sigma\in C\setminus\{\kappa\}} \times \Gamma_{\sigma\lambda}(\omega_{\sigma\nu} \mid \kappa\sigma)\right] + O(\Gamma^3).$$

The calculus of error is most advantageous for diatomic molecules since for three and more atomic molecules such simplifications are not possible.

The results for the numerical calculations of boron nitride (BN), fluorine (F_2), and lithium fluoride (LiF) are represented in Tables I–III. An all-electron minimal basis of Slater functions is utilized (five atomic orbitals at B, N, F, and two atomic orbitals at Li); the Slater exponents can be found in Clementi and Roetti [5]. The program DIATOM available at QCPE [6] is used for the calculation of repulsion integrals. Local orthogonalization was performed utilizing a Schmidt procedure. The bond distances read $d_{BN} = 1.281$ Å, $d_{FF} = 1.435$ Å, and $d_{LiF} = 1.510$ Å; the expansion coefficients are calculated by Legendre approximation (see Part II).

The tables provide a comparison of different integral types: The NDDO-surviving integrals G_{AA}^{AA} and G_{BB}^{AA} can be found in the first column. The three following columns describe the integral G_{AB}^{AA} (general type G_{CD}^{AA}) distinguished between equal or different orbitals in the one-center charge distribu-

TABLE I
Repulsion integrals of boron nitride.

Boron nitride (BN)	G_{AA}^{AA} / G_{BB}^{AA}	G_{AB}^{AA}, (G_{CD}^{AA}) $\mu = \nu$	$\mu \neq \nu$	$\mu \overset{=}{\neq} \nu$	G_{AB}^{AB} $(G_{AC}^{AB}, G_{CD}^{AB})$	All types
Total no. integrals	2500	1000	4000	5000	2500	10,000
Mean ϕ-basis: ${}^{\phi}(\mu\nu \mid \kappa\lambda)$	0.14979	0.10436	0.01091	0.04768	0.02266	0.08291
Mean λ-basis: ${}^{\lambda}(\mu\nu \mid \kappa\lambda)$	0.15042	0.02232	0.00400	0.01060	0.00189	0.07559
Mean ${}_{approx}^{\lambda}(\mu\nu \mid \kappa\lambda)$	0.14990	0.06680	0.00193	0.02992	0.00730	—
Mean diagonal-approx.	—	0.0	0.01020	0.00912	0.00991	—
Mean Mulliken approx.	0.01135	0.01468	0.00982	0.01096	0.00197	—
Mean mixed terms	—	0.00618	0.00585	0.00592	0.0	—
Mean all integral approx.	0.01135	0.01894	0.00651	0.01028	0.01061	0.01064
Mean 2nd-order expansion	0.03404	0.05758	0.00387	0.02598	0.01533	0.02619

TABLE II
Repulsion integrals of fluorine.

Fluorine (F_2)	G_{AA}^{AA} / G_{BB}^{AA}	G_{AB}^{AA}, (G_{CD}^{AA}) $\mu = \nu$	$\mu \neq \nu$	$\mu \overset{=}{\neq} \nu$	G_{AB}^{AB} $(G_{AC}^{AB}, G_{CD}^{AB})$	All types
Total no. integrals	2500	1000	4000	5000	2500	10,000
Mean ϕ-basis: $^{\phi}(\mu\nu \mid \kappa\lambda)$	0.22058	0.04086	0.00386	0.01860	0.00344	0.11108
Mean λ-basis: $^{\lambda}(\mu\nu \mid \kappa\lambda)$	0.22124	0.00771	0.00127	0.00363	0.00036	0.11065
Mean $_{approx}^{\lambda}(\mu\nu \mid \kappa\lambda)$	0.22100	0.00599	0.00004	0.00268	0.0001	—
Mean diagonal-approx.	—	0.0	0.00312	0.00279	0.00053	—
Mean Mulliken approx.	0.00147	0.00424	0.00310	0.00336	0.00028	—
Mean mixed terms	—	0.00025	0.00014	0.00017	0.0	—
Mean all integral approx.	0.00147	0.00426	0.00122	0.00220	0.00046	0.00173
Mean 2nd-order expansion	0.00033	0.00153	0.00009	0.00069	0.00012	0.00052

tion. In the second to last column, the repulsion integrals G_{AB}^{AB} (general types G_{CD}^{AB}, G_{AC}^{AB}) with only two-center charge distributions are investigated. Finally, in the last column, the means on all integral types are shown. For each integral type, first, the number of relating integrals and, then, the different means are given in the rows. The first mean is that of the integrals in the locally orthogonalized basis followed by that in the Löwdin basis.

The mean of the integrals $_{approx}^{\lambda}(\mu\nu \mid \kappa\lambda)$ is given by Eqs. (17), (19), (26), or (28), respectively. The diagonal-approximation is not applied to the transformation of the NDDO-surviving integrals. In the remaining cases, the mean of diagonal-aproximation is calculated by an addition of the terms r_{diag}, $(_{diag}^{\lambda}\Omega_{\mu\nu} \mid _{diag}^{\lambda}\Omega_{\kappa\lambda})$, $(_{tr}^{\lambda}\Omega_{\mu\nu} \mid _{diag}^{\lambda}\Omega_{\kappa\lambda})$, and $(_{diag}^{\lambda}\Omega_{\mu\nu} \mid _{tr}^{\lambda}\Omega_{\kappa\lambda})$ followed by the computation of the quadratic mean. Analogously, the means for the errors due to Mulliken approximation and the mixed terms can be calculated. The error of Mulliken approximation of the NDDO-surviving integrals is determined by (18). The mean of integral approximation errors is computed by an addition of the errors that are induced by the integral approximations for each integral followed by the calculation of the quadratic mean. (The proper sequence is essential!)

The error of the second-order expansion in $\mathbf{\Gamma}$ is now the mean of the difference of the correctly (without approximations) calculated integral $^{\lambda}(\mu\nu \mid \kappa\lambda)$ and the sum of $_{approx}^{\lambda}(\mu\nu \mid \kappa\lambda)$ with the various error terms. Some items in the tables are not defined and are therefore marked by a dash.

DISCUSSION OF THE RESULTS

At first, it can be seen that integrals with two-center charge distributions become small in the symmetrically orthogonalized basis (about of a factor of 10). This circumstance is already known from the frequency distribution diagrams of Part IV for boron nitride. The mean for the integrals of type

TABLE III
Repulsion integrals of lithium fluoride.

Lithium fluorine (LiF)	G_{AA}^{AA} / G_{BB}^{AA}	G_{AB}^{AA}, (G_{CD}^{AA}) $\mu = \nu$	$\mu \neq \nu$	$\mu \overset{=}{\neq} \nu$	G_{AB}^{AB} $(G_{AC}^{AB}, G_{CD}^{AB})$	All types
Total no. integrals	841	280	880	1160	400	2401
Mean ϕ-basis: $^{\phi}(\mu\nu \mid \kappa\lambda)$	0.27232	0.05778	0.00672	0.02898	0.00497	0.16244
Mean λ-basis: $^{\lambda}(\mu\nu \mid \kappa\lambda)$	0.27230	0.01531	0.00240	0.00781	0.00059	0.16125
Mean $_{approx}^{\lambda}(\mu\nu \mid \kappa\lambda)$	0.27273	0.00820	0.00003	0.00403	0.00000	—
Mean diagonal-approx.	—	0.0	0.00479	0.00417	0.00070	—
Mean Mulliken approx.	0.00208	0.01047	0.00654	0.00767	0.00044	—
Mean mixed terms	—	0.00009	0.00019	0.00017	0.0	—
Mean all integral approx.	0.00208	0.01048	0.00239	0.00555	0.00061	0.00406
Mean 2nd-order expansion	0.00028	0.00244	0.00006	0.00120	0.00007	0.00085

(iii), i.e., G^{AA}_{CD} and G^{AA}_{AD}, does not decrease in the same manner. The mean magnitude of the NDDO-surviving integrals does not vary much.

By inspection of the integrals that are neglected by NDDO, one can see that the mean of the sum of the integral approximation errors is of about the magnitude of the mean of the integrals in the symmetrically orthogonalized basis ${}^{\lambda}_{approx}(\mu\nu \mid \kappa\lambda)$. Moreover, the quadratic mean of the second-order expansion error is about of equal magnitude. Therefore, the transformations for the approximative representation of the integrals with two-center charge densities are almost useless. But its importance can be seen in the reproduction of the proportions of the mean magnitude of the integrals in the Löwdin basis; this provides the arguments for the justification of NDDO.

The error of Mulliken approximation is unavoidable because it is necessary for the substitution of two-center charge distributions. Also, diagonal-approximation produces great errors: The integrals G^{AA}_{AB} for $\mu \neq \nu$ are even underestimated, whereas the error of diagonal-approximation is of the magnitude of the considered integrals in the quadratic mean. This verifies the assumption that the diagonal-approximation serves mainly for a reduction of the mean magnitude of repulsion integrals in the Löwdin basis. The error that is introduced by the second-order expansion may be reduced by a polynomial ansatz of higher degree. But this increases the error caused by the Mulliken approximation; moreover, the corresponding equations are expected to be difficult to handle because of their complexity.

For the NDDO-surviving integrals, the situation seems to be favorable. These integrals have a quadratic mean in the ϕ- and λ-basis that is greater to orders of magnitude than the mean of errors. These integrals shall be investigated further: Let M be the set of NDDO-surviving integrals: $M = G^{AA}_{AA} \cup G^{AA}_{GG}$:

$$m_1 := \left(\frac{1}{|M|} \sum_{(\mu\nu \mid \kappa\lambda) \in M} [{}^{\phi}(\mu\nu \mid \kappa\lambda) - {}^{\lambda}(\mu\nu \mid \kappa\lambda)]^2 \right)^{1/2}$$

$$m_2 := \left(\frac{1}{|M|} \sum_{(\mu\nu \mid \kappa\lambda) \in M} [{}^{\lambda}_{approx}(\mu\nu \mid \kappa\lambda) - {}^{\lambda}(\mu\nu \mid \kappa\lambda)]^2 \right)^{1/2}.$$

The weighted quadratic mean m_1 describes the distance of the $|M|$-dimensional vectors of NDDO-surviving integrals in the ϕ- and λ-basis. The integrals ${}^{\lambda}(\mu\nu \mid \kappa\lambda)$ are to be calculated by a nonapproximative method (Table IV).

TABLE IV
Quadratic means m_1 and m_2 for diatomic molecules.

	m_1	m_2
HF	0.011032	0.014082
LiH	0.010667	0.005611
LiF	0.002847	0.002244
BeO	0.005730	0.005396
BN	0.011491	0.041612
CO	0.012389	0.041914
N_2	0.013260	0.053946
O_2	0.007920	0.014473
F_2	0.002212	0.001616

Let us discuss some of the diatomic molecules: As above, an all-electron minimal basis of Slater functions was utilized with single-zeta orbital coefficients following [5]. The bond distances read $d_{LiH} = 1.595$ Å, $d_{BeO} = 1.331$ Å, $d_{CO} = 1.128$ Å, $d_{NN} = 1.094$ Å, $d_{OO} = 1.207$ Å and $d_{HF} = 0.917$ Å; and the rest like in the last section.

Therefore, the NDDO-surviving integrals in the locally orthogonalized basis differ from that in the Löwdin basis about of the order of 10^{-2} to 10^{-3}. But the integrals ${}^{\lambda}_{approx}(\mu\nu \mid \kappa\lambda)$ provide for the molecules HF, BN, CO, N_2, and O_2 an often significantly less accurate result than do the integrals in the initial ϕ-basis ($m_2 > m_1$). In the remaining cases, only small improvements ($m_2 < m_1$) are realized. This means that m_1 and m_2 are of about the same order of magnitude as are the quadratic means of the approximation errors of the NDDO-surviving integrals. For instance, in the unfavorable case of boron nitride, the second-order expansion error of the NDDO-surviving integrals is 0.03404 (Table I), which is greater than $m_1 \approx 0.011491$; hence, it is responsible for the poor approximation of ${}^{\lambda}_{approx}(\mu\nu \mid \kappa\lambda)$ with $m_2 \approx 0.041692$. For fluorine and lithium fluoride (Tables II and III), the errors induced by the Mulliken approximation and the second-order expansion error are each smaller than m_1. Hence, the integrals ${}^{\lambda}_{approx}(\mu\nu \mid \kappa\lambda)$ represent a better approximation of the integrals in the Löwdin basis: compare m_2.

Therefore, one can agree with the identification of the NDDO-surviving integrals between the ϕ- and λ-basis as proposed by Chandler and Grader and others (cf. Part IV):

$${}^{\lambda}(\mu_A\nu_A \mid \kappa_B\lambda_B) \approx {}^{\phi}(\mu_A\nu_A \mid \kappa_B\lambda_B).$$

An integral scaling constant is available not only from an expansion of the zeroth degree but

also from an expansion of first degree, because by Eq. (17) one obtains for diatomic molecules ($\Gamma_{\mu\mu} = 0$):

$$_{approx}^{\lambda}(\mu\nu \mid \kappa\lambda) = {}^{\phi}(\mu\nu \mid \kappa\lambda)a^4 + O(\Gamma^2).$$

TO THE CONCEPT OF A SIMPLIFIED NONEMPIRICAL COMPUTATION METHOD

The results of Part IV and the calculus of error can be summarized as follows:

- NDDO approximation is not applicable to one-electron operators (core-integrals). They have to be calculated completely and then transformed into the Löwdin basis by

$$^{\lambda}\mathbf{M} = \Delta^{-1/2}\mathbf{M}\Delta^{-1/2}.$$

- NDDO is justified by the Γ-expansion technique for the two-electron integrals consisting only of two-electron charge distributions. These are the types G_{CD}^{AB}, G_{AC}^{AB}, and G_{AB}^{AB}.
- The integrals G_{BB}^{AA} and G_{AA}^{AA} are to be calculated in the locally orthogonalized basis. The approximative transformation of these integrals by the linear mapping (17) into the Löwdin basis is not recommended due to the error involved. Due to the analysis in the last section, identification of the integrals in both bases seems to be preferable.
- Consideration of the integrals G_{CD}^{AA} and G_{AD}^{AA} seems to be essential.

The last point requires further discussion: The two- and three-center integrals mentioned above are only insufficiently represented by the $_{approx}^{\lambda}(\mu\nu \mid \kappa\lambda)$ as stated in the section Discussion of the Results and cf. the section Integrals with Two-center Charge Distribution. Moreover, the different orders of magnitude (cf. Tables I–III) preclude an identification of the integrals as an easy method for changing the basis.

Two perspectives can be seen:

1. The integrals $G_{BB}^{AA}, G_{AA}^{AA}, G_{AD}^{AA}$, and G_{CD}^{AA} should be calculated in the locally orthogonalized basis. All integral transformations of Part IV are to deduced a second time, but the domain of the mapping from the ϕ- to λ-basis consists of the integrals above instead of the NDDO-surviving integrals only. All approximative transformations can then be analyzed by a calculus of error, analogously to the proceeding described above. One expects a reduced error due to the Mulliken approximation, but the error of the second-order expansion remains. The examples in Tables I–III shows that this error is of about the same magnitude as the discussed integrals. Therefore, this solution does not appear to be promising.
2. In accordance with Brown and Burton [7], one abandons the concept of the representation of integrals in the Löwdin basis and works in the locally orthogonalized basis directly. By comparison of Figure 4(c) and (d) of Part IV as well as Table I, one can see that the integrals of types G_{CD}^{AB}, G_{AC}^{AB}, and G_{AB}^{AB} are greater in the ϕ-basis. Some theoretical investigations still need to be carried out.

Summary and Conclusions

In this series, the justification of the NDDO approximation was critically reexamined. First, the Γ-expansion technique was developed for the replacement of the nonconvergent binomial expansion (**S**-expansion technique) and the slowly convergent **P**-expansion of Chandler and Grader [3]. This new technique was applied to the discussion of the examination of the justification of NDDO approximation. NDDO was not justified for the core integrals (one-electron operators) but was partially for the electron repulsion integrals. The results are summarized in the last section.

The calculus of error shows that the linear integral transformations of the Γ-expansion technique and the resulting arguments are of only restricted reliability and applicability. Some errors, due to the different employed approximations, are of the order of magnitude of the considered integrals in the Löwdin basis.

One should understand that the goal, of the investigations conducted, was to remove the often found weakness of insufficient control over the various introduced approximations while developing and justifying simplified, quantum chemical computation methods.

ACKNOWLEDGMENTS

The author is very grateful to Prof. Dr. F.F. Seelig as well as to Dr. W. Koch for the continuous

support and fruitful discussions of this work. This work was supported by the "Studienstiftung des deutschen Volkes."

References

1. N. A. B. Gray and J. Stone, Theor. Chim. Acta **18**, 389 (1970).
2. R. D. Brown and K. R. Roby, Theor. Chim. Acta **16**, 175 (1970).
3. G. S. Chandler and F. E. Grader, Theor. Chim. Acta **54**, 131 (1980).
4. R. S. Mulliken, J. Chim. Phys. **46**, 497 (1949).
5. E. Clementi and C. Roetti, Atom. Data Nucl. Data Tab. **14**, 177 (1974).
6. DIATOM–Diatomic Molecular Integral Program, Program Number 138 (Quantum Chemistry Program Exchange, Indiana University, Chemistry Department, Bloomington, IN).
7. R. D. Brown and P. G. Burton, Chem. Phys. Lett. **20**, 45 (1973).