Calculation of two-centre two-electron integrals over Slater-type orbitals revisited.  
I. Coulomb and hybrid integrals

MICHAL LESIUK* AND ROBERT MOSZYNSKI  
Faculty of Chemistry, University of Warsaw  
Pasteura 1, 02-093 Warsaw, Poland  
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In this paper, which constitutes the first part of the series, we consider calculation of two-centre Coulomb and hybrid integrals over Slater-type orbitals (STOs). General formulae for these integrals are derived with no restrictions on the values of the quantum numbers and nonlinear parameters. Direct integration over the coordinates of one of the electrons leaves us with the set of overlap-like integrals which are evaluated by using two distinct methods. The first one is based on the transformation to the ellipsoidal coordinates system and the second utilises a recursive scheme for consecutive increase of the angular momenta in the integrand. In both methods simple one-dimensional numerical integrations are used in order to avoid severe digital erosion connected with the straightforward use of the alternative analytical formulae. It is discussed that the numerical integration does not introduce a large computational overhead since the integrands are well-behaved functions, calculated recursively with decent speed. Special attention is paid to the numerical stability of the algorithms. Applicability of the resulting scheme over a large range of the nonlinear parameters is tested on examples of the most difficult integrals appearing in the actual calculations including at most 7\textit{r}-type functions ($l=6$).

I. INTRODUCTION

Slater-type orbitals [1, 2], or more general exponential-type orbitals, are the natural choice of basis set for applications in quantum chemistry and molecular or atomic physics. Their common origin is the analytical solution of the Schrödinger equation for the hydrogen atom. It can be shown that Slater-type orbitals behave correctly at the electron-nucleus coalescence points \textit{i.e.} they satisfy Kato's conditions [3]. Additionally, the Slater-type orbitals decay exponentially when an electron is far from the nucleus. This is in line with the theoretical findings of the asymptotic form of the electron density [4]. It is obvious that Gaussian orbitals [5], which have gained an enormous popularity in the last 50 years, are able to satisfy neither of the above conditions. Virtually the only issue which prohibited the widespread use of the Slater-type orbitals is calculation of the two-electron molecular integrals.

The main purpose of the present series of papers is to provide a complete set of methods for the evaluation of the two-electron two-centre integrals. The reliability of these methods needs to be sufficient to allow the use of Slater-type orbitals including high angular momentum functions for the diatomic systems. Our integral program based on the presented algorithms serves as a vehicle for the upcoming new \textit{ab-initio} quantum chemistry program package \textsc{Kolos}. This program combines basis set of Slater-type orbitals with state-of-the-art quantum chemical \textit{ab-initio} methods and is aimed at spectroscopically accurate (few cm\textsuperscript{-1}) results for the diatomic systems.

When considering our approach to the present problem, one issue needs to be clarified. To reach the spectroscopic accuracy it is not only necessary to use huge basis sets but also very accurate quantum chemistry methods. Let us now observe that calculations of the two-electron integral file scale as the fourth power of the size of the system ($N^4$) in the worst case scenario. This can be compared with the scaling of the accurate coupled cluster methods, $N^6$ for CCSD, $N^8$ for CCSDT \textit{etc.} [6–9]. As a result, one can expect that calculations of the integral file should not be a bottleneck in high-level calculations of the correlation energy. On the other hand, since we require the aforementioned accuracy in the molecular energy, we need the integrals to be calculated with higher precision than typical. We believe that the requirement for accuracy of 12 decimal places is reasonable.

The situation described above suggests that we should favour accuracy of the algorithms over their speed. In other words, if we had two algorithms - the first one being fast but less accurate, and the second one being somehow slower but significantly more accurate - we would pick up the second one. Of course, we still have limitations on the computational time and we cannot use arbitrary precision arithmetic, for instance. This philosophy of choosing and developing algorithms shall be perceptible throughout the whole series of papers.

This series of papers is organised as follows. In Paper I we deal with calculation of the Coulomb and hybrid integrals \textit{i.e.} $(aa|bb)$ and $(aa|ab)$, respectively, where $a$ and $b$ denote the nuclei at which orbitals are located. We use direct integration over the second electron in the same spirit as several previous investigators but we dif-

* e-mail: lesiuk@tiger.chem.uw.edu.pl
fer in methods of computation of almost all nontrivial basic quantities. Final forms of the working expressions are also completely reformulated. Moreover, we present the results of demanding tests of the numerical performance. In Paper II we apply the Neumann expansion to calculation of the exchange integrals, \((ab|ab)\). We report new methods of calculation of the most difficult auxiliary quantities appearing in the theory. Additionally, we discuss how new algorithms can be sewed together to form a sufficiently general method. Finally, in Paper III we provide the first application of the presented theory - \(ab-initio\) calculations for the beryllium dimer which is an interesting system from both spectroscopic and theoretical point of view. In these calculations we use STO basis sets ranging from double to sextuple zeta quality combined with high level \(ab-initio\) methods in order to provide spectrascopically accurate results.

The literature dealing with evaluation of the molecular integrals over Slater-type orbitals is extensive and a full bibliography would count hundreds of positions. Its detailed review is undoubtedly beyond the scope of the present report. Therefore, our introduction is, by necessity, limited and subjective. Nonetheless, let us recall several prominent and the most widely used general techniques for computation of the aforementioned integrals.

Single-centre expansions allow to expand STOs located at some point of space around a different centre. These methods were pioneered by Barnett and Coulson as the widely known \(\zeta\)-function method \((10–12)\) and later independently by Löwdin \((13)\) (\(\alpha\)-function method). In cases when the single-centre expansion terminates under the integral sign due to spherical symmetry of the integrand, it typically results in closed-form, compact and plausible expressions. However, in many cases, such as calculation of the exchange integrals, the single-centre expansions results in an infinite series which have a pathologically slow (i.e. logarithmic) convergence rate \((14)\). The problem does not have a satisfactory solution although several approaches \((15)\) were adopted to overcome it. The second problem of the single-centre expansions is the catastrophic digital erosion during calculations of the auxiliary quantities \((16, 17)\) which seems to be extremely difficult to overcome. A promising work-around is use of the symbolic computational environments such as MATHEMATICA \((18–20)\) but at present the symbolic methods are typically orders of magnitude slower than the numerical ones. Since the time the single-centre methods were first proposed, several new (or more general) expansion techniques has been developed. Examples are the works of Guseinov \((21)\), Harris and Michels \((22)\) and Rico et al. \((23, 24)\) and references therein.

The second class of methods which gained a significant interest is the Gaussian expansion methods and the Gaussian transform methods. The former is simply based on a least squares fit of a linear combination of Gaussian orbitals in order to mimic the shape of STOs. This idea, proposed first by Boys and Shavitt \((25)\) was the dominant method used in the early versions of the SMILES program \((26)\). The Gauss transform methods are more involved and use some integral representations in order to transform STO into a more computationally convenient form. The initial proposition of Shavitt and Karplus \((27–29)\) was to use the Laplace transform of the exponential function but now a handful of different schemes is in use, along with suitable discretisation techniques \((30)\).

The next prominent technique is the family of Fourier-transform methods which are usually used in conjunction with the so-called \(B\)-functions. These methods were primarily developed by the group of Steinborn \((31–41)\) and applied to many difficult cases of the many-centre integrals. The fact that \(B\)-functions, being essentially a linear combination of STOs, possess an exceptionally simple Fourier transform can be used to evaluate the integrals in the momentum space and reduce many important integrals to the combination of some one-dimensional integrals. However, these integrals contain highly oscillatory integrands (including the Bessel functions) which make numerical integration extremely difficult with standard Gaussian quadrature techniques. Some approaches were adopted to accelerate the convergence towards the actual value with increasing number of quadrature nodes. The prominent method is the SD-transform, put forward by Sidi \((42, 43)\), and later applied by Safouhi \((44, 45)\). Despite that, it seems that there is no general method reliable enough to evaluate the integrals in question in a black-box fashion.

There is also a number of less extensively studied techniques for evaluation of the molecular integrals over STOs. These include the Coulomb Sturmians introduced by Shull and Löwdin \((46)\) and used by some other authors \((47–50)\). The shift operator technique \((51–53)\) is a very elegant method which generates integrals with arbitrary STOs starting with the simplest integrals with 1s functions by application of the so-called shift operator. Gill et al. \((54, 55)\) introduced the Coulomb resolution techniques where the interaction potential is expanded in terms of the so-called potential functions resulting from the Poisson equation. This method has been recently pursued by Hoggan and coworkers \((56, 57)\) and included in their STOP program package \((58)\).

Remarkably, it has not been a well-known fact yet that all two-centre integrals over STOs were integrated analytically in a closed-form. In a recent work Pachucki \((59, 60)\) has shown that the so-called master integral with inverse powers of all interparticle distances can be obtained from the second order differential equation in the distance between the nuclei. The present authors also contributed to the development of this theory by extending it to the case of Slater geminals \((61)\). Pachucki used these expressions for calculations of the Born-Oppenheimer potential for the hydrogen molecule \((62, 63)\) and helium hydride ion \((64)\). However, an extreme level of complication of this theory along with drastic numerical instabilities occurring in the calculations have made its use limited to certain special forms of the basis set, applicable only to two-electron systems. We believe that some ingenious re-
formulation of this theory is necessary to circumvent the aforementioned difficulties.

We postpone the discussion of the methods based on the Neumann expansion of the interaction potential in the ellipsoidal coordinates. In the second paper of the series it is used to evaluate the exchange integrals and a proper separate introduction is given therein.

Let us now concentrate on methods designed specifically for treatment of the Coulomb and hybrid integrals. For the former ones there exists a plethora of independent methods which differ in both accuracy and speed. Probably the first attack on this problem was attempted by Barnett and Coulson [10] by using the single-centre expansion technique. Roothaan [65] pioneered the direct integration method in the ellipsoidal coordinates which was later pursued by several authors [66–72]. Later, it has become apparent that integration in the momentum space utilising the Fourier representation of STOs is very advantageous [34, 35, 73–77]. Gaussian transform techniques [27, 28, 87], refined translation/expansion methods [78–80] and several special approaches [81–87] were also successfully applied. For hybrid integrals the number of available methods is modest. Several prominent techniques, such as the Fourier transform, cannot be applied straightforwardly. The biggest effort was aimed at the direct integration [66, 88–90] or its combinations with the translation techniques [91–93]. Our unified approach to the Coulomb and hybrid integrals is based on the earlier experiences with the direct integration. By using the Laplace expansion of the interaction potential and analytic integration over the coordinates of the second electron the problem is reduced to the calculation of the standard overlap integrals and a set of overlap-like integrals. To calculate these integrals two distinct approaches are used. The first one is integration in the ellipsoidal coordinates and the second method is based on recursive techniques. In both cases a simple, one-dimensional numerical integration is used to avoid drastic digital erosion. This indicates some connections with the method of Miller [90]. Finally, we verify that when both methods are used together, in their respective regions of applicability, a loss of digits observed in the calculations by using some other methods can be avoided within a reasonable range of the nonlinear parameters.

Let us also note in passing that to perform actual calculations on the diatomic systems one also requires one-electron two-centre and two-electron one-centre (atomic) integrals. The former can be computed using various techniques among which the Fourier transform methods [31–41], recursive techniques for increasing the angular momenta in the integral [87, 94–99], and finally direct integration using the ellipsoidal coordinate system [65, 100–102] were intensively studied. The latter seems to be the method of choice for these integrals. Two-electron atomic integrals have been solved at least since the papers of Clementi and co-workers (see Refs. [103] and references therein). For the sake of completeness, a refined, simple, and numerically stable procedure for the computation of these integrals was included in the Supplementary Material [104].

II. PRELIMINARIES

Let us consider a diatomic system with the nuclei A and B centred at the positions \( \mathbf{R}_A = (0, 0, -R/2) \) and \( \mathbf{R}_B = (0, 0, R/2) \), respectively, in the ordinary Cartesian coordinate system. Slater-type orbitals (STOs) have the following general form:

\[
\chi_{nlm}(\mathbf{r}; \zeta) = S_n(\zeta) r^{n-1} e^{-\zeta r} Y_{lm}(\theta, \phi),
\]

Therefore, any STO is uniquely described by the quartet of parameters \((n, l, m, \zeta)\). We assume throughout that \( n, l \) are restricted to the positive integers \((n > l)\). The variables \( r, \theta, \phi \) denote the spherical coordinates located on the atom A with analogous notation for the centre B. In Eq. (1), \( S_n(\zeta) \) is the radial normalisation constant:

\[
S_n(\zeta) = \frac{(2\zeta)^{n+1/2}}{\sqrt{(2n)!}},
\]

and \( Y_{lm}(\theta, \phi) \) are the spherical harmonics defined according to the Condon-Shortley phase convention [105]:

\[
Y_{lm}(\mathbf{r}) = \Omega_{lm} P_l^m(\cos \theta) e^{im\phi} \sqrt{2\pi},
\]

where \( P_l^m \) are the (unnormalised) associated Legendre polynomials [106] and \( \Omega_{lm} \) is the angular normalisation constant:

\[
\Omega_{lm} = i^{m-|m|} \sqrt{\frac{2l + 1 (l - |m|)!}{2 (l + |m|)!}}.
\]

In actual calculations it is typical to use real versions of the spherical harmonics. However, the complex spherical harmonics are more convenient in the derivations and thus we use them throughout the paper. Transfer to the real spherical harmonics can be performed on the top of the presented algorithms by using standard relations.

Let us now introduce the prolate ellipsoidal coordinates \((\xi, \eta, \phi)\) by means of the following relations:

\[
\xi = \frac{r_a + r_b}{R}, \quad \eta = \frac{r_a - r_b}{R},
\]

so that \( 1 \leq \xi < \infty \), \(-1 \leq \eta \leq 1\) and \( 0 \leq \phi \leq 2\pi\). The spherical coordinates are expressed through the ellipsoidal coordinates by means of the well-known expressions:

\[
r = \frac{R}{2} (\xi + \kappa \eta), \quad \cos \theta = \frac{1 + \kappa \eta}{\xi + \kappa \eta},
\]

where the value of \( \kappa \) is equal to +1 if STO is located on the centre A or −1 if it is located on the centre B. The volume element becomes \( d\mathbf{r} = \left( \frac{R}{2} \right)^3 (\xi^2 - \eta^2) \, d\xi \, d\eta \, d\phi\).
The simplest way to express the product of two STOs (i.e., the charge distribution) in the ellipsoidal coordinates is to proceed in two steps. First, we transfer the following scaled product of the Legendre polynomials by means of the expression

\[
P_{l_a}^{(m_a)}(\cos \theta_a)P_{l_b}^{(m_b)}(\cos \theta_b)r_a^{e_a}r_b^{e_b} = \left( \frac{R}{2} \right)^{\frac{3}{2}} \left( \xi^2 - 1 \right)^{(1 - \eta^2)^{\frac{M}{2}}} \sum_{p=0}^{\infty} \sum_{q=0}^{\infty} \left( \Xi_{l_a,l_b}^{M} \right)_{pq} \xi^p \eta^q
\]

(7)

where \( M = m_a - m_b \), \( \Gamma = l_a + l_b \) and \( \Xi_{l_a,l_b}^{M} \) are square matrices of dimension \( \Gamma \). The values of the latter depend on the locations of the orbitals and their quantum numbers. Explicit forms of these matrices can easily be deduced from the general expressions available in the literature [107–111]. We tabulated the values of \( \Xi_{l_a,l_b}^{M} \) up to the maximum value of \( l_a + l_b \) equal to 24. These tables, along with Mathematica code [112] used for their generation, can be obtained from the authors on demand.

The remainder can be transferred to the ellipsoidal coordinates by using the following formula:

\[
f_a^{n_a} f_b^{n_b} = \sum_{k=0}^{k_{max}} B_k^{n_a,n_b} \xi^k \eta^{k_{max} - k},
\]

(8)

with \( k_{max} = n_a + n_b \). The above expression has been extensively used by many authors [110, 113, 114] who presented explicit expressions for the coefficients \( B_k^{n_a,n_b} \) (the so-called generalised binomial coefficients). We found it simpler to tabulate these coefficients as series of one-dimensional look-up tables.

Making use of the transfer relations (7) and (8) one can write down the explicit expression for the STOs charge distribution in terms of the ellipsoidal coordinates. The result reads (for convenience, we additionally included the Jacobian):

\[
\left( \frac{R}{2} \right)^{\frac{3}{2}} \xi^2 - 1)^{(1 - \eta^2)^{\frac{M}{2}}} e^{iM \phi} \sum_{k=0}^{k_{max}} B_k^{n_a,n_b} \xi^k \eta^{k_{max} - k},
\]

(9)

with \( M = m_a - m_b \), \( k_{max} = n_a - l_a + n_b - l_b \) and \( \Gamma = l_a + l_b \). Additionally, in Eq. (9) we introduced several new quantities: \( \alpha = \frac{R}{2}(\zeta_a + \zeta_b) \), \( \beta = \frac{R}{2}(\kappa_a \zeta_a + \kappa_b \zeta_b) \), \( K_{ab} = S_{n_a}(\zeta_a)S_{n_b}(\zeta_b) \Omega_{l_a,l_b} \Omega_{l_b,l_a} (\frac{R}{2})^{n_a+n_b+1} \). The above formulation is quite explicit and rather transparent at the same time. Apart from that, it remains valid for “singular” orbitals such as 0s which is advantageous from the point of view of some developments.

Before passing further let us introduce three useful auxiliary functions:

\[
A_p(\alpha) = \int_{1}^{\infty} d\xi \xi^p e^{-\alpha \xi},
\]

(10)

\[
B_q(\beta) = \int_{-1}^{1} d\eta \eta^q e^{-\beta \eta},
\]

(11)

\[
ap(\alpha) = \int_{0}^{1} d\xi \xi^p e^{-\alpha \xi}.
\]

(12)

The first two of the above functions are the so-called Mulliken integrals [100]. Accurate and stable calculation of these integrals was considered by many authors, the works of Corbató [101] and a recent paper of Harris [115] need to be mentioned in this respect. The third integral, Eq. (12), can be considered complementary to the first integral, Eq. (10), and has strong connections with the lower incomplete gamma functions. Integrals (12) have to be computed by using the Miller algorithm [116], as discussed by Harris [117].

### III. COULOMB AND HYBRID INTEGRALS

In this section we attack the main objectives of this paper - calculation of the coulomb \( (I_C) \) and hybrid \( (I_H) \) integrals. With the notation developed in the previous section they take the following form:

\[
I_C = \int dr_1 \int dr_2 \chi_n^{*}_{l_1,m_1}(\mathbf{r}_{1a};\zeta_1)\chi_{n_2,l_2,m_2}(\mathbf{r}_{1a};\zeta_2) \times \frac{1}{r_{12}} \chi_{n_3,l_3,m_3}(\mathbf{r}_{2b};\zeta_3)\chi_{n_4,l_4,m_4}(\mathbf{r}_{2b};\zeta_4),
\]

(13)

\[
I_H = \int dr_1 \int dr_2 \chi_n^{*}_{l_1,m_1}(\mathbf{r}_{1a};\zeta_1)\chi_{n_2,l_2,m_2}(\mathbf{r}_{1b};\zeta_2) \times \frac{1}{r_{12}} \chi_{n_3,l_3,m_3}(\mathbf{r}_{2b};\zeta_3)\chi_{n_4,l_4,m_4}(\mathbf{r}_{2b};\zeta_4).
\]

(14)

Let us note that in the above expressions we have adapted a particular, fixed location of the STOs. This convention is very useful from the point of view of the upcoming derivation. Other possible options for the orbitals location within the class of the Coulomb and hybrid integrals can be obtained by using the usual eightfold permutational symmetry of the integrals.

#### A. Initial reduction to the overlap-like integrals

Before proceeding with the integration of \( I_C \) and \( I_H \) let us simplify the formulas by using the Clebsch-Gordan expansion of the products of the spherical harmonics. In the case of the Coulomb integrals one expands pairs of the spherical harmonics on both centres; in case of the hybrid integrals, only the pair dependent on the coordinates of the second electron can be expanded. Once the Clebsch-Gordan expansion is used and the resulting integrals are written explicitly, it becomes obvious that the problem
reduces now to the calculation of the following families of the integrals

\[ \tilde{I}_C = \int dr_1 \int dr_2 r_{1a}^{n_{12} - 2} Y_{L_1 M_1}^*(\cos \theta_{1a}, \phi) \frac{1}{r_{12}} \times r_{2b}^{n_{34} - 2} Y_{L_2 M_2}^*(\cos \theta_{2b}, \phi) e^{-\zeta_1 r_{1a}} \]

\[ \tilde{I}_H = \int dr_1 \int dr_2 r_{1a}^{n_{12} - 1} Y_{L_1 M_1}^*(\cos \theta_{1a}, \phi) e^{-\zeta_1 r_{1a}} \times r_{1b}^{n_{21} - 1} Y_{L_2 M_2}^*(\cos \theta_{1b}, \phi) e^{-\zeta_2 r_{1b}} \times r_{2b}^{n_{34} - 2} Y_{L_2 M_2}^*(\cos \theta_{2b}, \phi) e^{-\zeta_3 r_{2b}}, \]

where \( n_{12} = n_1 + n_2, \zeta_1 = \zeta_1 + \zeta_2 \ldots \) and \( r_{ij} \) denote the interparticle distances. It is evident that any Coulomb integral \( (I_C) \) can be written as a linear combination of

\[ \int dr_2 r_{2b}^{n_{34} - 2} Y_{L_2 M_2}^*(\cos \theta_{2b}, \phi) e^{-\zeta_3 r_{2b}} = \frac{4\pi}{2L_2 + 1} \frac{Y_{L_2 M_2}^*(\cos \theta_{1b}, \phi)}{\zeta_{34}^{n_{34}}} \left[ (\zeta_{34} r_{1b})^{n_{34}} a_{n_{34} + L_2} (\zeta_{34} r_{1b}) \right] \]

\[ + (n_{34} - L_2 - 1)! e^{-\zeta_3 r_{1b}} \sum_{j=L_2}^{n_{34}-1} (\zeta_{34} r_{1b})^j \left[ (\zeta_{34} r_{1b})^{n_{34}-j} \right] \]

where \( a_n \) is given by Eq. (12). To bring the above expression into a more familiar and simplified form we could use the following obvious relationships

\[ a_n(\alpha) = \frac{n!}{\alpha^{n+1}} - A_n(\alpha), \]

\[ A_n(\alpha) = e^{-\alpha} n! \sum_{k=0}^{n} \frac{\alpha^k}{k!} \]

By doing so, one expresses the integral (17) explicitly through the elementary functions only. It seems to be advantageous but there are two main problems connected with use of Eqs. (18) and (19). Firstly, these expressions introduce spurious singularities (high inverse powers of \( r_{1b} \)) and generate integrals which have to be treated with special methods. Secondly, and more importantly, Eq. (18) by itself is numerically badly conditioned and these problems propagate to the final expressions for the Coulomb and hybrid integrals. Precisely speaking, unless the relationship \( n \gg \alpha \) holds, Eq. (18) consists of subtraction of two large numbers to a relatively small result. Therefore, a huge digital erosion occurs, especially when large values of the quantum numbers are necessary.

This leads to the conclusion that in order to preserve a good numerical stability of the method, we have to abandon the use of Eqs. (18) and (19) and exploit Eq. (17) as it stands. By inserting Eq. (17) into the initial expressions for \( I_C \) one obtains the formula

\[ \tilde{I}_C = \frac{4\pi}{2L_2 + 1} \frac{1}{\zeta_{34}^{n_{34}}} \int dr_1 r_{1a}^{n_{12} - 2} Y_{L_1 M_1}^*(\cos \theta_{1a}, \phi) e^{-\zeta_1 r_{1a}} r_{1b}^{n_{34} - 2} Y_{L_2 M_2}^*(\cos \theta_{1b}, \phi) a_{n_{34} + L_2} (\zeta_{34} r_{1b}) \]

\[ + (n_{34} - L_2 - 1)! \sum_{j=L_2}^{n_{34}-1} \frac{\zeta_{34}^j}{(j - L_2)!} \int dr_1 r_{1a}^{n_{12} - 2} Y_{L_1 M_1}^*(\cos \theta_{1a}, \phi) e^{-\zeta_1 r_{1a}} r_{1b}^j Y_{L_2 M_2}^*(\cos \theta_{1b}, \phi) e^{-\zeta_3 r_{1b}} \]

For the hybrid integrals, the manipulations are slightly more involved. After inserting Eq. (17) into the formula
for $\tilde{I}_H$ one is left with three spherical harmonics under the integral sign. Two of these spherical harmonics are centred at the nucleus B and therefore can be expanded in the Clebsch-Gordan series. The result of this manipulations is as follows (the usual notation for the Wigner 3J symbols is used):

$$
\tilde{I}_H = \frac{(-1)^{m_2}}{c_{n_3}^{m_2}} \sqrt{(2l_2 + 1)(2L_2 + 1)} \sum_{L_1=|l_2-L_2|}^{l_2+l_2} \sqrt{\frac{4\pi}{2L_1 + 1}} \left( \begin{array}{ccc} l_2 & L_2 & L_1 \\ -m_2 & -M & m_1 \end{array} \right) \int dr_1 r_1^{n_1-1} Y_{l_1m_1}(\cos \theta_1, \phi) e^{-\zeta_1r_1} r_1^{n_2+n_3-1} Y_{L_1m_1}(\cos \theta_1, \phi) e^{-\zeta_2r_{1b}} a_{n_3+L_2}(\zeta_3r_{1b})
$$

(21)

Let us now investigate the above formulae in a greater detail. It is obvious that Eqs. (20) and (21) include two basic types of integrals which take the following general forms

$$
S_{n_1l_1m}(\zeta_1, \zeta_2) = \int dr_1 r_1^{n_1-1} Y_{l_1m}(\cos \theta_1, \phi) e^{-\zeta_1r_1} r_1^{n_2-1} Y_{l_2m}(\cos \theta_1, \phi) e^{-\zeta_2r_{1b}},
$$

(22)

$$
\bar{S}_{n_1l_1m}(n_3; \zeta_1, \zeta_2, \zeta_3) = \int dr_1 r_1^{n_1-1} Y_{l_1m}(\cos \theta_1, \phi) e^{-\zeta_1r_1} r_1^{n_2-1} Y_{l_2m}(\cos \theta_1, \phi) e^{-\zeta_3r_{1b}} a_{n_3}(\zeta_3r_{1b}),
$$

(23)

B. Calculation of the overlap-like integrals by the ellipsoidal coordinates method

For the calculation of the overlap-like integrals the use of ellipsoidal coordinates seems to be a natural approach because the standard one-electron integrals separate into a product of simple one-dimensional integrals. It is obvious, however, that due to the presence of the factor $a_n$ in Eq. (23) this separation can no longer be performed straightforwardly. Not discouraged by this fact, we proceed in a conventional manner and utilise Eq. (9) to express the integrand in Eq. (23) in ellipsoidal coordinates. Noting that the axial symmetry of the integrand requires $M = 0$ in the transfer formula (9) we arrive at the expression

$$
\bar{S}_{n_1l_1m}(n_3; \zeta_1, \zeta_2, \zeta_3) = K_{12} \sum_{k=0}^{k_{\text{max}}} P_k^{n_1-l_1,n_2-l_2} \sum_{p=0}^{\Gamma} \sum_{q=0}^{\Gamma} (\Xi_{l_1l_2})^{pq} \int_{-1}^{1} d\xi \int_{-1}^{1} d\eta \xi^{p+k} \eta^{q+k_{\text{max}}-k} e^{-\alpha \xi - \beta \eta} a_{n_3} \left[ \gamma(\xi + \eta) \right],
$$

(24)

after an elementary integration over the angle $\phi$. In the above expression $K_{12} = (R/2)^{n_1+n_2+3} \Omega_{l_1m_1} \Omega_{l_2m_2},$

$k_{\text{max}} = n_1 - l_1 + n_2 - l_2,$ $\alpha$ and $\beta$ are defined analogously...
as in Eq. (9) and \( \gamma = R \cdot \zeta_3/2 \). Let us now consider the inner integrals in the above expression and define the auxiliary integrals class:

\[
J_\lambda(p,q;\alpha,\beta,\gamma) = \int_0^\infty dt \int d\xi \int d\eta \xi^p \eta^q e^{-\alpha \xi - \beta \eta} \alpha_{\lambda}(\xi + \eta).
\]

(25)

The above integrals do not separate to a product of one-dimensional integrals and are also very resistant to the numerical integration. However, let us insert the integral representation (12) and change the order of integration so that integrations over \( \xi \) and \( \eta \) are performed at the end. One easily recognises that the inner integrals are the Mulliken integrals defined in Eqs. (10); (11) and the integrals (25) can be written as

\[
J_\lambda(p,q;\alpha,\beta,\gamma) = \int_0^\infty dt A_p(\alpha + \gamma t) B_q(\beta - \gamma t).
\]

(26)

Note that, apart from reducing the dimensionality of the integral, we have obtained a form which is very convenient for the numerical integration. The Mulliken integrals are smooth, continuous functions of the real variable with no singularities on the integration line or unwanted oscillatory behaviour. Therefore, there is no need to use numerical quadratures with overwhelmingly large number of points. Additionally, the Mulliken integrals can be calculated extremely efficiently in a recursive fashion for arbitrary values of the parameters.

Despite the obvious advantages of the numerical integration of Eq. (26) this approach still has to be justified to some extent. One may ask what is the point of using numerical integration since integrals (26) can be worked out analytically. One can do that, for instance, by inserting in Eq. (26) the explicit expressions for the Mulliken integrals, which are available in the literature [100].

Next, the integral over \( t \) can be expressed as a hypergeometric function of two integer parameters and with help of the so-called contiguous relations one can reduce the initial integrals to combinations of the well-known basic functions. This approach seems to be particularly attractive for the Coulomb integrals (when \( \zeta_2 = 0 \)) since, as pointed out by Tai [81], the final explicit expressions contain only elementary functions of the real variables. Therefore, the numerical approach to the integrals (26) seems to be an unwise decision at first glance.

However, the actual situation is more complicated. Taking Eq. (26) as a starting point, we note that the explicit expressions for \( B_q \) functions are badly conditioned due to cancellation of two large terms to a relatively small result. That is why computation of \( B_q \) from the analytic expressions is unstable and alternate methods need to be utilised [101, 115]. This instability propagates further to the integrals (26) and becomes more pronounced as the value of \( q \) increases. Nonetheless, with help of the symbolic algebra package, such as MATHEMATICA, one can derive explicit expressions for \( J_\lambda \) in order to verify their usefulness. We found that for \( \beta \approx \gamma \) the loss of digits is enormous, even when the values of \( q \) are not large. Therefore, a prohibitively high arithmetic precision is required to obtain any useful information about the values of \( J_\lambda \).

Taking into consideration the philosophy presented in the introduction (favouring accuracy over speed within reasonable limits), the above observation seems to state a deadly argument against the analytic approach. In other words, the numerical integration can be understood as a simple way to avoid a severe digital erosion.

For the benchmarking purposes, we show results of the calculation of two integrals, \( S_{1312m}^{1512m}(26;\zeta_1,0,\zeta_3) \) and \( S_{7,6,m}^{21,18,m}(26;\zeta_1,\zeta_1,\zeta_3) \), within the reasonable range of values of the nonlinear parameters \( \zeta_1, \zeta_3 \). We are free to set \( R = 1 \) since an increase of \( R \) results only in scaling of the nonlinear parameters by \( R \) (up to a trivial multiplicative constant). All necessary \( J_\lambda \) integrals were calculated numerically using 100 or 200 grid points of the Tanh-Sinh quadrature [124, 125] for double and quadruple arithmetic precision, respectively. Under these conditions, \( J_\lambda \) integrals are typically calculated with full precision allowed by the arithmetic.

The integrals, \( S_{1312m}^{1512m}(26;\zeta_1,0,\zeta_3) \) and \( S_{7,6,m}^{21,18,m}(26;\zeta_1,\zeta_1,\zeta_3) \), are the most difficult quantities (in terms of the angular momentum) encountered in the calculation of the Coulomb and hybrid integrals, respectively, including at most 71 functions. We set \( \zeta_2 = \zeta_1 \) in the second integral for illustrative purposes - the overall picture changes very slightly when the value of \( \zeta_2 \) is distorted. The results are presented in Table 1 for the first integral and in Table 2 for the second integral. One observes a progressive loss of digits when one of the nonlinear parameters is large and the second is small. This digital erosion is due to the cancellation of large numbers during summations in Eq. (24) and it cannot be avoided in the ellipsoidal coordinates method. The use of quadruple precision improves the situation a lot but it is not sufficient to cope with the most difficult cases. Of course, for lower angular momentum functions the changes are less sharp but the overall trend remains the same. Concluding, our observations signal that the ellipsoidal coordinates method alone is not sufficient to calculate the desired integrals with the prescribed accuracy and need to be supplemented by a different algorithm.

In the present series of papers we do not go into technical details of the implementation etc., but let us give a short remark on the timings in the present algorithm. The numerical integration of the integrals \( J_\lambda \) typically consumes about a half of the total time necessary to calculate a given shell of integrals. Only for the smallest values of the quantum numbers this ratio is higher, but these integrals are very cheap anyway. The remaining time is spent on the lengthy summations in Eq. (24), formation of \( \tilde{I}_{C/H} \), Eqs. (20) and (21), and summation of the initial Clebsh-Gordan expansion to finally arrive at the value of \( I_{C/H} \). Therefore, the numerical integration is not connected with a drastic overhead as might
have been initially expected. A faster scheme for the calculation of \( F_a \) shall not result in a significant overall speed-up. Typically, the Coulomb and hybrid integrals are obtained in 1-100 \( \mu \)s per integral, depending on the values of quantum numbers, with hybrid integrals being slightly more expensive.

**C. Calculation of the overlap-like integrals by the recursive method**

For the calculation of the overlap-like integrals by using the recursive method it is more convenient to introduce different basic integrals, so that the final expressions take a simpler form. Let us note that Eq. (23) can be rewritten as

\[
\tilde{S}^{15,12, \alpha}_{\beta \gamma \delta} (26; \zeta_1, \zeta_2, \zeta_3) = \frac{1}{R} \Omega_{\alpha \beta \gamma \delta}(\phi_{\alpha \beta} | \phi_{\gamma \delta}) \times P^m_{\alpha \beta} \sin \theta_{\gamma \delta}, \tag{27}
\]

where

\[
\langle \phi_{\alpha \beta} | \phi_{\gamma \delta} \rangle = \int_0^\pi dr_\alpha \int_{\cos \theta_{\alpha \beta}}^{\cos \theta_{\gamma \delta}} dr_{\gamma \delta} P^m_{\alpha \beta} \sin \theta_{\alpha \beta} e^{-r_\alpha - r_{\gamma \delta} \sin \theta_{\alpha \beta}} \times P^m_{\gamma \delta} \sin \theta_{\gamma \delta}. \tag{28}
\]

In the second expression we changed the variables from the Cartesian coordinates to the internal coordinate system \((r_a, r_b, \theta)\) and integrated over the angle. Note, that the notation for the nonlinear parameters and for the variable \( n_3 \) was suppressed since these quantities do not change during the recursive process. We have to stress that all formulae presented here are valid only for \( m > 0 \). There is no need to consider the negative values of \( m \) because of the axial symmetry of the integrands.

Generally speaking, to establish a recursive process which is able to increase the values of \( \ell_1, \ell_2 \) and \( m \), starting with provided values of \( \langle r_{\alpha \beta} | r_{\gamma \delta} \rangle \) we need to use the well-known recursion relations for the Legendre polynomials \( P^m_l \). A similar idea was applied by several authors to the calculation of various important matrix elements [87, 94-99]. Let us first derive a recursion relation connecting \( \langle r_{\alpha \beta} | r_{\gamma \delta} \rangle \) with different \( m \) by recalling the following expression for the Legendre polynomials with \( \ell = m \):

\[
P^m_m (\cos \theta) = \frac{(2m)!}{2^m m!} \sin^m \theta, \tag{29}
\]

so that

\[
P^{m+1}_m (\cos \theta) = P^m_m (\cos \theta) (2m + 1) \sin \theta. \tag{30}
\]

By combining two expressions like the above for \( \cos \theta_a \) and \( \cos \theta_b \) and using the obvious relationship \( r_a \sin \theta_a = r_b \sin \theta_b \) one finds

\[
P^{m+1}_m (\cos \theta_a) P^{m+1}_m (\cos \theta_b) = P^m_m (\cos \theta_a) P^m_m (\cos \theta_b) (2m + 1)^2 \frac{r_a}{r_b} \sin^2 \theta_a, \tag{31}
\]

and the expression for \( \sin^2 \theta_a \) in terms of \( r_a, r_b \) is elementary. Finally, this leads to the recursion relation for the
TABLE II. Calculation of $S_{7.6,m}^{21,18,m}(26; \zeta_1, \zeta_2, \zeta_3)$ using the method based on the ellipsoidal coordinates. The values of $\zeta_1, \zeta_3$ increase along the columns or rows, respectively. The values presented are in the form $d-q$ which denotes (rounded) decimal logarithms of the relative error obtained in double and quadruple arithmetic precision, respectively. Therefore, these values roughly represent the number of correct significant digits obtained using the present algorithm. Values obtained in quadruple precision were denoted to double precision before the comparison since these are the values used in the actual calculations. The worst result obtained within the possible range of $m$ was chosen in all cases. Reference values were obtained from calculations in extended arithmetic precision of 128 significant digits.

| $\zeta_1/\zeta_3$ | 0.1250 | 0.2500 | 0.5000 | 1.0000 | 2.0000 | 4.0000 | 8.0000 | 16.000 | 32.000 | 64.000 | 128.00 | 256.00 |
|------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| 0.1250           | 0−9    | 0−10   | 0−12   | 0−16   | 1−16   | 1−16   | 1−16   | 7−16   | 7−16   | 6−16   | 6−16   | 4−16   | 4−16   |
| 0.2500           | 0−10   | 0−10   | 0−13   | 0−16   | 2−16   | 5−16   | 8−16   | 7−16   | 6−16   | 7−16   | 6−16   | 4−16   | 4−16   |
| 0.5000           | 0−10   | 0−10   | 0−13   | 0−16   | 3−16   | 6−16   | 7−16   | 7−16   | 6−16   | 7−16   | 6−16   | 4−16   | 4−16   |
| 1.0000           | 0−11   | 0−11   | 0−14   | 0−16   | 2−16   | 5−16   | 7−16   | 7−16   | 7−16   | 7−16   | 5−16   | 5−16   | 5−16   |
| 2.0000           | 0−12   | 0−13   | 0−15   | 0−16   | 2−16   | 5−16   | 7−16   | 6−16   | 6−16   | 6−16   | 5−16   | 5−16   | 5−16   |
| 4.0000           | 0−14   | 0−15   | 0−16   | 0−16   | 2−16   | 4−16   | 6−16   | 5−16   | 6−16   | 6−16   | 5−16   | 5−16   | 5−16   |
| 8.0000           | 0−16   | 0−16   | 0−16   | 0−16   | 2−16   | 3−16   | 4−16   | 4−16   | 4−16   | 4−16   | 7−16   | 5−16   | 5−16   |
| 16.000           | 0−16   | 0−16   | 0−16   | 0−16   | 1−16   | 1−16   | 1−16   | 2−16   | 2−16   | 2−16   | 4−16   | 3−16   | 5−16   |
| 32.000           | 0−13   | 0−14   | 0−13   | 0−14   | 0−15   | 0−15   | 0−15   | 0−16   | 0−16   | 0−16   | 0−15   | 0−14   | 5−16   |
| 64.000           | 0−6    | 0−6    | 0−6    | 0−7    | 0−7    | 0−8    | 0−9    | 0−9    | 0−9    | 0−6    | 5−5    | 0−4    | 0−4    |
| 128.00           | 0−0    | 0−0    | 0−0    | 0−0    | 0−0    | 0−0    | 0−1    | 0−2    | 0−2    | 0−4    | 0−3    | 0−2    | 0−2    |

The desired set of integrals

$$\langle \varphi_{m+n+1}^{m+1} | \varphi_{m+n+1}^{m+1} \rangle \equiv \frac{(m+1)^2}{2R^2} \times$$

$$\left[ R^2 \langle \varphi_{n_1}^{m+1} | \varphi_{n_2}^{m+1} \rangle + R^2 \langle \varphi_{n_1-1}^{m+1} | \varphi_{n_2+1}^{m+1} \rangle \right.$$ $$+ \langle \varphi_{n_1+1}^{m+1} | \varphi_{n_2-1}^{m+1} \rangle - \frac{1}{2} R^4 \langle \varphi_{n_1-1}^{m+1} | \varphi_{n_2+1}^{m+1} \rangle,$$

$$- \frac{1}{2} \langle \varphi_{n_1+1}^{m+1} | \varphi_{n_2+1}^{m+1} \rangle - \frac{1}{2} \langle \varphi_{n_1-1}^{m+1} | \varphi_{n_2-1}^{m+1} \rangle \right].$$

(32)

The second ingredient of the recursive process is a relation that allows to increase the values of $l_1$ and $l_2$ independently, starting with the just considered $\langle \varphi_{n_1}^{m+1} | \varphi_{n_2}^{m+1} \rangle$ integrals. The following recursion relation for the Legendre polynomials is useful

$$(l - m + 1) P_{l+1}^{m}(x) + (l + m) P_{l-1}^{m}(x) = (2l + 1)x P_{l}^{m}(x).$$

(33)

If one uses the above relation for $P_{l_1}^{m}(\cos \theta_a)$ in Eq. (28) and subsequently expresses $\cos \theta_a$ through $r_a$ and $r_b$ from the cosine theorem, the following recursion is obtained

$$\frac{1}{2R^2} \left[ \langle \varphi_{n_1}^{m} | \varphi_{n_2}^{m} \rangle - \langle \varphi_{n_1-1}^{m} | \varphi_{n_2+1}^{m} \rangle + R^2 \langle \varphi_{n_1-1}^{m} | \varphi_{n_2+1}^{m} \rangle \right.$$ $$\left. = (l_1 - m + 1) \langle \varphi_{n_1-1}^{m} | \varphi_{n_2+1}^{m} \rangle + (l_1 + m) \langle \varphi_{n_1-1}^{m} | \varphi_{n_2+1}^{m} \rangle, \right.$$ (34)

which can be used to increase $l_1$ at cost of $n_1$ and $n_2$. A corresponding expression for increasing $l_2$ can be obtained by repeating the derivation for $P_{l_2}^{m}(\cos \theta_b)$. Therefore, by using Eq. (34) and its counterpart for the centre $b$, we can build all $\langle \varphi_{n_1}^{m} | \varphi_{n_2}^{m} \rangle$ starting with integrals with $l_1 = l_2 = m$ and higher $n_1$, $n_2$.

Having said this, the only thing that remains in question is the calculation of the pertinent integrals $\langle n_100 | n_200 \rangle$. Let us return to Eq. (28)

$$\langle \varphi_{n_1}^{00} | \varphi_{n_2}^{00} \rangle = \int_0^{\infty} dr_a \int_{|r_a-R|} r_a n_1 r_b n_2$$

$$\times e^{-\zeta_1 r_a - \zeta_2 r_b} a_n \zeta_3 R_{1b},$$

(35)

use the integral representation of $a_n$, Eq. (12), and reverse the order of integration. By doing so we obtain an equivalent representation of the basic integrals

$$\langle \varphi_{n_1}^{00} | \varphi_{n_2}^{00} \rangle = \int_0^{1} dt m \Gamma_{n_1 n_2}(R; \zeta_1, \zeta_2 + t \zeta_3),$$

(36)

where $\Gamma_{mn}$ are the usual overlap integrals between $n$-type orbitals

$$\Gamma_{mn}(R; \zeta_1, \zeta_2) = \int_0^{1} dr_a \int_{|r_a-R|} r_a n_1 r_b n_2 e^{-\zeta_1 r_a - \zeta_2 r_b}.$$

(37)

In our approach, the outer integral in (36) is carried out numerically. The arguments for this approach are virtually the same as in the ellipsoidal coordinates method. Roughly speaking, numerical integration serves as a way to avoid numerical instabilities which inevitably appear when the analytic approaches are used. However, now we require a robust scheme for the calculation of $\Gamma_{mn}$, so that these integrals can be computed at each point of the grid without a great overhead. In fact, the main advantage of the numerical integration in the ellipsoidal coordinates method was that the integrand in Eq. (26) could be evaluated extremely efficiently and with a strictly controlled precision. On the other hand, the desired algorithm has to preserve a decent accuracy up to large values of $m$ and $n$ (several tens, say). Determination of such
an algorithm still presents a challenge from the practical point of view.

The basic integrals $\Gamma_{mn}$ are well-known in the literature. Many authors considered their computation by using several different algorithms which varied in accuracy and speed. Let us note, however, that in the calculation of the integrals (37) the main issue is the numerical stability. The actual expressions for these integrals are not difficult to derive and include only simple elementary functions. Unfortunately, these expressions consist of finite series with terms of alternating signs. When $m$, $n$ are increased these terms grow exponentially while the sum remains by orders of magnitude smaller. As a result, a gross digital erosion is inevitable. In a large fraction of works which considered calculation of the integrals (37), or used them as a part of different algorithms, the issue of numerical stability was completely disregarded or treated very lightly. The common justification for this fact is that authors were mainly interested in low quantum numbers or devised their algorithms to verify the correctness of the approach more than to perform general calculations.

Let us begin by noting that all integrals (37) can be generated by a consecutive differentiation of $\Gamma_{00}$ with respect to the nonlinear parameters $\zeta_1, \zeta_2$ i.e.

$$\Gamma_{mn}(R; \zeta_1, \zeta_2) = \left( -\frac{\partial}{\partial \zeta_1} \right)^m \left( -\frac{\partial}{\partial \zeta_2} \right)^n \Gamma_{00}(\zeta_1, \zeta_2), \quad (38)$$

which is, in substance, a trivial case of the so-called shift method of Fernández Rico et al. [51–53]. The simplest integrals $\Gamma_{00}$ are elementary

$$\Gamma_{00}(R; \zeta_1, \zeta_2) = \frac{2}{\zeta_1 + \zeta_2} e^{-\zeta_2 R} - e^{-\zeta_1 R \zeta_2}. \quad (39)$$

It is now convenient to define $g_{00}$ by

$$g_{00}(R; \zeta_1, \zeta_2) = 2 e^{-\zeta_2 R} - e^{-\zeta_1 R \zeta_2}, \quad (40)$$

so that $\Gamma_{00} = g_{00}/(\zeta_1 + \zeta_2)$, and the definition of $g_{mn}$ is analogous

$$g_{mn}(R; \zeta_1, \zeta_2) = \left( -\frac{\partial}{\partial \zeta_1} \right)^m \left( -\frac{\partial}{\partial \zeta_2} \right)^n g_{00}(\zeta_1, \zeta_2). \quad (41)$$

Let us now multiply both sides of Eq. (39) by $\zeta_1 + \zeta_2$, rewrite the result in terms of $g_{00}$ and differentiate both sides $m$ with respect to $-\zeta_1$ and $n$ times with respect to $-\zeta_2$. After some rearrangements, the final result can be written as

$$\Gamma_{mn} = \frac{1}{\zeta_1 + \zeta_2} \left[ g_{mn} + m \Gamma_{m-1,n} + n \Gamma_{m,n-1} \right], \quad (42)$$

where the notation for the nonlinear parameters is suppressed for brevity. The above expression is an inhomogeneous linear recursion relation for $\Gamma_{mn}$. Note, that all integrals $\Gamma_{mn}$ are positive and so are the values of $g_{mn}$.

Therefore, the above recursion relation is completely stable. This approach is reminiscent of the treatment of the one-centre integrals by Sack et al. [126].

The problem is now reduced to an efficient calculation of $g_{mn}$. Explicit differentiation is not an option because of similar cancellations as for the initial $\Gamma_{mn}$ integrals. However, let us observe that $g_{00}$ can also be rewritten as

$$g_{00}(\zeta_1, \zeta_2) = \frac{R}{2} e^{-\zeta_1 R} M[1, 2, (\zeta_1 - \zeta_2)R], \quad (43)$$

where $M(a, b, z)$ is the confluent hypergeometric function [106] (denoted as $\, _1F_1$ by some authors). By using two differentiation formulae for $M(a, b, z)$

$$\frac{\partial^n}{\partial z^n} M(a, b, z) = \frac{(a)_n}{(b)_n} M(a + n, b + n, z), \quad (44)$$

$$\frac{\partial^n}{\partial z^n} \left[ e^{-z} M(a, b, z) \right] = (-1)^n \frac{(b - a)_n}{(b)_n} e^{-z} M(a, b + n, z), \quad (45)$$

one easily arrives at the new formula for $g_{mn}$

$$g_{mn}(\zeta_1, \zeta_2) = \frac{1}{2} e^{-\zeta_1 R \zeta_2} \left[ e^{-\zeta_2 R} R^{m+n+1} \times M[1 + n, 2 + m + n, (\zeta_1 - \zeta_2)R] \right]. \quad (46)$$

At this point the problem can be considered to be solved because methods of calculation of $M(a, b, z)$ for arbitrary real (or even complex) values of the parameters $a$, $b$, and $z$ exist. Let us note that here we deal with an exceptionally special case of $M(a, b, z)$ with both $a$ and $b$ being strictly positive integers, and additionally $b > a$ always holds. Moreover, we can use the symmetry of the initial integrals, $(\varphi^{00}_{n_1} \varphi^{00}_{n_2}) = (\varphi^{00}_{n_2} \varphi^{00}_{n_1})$, in order to impose the restriction $\zeta_1 \geq \zeta_2$, which gives $z \geq 0$. All these conditions signal that we should design a dedicated procedure for the calculation of $M(a, b, z)$ in this special case and avoid using general algorithms which are drastically more complicated and involve a large computational overhead.

In Appendix we present a recursive method which is able to calculate $M(a, b, z)$ in our special case with a decent speed, at the same time preserving full accuracy allowed by the arithmetic.

In Tables 3 and 4 we present results of the benchmark calculations for the same representative integrals, $S^7_{112m}(26; \zeta_1, 0, \zeta_3)$ and $S_{7.6.6}^{21,18,m}(26; \zeta_1, \zeta_1, \zeta_3)$, as in the previous subsection. We use the same numerical quadrature as before and typically a machine precision is obtained in Eq. (36). One sees that the recursive algorithm fails completely, even in the quadruple arithmetic precision, when nonlinear parameters are both small. On the other hand, as they get large the accuracy gradually improves which is exactly the opposite behaviour to the one found in the ellipsoidal method. Therefore, two methods presented in this paper can be considered fully complementary and together are able to cover a sufficiently large range of the nonlinear parameters. Outside this range, hybrid integrals are usually very small and are typically
TABLE III. Calculation of $\zeta_{12, 13; m}^{15, 12}$ (26; $\zeta_1, \zeta_3$) using the recursive method. The values of $\zeta_1$, $\zeta_3$ increase along the columns or rows, respectively. The values presented are in the form d-q which denotes (rounded) decimal logarithms of the relative error obtained in double and quadruple arithmetic precision, respectively. Therefore, this values roughly represent the number of correct significant digits obtained using the present algorithm. Values obtained in quadruple precision were demoted to double precision before the comparison since these are the values used in the actual calculations. The worst result obtained within the possible range of $m$ was chosen in all cases. Reference values were obtained from calculations in extended arithmetic precision of 128 significant digits.

| $\zeta_1/\zeta_3$ | 0.1250 | 0.2500 | 0.5000 | 1.0000 | 2.0000 | 4.0000 | 8.0000 | 16.000 | 32.000 | 64.000 | 128.00 | 256.00 |
|------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| 0.1250           | 0-0    | 0-0    | 0-0    | 0-0    | 0-0    | 0-5    | 0-11   | 1-16   | 4-16   | 5-16   | 1-16   | 0-11   |
| 0.2500           | 0-0    | 0-0    | 0-0    | 0-0    | 0-0    | 0-5    | 0-11   | 1-16   | 4-16   | 5-16   | 1-16   | 0-11   |
| 0.5000           | 0-0    | 0-0    | 0-0    | 0-0    | 0-0    | 0-5    | 0-11   | 1-16   | 4-16   | 5-16   | 1-16   | 0-11   |
| 1.0000           | 0-0    | 0-0    | 0-0    | 0-0    | 0-0    | 0-5    | 0-11   | 1-16   | 4-16   | 5-16   | 1-16   | 0-11   |
| 2.0000           | 0-0    | 0-0    | 0-0    | 0-0    | 0-0    | 0-5    | 0-11   | 1-16   | 4-16   | 5-16   | 1-16   | 0-11   |
| 4.0000           | 0-6    | 0-6    | 0-6    | 0-6    | 0-5    | 0-11   | 1-16   | 3-16   | 4-16   | 1-16   | 0-12   |
| 8.0000           | 0-12   | 0-12   | 0-12   | 0-10   | 0-12   | 0-10   | 1-16   | 3-16   | 2-16   | 1-16   | 0-12   |
| 16.000           | 1-16   | 1-16   | 1-16   | 1-16   | 0-14   | 1-16   | 1-16   | 2-16   | 1-16   | 0-15   | 0-11   |
| 32.000           | 4-16   | 4-16   | 4-16   | 4-16   | 3-16   | 3-16   | 3-16   | 5-16   | 6-16   | 2-16   | 1-16   |
| 64.000           | 5-16   | 5-16   | 5-16   | 4-16   | 3-16   | 4-16   | 7-16   | 9-16   | 6-16   | 1-16   | 0-15   |
| 128.00           | 1-16   | 1-16   | 1-16   | 1-16   | 0-14   | 1-16   | 1-16   | 4-16   | 3-16   | 0-16   | 0-13   |
| 256.00           | 0-12   | 0-12   | 0-12   | 0-10   | 0-12   | 0-12   | 0-13   | 0-13   | 0-14   | 0-14   | 0-12   |

Table IV. Calculation of $\zeta_{7, 6; m}^{21, 18}$ (26; $\zeta_1, \zeta_3$) using the recursive method. The values of $\zeta_1$, $\zeta_3$ increase along the columns or rows, respectively. The values presented are in the form d-q which denotes (rounded) decimal logarithms of the relative error obtained in double and quadruple arithmetic precision, respectively. Therefore, this values roughly represent the number of correct significant digits obtained using the present algorithm. Values obtained in quadruple precision were demoted to double precision before the comparison since these are the values used in the actual calculations. The worst result obtained within the possible range of $m$ was chosen in all cases. Reference values were obtained from calculations in extended arithmetic precision of 128 significant digits.

| $\zeta_1/\zeta_3$ | 0.1250 | 0.2500 | 0.5000 | 1.0000 | 2.0000 | 4.0000 | 8.0000 | 16.000 | 32.000 | 64.000 | 128.00 | 256.00 |
|------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| 0.1250           | 0-0    | 0-0    | 0-0    | 0-0    | 0-0    | 0-0    | 0-0    | 0-0    | 0-0    | 0-0    | 0-0    | 0-0    |
| 0.2500           | 0-0    | 0-0    | 0-0    | 0-0    | 0-0    | 0-0    | 0-0    | 0-0    | 0-0    | 0-0    | 0-0    | 0-0    |
| 0.5000           | 0-0    | 0-0    | 0-0    | 0-0    | 0-0    | 0-0    | 0-0    | 0-0    | 0-0    | 0-0    | 0-0    | 0-0    |
| 1.0000           | 0-0    | 0-0    | 0-0    | 0-0    | 0-0    | 0-0    | 0-0    | 0-0    | 0-0    | 0-0    | 0-0    | 0-0    |
| 2.0000           | 0-0    | 0-0    | 0-0    | 0-0    | 0-0    | 0-0    | 0-0    | 0-0    | 0-0    | 0-0    | 0-0    | 0-0    |
| 4.0000           | 0-0    | 0-0    | 0-0    | 0-0    | 0-0    | 0-0    | 0-0    | 0-0    | 0-0    | 0-0    | 0-0    | 0-0    |
| 8.0000           | 0-5    | 0-5    | 0-5    | 0-5    | 0-5    | 0-5    | 0-6    | 0-6    | 0-6    | 0-5    | 0-4    |
| 16.000           | 0-12   | 0-12   | 0-12   | 0-12   | 0-12   | 0-12   | 0-13   | 0-13   | 0-13   | 0-12   | 0-11   |
| 32.000           | 6-16   | 6-16   | 6-16   | 6-16   | 6-16   | 6-16   | 6-16   | 7-16   | 7-16   | 4-16   | 0-14   |
| 64.000           | 8-16   | 8-16   | 8-16   | 8-16   | 8-16   | 8-16   | 8-16   | 8-16   | 8-16   | 9-16   | 10-16  |
| 128.00           | 4-16   | 4-16   | 4-16   | 4-16   | 4-16   | 4-16   | 4-16   | 4-16   | 4-16   | 6-16   | 7-16   | 2-16   |

neglected in advance by the Schwarz screening technique or a similar scheme. Coulomb integrals with bigger values of the nonlinear parameters may still be non-negligible. However, they can be computed with different standard techniques such as the multipole expansion. It is mandatory for a general program to include such a method as an option.

IV. CONCLUSIONS

Concluding, we derived new expressions for the Coulomb and hybrid integrals over the Slater-type orbitals, with no restrictions on the values of the quantum numbers, starting by a direct integration over coordinates of the second electron. In this way the desired integrals reduce to combinations of ordinary overlap integrals and a set of the so-called overlap-like integrals. These basic integrals are evaluated by using two distinct methods -
direct integration in the ellipsoidal coordinate system or with a recursive scheme for increasing angular momenta in the integrand. One of the biggest problems in actual computations is numerical stability of the resulting algorithms. Many formulations available in the literature contain numerically badly conditioned expressions which introduce a significant loss of digits when evaluated in a finite arithmetic precision. We show how these instabilities can be avoided if a simple, one-dimensional numerical integration is used instead. We discuss that this numerical approach introduces an acceptable computational overhead due to well-behaved and simple form of the integrands. We also show that the remaining numerical instabilities can be easily controlled. Extensive numerical tests are presented, verifying the usefulness and applicability of the method.

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Appendix: Calculation of $M(a, b, z)$ for $a, b \in \mathbb{Z}_+, b > a, z \geq 0$

Let us start by recalling some of the useful formulae obeyed by $M(a, b, z)$. The first one is the Gautschi representation of the continued fraction (GCF) \(^{[127]}\) which states that

$$
\frac{M(a + 1, b, z)}{M(a, b, z)} = 1 + \frac{z}{a} \sum_{k=0}^{\infty} p_k,
$$

where

$$
p_0 = 1, \quad p_k = \prod_{i=1}^{k} r_i,
$$

$$
 r_0 = 0, \quad r_k = -\frac{a_k(1 + r_{k-1})}{1 + a_k(1 + r_{k-1})},
$$

$$
 a_k = \frac{(a + k)z}{(b - z + k - 1)(b - z + k)}.
$$

The second useful expression is the recursion relation which allows to increase the value of $a$ at constant $b$:

$$(b - a)M(a - 1, b, z) + (2a - b + z)M(a, b, z) - aM(a + 1, b, z) = 0. \tag{A.2}
$$

The region $a, b \in \mathbb{Z}_+, b > a, z \geq 0$ needs to be divided into three subregions and different algorithms have to be used in each of them. They are as follows:

- $b \geq 2a + z$,
  one first uses GCF, Eq. (A.1), in order to obtain the ratio $\frac{M(a + 1, b, z)}{M(a, b, z)}$ for the maximal desired $b$ and $a = \left\lfloor \frac{(b - z)/2} \right\rfloor$ (\(\left\lfloor \cdot \right\rfloor\) is the ceiling function). The recursion (A.2) can be rewritten as

$$
r_{a-1} = \frac{b - a}{ar_a + b - 2a - z} \tag{A.3}
$$

where $r_a = M(a + 1, b, z)/M(a, b, z)$. This recursion is then carried out downward, starting with the value of the ratio obtained from GCF, until $r_0$ is reached. Since $M(0, b, z) = 1$, it turns out that $r_0 = M(1, b, z)$ and other values can be obtained by using the definition of $r_a$ e.g. $M(2, b, z) = r_1 M(1, b, z)$.

- $b < 2a + z, b \geq z$,
  again, the relation (A.2) is transformed into a Miller-like two-step recursion

$$
r_a = \frac{b - a}{a} r_{a-1} + 2 + \frac{z - b}{a} \tag{A.4}
$$

with $r_a$ being defined in the same way as previously. Starting with an arbitrary value of $r_0$, this recursion is carried out upward up to the line $a = b$ (corresponding to $r_{b-1}$). Using the the value of $M(1, b, z)$ is reached.

- $b < 2a + z, b < z$,
  this is the so-called anomalous convergence region of GCF i.e. the expression (A.1) converges to the wrong result \(^{[127]}\) and therefore cannot be used. However, in this region the initial upward recursion (A.2) is totally stable since all terms in (A.2) are positive. The starting (exact) values are

$$
M(0, b, z) = 1, \tag{A.5}
$$

$$
M(1, b, z) = (b - 1)e^z a_{b-2}(z), \tag{A.6}
$$

where $a_n$ are given by Eq. (12). The second relationship breaks down when $b = 1$ but in this case we obtain independently $M(1, 1, z) = e^z$, as noted beforehand.

Let us also add in passing that the power series expansion of $M(a, b, z)$ around $z = 0$ can additionally be used for small $z$

$$
M(a, b, z) = \sum_{s=0}^{\infty} \frac{(a)_s}{(b)_s s!} z^s, \tag{A.7}
$$

since it typically converges very fast in the vicinity of the origin, $z \approx 0$. Similar conclusion holds for the asymptotic expansion of $M(a, b, z)$ as $z$ is large. Remarkably, when the values of $M(a, b, z)$ are calculated as described in this Appendix, no loss of digits is observed, and thus $\langle P_{n_1} \rangle^{00_0}$ can be obtained with full precision up to very large values of $n_1$ and $n_2$. 
Supplemental Material.

Calculation of two-centre two-electron integrals over Slater-type orbitals revisited.
I. Coulomb and hybrid integrals

Michal Lesiuk and Robert Moszynski
Faculty of Chemistry, University of Warsaw
Pasteura 1, 02-093 Warsaw, Poland
(Dated: October 23, 2014)

The present document serves as a supplemental material for the publication Calculation of two-centre two-electron integrals over Slater-type orbitals revisited. I. Coulomb and hybrid integrals. It contains data or derivations which are of some importance but are not necessary for an overall understanding of the manuscript. However, the material presented here will be useful for a reader who wishes to repeat all of our derivations in details. Researchers who wish to repeat some of the calculations independently may also benefit from these additional data.

a e-mail: lesiuk@tiger.chem.uw.edu.pl
I. SUPPLEMENTAL MATERIAL FOR PAPER I

Let us consider an atomic integral

\[ I = \int dr_1 \int dr_2 \chi_{n_1 l_1} (r_1; \zeta_1) \chi_{n_2 l_2} (r_1; \zeta_2) \frac{1}{r_{12}} \chi_{n_3 l_3} (r_2; \zeta_3) \chi_{n_4 l_4} (r_2; \zeta_4), \]  

where all orbitals are located at the same point of space. By using the Laplace expansion for the term \( \frac{1}{r_{12}} \) and integrating over the angular coordinates of both electrons one gets

\[ I = (-1)^{m_1 + m_3} \sqrt{\frac{A}{2\pi}} \sum_{L=1}^{\infty} \left( \frac{l_1 l_2 l_3 l_4}{0 0 0} \right) \times \left[ I_L^1 (n_{12} + 2, n_{34} + 2; \zeta_{12}, \zeta_{34}) + I_L^2 \right], \]

where \( n_{12} = n_1 + n_2, \zeta_{12} = \zeta_1 + \zeta_2 \) and the same notation is used for the second electron. The summation over \( L \) in the above expression is finite i.e. only terms with max(\(|l_1 - l_2|, |l_3 - l_4|\)) \( \leq L \leq \min(l_1 + l_2, l_3 + l_4) \) survive. Let us first consider the integral \( I_L^1 \) which takes the form

\[ I_L^1 (n_1, n_2; \alpha_1, \alpha_2) = \int_0^\infty dr_1 r_1^{n_1 + L - 1} e^{-\alpha_1 r_1} \int_0^\infty dr_2 r_2^{n_2 - L - 1} e^{-\alpha_2 r_2}, \]

where the notation for the parameters was simplified for better readability. This integral can be integrated by using elementary methods to give

\[ I_L^1 (n_1, n_2; \alpha_1, \alpha_2) = \frac{\alpha_2^{-n_2} (n_2 - L - 1)!}{(\alpha_1 + \alpha_2)^{n_1 + L + 1}} \times \sum_{j=0}^{n_2 - L - 1} \frac{(n_1 + L + j)!}{j!} \left( \frac{\alpha_2}{\alpha_1 + \alpha_2} \right)^j. \]

Note all terms present in the above sum are positive and thus no cancellation of huge numbers to a relatively small result can occur. The above expression can be put even in a more compact form by using the Pochhammer symbols.

Let us now pass to the second class of integrals (\( I_L^2 \)) which are defined as

\[ I_L^2 (n_1, n_2; \alpha_1, \alpha_2) = \int_0^\infty dr_1 r_1^{n_1 - L - 1} e^{-\alpha_1 r_1} \int_0^\infty dr_2 r_2^{n_2 + L} e^{-\alpha_2 r_2}. \]

In some works, the first step to bring the above integrals into a closed form is to manipulate the integration range in the inner integral by inserting an obvious identity \( \int_0^{r_1} = \int_0^\infty - \int_{r_1}^\infty \). The advantage of this idea is that all resulting integrals are solved immediately in the same way as \( I_L^1 \). However, for some combinations of \( \alpha_2 \) and \( r_1 \) the two resulting integrals are nearly equal in magnitude. Therefore, subtraction will cause a significant loss of accuracy. This effect is particularly considerable when the values of the quantum numbers are large.

In the alternative approach, the integration variable in the inner integrand of Eq. (5) \( r_2 \) is changed to \( t = r_2/r_1 \). If the order of integration is reversed, the integration over \( r_1 \) can be carried out easily and one is left with the following one-dimensional integration

\[ I_L^2 (n_1, n_2; \alpha_1, \alpha_2) = (n_1 + n_2)! \int_0^1 dt \frac{t^{n_2 + L}}{(\alpha_1 + \alpha_2)^{n_1 + n_2 + 1}}. \]

The above integrand is a rational function and the integration can be carried out by using general methods. Taking into account that the relationship \( L \leq n_2 \) always holds, the final result can be cast into the form

\[ I_L^2 (n_1, n_2; \alpha_1, \alpha_2) = \frac{1}{\alpha_1} \frac{(n_2 + L)!}{(n_1 - L + 1)!} \sum_{k=0}^{n_1 - L - 1} \left( \frac{n_1 + n_2}{n_1 - L - 1 - k} \right)^k \left( \frac{\alpha_2}{\alpha_1} \right)^k. \]

The above summation includes only terms with positive signs and therefore the whole procedure is completely stable. Moreover, no special functions or infinite summations are required as contrasted to some of the formulations available in the literature.