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Electric and magnetic multipole integrals in STO basis sets: an analytical approach

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Abstract. A new method for the evaluation of one- and two-centre magnetic and electric multipole integrals for Slater-type functions is presented. The method is strictly analytical in that no approximations of any kind are involved. Two simple functions, $\mathscr{I}_1^{\text{aug}}$ and $\mathscr{I}_2^{\text{aug}}$, are introduced, which employ only functions that are well known in electronic structure theory. With the use of augmentation exponents these functions apply to multipole integrals as well as other one-electron integrals, such as nuclear attraction integrals. The proposed method includes the analytic determination of derivatives of the integrals with respect to atomic displacements. Some illustrative test calculations are presented and compared to results from the literature.

Key words: Slater-type orbitals – Electric multipole – Magnetic multipole – Molecular integrals – Derivatives

1 Introduction

For the theoretical determination of static or transition multipole moments it is necessary to represent the appropriate operators in a given basis, irrespective of the quantum chemical model used. In time-independent theory the basis is usually composed of atomic orbitals. The "quality" of the overall wave function depends heavily on

1. The size of the basis set (minimal, double zeta, ...).
2. Inclusion of property orbitals (diffuse or polarisation functions, Rydberg functions, etc.).
3. The functional form of the orbitals.

Slater-type orbitals (STOs) [1] model the radial part of exact hydrogen-like atomic orbitals quite accurately but lead to difficulties in the evaluation of many-centre integrals. To overcome this problem, Boys [2] introduced Gaussian-type orbitals (GTOs). GTOs suffer from their unphysical behaviour close to and far away from the nucleus. STOs are still used in most semiempirical methods, usually as minimal valence sets, sometimes including *d* functions [3, 4]. In ab intio theory, GTOs are now widely established, except for atomic ab intio calculations which often employ STO bases (see, e.g. [5–7]) and some benchmark STO calculations on small molecules [8–11]. A comparison of STO and GTO bases of various size showed that a GTO basis needs about twice the size of a STO basis to obtain comparable accuracy [9, 10]. Thus STO bases are still very attractive.

Some classical work on one-electron integrals over STOs can be found in Refs. [12–15]. A variety of approaches for the evaluation of molecular two-electron multicentre integrals in STO bases also exists for example one-centre expansions [16–18], recurrence schemes [19–23], integral transformation methods [24, 25], and other methods [11, 26–29].

The present work deals with one-electron integrals of the general operator $x^i y^j z^k \left(r^{-1}\right)^l \nabla^m$ ($i, j, k \geq 0$ and $l, m = 0, 1$; ∇ denotes the gradient operator) and with derivatives of these integrals with respect to atomic displacements. The most prominent operators of this kind correspond to the electric and magnetic dipole moment and to the electric quadrupole moment. These quantities determine spectroscopic properties, such as the oscillator strength or the natural or field induced rotatory strength [30]. The calculation of each of these properties remains a challenging problem in theoretical chemistry.

Augspurger [31] has studied an operator similar to $x^i y^j z^k \times \left(r^{-1}\right)^l \nabla^m$ for GTOs. McMurchie and Davidson [32] have solved integrals containing spatial derivatives of GTOs. Analytical expressions for electric dipole integrals and *s*- and *p*STOs with principal quantum numbers $n = 1, \ldots, 5$ were derived by Suzuki et al. [33]. Hug and Wagniere [34] calculated magnetic dipole integrals for 1*s*, 2*s* and 2*p* STOs. The first general approach for the solution of magnetic two-centre integrals with the origin fixed in-between the two centres is due to

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Ichimura and Rauk [35]. Guseinov [36] expressed magnetic multipole integrals in terms of Ruedenberg's C functions. Another approach is to calculate magnetic dipole integrals numerically or to solve the integrals in a GTO basis and project the results back onto the STO basis [37]. The method proposed in this paper derived its basic impact from two recent publications on STO integrals [38, 39]. Carbo and Besalu [38] investigated both molecular one- and two-electron operators as well as operators of the type $x^i y^j z^k$. In a work specialised on electric multipole operators, Zheng and Zerner [39] proposed an analytic procedure using some ideas similar to those of Carbo and Besalu.

To the best of our knowledge, no approaches for analytic derivatives of electric and magnetic multipole integrals have been published up to now.

2 Preliminaries

In the following derivations, we deal with Cartesian monomials of the type $x^i y^j z^k$, where x, y and z are Cartesian coordinates and i, j and k are positive integers or zero and we use the notation introduced in Ref. [39]

$$(i,j,k)_{\mathrm{P}} := x_{\mathrm{P}}^i \; y_{\mathrm{P}}^j \; z_{\mathrm{P}}^k \quad . \tag{1}$$

P indicates the point in three-dimensional space to which x, y and z refer. Details concerning the translational and rotational behaviour of Cartesian monomials can be found in Ref. [38, 39]. We will use the capital letters O, A and B to denote the origin of the coordinate system and two additional points in space. The coordinates of a point A with respect to O are A_x, A_y and A_z. Terms like x_{A}, y_{A}, z_{A} etc. denote coordinate functions with respect to A.

It has been shown that it is always possible to express a real spherical harmonic centred in P in terms of Cartesian monomials [11, 39, 40]:

$$r^l Y_{l,m} = \sum_{i+j+k=l} c_{i,j,k} (i,j,k)_{\mathrm{P}} \quad . \tag{2}$$

$c_{i,j,k}$ are appropriate real coefficients. The sum runs over all (i,j,k) with $i+j+k=l$. A STO [1] is defined as

$$\chi_{n,l,m}^{\mathrm{STO}} := \sqrt{\frac{(2\zeta)^{2n+1}}{(2n)!}} \; r^{n-1} \; \exp(-\zeta r) Y_{l,m}(\theta,\phi)$$

Substituting Eq. (2) we get

$$\chi_{n,l,m}^{\mathrm{STO}} = \sqrt{\frac{(2\zeta)^{2n+1}}{(2n)!}} \; r^{n-l-1} \exp(-\zeta r) \times \sum_{i+j+k=l} c_{i,j,k} (i,j,k) \quad . \tag{3}$$

Each $\chi_{n,l,m}^{\mathrm{STO}}$ can be expressed as a linear combination of unnormalised primitive STOs

$$\chi = r^{n-l-1} \mathrm{e}^{-\zeta r} (i,j,k) \quad . \tag{4}$$

We will use primitive STOs in all our derivations.

Electric multipole operators can be defined as [41]:

$$\hat{M}_{l,m}^{\mathrm{electric}} := -|\mathrm{e}| \; Y_{l,m} r^l \tag{5}$$

Each electric multipole operator can be written as a linear combination of Cartesian monomials $(i,j,k)_{\mathrm{O}}$. We will therefore refer to $(i,j,k)_{\mathrm{O}}$ as a primitive electric operator. Each primitive electric operator is hermitian.

As long as we neglect any spin dependence, the magnetic dipole operator is essentially the angular momentum operator, $\hat{\mathbf{l}}$. Beyond that, there is no generally accepted definition of magnetic multipole operators [42, 43]. The most widely accepted definition [43, 44] contains terms like

$$r_\beta r_\gamma \cdots r_\omega \hat{l}_\alpha + \hat{l}_\alpha r_\beta r_\gamma \cdots r_\omega \quad , \tag{6}$$

where the Greek indices denote Cartesian x, y or z components. These operators can be reduced to linear combinations of primitive magnetic operators, $(i,j,k)_{\mathrm{O}}\nabla$, which are in general neither hermitian nor anti hermitian. Equation (6) yields an anti hermitian formulation.

In the first part of this paper we will solve integrals of the types $\langle \chi_A | (i,j,k)_{\mathrm{O}} | \chi_{\mathrm{B}} \rangle$ and $\langle \chi_{\mathrm{A}} | (i,j,k)_{\mathrm{O}} \nabla | \chi_{\mathrm{B}} \rangle$ analytically for the one- and the two-centre cases. With these integrals it is possible to calculate the matrix representation of any electric and magnetic multipole operator in a STO basis. Therefore, we refer to these integrals as primitive electric and primitive magnetic integrals, respectively. Later on, we will apply the same ansatz to the evaluation of derivatives of these integrals with respect to atomic displacements.

3 Results

3.1 One-centre integrals

In one-centre integrals $\langle \chi_{\mathrm{a}}|$ and $|\chi_{\mathrm{b}}\rangle$ are located at A. For the evaluation of the integral we use a spherical polar coordinate system centred at A, with radial distance r, azimuthal angle θ and polar angle ϕ. The primitive electric operator $(i,j,k)_{\mathrm{O}}$ is defined with respect to the origin O. In order to express the primitive electric operator $(i,j,k)_{\mathrm{O}}$ in the polar coordinate system located at A we write the vector $\mathbf{P}_{\mathrm{O}}$ which points from O to an arbitrary point P as $\mathbf{P}_{\mathrm{O}} = \mathbf{A} + \mathbf{r}_{\mathrm{A}}$, where $\mathbf{A}$ points from O to A and $\mathbf{r}_{\mathrm{A}}$ points from A to P. Then we insert this into the definition of $(i,j,k)_{\mathrm{O}}$ and apply the binomial theorem 3 times (cf. Ref. [38]). With the following shorthand notation for the binomial sum (cf. the "nested summation symbol" in Ref. [38])

$$\sum_{m,n,l}^{i,j,k} \mathrm{B} := \sum_{m=0}^{i} \sum_{n=0}^{j} \sum_{l=0}^{k} \binom{i}{m} \binom{j}{n} \binom{k}{l} \times \cdots \tag{7}$$

we obtain:

$$(i,j,k)_{\mathrm{O}} = \sum_{m,n,l}^{i,j,k} \mathrm{B} \, A_x^{i-m} A_y^{j-n} A_z^{k-l} r^{l+m+n} \times \cos(\phi)^m \cos(\theta)^l \sin(\phi)^n \sin(\theta)^{m+n} \quad . \tag{8}$$

The primitive magnetic operators are obtained by multiplying Eq. (8) by ∇ expressed in spherical polar coordinates. Two unnormalised primitive STOs centred at A are obtained by transforming the definition of Eq. (4) to spherical polar coordinates:

$$
\begin{aligned}
\chi_{\mathrm{a}} &= r^{-1+i_{\mathrm{a}}+j_{\mathrm{a}}+k_{\mathrm{a}}-l_{\mathrm{a}}+n_{\mathrm{a}}}\cos(\phi)^{i_{\mathrm{a}}}\cos(\theta)^{k_{\mathrm{a}}} \\
&\quad\times \sin(\phi)^{j_{\mathrm{a}}}\sin(\theta)^{i_{\mathrm{a}}+j_{\mathrm{a}}}\exp(-\zeta_{\mathrm{a}}r) \\
\chi_{\mathrm{b}} &= r^{-1+i_{\mathrm{b}}+j_{\mathrm{b}}+k_{\mathrm{b}}-l_{\mathrm{b}}+n_{\mathrm{b}}}\cos(\phi)^{i_{\mathrm{b}}}\cos(\theta)^{k_{\mathrm{b}}} \\
&\quad\times \sin(\phi)^{j_{\mathrm{b}}}\sin(\theta)^{i_{\mathrm{b}}+j_{\mathrm{b}}}\exp(-\zeta_{\mathrm{b}}r)\ . \qquad (9)
\end{aligned}
$$

By definition, $i_{\mathrm{a,b}} + j_{\mathrm{a,b}} + k_{\mathrm{a,b}} - l_{\mathrm{a,b}} = 0$ for STOs. As we want the treatment of the integrals to be as general as possible, we keep the full exponent of r as it appears in Eq. [9].

3.1.1 $(i,j,k)_{\mathrm{O}}$ integrals

The combination of Eqs. (8) and (9) leads to the following formulation of a primitive electric one-centre integral:

$$
\begin{aligned}
\mathscr{I}_1 &= \langle\chi_{\mathrm{a}}|(i,j,k)_{\mathrm{O}}|\chi_{\mathrm{b}}\rangle \\
&= \int\limits_{r,\theta,\phi=0}^{\infty,\pi,2\pi} dr\ d\theta\ d\phi \sum_{m,n,l}^{i,j,k} \mathbf{B}\, A_x^{i-m}A_y^{j-n}A_z^{k-l} \\
&\quad\times \exp\left[-(\zeta_{\mathrm{a}}+\zeta_{\mathrm{b}})r\right] r^{l+m+n+T}\cos(\phi)^{m+I}\sin(\phi)^{n+J} \\
&\quad\times \cos(\theta)^{l+K}\sin(\theta)^{1+m+n+I+J}\ , \qquad (10)
\end{aligned}
$$

with $I = i_{\mathrm{a}} + i_{\mathrm{b}},\ J = j_{\mathrm{a}} + j_{\mathrm{b}},\ K = k_{\mathrm{a}} + k_{\mathrm{b}},\ L = l_{\mathrm{a}} + l_{\mathrm{b}}$, $N = n_{\mathrm{a}} + n_{\mathrm{b}}$ and $T = I + J + K + N - L$. The integral separates into the well-known standard integrals $\mathscr{R}$, $\mathscr{F}$, and $\mathscr{G}$ (Appendix 1):

$$
\begin{aligned}
&\mathscr{I}_1(n_{\mathrm{a}}, l_{\mathrm{a}}, i_{\mathrm{a}}, j_{\mathrm{a}}, k_{\mathrm{a}}, i, j, k, n_{\mathrm{b}}, l_{\mathrm{b}}, i_{\mathrm{b}}, j_{\mathrm{b}}, k_{\mathrm{b}}, \zeta_{\mathrm{a}}, \zeta_{\mathrm{b}}, A_x, A_y, A_z) \\
&\quad := \mathscr{N}\sum_{l,m,n}^{k,i,j} \mathbf{B}\, A_x^{i-m}A_y^{j-n}A_z^{k-l} \\
&\quad\times \mathscr{R}(T+l+m+n, \zeta_{\mathrm{a}}+\zeta_{\mathrm{b}}) \\
&\quad\times \mathscr{F}(I+m, J+n) \\
&\quad\times \mathscr{G}(K+l, 1+I+J+m+n)\ , \qquad (11)
\end{aligned}
$$

where $\mathscr{N}$ is the usual normalisation factor. Equation 11 differs from the corresponding equation in the treatment of Zheng and Zerner [39] only in that it does need master formulae. Their one-centre results are special cases of Eq. (11).

3.1.2 $(i,j,k)_{\mathrm{O}}\nabla$ integrals

To treat primitive magnetic integrals we first introduce another shorthand notation:

$$
\overset{\mathrm{p}}{\sum\!\!\!\!\!\!\int} = \int\limits_{r,\theta,\phi=0}^{\infty,\pi,2\pi} dr\ d\theta\ d\phi \sum_{m,n,l}^{i,j,k} \mathbf{B}\, A_x^{i-m}A_y^{j-n}A_z^{k-l} \times \exp[-(\zeta_{\mathrm{a}}+\zeta_{\mathrm{b}})r] \times \ldots \qquad (12)
$$

A primitive magnetic integral then reads:

$$
\begin{aligned}
&\langle\chi_{\mathrm{a}}|(i,j,k)_{\mathrm{O}}\nabla_x|\chi_{\mathrm{b}}\rangle \\
&= i_{\mathrm{b}} \overset{\mathrm{p}}{\sum\!\!\!\!\!\!\int} r^{-1+l+m+n+T}\cos(\phi)^{m-1+I}\sin(\phi)^{n+J} \\
&\quad\times \cos(\theta)^{l+K}\sin(\theta)^{m+n+I+J} + (n_{\mathrm{b}} - l_{\mathrm{b}} - 1) \\
&\quad\times \overset{\mathrm{p}}{\sum\!\!\!\!\!\!\int} r^{-1+l+m+n+T}\cos(\phi)^{1+m+I}\sin(\phi)^{n+J} \\
&\quad\times \cos(\theta)^{l+K}\sin(\theta)^{2+m+n+I+J} \\
&\quad - \zeta_{\mathrm{b}} \overset{\mathrm{p}}{\sum\!\!\!\!\!\!\int} r^{l+m+n+T}\cos(\phi)^{1+m+I}\sin(\phi)^{n+J} \\
&\quad\times \cos(\theta)^{l+K}\sin(\theta)^{2+m+n+I+J}\ . \qquad (13)
\end{aligned}
$$

Similar expressions are obtained for the y and z components of the primitive magnetic operator. All the integrals that appear in Eq. (13) differ from those appearing in Eq. (10) only by some of the exponents of r, $\cos(\phi)$, $\sin(\phi)$ $\cos(\theta)$ and $\sin(\theta)$. This calls for a generalisation of Eq. (11):

$$
\begin{aligned}
&\mathscr{I}_1^{\mathrm{aug}}(n_{\mathrm{a}}, l_{\mathrm{a}}, i_{\mathrm{a}}, j_{\mathrm{a}}, k_{\mathrm{a}}, i, j, k, n_{\mathrm{b}}, l_{\mathrm{b}}, i_{\mathrm{b}}, j_{\mathrm{b}}, k_{\mathrm{b}}, \\
&\quad \zeta_{\mathrm{a}}, \zeta_{\mathrm{b}}, A_x, A_y, A_z, r^+, f_1^+, f_2^+, g_1^+, g_2^+) \\
&\quad = \mathscr{N}\sum_{l,m,n}^{k,i,j} \mathbf{B}\, A_x^{i-m}A_y^{j-n}A_z^{k-l} \\
&\quad\times \mathscr{R}(r^+ + T + l + m + n, \zeta_{\mathrm{a}}+\zeta_{\mathrm{b}}) \\
&\quad\times \mathscr{F}(f_1^+ + I + m, f_2^+ + J + n) \\
&\quad\times \mathscr{G}(g_1^+ + K + l, g_2^+ + 1 + I + J + m + n)\ . \qquad (14)
\end{aligned}
$$

We call the integers r^+, f_1^+, f_2^+, g_1^+ and g_2^+ augmentation exponents (AE). $f_1^+ = 2$, for example, means that $\cos(\phi)$ has to be taken to the $(I+m+2)$th power instead of to the $(I+m)$th power in which it appears in Eq. (10). Equation (14) is valid for all choices of AEs which do not lead to negative exponents. The range of valid values is given in the third column of Table 1. With the concept of AEs our approach gains both applicability to a wide range of integrals and simplicity in handling and programming.

With $\mathscr{I}_1^{\mathrm{aug}}$ at hand, we are able to solve the integrals in Eq. (13) by comparing the exponents of the integrands with those in Eq. (10). We only give the values for the AEs explicitly, using the same order as in Eq. (14).

$$
\begin{aligned}
&\langle\chi_{\mathrm{a}}|(i,j,k)_{\mathrm{O}}\nabla_x|\chi_{\mathrm{b}}\rangle \\
&\quad = i_{\mathrm{b}}\ \mathscr{I}_1^{\mathrm{aug}}(\ldots, -1, -1, 0, 0, -1) \\
&\quad\quad + (n_{\mathrm{b}} - l_{\mathrm{b}} - 1)\ \mathscr{I}_1^{\mathrm{aug}}(\ldots, -1, 1, 0, 0, 1) \\
&\quad\quad - \zeta_{\mathrm{b}}\ \mathscr{I}_1^{\mathrm{aug}}(\ldots, 0, 1, 0, 0, 1) \qquad (15)
\end{aligned}
$$

Table 1. Augmentation exponents (AE) for one-centre integrals

AE	Term	Validity range
r^+	r	$r^+ \geq -T$
f_1^+	$\cos(\phi)$	$f_1^+ \geq -I$
f_2^+	$\sin(\phi)$	$f_2^+ \geq -J$
g_1^+	$\cos(\theta)$	$g_1^+ \geq -K$
g_2^+	$\sin(\theta)$	$g_2^+ \geq -(I+J)$

$$\langle\chi_a|(i,j,k)_O\nabla_y|\chi_b\rangle = j_b\ \mathscr{I}_1^{aug}(\ldots,-1,0,-1,0,-1) + (n_b-l_b-1)\ \mathscr{I}_1^{aug}(\ldots,-1,0,1,0,1) - \zeta_b\ \mathscr{I}_1^{aug}(\ldots,0,0,1,0,1) \quad (16)$$

$$\langle\chi_a|(i,j,k)_O\nabla_z|\chi_b\rangle = k_b\ \mathscr{I}_1^{aug}(\ldots,-1,0,0,-1,0) + (n_b-l_b-1)\ \mathscr{I}_1^{aug}(\ldots,-1,0,0,1,0) - \zeta_b\ \mathscr{I}_1^{aug}(\ldots,0,0,0,1,0)\ . \quad (17)$$

$\mathscr{I}_1^{aug}$ is valid in all the above equations. Consider a "worst case": for $\langle 1s|(i,j,k)_O\nabla_x|1s\rangle$ we have $I=J=K=0$ and g_2^+ is restricted to positive integers or zero. The term $\mathscr{I}_1^{aug}(\ldots,-1,-1,0,0,g_2^+=-1)$ in Eq. (15) is not allowed; however this term is multiplied by $i_b=0$ and we do not need to worry. By similar arguments it is possible to show that all cases which lead to negative exponents in $\mathscr{I}_1^{aug}$ are zero.

3.2 Two-centre integrals

3.2.1 Coordinate system and operators

Two-centre integrals involve two STOs located at two different centres A and B and an operator which is defined with respect to the origin O of the molecular coordinate system (MCS). For a given molecule this origin is chosen once, usually by symmetry arguments. The MCS is a Cartesian coordinate system defined by a tripod centred at the origin (Fig. 1a).

For the evaluation of an individual two-centre integral we start with the introduction of a local coordinate system (LCS). For any pair of atoms a LCS is defined as follows (Fig. 1b). At atom A a right-handed tripod is centred with the z-axis pointing towards atom B. The corresponding tripod in B is left handed. Its z-axis points towards A. The x- and y-axes in A are parallel to the x- and y-axes in B. The tripod for the operator located at O is chosen parallel to the one in A. In such a LCS bi-focal elliptical coordinates μ, v and ϕ can be defined as follows [19, 38]:

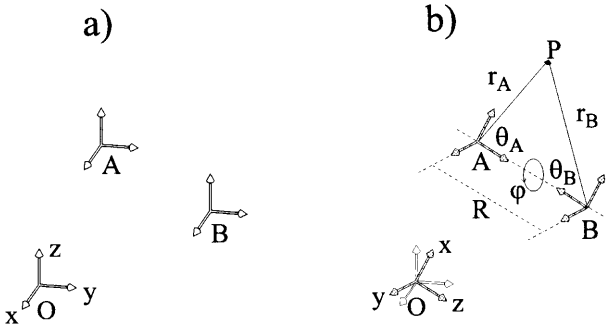

Fig. 1a, b Coordinate systems employed for two centre integrals. **a** Molecular coordinate system and **b** one possible local coordinate system. See text for details

$$x_A = x_B = \frac{\sqrt{-1+\mu^2}\ \sqrt{1-v^2}\ R\cos(\phi)}{2}$$
$$y_A = y_B = \frac{\sqrt{-1+\mu^2}\ \sqrt{1-v^2}\ R\sin(\phi)}{2} \quad (18)$$
$$z_A = R - z_B = \frac{(1+\mu v)R}{2}\ ,$$

R denotes the interatomic distance. Note that ϕ is positively oriented with respect to the tripod in A, ranging from 0 to 2π. The coordinates v and μ range from -1 to $+1$ and from $+1$ to $+\infty$, respectively. The differential volume is $d\tau = \left(\frac{R}{2}\right)^3(\mu^2-v^2)d\mu\ dv\ d\phi$. As the labelling of the two atoms is arbitrary, there are always two equivalent types of LCSs for any given pair of atoms depending on which of the two atoms is labelled "A" or "B". We have to ensure that this arbitrariness does not affect our results.

In a way analogous to the one-centre case we find for the electric operator $(i,j,k)_O$:

$$(i,j,k)_O = \sum_{l,m,n}^{i,j,k} B\left(\frac{R}{2}\right)^{l+m+n} A_x^{i-m}A_y^{j-n}A_z^{k-l} \times \left(-1+\mu^2\right)^{\frac{m}{2}+\frac{n}{2}}(1+\mu v)^l\left(1-v^2\right)^{\frac{m}{2}+\frac{n}{2}} \times \cos(\phi)^m\sin(\phi)^n \quad (19)$$

The gradient operator in elliptical bi-focal coordinates can be obtained in a straightforward manner (Appendix 2). The STOs located at A and B are:

$$\chi_A = \left(\frac{R}{2}\right)^{-1-l_a+n_a}\left(-1+\mu^2\right)^{\frac{i_a}{2}+\frac{j_a}{2}}(\mu+v)^{-1-l_a+n_a} \times (1+\mu v)^{k_a}(1-v^2)^{\frac{i_a}{2}+\frac{j_a}{2}} \times \cos(\phi)^{i_a}\ \sin(\phi)^{j_a}\ \exp\left[-\frac{(\mu+v)R\zeta_a}{2}\right] \quad (20)$$

$$\chi_B = \left(\frac{R}{2}\right)^{-1+n_b}\left(-1+\mu^2\right)^{\frac{i_b}{2}+\frac{j_b}{2}}(\mu-v)^{-1-l_b+n_b} \times (1-\mu v)^{k_b}\left(1-v^2\right)^{\frac{i_b}{2}+\frac{j_b}{2}} \times \cos(\phi)^{i_b}\sin(\phi)^{j_b}\exp\left[-\frac{(\mu-v)R\zeta_b}{2}\right]\ . \quad (21)$$

3.2.2 $(i,j,k)_O$ integrals

We now have to solve the following integral (Similar integrands appear, for example, in Refs. [14, 15, 38, 39]):

$$\langle\chi_A|(i,j,k)_O|\chi_B\rangle = \int_{\phi=0,\mu=1,v=-1}^{2\pi,\infty,1} d\phi\ d\mu\ dv \sum_{l,m,n}^{i,j,k} B\left(\frac{R}{2}\right)^{1+T+l+m+n} \times A_x^{i-m}A_y^{j-n}A_z^{k-l}\exp(-\rho\mu-\rho\tau v) \times \left(-1+\mu^2\right)^{\frac{I+J+m+n}{2}}(\mu-v)^{-l_b+n_b} \times (\mu+v)^{-l_a+n_a}(1-\mu v)^{k_b}(1+\mu v)^{k_a+l} \times \left(1-v^2\right)^{\frac{I+J+m+n}{2}}\cos(\phi)^{I+m}\ \sin(\phi)^{J+n}\ , \quad (22)$$

where $\rho = \frac{R}{2}(\zeta_a + \zeta_b)$ and $\tau = \frac{\zeta_a - \zeta_b}{\zeta_a + \zeta_b}$ [12]. For later use we define the operator:

$$\overset{e}{\int\!\!\!\!\!\!\int} := \int_{\phi=0,\mu=1,\nu=-1}^{2\pi,\infty,1} d\phi\ d\mu\ d\nu \sum_{l,m,n}^{i,j,k} B \left(\frac{R}{2}\right)^{l+m+n+T} \times A_x^{i-m} A_y^{j-n} A_z^{k-l} e^{-\rho\mu - \rho\tau\nu} \times \cdots \quad (23)$$

The integration over the polar angle can be separated. This part of the integral is solved by $F(I+m, J+n)$ (Appendix). F yields nonzero values only if both arguments are even integers. The only terms in the sum we need to consider are for those m and n which leave $I+m$ and $J+m$ even. This ensures that any bracketed term in Eq. (22) can be expanded binomially. We arrive at a finite sum of separable integrals of the form $\int d\mu\ d\nu\ \nu^q \mu^w \exp(-\rho\mu) \exp(-\rho\tau\nu)$, with integers q and w. These integrals can be expressed by Mulliken's A and B integrals [12]. A detailed discussion of their properties can be found in Ref. [38]. Putting all terms together, we arrive at

$$\begin{aligned}
&\mathcal{I}_2(n_a, l_a, i_a, j_a, k_a, i, j, k, n_b, l_b, i_b, j_b, k_b, R, \\
&\quad \zeta_a, \zeta_b, A_x, A_y, A_z) \\
&\quad := \mathcal{N}\mathcal{P}(k_a, k_b) \sum_{\alpha}^{n_a - l_a} B \sum_{\beta}^{n_b - l_b} B \sum_{\kappa_a, \kappa_b}^{k_a, k_b} B \sum_{\iota,\lambda,\eta}^{i,j,k} B \sum_{\epsilon}^{\eta} B \\
&\qquad \times \sum_{\xi_\nu}^{\frac{I+J+\iota+\lambda}{2}} B \sum_{\xi_\mu}^{\frac{I+J+\iota+\lambda}{2}} B \left(\frac{R}{2}\right)^{1+T+\eta+\iota} A_x^{\,i-\iota} A_y^{\,j-\lambda} A_z^{\,-\eta+k} \\
&\qquad \times (-1)^{-\beta+\kappa_b+\frac{I+\iota+J+\lambda}{2}-l_b+n_b-\xi_\mu+\xi_\nu} \times F(I+\iota, J+\lambda) \\
&\qquad \times A(\alpha+\beta+\epsilon+\kappa_a+\kappa_b+2\xi_\mu, \rho) \\
&\qquad \times B(-\alpha-\beta+\epsilon+\kappa_a+\kappa_b-L+N+2\xi_\nu, \rho, \tau) \quad (24)
\end{aligned}$$

with

$$\mathcal{P}(k_a, k_b) := \begin{cases} 1; & g(k_a) \wedge g(k_b) \vee u(k_a) \wedge g(k_b) \\ -1; & \text{otherwise} \end{cases} . \quad (25)$$

$\wedge$ and $\vee$ denote the Boolean operators "and" and "or". Equation (24) bears some resemblance to the Z function introduced by Zheng and Zerner [39]. We postpone a detailed comparison to the "Discussion". $\mathcal{P}(k_a, k_b)$ is a phase correction that takes care of the left-handedness of the tripod in B. Consider for example the overlap of two p_z orbitals at the atoms A and B, pointing to one another. This overlap is surely negative. Without $\mathcal{P}$ the function $\mathcal{I}_2$ would yield a positive value, because the two z-axes in A and B are anti-parallel. In the example, this is corrected by $\mathcal{P}(1,1) = -1$. If $\mathcal{P}(k_a, k_b)$ is neglegted in Eq. (24), the phase correction has to be done during the transformation of the integral from the LCS into the MCS.

3.2.3 $(i,j,k)_O\nabla$ integrals

The calculation of the magnetic integrals is somewhat more laborious, which is caused mainly by the complicated structure of the gradient operator (Appendix 2, Eq. A7). Because of the similarity of the arguments with those in the previous section, we only give a sketch of the derivation. After some rearrangement, the integral for the $(i,j,k)_O\nabla_x$ operator reads

$$\begin{aligned}
&\langle \chi_A | (i,j,k)_O \frac{\partial}{\partial x} | \chi_B \rangle \\
&\quad = (n_b - l_b - 1) \overset{e}{\int\!\!\!\!\!\!\int} \Big(\mu(\mu-\nu)^{-2-l_b+n_b} (\mu+\nu)^{-1-l_a+n_a} \\
&\qquad \times (1-\mu\nu)^{k_b} (1+\mu\nu)^{k_a} \\
&\qquad \times \left(1-\nu^2\right)^{\frac{1}{2}+\frac{I}{2}+\frac{J}{2}+\frac{m}{2}+\frac{n}{2}} \\
&\qquad \times \left(-1+\mu^2\right)^{\frac{1}{2}+\frac{I}{2}+\frac{J}{2}+\frac{m}{2}+\frac{n}{2}} \\
&\qquad \times \cos(\phi)^{m+1+I} \sin(\phi)^{n+I} \\
&\qquad + \nu(\mu-\nu)^{-2-l_b+n_b} (\mu+\nu)^{-1-l_a+n_a} \\
&\qquad \times (1-\mu\nu)^{k_b} (1+\mu\nu)^{k_a} \\
&\qquad \times \left(1-\nu^2\right)^{\frac{1}{2}+\frac{I+J}{2}+\frac{m}{2}+\frac{n}{2}} \\
&\qquad \times \left(-1+\mu^2\right)^{\frac{1}{2}+\frac{I+J}{2}+\frac{m}{2}+\frac{n}{2}} \\
&\qquad \times \cos(\phi)^{m+1+I} \sin(\phi)^{n+I} \Big) \\
&\quad + (i_b + j_b) \overset{e}{\int\!\!\!\!\!\!\int} \Big(\mu^2(\mu-\nu)^{-1-l_b+n_b} (\mu+\nu)^{-1-l_a+n_a} \\
&\qquad \times (1-\mu\nu)^{k_b} (1+\mu\nu)^{k_a} \\
&\qquad \times \left(1-\nu^2\right)^{\frac{1}{2}+\frac{I+J}{2}+\frac{m}{2}+\frac{n}{2}} \\
&\qquad \times \left(-1+\mu^2\right)^{-\frac{1}{2}+\frac{I+J}{2}+\frac{m}{2}+\frac{n}{2}} \\
&\qquad \times \cos(\phi)^{m+1+I} \sin(\phi)^{n+I} \\
&\qquad + \nu^2(\mu-\nu)^{-1-l_b+n_b} (\mu+\nu)^{-1-l_a+n_a} \\
&\qquad \times (1-\mu\nu)^{k_b} (1+\mu\nu)^{k_a} \\
&\qquad \times \left(1-\nu^2\right)^{-\frac{1}{2}+\frac{I+J}{2}+\frac{m}{2}+\frac{n}{2}} \\
&\qquad \times \left(-1+\mu^2\right)^{\frac{1}{2}+\frac{I+J}{2}+\frac{m}{2}+\frac{n}{2}} \\
&\qquad \times \cos(\phi)^{m+1+I} \sin(\phi)^{n+I} \Big) \\
&\quad - \zeta_b \frac{R}{2} \overset{e}{\int\!\!\!\!\!\!\int} \Big(\mu(\mu-\nu)^{-1-l_b+n_b} (\mu+\nu)^{-1-l_a+n_a} \\
&\qquad \times (1-\mu\nu)^{k_b} (1+\mu\nu)^{k_a} \\
&\qquad \times \left(1-\nu^2\right)^{\frac{1}{2}+\frac{I+J}{2}+\frac{m}{2}+\frac{n}{2}} \\
&\qquad \times \left(-1+\mu^2\right)^{\frac{1}{2}+\frac{I+J}{2}+\frac{m}{2}+\frac{n}{2}} \\
&\qquad \times \cos(\phi)^{m+1+I} \sin(\phi)^{n+I} \\
&\qquad + \nu(\mu-\nu)^{-1-l_b+n_b} (\mu+\nu)^{-1-l_a+n_a} \\
&\qquad \times (1-\mu\nu)^{k_b} (1+\mu\nu)^{k_a} \\
&\qquad \times \left(1-\nu^2\right)^{\frac{1}{2}+\frac{I+J}{2}+\frac{m}{2}+\frac{n}{2}} \\
&\qquad \times \left(-1+\mu^2\right)^{\frac{1}{2}+\frac{I+J}{2}+\frac{m}{2}+\frac{n}{2}} \\
&\qquad \times \cos(\phi)^{m+1+I} \sin(\phi)^{n+I} \Big)
\end{aligned}$$

$$
\begin{aligned}
&+ (i_\mathrm{b} - j_\mathrm{b}) \sum_{\mathrm{e}} \Big(\mu^2 (\mu - v)^{-1-l_\mathrm{b}+n_\mathrm{b}} (\mu + v)^{-1-l_\mathrm{a}+n_\mathrm{a}} \\
&\times (1 - \mu v)^{k_\mathrm{b}} (1 + \mu v)^{k_\mathrm{a}} \\
&\times \left(1 - v^2\right)^{-\frac{1}{2}+\frac{I+J}{2}+\frac{m}{2}+\frac{n}{2}} \\
&\times \left(-1 + \mu^2\right)^{-\frac{1}{2}+\frac{I+J}{2}+\frac{m}{2}+\frac{n}{2}} \\
&\times \cos(\phi)^{m+1+I} \sin(\phi)^{n+I} \\
&- v^2 (\mu - v)^{-1-l_\mathrm{b}+n_\mathrm{b}} (\mu + v)^{-1-l_\mathrm{a}+n_\mathrm{a}} \\
&\times (1 - \mu v)^{k_\mathrm{b}} (1 + \mu v)^{k_\mathrm{a}} \\
&\times \left(1 - v^2\right)^{-\frac{1}{2}+\frac{I+J}{2}+\frac{m}{2}+\frac{n}{2}} \\
&\times \left(-1 + \mu^2\right)^{-\frac{1}{2}+\frac{I+J}{2}+\frac{m}{2}+\frac{n}{2}} \\
&\times \cos(\phi)^{m+1+I} \sin(\phi)^{n+I} \Big) \ . \qquad (26)
\end{aligned}
$$

A corresponding expression is obtained for the $(i,j,k)_\mathrm{O}\nabla_y$ operator. The expression for the $(i,j,k)_\mathrm{O}\nabla_z$ operator contains nearly twice as many terms. By comparing the individual terms in these integrals to those appearing in Eq. (22) we arrive at an augmented version of the function $\mathscr{I}_2$:

$$
\begin{aligned}
&\mathscr{I}_2^{\mathrm{aug}}(n_\mathrm{a}, l_\mathrm{a}, i_\mathrm{a}, j_\mathrm{a}, k_\mathrm{a}, i, j, k, n_\mathrm{b}, l_\mathrm{b}, i_\mathrm{b}, j_\mathrm{b}, k_\mathrm{b}, R, \zeta_\mathrm{a}, \zeta_\mathrm{b}, A_x, \\
&\quad A_y, A_z, R^+, r_\mathrm{a}^+, r_\mathrm{b}^+, z_\mathrm{a}^+, z_\mathrm{b}^+, \mu^+, v^+, \mu_2^+, v_2^+, s^+, c^+) \\
&:= N \mathscr{P}(k_\mathrm{a}, k_\mathrm{b}) \sum_{\alpha}^{-l_\mathrm{a}+n_\mathrm{a}+r_\mathrm{a}^+} \mathrm{B} \sum_{\beta=0}^{n_\mathrm{b}-l_\mathrm{b}+r_\mathrm{b}^+} \mathrm{B} \sum_{\kappa_\mathrm{a}}^{k_\mathrm{a}+z_\mathrm{a}^+} \mathrm{B} \sum_{\kappa_\mathrm{b}}^{k_\mathrm{b}+z_\mathrm{b}^+} \mathrm{B} \\
&\quad \times \sum_{\iota}^{i} \mathrm{B} \sum_{\lambda}^{j} \mathrm{B} \sum_{\eta}^{k} \mathrm{B} \sum_{\epsilon}^{\eta} \mathrm{B} \sum_{\xi_\nu}^{\frac{I+J+\iota+\lambda+v_2^+}{2}} \mathrm{B} \sum_{\xi_\mu}^{\frac{I+J+\iota+\lambda+v_2^+}{2}} \mathrm{B} \\
&\quad \times (-1)^{n_\mathrm{b}-l_\mathrm{b}+r_\mathrm{b}^+-\beta+\kappa_\mathrm{b}+\frac{I+J+\iota+\lambda+\mu_2^+}{2}-l_\mathrm{b}+n_\mathrm{b}-\xi_\mu+\xi_\nu} \\
&\quad \times \left(\frac{R}{2}\right)^{1+T+\eta+\iota+\lambda+R^+} A_x^{i-\iota} A_y^{j-\lambda} A_z^{-\eta+k} \\
&\quad \times F(I+\iota+c^+, J+\lambda+s^+) \\
&\quad \times A(\alpha+\beta+\epsilon+\kappa_\mathrm{a}+\kappa_\mathrm{b}+2\xi_\mu+\mu^+, \rho) \\
&\quad \times B(-\alpha-\beta+\epsilon+\kappa_\mathrm{a}+\kappa_\mathrm{b}-L+N+2\xi_\nu+v^+, \rho, \tau) \ . \qquad (27)
\end{aligned}
$$

The AEs are given in Table 2. In contrast to the $\mathscr{I}_1^{\mathrm{aug}}$ function, the AEs have to be chosen very carefully in $\mathscr{I}_2^{\mathrm{aug}}$. Because of their complicated interplay it is not possible to derive validity ranges as simple as those given in Table 1. Instead, some allowed configurations of AEs are listed in Table 2. If, for example, s^+ is an odd and c^+ is an even integer, μ_2^+ and v_2^+ must both be odd. Equation (27) is valid for all combinations of AEs used in this work; however, if used for other integrals one has to make sure that there are no terms with noninteger exponents.

With $\mathscr{I}_2^{\mathrm{aug}}$ the integrals of the $(i,j,k)_\mathrm{O}\nabla$ operator can be solved by inspection of the exponents appearing in the integrands. Again, we specify only the augmentation exponents.

Table 2. AEs for the functions $\mathscr{I}_2$ and $\mathscr{D}_2$

AE	Term	Validity conditions				
μ^+	μ	$\mu^+ \geq 0$				
v^+	v	$v^+ \geq -(r_\mathrm{a}^+ + r_\mathrm{a}^+)$				
μ_2^+	$(-1+\mu^2)^{\frac{1}{2}}$		g^a	u	u	g
v_2^+	$(1-v^2)^{\frac{1}{2}}$		g	u	u	g
s^+	$\sin(\phi)$	$s^+ \geq -J$	g	g	u	u
c^+	$\cos(\phi)$	$c^+ \geq -I$	g	u	g	u
R^+	$(\frac{R}{2})$	any integer				
r_a^+	$(\mu + v)$	$r_\mathrm{a}^+ \geq -1 - n_\mathrm{a} + l_\mathrm{a}$				
r_b^+	$(\mu - v)$	$r_\mathrm{b}^+ \geq -1 - n_\mathrm{b} + l_\mathrm{b}$				
z_a^+	$(1 + \mu v)$	$z_\mathrm{a}^+ \geq -k_\mathrm{a}$				
z_b^+	$(1 - \mu v)$	$z_\mathrm{b}^+ \geq -k_\mathrm{b}$				

[a] $g \leftrightarrow$ even integer, $u \leftrightarrow$ odd integer

$$
\begin{aligned}
&\langle \chi_\mathrm{A} | (i,j,k)_\mathrm{O} \frac{\partial}{\partial x} | \chi_\mathrm{B} \rangle \\
&\quad = (-1 - l_\mathrm{b} + n_\mathrm{b}) \Big(\mathscr{I}_2^{\mathrm{aug}}(-1,-1,-2,0,0,0,1,1,1,0,1) \\
&\qquad + \mathscr{I}_2^{\mathrm{aug}}(-1,-1,-2,0,0,1,0,1,1,0,1) \Big) \\
&\qquad + (i_\mathrm{b} - j_\mathrm{b}) \Big(\mathscr{I}_2^{\mathrm{aug}}(-1,-1,-1,0,0,2,0,-1,-1,0,1) \\
&\qquad - \mathscr{I}_2^{\mathrm{aug}}(-1,-1,-1,0,0,0,2,-1,-1,0,1) \Big) \\
&\qquad + (i_\mathrm{b} + j_\mathrm{b}) \Big(\mathscr{I}_2^{\mathrm{aug}}(-1,-1,-1,0,0,0,2,1,-1,0,1) \\
&\qquad + \mathscr{I}_2^{\mathrm{aug}}(-1,-1,-1,0,0,2,0,-1,1,0,1) \Big) \\
&\qquad - \zeta_\mathrm{b} \Big(\mathscr{I}_2^{\mathrm{aug}}(0,-1,-1,0,0,0,1,1,1,0,1) \\
&\qquad + \mathscr{I}_2^{\mathrm{aug}}(0,-1,-1,0,0,1,0,1,1,0,1) \Big) \ , \qquad (28)
\end{aligned}
$$

$$
\begin{aligned}
&\langle \chi_\mathrm{A} | (i,j,k)_\mathrm{O} \frac{\partial}{\partial y} | \chi_\mathrm{B} \rangle \\
&\quad = (-1 - l_\mathrm{b} + n_\mathrm{b}) \Big(\mathscr{I}_2^{\mathrm{aug}}(-1,-1,-2,0,0,0,1,1,1,1,0) \\
&\qquad + \mathscr{I}_2^{\mathrm{aug}}(-1,-1,-2,0,0,1,0,1,1,1,0) \Big) \\
&\qquad + (i_\mathrm{b} - j_\mathrm{b}) \Big(\mathscr{I}_2^{\mathrm{aug}}(-1,-1,-1,0,0,0,2,-1,-1,1,0) \\
&\qquad - \mathscr{I}_2^{\mathrm{aug}}(-1,-1,-1,0,0,2,0,-1,-1,1,0) \Big) \\
&\qquad + (i_\mathrm{b} + j_\mathrm{b}) \Big(\mathscr{I}_2^{\mathrm{aug}}(-1,-1,-1,0,0,0,2,1,-1,1,0) \\
&\qquad + \mathscr{I}_2^{\mathrm{aug}}(-1,-1,-1,0,0,2,0,-1,1,1,0) \Big) \\
&\qquad - \zeta_\mathrm{b} \Big(\mathscr{I}_2^{\mathrm{aug}}(0,-1,-1,0,0,0,1,1,1,1,0) \\
&\qquad + \mathscr{I}_2^{\mathrm{aug}}(0,-1,-1,0,0,1,0,1,1,1,0) \Big) \ , \qquad (29)
\end{aligned}
$$

$$
\begin{aligned}
&\langle \chi_\mathrm{A} | (i,j,k)_\mathrm{O} \frac{\partial}{\partial z} | \chi_\mathrm{B} \rangle \\
&\quad = (-1 - l_\mathrm{b} + n_\mathrm{b}) \Big(- \mathscr{I}_2^{\mathrm{aug}}(-1,-1,-2,0,0,0,1,0,0,0,0) \\
&\qquad - \mathscr{I}_2^{\mathrm{aug}}(-1,-1,-2,0,0,1,0,0,0,0,0)
\end{aligned}
$$

$$
\begin{aligned}
&+ \mathscr{I}_2^{\mathrm{aug}}(-1,-1,-2,0,0,1,2,0,0,0,0)\\
&+ \mathscr{I}_2^{\mathrm{aug}}(-1,-1,-2,0,0,2,1,0,0,0,0)\Big)\\
&+ k_{\mathrm{b}}\Big(\mathscr{I}_2^{\mathrm{aug}}(-1,-1,-1,0,-1,0,2,0,0,0,0)\\
&- \mathscr{I}_2^{\mathrm{aug}}(-1,-1,-1,0,-1,2,0,0,0,0,0)\Big)\\
&+ (i_{\mathrm{b}}+j_{\mathrm{b}})\Big(-\mathscr{I}_2^{\mathrm{aug}}(-1,-1,-1,0,0,1,1,-2,0,0,0)\\
&- \mathscr{I}_2^{\mathrm{aug}}(-1,-1,-1,0,0,1,1,0,-2,0,0)\\
&+ \mathscr{I}_2^{\mathrm{aug}}(-1,-1,-1,0,0,1,3,0,-2,0,0)\\
&+ \mathscr{I}_2^{\mathrm{aug}}(-1,-1,-1,0,0,3,1,-2,0,0,0)\Big)\\
&+ \zeta_{\mathrm{b}}\Big(\mathscr{I}_2^{\mathrm{aug}}(0,-1,-1,0,0,0,1,0,0,0,0)\\
&+ \mathscr{I}_2^{\mathrm{aug}}(0,-1,-1,0,0,1,0,0,0,0,0)\\
&- \mathscr{I}_2^{\mathrm{aug}}(0,-1,-1,0,0,1,2,0,0,0,0)\\
&- \mathscr{I}_2^{\mathrm{aug}}(0,-1,-1,0,0,2,1,0,0,0,0)\Big)\ . \qquad (30)
\end{aligned}
$$

All two-centre integrals that appear for a given molecule can now be calculated in an appropriate LCS. Finally, the resulting integrals have to be transferred into the common MCS. This can be done by procedures similar to those described in [38, 45]. The only task of such a transformation is the rotation of the z-axis into a proper direction. One Eulerian angle is arbitrary which leads to an infinite number of equivalent LCSs for a given A–B pair. For a primitive electric integral the transformation involves three distinct rotations: two for the spherical harmonics employed in the two STOs and one for the operator. In primitive magnetic integrals, an additional rotation of the gradient operator must be performed.

3.3 Derivatives with respect to normal coordinates

One of the possible applications of the integrals discussed so far is the calculation of various expectation values for electronic transitions including, for example, natural and magnetic field induced optical activity tensors [30, 46]. If we want to go a step further and include vibrational excitations [47, 48] or vibronic coupling [49] we need derivatives of the primitive integrals with respect to normal coordinates. The simplest approach to solve this problem is the use of numerical methods, for example, the application of finite displacements. Our newly developed formalism offers an alternative as it allows not only the evaluation of the integrals themselves but also the direct analytical determination of the necessary derivatives.

A normal coordinate q_j can be formulated in terms of $3N$ Cartesian displacements ξ:

$$
{}_j = \sum_{i=1}^{3N} a_{ji}\xi_i\ . \qquad (31)
$$

The coefficients a_{ji} result from a standard normal coordinate analysis [48, 50]. The derivative with respect to the jth normal coordinate is given by

$$
\begin{aligned}
\frac{\partial}{\partial q_j} &= \sum_{i=1}^{3N}\frac{\partial \xi_i}{\partial q_j}\frac{\partial}{\partial \xi_i}\\
&= \sum_{i=1}^{3N} a_{ij}\frac{\partial}{\partial \xi_i}\ . \qquad (32)
\end{aligned}
$$

In the derivation of Eq. (32) we used the assumption that the a_{ij} matrix (with translations and rotations included) is unitary. Because of Eq. (32) it is sufficient to determine the derivatives with respect to Cartesian displacements.

We consider the function $\mathscr{I}_1^{\mathrm{aug}}$ as a function of the coordinates of centre A defined in the MCS, $\mathscr{I}_1^{\mathrm{aug}} = \mathscr{I}_1^{\mathrm{aug}}(A_x, A_y, A_z)$. Using Eq. (32), the derivative of $\mathscr{I}_1^{\mathrm{aug}}$ with respect to the jth normal coordinate is

$$
\begin{aligned}
\frac{\partial}{\partial q_j}\mathscr{I}_1^{\mathrm{aug}} &= \sum_{i=1}^{3N} a_{ij}\frac{\partial}{\partial \xi_i}\mathscr{I}_1^{\mathrm{aug}}\\
&= a_{A_x,j}\partial_{A_x}\mathscr{I}_1^{\mathrm{aug}} + a_{A_y,j}\partial_{A_y}\mathscr{I}_1^{\mathrm{aug}}\\
&\quad + a_{A_z,j}\partial_{A_z}\mathscr{I}_1^{\mathrm{aug}}\ . \qquad (33)
\end{aligned}
$$

Here, ∂_{A_x} abbreviates $\frac{\partial}{\partial \xi_{A_x}}$, where ξ_{A_x} is the Cartesian displacement of A in the x direction. Similarly we treat $\mathscr{I}_2^{\mathrm{aug}}$ as $\mathscr{I}_2^{\mathrm{aug}}(A_x, A_y, A_z; B_x, B_y, B_z)$.

$$
\begin{aligned}
\frac{\partial}{\partial q_j}\mathscr{I}_2^{\mathrm{aug}} &= \sum_{i=1}^{3N} a_{ij}\frac{\partial}{\partial \xi_i}\mathscr{I}_2^{\mathrm{aug}}\\
&= a_{A_x,j}\partial_{A_x}\mathscr{I}_2^{\mathrm{aug}} + a_{A_y,j}\partial_{A_y}\mathscr{I}_2^{\mathrm{aug}}\\
&\quad + a_{A_z,j}\partial_{A_z}\mathscr{I}_2^{\mathrm{aug}} + a_{B_x,j}\partial_{B_x}\mathscr{I}_2^{\mathrm{aug}}\\
&\quad + a_{B_y,j}\partial_{B_y}\mathscr{I}_2^{\mathrm{aug}} + a_{B_z,j}\partial_{B_z}\mathscr{I}_2^{\mathrm{aug}}\\
&= (a_{A_x,j} - a_{B_x,j})\partial_{A_x}\mathscr{I}_2^{\mathrm{aug}}\\
&\quad + (a_{A_y,j} - a_{B_y,j})\partial_{A_y}\mathscr{I}_2^{\mathrm{aug}}\\
&\quad + (a_{A_z,j} - a_{B_z,j})\partial_{A_z}\mathscr{I}_2^{\mathrm{aug}}\ . \qquad (34)
\end{aligned}
$$

In the last step we used $\partial_{A_x} = -\partial_{B_x}$, $\partial_{A_y} = -\partial_{B_y}$, and $\partial_{A_z} = -\partial_{B_z}$ in the MCS. Thus only three derivatives have to be calculated and stored for any one- or two-centre integral.

3.3.1 Derivatives of one-centre integrals

The derivatives of the function $\mathscr{I}_1^{\mathrm{aug}}$ follow directly from Eq. (14).

$$
\begin{aligned}
\partial_{A_x}\mathscr{I}_1^{\mathrm{aug}} = \ & \mathscr{N}\sum_{l,m,n}^{k,i,j}{}^{\mathrm{B}}(i-m)A_x^{i-m-1}A_y^{j-n}A_z^{k-l}\\
&\times \mathscr{R}(r^+ + T + l + m + n, \zeta_{\mathrm{a}} + \zeta_{\mathrm{b}})\\
&\times \mathscr{F}(f_1^+ + I + m, f_2^+ + J + n)\\
&\times \mathscr{G}(g_1^+ + K + l, g_2^+ + 1 + I + J + m + n)
\end{aligned}
$$

$$\partial_{A_y}\mathscr{I}_1^{\text{aug}} = \mathscr{N}\sum_{l,m,n}^{k,i,j}\mathrm{B}(j-n)A_x^{i-m}A_y^{j-n-1}A_z^{k-l}$$
$$\times\mathscr{R}(r^+ + T + l + m + n, \zeta_\mathrm{a} + \zeta_\mathrm{b})$$
$$\times\mathscr{F}(f_1^+ + I + m, f_2^+ + J + n)$$
$$\times\mathscr{G}(g_1^+ + K + l, g_2^+ + 1 + I + J + m + n)$$

$$\partial_{A_z}\mathscr{I}_1^{\text{aug}} = \mathscr{N}\sum_{l,m,n}^{k,i,j}\mathrm{B}(k-l)A_x^{i-m}A_y^{j-n}A_z^{k-l-1}$$
$$\times\mathscr{R}(r^+ + T + l + m + n, \zeta_\mathrm{a} + \zeta_\mathrm{b})$$
$$\times\mathscr{F}(f_1^+ + I + m, f_2^+ + J + n)$$
$$\times\mathscr{G}(g_1^+ + K + l, g_2^+ + 1 + I + J + m + n)\ .$$

By comparison with Eq. (10) we obtain:

$$\begin{aligned}\partial_{A_x}\mathscr{I}_1^{\text{aug}} &= i\mathscr{I}_1^{\text{aug}}(i \to i-1)\\ \partial_{A_y}\mathscr{I}_1^{\text{aug}} &= j\mathscr{I}_1^{\text{aug}}(j \to j-1)\\ \partial_{A_z}\mathscr{I}_1^{\text{aug}} &= k\mathscr{I}_1^{\text{aug}}(k \to k-1)\ .\end{aligned} \tag{35}$$

$\mathscr{I}_1(i \to i-1)$ indicates that i is replaced by $i-1$ and the remaining arguments remain the same. Substitution of Eq. (35) into Eqs. (15)–(17) leads to derivatives of primitive magnetic integrals.

3.3.2 Derivatives of two-centre integrals

For the LCS it follows by definition that

$$\begin{aligned}\partial_{A_x}^{\text{local}} &= \partial_{B_x}^{\text{local}}\\ \partial_{A_y}^{\text{local}} &= \partial_{B_y}^{\text{local}}\\ \partial_{A_z}^{\text{local}} &= -\partial_{B_z}^{\text{local}}\ ,\end{aligned} \tag{36}$$

The suffix "local" indicates that we are dealing with a LCS. Analogous to Eq. (35) we obtain

$$\begin{aligned}\partial_{A_x}^{\text{local}}\mathscr{I}_2^{\text{aug}} &= i\mathscr{I}_2^{\text{aug}}(i \to i-1)\\ \partial_{A_y}^{\text{local}}\mathscr{I}_2^{\text{aug}} &= j\mathscr{I}_2^{\text{aug}}(j \to j-1)\\ \partial_{A_z}^{\text{local}}\mathscr{I}_2^{\text{aug}} &= k\mathscr{I}_2^{\text{aug}}(k \to k-1) - \mathscr{D}_2^{\text{aug}}\ .\end{aligned} \tag{37}$$

$\mathscr{D}_2^{\text{aug}}$ arises from the implicit dependence of the Mulliken integrals $A(k,\rho)$ and $B(k,\rho,\tau)$ and of $\left(\frac{R}{2}\right)^{1+\eta+i_\mathrm{a}+\cdots}$ on A_z.

$$\mathscr{D}_2^{\text{aug}}(n_\mathrm{a}, l_\mathrm{a}, i_\mathrm{a}, j_\mathrm{a}, k_\mathrm{a}, i, j, k, n_\mathrm{b}, l_\mathrm{b}, i_\mathrm{b}, j_\mathrm{b}, k_\mathrm{b}, R, \zeta_\mathrm{a}, \zeta_\mathrm{b}, A_x,$$
$$A_y, A_z, R^+, r_\mathrm{a}^+, r_\mathrm{b}^+, z_\mathrm{a}^+, z_\mathrm{b}^+, \mu^+, v^+, \mu_2^+, v_2^+, s^+, c^+)$$
$$= \mathscr{N}\mathscr{P}(k_\mathrm{a}, k_\mathrm{b})\sum_{\alpha}^{-l_\mathrm{a}+n_\mathrm{a}+r_\mathrm{a}^+}\mathrm{B}\sum_{\beta}^{n_\mathrm{b}-l_\mathrm{b}+r_\mathrm{b}^+}\mathrm{B}\sum_{\kappa_\mathrm{a}}^{k_\mathrm{a}+z_\mathrm{a}^+}\mathrm{B}\sum_{\kappa_\mathrm{b}}^{k_\mathrm{b}+z_\mathrm{b}^+}\mathrm{B}$$
$$\times\sum_{\iota}^{i}\mathrm{B}\sum_{\lambda}^{j}\mathrm{B}\sum_{\eta}^{k}\mathrm{B}\sum_{\epsilon}^{\eta}\mathrm{B}\sum_{\xi_v}^{\frac{I+J+\iota+\lambda+v_2^+}{2}}\mathrm{B}\sum_{\xi_\mu}^{\frac{I+J+\iota+\lambda+\mu_2^+}{2}}\mathrm{B}$$
$$\times(-1)^{n_\mathrm{b}-l_\mathrm{b}+r_\mathrm{b}^+-\beta+\kappa_\mathrm{b}+\frac{I+J+\iota+\lambda+\mu_2^+}{2}-l_\mathrm{b}+n_\mathrm{b}-\xi_\mu+\xi_v}$$
$$\times A_x^{i-\iota}A_y^{j-\lambda}A_z^{-\eta+k}\left(\frac{R}{2}\right)^{\eta+T+\iota+\lambda+R^+}$$
$$\times F(I+\iota+c^+, J+\lambda+s^+)$$
$$\times\Big[(1+T+\eta+\iota+\lambda+R^+)$$
$$\times A(\alpha+\beta+\epsilon+\kappa_\mathrm{a}+\kappa_\mathrm{b}+2\xi_\mu+\mu^+,\rho)$$
$$\times B(-\alpha-\beta+\epsilon+\kappa_\mathrm{a}+\kappa_\mathrm{b}-L+N$$
$$+2\xi_v+v^+,\rho,\tau)$$
$$-\frac{\zeta_\mathrm{a}+\zeta_\mathrm{b}}{2}\frac{R}{2}A(1+\alpha+\beta+\epsilon+\kappa_\mathrm{a}+\kappa_\mathrm{b}$$
$$+2\xi_\mu+\mu^+,\rho)$$
$$\times B(-\alpha-\beta+\epsilon+\kappa_\mathrm{a}+\kappa_\mathrm{b}-L+N$$
$$+2\xi_v+v^+,\rho,\tau)$$
$$-\frac{\zeta_\mathrm{a}-\zeta_\mathrm{b}}{2}\frac{R}{2}A(\alpha+\beta+\epsilon+\kappa_\mathrm{a}+\kappa_\mathrm{b}$$
$$+2\xi_\mu+\mu^+,\rho)$$
$$\times B(1-\alpha-\beta+\epsilon+\kappa_\mathrm{a}+\kappa_\mathrm{b}-L+N$$
$$+2\xi_v+v^+,\rho,\tau)\Big]\ . \tag{38}$$

The same rules apply to the AEs in $\mathscr{D}_2^{\text{aug}}$ as they apply to $\mathscr{I}_2^{\text{aug}}$ (Table 2). For the derivation of Eq. (38) we used

$$\partial_{A_z}^{\text{local}} = -\partial_R = -\frac{\zeta_\mathrm{a}+\zeta_\mathrm{b}}{2}\partial_\rho \tag{39}$$

and the fact that the derivatives of the Mulliken integrals with respect to ρ are simply

$$\begin{aligned}\frac{\partial}{\partial\rho}A(k,\rho) &= -A(k+1,\rho)\\ \frac{\partial}{\partial\rho}B(k,\rho,\tau) &= -\tau B(k+1,\rho,\tau)\ .\end{aligned} \tag{40}$$

For the final rotation of the derivative of a two-centre integral from the LCS into the MCS we need not only the derivatives of the integral but also the derivatives of the rotation matrix. These can be written as

$$\partial^{\text{MCS}}\mathscr{I}_2^{\text{aug}} = \sum\text{Rotation}\ \partial^{\text{LCS}}\mathscr{I}_2^{\text{aug}}$$
$$+\sum\left(\partial^{\text{LCS}}\text{Rotation}\right)\mathscr{I}_2^{\text{aug}}\ . \tag{41}$$

∂^{LCS} Rotation is easily obtained by standard procedures.

3.4 Nuclear attraction integrals

Although not the primary goal of this work, nuclear attraction integrals are most easily evaluated with the concept of AEs. We obtain

$$\left\langle\chi_\mathrm{a}\right|-\frac{Z_\mathrm{A}}{r_\mathrm{A}}\left|\chi_\mathrm{b}\right\rangle$$
$$= -Z_\mathrm{A}\mathscr{I}_1^{\text{aug}}\ (i=0, j=0, k=0, r^+=-1) \tag{42}$$

for one-centre nuclear attraction integrals and

$$\left\langle \chi_A \left| -\frac{Z_A}{r_A} \right| \chi_B \right\rangle = -Z_A \mathscr{I}_2^{aug} \quad (i=0, j=0, k=0, R^+ = -1, r_a^+ = -1, r_b^+ = 0) \tag{43}$$

$$\left\langle \chi_A \left| -\frac{Z_B}{r_B} \right| \chi_B \right\rangle = -Z_B \mathscr{I}_2^{aug} \quad (i=0, j=0, k=0, R^+ = -1, r_a^+ = 0, r_b^+ = -1) \tag{44}$$

for- two-centre nuclear attraction integrals. All AEs which are not shown explicitly default to zero. Integrals of the Laplacian and thereby kinetic energy integrals can also be calculated with $\mathscr{I}_{1,2}^{aug}$. Unfortunately, the number of primitive integrals involved becomes quite large in this case and the methods cited in the Introduction are clearly superior for the calculation of kinetic energy integrals.

4. Discussion

4.1 Numerical aspects

4.1.1 Tests for I_1^{aug} and I_2^{aug}

The methods derived in the foregoing sections have been implemented in the program `eXcite` using the Fortran90 programming language. In order to check the routines, a number of test calculations have been performed for comparison with published results. Unfortunately, there are only few published results for multipole integrals that give explicit values. However, because of the general applicability of the two functions $\mathscr{I}_1^{aug}$ and $\mathscr{I}_2^{aug}$, we were able to check against some overlap, angular momentum, and nuclear attraction integrals (Table 3). `eXcite` has been compiled in two versions, one with the standard double-precision word length of 64 bits, and one with twice that word length. The size of the binary code increases by only about 40% when using a word length of 128 bits but the program becomes about 8 times slower on a DEC Alpha workstation. From Table 3 we learn that the calculations which use 128 bit double-precision variables reproduce precisely the overlap and $1/r$-integrals found by Fernandez Rico et al. [20] and the angular momentum integrals calculated by Hug and Wagniere [34]. The differences between the values which we obtained either with 64 or with 128 bit double-precision variables are only minor. The respective values coincide within 13–15 digits. To emphasize this result it should be mentioned that

1. `eXcite` was programmed in the most straightforward manner with no special treatment of numerically critical routines.
2. The calculation of each integral in Table 3 employs a linear combination of two to nine primitive integrals, summing up the numerical errors of each primitive integral.

We therefore conclude that the proposed method is of high numerical stability.

Table 3. Some test calculations for the use of $\mathscr{I}_1^{aug}$ and $\mathscr{I}_2^{aug}$ in comparison to values from the literature. All values in atomic units. For the 64 bit values, the digits differing from the 128 bit value are underlined

Integral	This work		Literature
	64 bit[a]	128 bit[a]	
Overlaps and nuclear attraction integrals			Ref. [20]
$\langle 3d, m_a = 0 \vert 3d, m_b = 0\rangle$[b]	$0.12547638617814\underline{673} \times 10^{-01}$	$0.12547638617816214 \times 10^{-01}$	$0.125476386178162 \times 10^{-01}$
$\langle 3d, \vert m_a\vert = 1 \vert 3d, \vert m_b\vert = 1\rangle$[b]	$-0.69911744322628\underline{290} \times 10^{-02}$	$-0.69911744322628676 \times 10^{-02}$	$-0.699117443226285 \times 10^{-02}$
$\langle 3d, \vert m_a\vert = 2 \vert 3d, \vert m_b\vert = 2\rangle$[b]	$0.1104965093297\underline{7856} \times 10^{-02}$	$0.11049650932976334 \times 10^{-02}$	$0.110496509329763 \times 10^{-02}$
$\langle 3d, m_a = 0 \vert -Z_a/r_a \vert 3d, m_b = 0\rangle$[c]	$-0.486277949158\underline{83660} \times 10^{+00}$	$-0.48627794915885689 \times 10^{+00}$	$-0.486277949158857 \times 10^{+00}$
$\langle 3d, \vert m_a\vert = 1 \vert -Z_a/r_a \vert 3d, \vert m_b\vert = 1\rangle$[c]	$0.265448562634\underline{63512} \times 10^{+00}$	$0.26544856263464321 \times 10^{+00}$	$0.265448562634643 \times 10^{+00}$
$\langle 3d, \vert m_a\vert = 2 \vert -Z_a/r_a \vert 3d, \vert m_b\vert = 2\rangle$[c]	$-0.413875309079\underline{66347} \times 10^{-01}$	$-0.41387530907973784 \times 10^{-01}$	$-0.413875309079738 \times 10^{-01}$
$\langle 3d, m_a = 0 \vert -Z_b/r_b \vert 3d, m_b = 0\rangle$[c]	$-0.865697113601\underline{55718} \times 10^{-01}$	$-0.86569711360165005 \times 10^{-01}$	$-0.865697113601649 \times 10^{-01}$
$\langle 3d, \vert m_a\vert = 1 \vert -Z_b/r_b \vert 3d, \vert m_b\vert = 1\rangle$[c]	$0.397046469000\underline{43952} \times 10^{-01}$	$0.39704646900044243 \times 10^{-01}$	$0.397046469000443 \times 10^{-01}$
$\langle 3d, \vert m_a\vert = 2 \vert -Z_b/r_b \vert 3d, \vert m_b\vert = 2\rangle$[c]	$-0.539466601538\underline{48178} \times 10^{-02}$	$-0.53946660153853615 \times 10^{-02}$	$-0.539466601538536 \times 10^{-02}$
Magnetic dipole integrals			Ref. [34]
$\langle 2s^{C1} \vert x\partial_y - y\partial_x \vert 2p_y^{C1}\rangle$[d]	$-0.673709874191379\underline{07} \times 10^{+00}$	$-0.67370987419137894 \times 10^{+00}$	-0.6737
$\langle 2p_x^{C1} \vert x\partial_y - y\partial_x \vert 2p_y^{C1}\rangle$[d]	$-0.999999999999999\underline{89} \times 10^{+01}$	$-0.10000000000000000 \times 10^{+01}$	-1.0000
$\langle 2p_y^{C1} \vert x\partial_y - y\partial_x \vert 2p_x^{C2}\rangle$[d]	$0.000000000000000\underline{10} \times 10^{+00}$	$0.00000000000000000 \times 10^{+00}$	0.0000
$\langle 2s^{C1} \vert x\partial_y - y\partial_x \vert 2p_y^{C2}\rangle$[d]	$-0.186041455761480\underline{29} \times 10^{+00}$	$-0.18604145576148015 \times 10^{+00}$	-0.1861
$\langle 2p_y^{C1} \vert x\partial_y - y\partial_x \vert 2p_y^{C2}\rangle$[d]	$0.658371816561391\underline{93} \times 10^{-01}$	$0.65837181656139083 \times 10^{-01}$	0.0658
$\langle 2p_y^{C1} \vert x\partial_y - y\partial_x \vert 2p_y^{O2}\rangle$[d]	$-0.516280939549\underline{57016} \times 10^{-01}$	$-0.51628093954956813 \times 10^{-01}$	-0.0516
$\langle 2p_y^{C1} \vert x\partial_y - y\partial_x \vert 2p_x^{O2}\rangle$[d]	$-0.524124729631\underline{85429} \times 10^{-01}$	$-0.52412472963185210 \times 10^{-01}$	-0.0522
$\langle 2p_y^{C1} \vert x\partial_y - y\partial_x \vert 2p_y^{O2}\rangle$[d]	$0.115834054506\underline{86264} \times 10^{-01}$	$0.11583405450686106 \times 10^{-01}$	0.0116

[a] Double-precision word length
[b] $\zeta_a = 6.5197$, $\zeta_b = 2.0387$, $R = 3.75$
[c] $\zeta_a = 6.5197$, $\zeta_b = 2.0387$, $R = 3.75$; the nuclear charges are $Z_a = 35$ and $Z_b = 17$
[d] Integrals for glyoxal in a minimal valence STO basis. $\zeta_{C}1 = \zeta_{C}2 = \zeta 1.625, \zeta_{O2} = 2.275$. Coordinates: C1: {1.43618429, 0.0, 0.0}, C1: {1.43618429, 0.0, 0.0}, and O2: {2.70229412, −2.01065800, 0.83336483}

4.1.2 Tests for $\partial_{A_{x,y,z}} I_2^{\text{aug}}$: analytic derivatives versus numerical derivatives

As an example for the use of Eqs. (37) and (38) we studied the integral $\langle 3p_y|xz|3d_{xy}\rangle$ with Slater exponents 2.3561 and 6.5197 in its LCS with $\{2,3,4\}$ as coordinates for A at various inter atomic distances R (Table 4). The analytical derivatives were calculated with Eq. (37). The results were compared to numerical derivatives of $\mathscr{I}_2^{\text{aug}}$ found in the most fundamental way by direct evaluation of the differential quotient with a finite displacement of the Cartesian coordinates

$$\begin{aligned}
\partial_{A_x}\mathscr{I}_2^{\text{aug}} &\approx \frac{1}{\Delta}\left[\mathscr{I}_2^{\text{aug}}(A_x+\Delta) - \mathscr{I}_2^{\text{aug}}(A_x)\right] \\
\partial_{A_y}\mathscr{I}_2^{\text{aug}} &\approx \frac{1}{\Delta}\left[\mathscr{I}_2^{\text{aug}}(A_y+\Delta) - \mathscr{I}_2^{\text{aug}}(A_y)\right] \\
\partial_{A_z}\mathscr{I}_2^{\text{aug}} &\approx \frac{1}{\Delta}\left[\mathscr{I}_2^{\text{aug}}(R-\Delta;A_z+\Delta) - \mathscr{I}_2^{\text{aug}}(R;A_z)\right]
\end{aligned} \tag{45}$$

with sufficiently small Δ.

The integral $\langle 3p_y|xz|3d_{xy}\rangle$ for $R = 0.0$ a.u. was calculated with the one-centre function I_1^{aug}. From the second column of Table 4 we learn that the 64 bit and the 128 bit version of the program yield practically the same value of the two-centre integral for an interatomic distance of $R = 2.0$ a.u. The difference increases for larger as well as for smaller R but for all practical purposes it is negligibly small. At $R = 25$ a.u., for example, the two values coincide in only eight nonzero digits, but the absolute difference is less than 10^{-30} a.u.

The analytic derivatives show similar trends (Table 4, central column), but the difference between the two word lengths is no longer negligible. The numerical derivatives have been calculated using various finite displacements Δ of centre B that range from $\Delta = 0.1$ to 10^{-30} a.u. In Fig. 2 the logarithmic relative error, log[(numerical derivative − analytical derivative)/analytical derivative], has been plotted against $\log\Delta$ for some of the two-centre integrals shown in Table 4. The plots that result for other integrals are similar. With decreasing Δ the numerical derivatives converge towards the analytical value. At a certain point, however, the relative error starts to increase again.

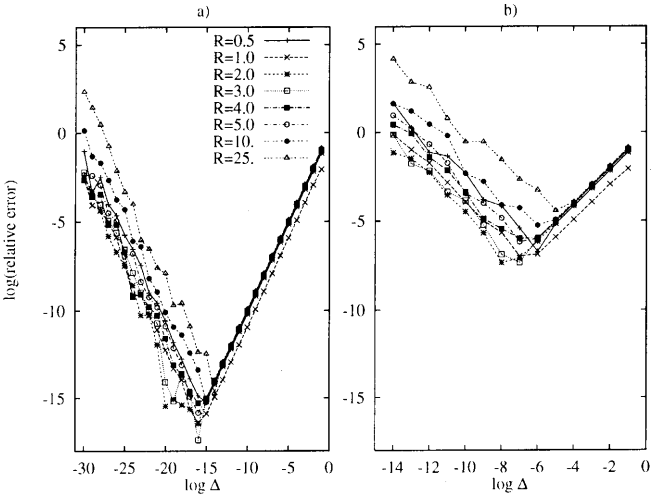

Fig. 2a, b Accuracy of Eq. (45) compared to the analytical solution Eq. (37) as a function of Δ for the integrals in Table 4. Note that both axes are logarithmic. **a** 128 bit double-precision variables and **b** 64 bit double-precision variables

Table 4. An unnormalised integral and its derivatives for various interatomic distances R. All values in atomic units. The digits in which the 64 bit values differ from the 128 bit values are underlined. In the column for the numerical derivatives the digits differing from the analytic values are overlined

R [a.u.]	$\langle 3p_y\|xz\|3d_{xy}\rangle$[a]		$\partial A_x\langle 3p_y\|xz\|3d_{xy}\rangle$[a]		
			Analytical, Eqs. (37) and (38)	Numerical, Eq. (45)	$-\log\Delta$
0.0[b]	64 bit:	$1.107391551149960 \times 10^{-00}$	$0.27684788778748998 \times 10^{+00}$	$0.27684788778747915 \times 10^{+00}$	3
	128 bit:	$1.107391551149959 \times 10^{-00}$	$0.27684788778748980 \times 10^{+00}$	$0.27684788778748980 \times 10^{+00}$	1, …, 16[c]
0.5	64 bit:	$1.074880332905100 \times 10^{-00}$	$0.60184248724280209 \times 10^{+00}$	$0.60184237771210292 \times 10^{+00}$	6
	128 bit:	$1.074880332905336 \times 10^{-00}$	$0.60184248724002855 \times 10^{+00}$	$0.60184248724002820 \times 10^{+00}$	15
1.0	64 bit:	$0.799575072849274 \times 10^{-00}$	$0.82863448843220899 \times 10^{+00}$	$0.82863457206983071 \times 10^{+00}$	7
	128 bit:	$0.799575072849282 \times 10^{-00}$	$0.82863448843214731 \times 10^{+00}$	$0.82863448843214734 \times 10^{+00}$	16
2.0	64 bit:	$0.248023186957969 \times 10^{-00}$	$0.39911100454010934 \times 10^{+00}$	$0.39911102200917981 \times 10^{+00}$	7
	128 bit:	$0.248023186957969 \times 10^{-00}$	$0.39911100454010168 \times 10^{+00}$	$0.39911100454010169 \times 10^{+00}$	16
3.0	64 bit:	$5.032281600899088 \times 10^{-02}$	$0.94261663714525712 \times 10^{-01}$	$0.94261659588923408 \times 10^{-01}$	7
	128 bit:	$5.032281600899074 \times 10^{-02}$	$0.94261663714524067 \times 10^{-01}$	$0.94261663714524068 \times 10^{-01}$	16
4.0	64 bit:	$8.253124448397308 \times 10^{-03}$	$0.16587687439802254 \times 10^{-01}$	$0.16587704161630246 \times 10^{-01}$	7
	128 bit:	$8.253124448398339 \times 10^{-03}$	$0.16587687439802685 \times 10^{-01}$	$0.16587687439802694 \times 10^{-01}$	16
5.0	64 bit:	$1.198420805761383 \times 10^{-03}$	$0.25046273743765256 \times 10^{-02}$	$0.25046289781754938 \times 10^{-02}$	7
	128 bit:	$1.198420805761296 \times 10^{-03}$	$0.25046273743778760 \times 10^{-02}$	$0.25046273743778757 \times 10^{-02}$	16
10.0	64 bit:	$3.464670984979476 \times 10^{-08}$	$0.77519948952131252 \times 10^{-07}$	$0.77520382904779132 \times 10^{-07}$	6
	128 bit:	$3.464670984986729 \times 10^{-08}$	$0.77519948952538339 \times 10^{-07}$	$0.77519948952538294 \times 10^{-07}$	15
25.0	64 bit:	$9.187009549920457 \times 10^{-23}$	$0.21248989391855453 \times 10^{-21}$	$0.21249781685337931 \times 10^{-21}$	5
	128 bit:	$9.187009551872945 \times 10^{-23}$	$0.21248989373179528 \times 10^{-21}$	$0.21248989373179487 \times 10^{-21}$	14

[a] Without normalisation, $\zeta_a = 2.3561$, $\zeta_b = 6.5197$. The Cartesian coordinates of A are {2,3,4}
[b] The one-centre integral and its derivatives have been calculated using Eqs. (11) and (35)
[c] This numeric derivative does not seem to depend on the value of Δ

The optimal Δ values and the corresponding numerical derivatives are shown in the last two columns of Table 4. In the numerically stable region, the relation between relative error and Δ exhibits nearly linearly decreasing behaviour in the double logarithmic plot (Fig. 2). The slope of this part is fairly independent of R and the word length. The numerical instability starts earlier with decreasing Δ the larger R becomes. This is not surprising as the integrals themselves approach zero. The important point is that unlike the analytical results, the word length influences the accuracy of the numerical derivatives by several orders of magnitude. Moreover, the minimum relative errors are reached for different Δs depending on R and word length. Thus, one should prefer the analytical procedure whenever possible.

4.2 Comparison to other methods

As mentioned earlier, a similar ansatz for the solution of electric multipole integrals has been proposed by Carbo and Besalu [38] and by Zheng and Zerner [39]. In the latter approach, the primitive electric operator $(i,j,k)_{\mathrm{O}}$ and the Cartesian monomials $(i,j,k)_{\mathrm{A}}$ of the spherical harmonic in χ_{A} are both translated into centre B. These translations are performed using master formulae, which have to be known explicitly for each operator and each orbital. After the translation, one is left with a linear combination of overlap integrals of s-type orbitals in A and orbitals with usually high angular momentum in B. The functions proposed by Zheng and Zerner are essentially special cases of the nonaugmented functions $\mathscr{I}_1$ and $\mathscr{I}_2$. Master formulae are not needed in the present derivation. The main problem with the use of master formulae is that they are not invariant to rotations of the coordinate system. For each LCS one has to find new master formulae. In the approach proposed here, the task of master formulae is taken over by the $\sum^{\mathrm{B}}$ symbols. In contrast to Zheng and Zerner but similar to Carbo and Besalu [38] we do not translate $(i,j,k)_{\mathrm{A}}$. Carbo and Besalu did not write the operators for two-centre integrals in terms of bi-focal coordinates but applied them directly to one of the orbitals. The main difference between their solution and the one proposed here, besides the functional form of the solutions, appears in the rotation of the results from the LCS into the MCS.

Fernandez Rico et al. [20] developed recurrence formulae for the calculation of two-centre one-electron integrals that result from the one-electron Hamiltonian. Their method involves the evaluation of infinite sums or sums of values close to zero depending on the values of their (x,y) parameters. Neither such sums nor master formulae are needed in the method presented in this contribution.

5. Conclusion

A new method for the calculation of arbitrary electric and magnetic multipole integrals has been developed. Only two functions, $\mathscr{I}_1^{\mathrm{aug}}$ and $\mathscr{I}_2^{\mathrm{aug}}$ for one- and two-centre integrals are needed for this purpose. Due to the introduction of AEs, $\mathscr{I}_1^{\mathrm{aug}}$ and $\mathscr{I}_2^{\mathrm{aug}}$ are widely applicable, as shown for the example of nuclear attraction integrals. The use of AEs in particular allows a completely analytical determination of the derivatives of all the integrals mentioned with respect to atomic displacements. Only one additional auxiliary function, $\mathscr{D}_2^{\mathrm{aug}}$, is needed for this purpose. $\mathscr{I}_1^{\mathrm{aug}}$, $\mathscr{I}_2^{\mathrm{aug}}$ and $\mathscr{D}_2^{\mathrm{aug}}$ reduce to standard integrals which are well known and broadly employed in integral evaluation with STOs.

The present approach does not involve the use of master formulae. The operators are translated implicitly. There is no translation of orbitals at all. The choice of the origin is totally free for all integrals and derivatives. Moreover, there are no infinite sums involved, so we do not need to worry about convergence radii. The method was implemented in a Fortran90 code which is numerically stable. The numerical values obtained in test calculations agree with those found in the literature for some of the relevant integrals.

Possible fields of application include the treatment of electronic as well as vibronic nonlinear spectroscopic effects and studies of higher electric and magnetic moments.

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Appendix

1 Basic integrals

The radial integral $\mathscr{R}$ is simply:

$$\mathscr{R}(k,\rho) = \int_{r=0}^{\infty} dr\, r^k \exp(-\rho r) = \frac{k!}{\rho^{k+1}} \quad . \tag{A1}$$

The solutions of the integrals over ϕ and θ are

$$\begin{aligned}\mathscr{F}(m,n) &= \int_{\phi=0}^{2\pi} d\phi \cos^m(\phi)\sin^m(\phi) \\ &= \begin{cases} F(m,n); & g(m) \wedge g(n) \\ 0; & \text{otherwise} \end{cases} .\end{aligned} \tag{A2}$$

$$\begin{aligned}\mathscr{G}(m,n) &= \int_{\theta=0}^{\pi} d\theta \cos^m(\theta)\sin^m(\theta) \\ &= \begin{cases} \frac{F(m,n)}{2}; & g(m) \wedge g(n) \\ G(m,n); & g(m) \wedge u(n) \\ 0; & \text{otherwise} \end{cases} .\end{aligned} \tag{A3}$$

In these equations, $\wedge$ denotes the Boolean "and". g is a Boolean function yielding "true" for even integer arguments ($u \mapsto \neg g$). F and G were taken from Ref. [39]:

$$F(m,n) := 2\pi \frac{(n-1)!!(m-1)!!}{(n+m)!!} \tag{A4}$$

$$G(m,n) := \frac{2^n}{n!}\frac{n!!(m-1)!!}{(n+m)!!}\left[\left(\frac{n-1}{2}\right)!\right]^2 \quad . \tag{A5}$$

A particularly useful relation for programming is

$$\mathscr{F}(m,n)\mathscr{G}(m,n+1) = F(m,n)G(m,n+1) \tag{A6}$$

which saves quite a few "if" statements.

2 The ∇- and $\mathbf{r}\times\nabla$-operators in elliptic bifocal coordinates

After some lengthy, but straightforward algebra, the gradient operator with respect to the LCS depicted in Fig. 1b reads:

$$\nabla = \begin{pmatrix} \frac{2\mu S\cos(\phi)}{(\mu^2-v^2)R}\partial_\mu + \frac{2vS\cos(\phi)}{(-\mu^2+v^2)R}\partial_v - \frac{2\sin(\phi)}{SR}\partial_\phi \\ \frac{2\mu S\sin(\phi)}{(\mu^2-v^2)R}\partial_\mu + \frac{2vS\sin(\phi)}{(-\mu^2+v^2)R}\partial_v + \frac{2\cos(\phi)}{SR}\partial_\phi \\ \frac{2(1-\mu^2)v}{(-\mu^2+v^2)R}\partial_\mu + \frac{2\mu(-1+v^2)}{(-\mu^2+v^2)R}\partial_v \end{pmatrix} , \tag{A7}$$

where $S = \sqrt{-1+\mu^2}\,\sqrt{1-v^2}$. The angular momentum operator, $\mathbf{r}\times\nabla$, with $\mathbf{r}$ defined with respect to B, aquires the form:

$$\mathbf{l} = i\hbar \begin{pmatrix} \frac{-P\sin(\phi)\partial_\mu + P\sin(\phi)\partial_v + P'\cos(\phi)\partial_\phi}{S(\mu-v)} \\ \frac{P\cos(\phi)\partial_\mu - P\cos(\phi)\partial_v + P'\sin(\phi)\partial_\phi}{S(\mu-v)} \\ -\partial_\phi \end{pmatrix} , \tag{A8}$$

with $P = (1-v^2-\mu^2+\mu^2v^2)$ and $P' = (\mu - v + \mu^2 v - \mu v^2)$. Although this operator seems to be rather simple, it acquires quite a bit of length and complexity when $\mathbf{r}$ is defined with respect to an origin outside the line joining A and B. Therefore, we did not use Eq. (A8), for the evaluation of magnetic two-centre integrals.

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