Recurrence Relations for Four-Electron Integrals Over Gaussian Basis Functions

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Abstract

In the spirit of the Head-Gordon–Pople algorithm, we report vertical, transfer, and horizontal recurrence relations for the efficient and accurate computation of four-electron integrals over Gaussian basis functions. Our recursive approach is a generalization of our algorithm for three-electron integrals (Barca et al., 2016). The RRs derived in the present study can be applied to a general class of multiplicative four-electron operators. In particular, we consider various types of four-electron integrals that may arise in explicitly correlated F12 methods.

1. INTRODUCTION

In 1985, starting from the Hylleraas functional[1–3] and using the inter-electronic distance $r_{12} = |r_1 - r_2|$ as a correlation factor, Kutzelnigg derived

the seminal form of the MP2-R12 equations.[4] This explicitly correlated method (more formally stated together with Klopper in 1987[5]) was later extended to higher level of theory and more accurate correlation factors $f_{12} = f(r_{12})$,[6–15] such as Gaussian geminals

$$f_{12} = \exp\left(-\lambda r_{12}^2\right), \tag{1}$$

or Slater geminals

$$f_{12} = \exp\left(-\lambda r_{12}\right). \tag{2}$$

The resulting "F12 methods" achieve chemical accuracy for small organic molecules with relatively small Gaussian basis sets[16–21] and are quickly becoming the first-choice method for high accuracy.[19,20]

However, the inclusion of the correlation factor f_{12} dredged up an old problem: in addition to two-electron integrals (traditional ones and new ones), three-electron integrals over $f_{13}f_{23}$, $r_{12}^{-1}f_{13}$, and $r_{12}^{-1}f_{13}f_{23}$, as well as four-electron integrals over $r_{12}^{-1}f_{14}f_{23}$, $r_{12}^{-1}f_{13}f_{34}$, and $r_{12}^{-1}f_{13}f_{14}$ arise. These integrals are not known analytically except when Gaussian geminals are used,[22,23] and, at that time, the only way to evaluate them would have been via expensive Gauss–Legendre quadratures.[24,25] Additionally, citing Kutzelnigg and Klopper,[26] "even if fast procedures for the evaluation of these integrals were available, one would have to face the problem of the large number of these integrals; while that of two-electron integrals is $\sim N^4$, there are $\sim N^6$ three-electron and $\sim N^8$ four-electron integrals. The storing and manipulating of these integrals could be handled only for extremely small basis sets."

Undoubtedly, in the late 1980s, the two-electron integrals technology was still in development.[27–34] Nowadays, though still challenging, these integrals could be computed much more effectively via judicious recursive schemes, designing the quadrature only to the fundamental integrals.[35] Another important remark is that the actual number of significant (i.e., greater than a given threshold) three- and four-electron integrals in a large system, is, at worst, $\mathcal{O}(N^3)$ or $\mathcal{O}(N^4)$. Such scaling results, e.g., by exploiting robust density fitting[36] or upper bound-based screening methods.[37]

Nevertheless, the success of the R12 method was due to the decision of avoiding three- and four-electron integrals entirely through the insertion of the resolution of the identity (RI)[17,26,38]

$$\hat{I} \approx \sum_{\mu}^{N_{RI}} |\chi_{\mu}\rangle\langle\chi_{\mu}|. \tag{3}$$

In this way, three- and four-electron integrals are approximated as linear combinations of products of more conventional two-electron integrals. Of course, the accuracy of the RI approximation (3) relies entirely on the assumption that the auxiliary basis set is sufficiently large ($N_{RI} \gg N$). Thus, in the general context of explicitly correlated methods, it is licit to ask: what is the suitable method to evaluate three- and four-electron integrals?

The use of RI as method of choice does not seem definitive to us. In fact, eschewing the RI approximation would offer at least two advantages:

(i) smaller one-electron basis as the larger auxiliary basis set would not be required anymore;

(ii) the three- and four-electron integrals would be computed exactly.

Moreover, one could avoid the commutator rearrangements involved in the computation of integrals over the kinetic energy operator.[39]

In a recent paper,[35] we reported recurrence relations (RRs) to compute three-electron integrals over Gaussian basis functions for multiplicative general operators of the form $f_{12}g_{13}h_{23}$. Here, we generalize our previous study to four-electron integrals.

The present chapter is organized as follows. In Section 2, we introduce notations and we define various key quantities. Section 3 explains how to calculate fundamental integrals required to start the recursive scheme. In Section 4, we reports vertical, transfer, and horizontal RRs for four-electron integrals. Finally, in Section 5, we propose a recursive scheme based on these RRs to calculate classes of four-electron integrals. Atomic units are used throughout.

2. FOUR-ELECTRON INTEGRALS

A primitive Gaussian-type function (PGF) is specified by an orbital exponent α, a center $\mathbf{A} = (A_x, A_y, A_z)$, and angular momentum $\boldsymbol{a} = (a_x, a_y, a_z)$:

$$\varphi_{\boldsymbol{a}}^{\mathbf{A}}(\boldsymbol{r}) = (x - A_x)^{a_x}(y - A_y)^{a_y}(z - A_z)^{a_z}e^{-\alpha|\boldsymbol{r}-\mathbf{A}|^2}. \tag{4}$$

A contracted Gaussian-type function (CGF) is defined as a normalized sum of PGFs

$$\psi_a^{\mathbf{A}}(\mathbf{r}) = \sum_{k=1}^{K_A} D_{ak}(x - A_x)^{a_x}(y - A_y)^{a_y}(z - A_z)^{a_z} e^{-\alpha_k|\mathbf{r}-\mathbf{A}|^2}, \tag{5}$$

where K_A is the degree of contraction and the D_{ak} are contraction coefficients. Throughout this chapter, we use physicist's notations, and we write the integral over a four-electron operator f_{1234} of CGFs as

$$\langle a_1 a_2 a_3 a_4 | b_1 b_2 b_3 b_4 \rangle \equiv \langle a_1 a_2 a_3 a_4 | f_{1234} | b_1 b_2 b_3 b_4 \rangle$$
$$= \iiint \psi_{a_1}^{\mathbf{A}_1}(\mathbf{r}_1)\psi_{a_2}^{\mathbf{A}_2}(\mathbf{r}_2)\psi_{a_3}^{\mathbf{A}_3}(\mathbf{r}_3)\psi_{a_4}^{\mathbf{A}_4}(\mathbf{r}_4) f_{1234} \psi_{b_1}^{\mathbf{B}_1}(\mathbf{r}_1) \quad (6)$$
$$\psi_{b_2}^{\mathbf{B}_2}(\mathbf{r}_2)\psi_{b_3}^{\mathbf{B}_3}(\mathbf{r}_3)\psi_{b_4}^{\mathbf{B}_4}(\mathbf{r}_4) d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4.$$

Additionally, square-bracketed integrals denote integrals over PGFs:

$$[a_1 a_2 a_3 a_4 | b_1 b_2 b_3 b_4] \equiv [a_1 a_2 a_3 a_4 | f_{1234} | b_1 b_2 b_3 b_4]$$
$$= \iiint \varphi_{a_1}^{\mathbf{A}_1}(\mathbf{r}_1)\varphi_{a_2}^{\mathbf{A}_2}(\mathbf{r}_2)\varphi_{a_3}^{\mathbf{A}_3}(\mathbf{r}_3)\varphi_{a_4}^{\mathbf{A}_4}(\mathbf{r}_4) f_{1234} \varphi_{b_1}^{\mathbf{B}_1}(\mathbf{r}_1) \quad (7)$$
$$\varphi_{b_2}^{\mathbf{B}_2}(\mathbf{r}_2)\varphi_{b_3}^{\mathbf{B}_3}(\mathbf{r}_3)\varphi_{b_4}^{\mathbf{B}_4}(\mathbf{r}_4) d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4.$$

The fundamental integral (i.e., the integral in which all eight basis functions are s-type PGFs) is defined as $[\mathbf{0}] \equiv [0000|0000]$ with $\mathbf{0} = (0,0,0)$. The Gaussian product rule reduces it from eight to four centers:

$$[\mathbf{0}] = S_1 S_2 S_3 S_4 \iiint \varphi_{\mathbf{0}}^{\mathbf{Z}_1}(\mathbf{r}_1)\varphi_{\mathbf{0}}^{\mathbf{Z}_2}(\mathbf{r}_2)\varphi_{\mathbf{0}}^{\mathbf{Z}_3}(\mathbf{r}_3)\varphi_{\mathbf{0}}^{\mathbf{Z}_4}(\mathbf{r}_4) f_{1234} d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4, \tag{8}$$

where

$$\zeta_i = \alpha_i + \beta_i, \quad \mathbf{Z}_i = \frac{\alpha_i \mathbf{A}_i + \beta_i \mathbf{B}_i}{\zeta_i}, \quad S_i = \exp\left(-\frac{\alpha_i \beta_i}{\zeta_i}|\mathbf{A}_i\mathbf{B}_i|^2\right), \tag{9}$$

with $\mathbf{A}_i\mathbf{B}_i = \mathbf{A}_i - \mathbf{B}_i$. For conciseness, we will adopt a notation in which missing indices represent s-type Gaussians. For example, $[a_2 a_3]$ is a shorthand for $[0a_2 a_3 0|0000]$. We will also use unbold indices, e.g., $[a_1 a_2 a_3 a_4 | b_1 b_2 b_3 b_4]$ to indicate a complete class of integrals from a shell–octet.

2.1 Four-Electron Operators

In the present study, we are particularly interested in the four-electron operators $g_{13}h_{23}i_{34}$ (trident) and $f_{12}h_{23}i_{34}$ (four-electron chain or 4-chain) because they can be required in explicitly correlated methods such as F12

methods.[17–20] Explicitly correlated calculations may also require three–electron integrals over the (3-chain) $f_{12}h_{23}$ and (cyclic) $f_{12}g_{13}h_{23}$ operators, as well as two–electron integrals over f_{12}. However, we will eschew the study of the two–electron integrals here as they have been extensively studied in the past 25 years.[11,13,15,26,40–49] Note that the nuclear attraction integrals can be easily obtained by taking the large-exponent limit of a s-type shell–pair. We refer the interested reader to Refs. 34 and 50 for more details about the computation of nuclear attraction integrals.

The structure of these operators is illustrated in Fig. 1, where we have adopted a diagrammatic representation. Starting with the "pacman" opera–tor $f_{12}g_{13}h_{23}i_{34}$, we are going to show that one can easily derive all the RRs required to compute two-, three-, and four-electron integrals following simple rules. Therefore, in the following, we will focus our analysis on this master "pacman" operator.
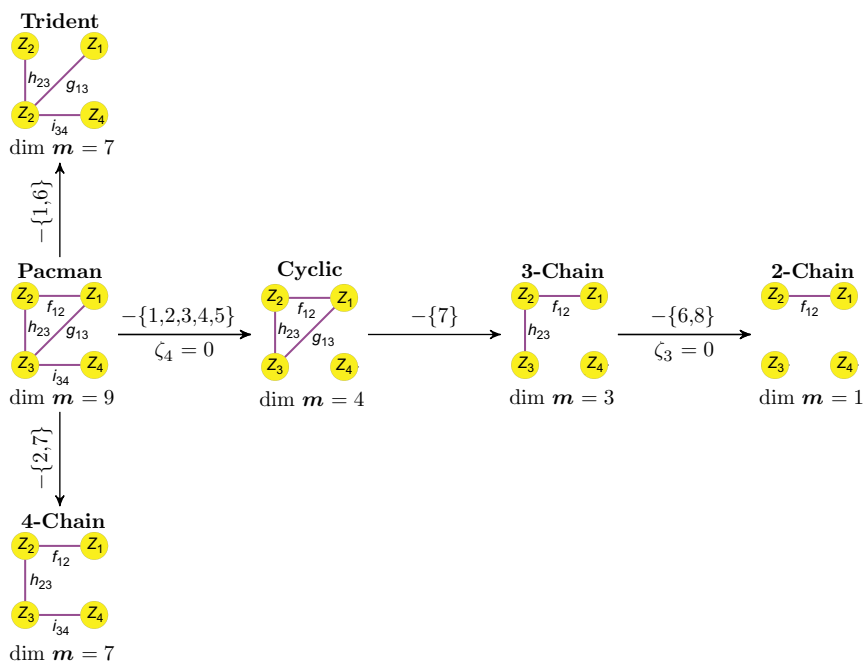

Fig. 1 Diagrammatic representation of various four-, three-, and two-electron integrals involved in explicitly correlated methods. dim m refers to the dimensionality of the aux-iliary index m (see Eq. (15)). The values in the *curly brackets* indicate which components of the auxiliary index vector m must be removed.

3. FUNDAMENTAL INTEGRALS

The first step required to compute integrals of arbitrary angular momentum is the computation of the (momentumless) fundamental integrals [0]. These are derived starting from Eq. (8) using the Gaussian integral representation of each two-electron operator. For instance, we have

$$f_{12} = \int_0^\infty F(t_{12}) \exp\left(-t_{12}^2 r_{12}^2\right) dt_{12}, \tag{10}$$

where $F(t_{12})$ is a Gaussian kernel. Table 1 contains kernels $F(t)$ for a variety of important two-electron operators f_{12}. From the formulas in Table 1, one can also easily deduce the kernels for related functions, such as f_{12}^2, f_{12}/r_{12}, and $\nabla^2 f_{12}$, which are of interest in explicitly correlated methods. More general kernels can be found in Ref. 35.

Next, the integration over r_1, r_2, r_3, and r_4 can be carried out, yielding

$$[0] = S_1 S_2 S_3 S_4 \iiiint F(t_{12}) \, G(t_{13}) \, H(t_{23}) \, I(t_{34}) \, w_0(t) \, dt, \tag{11}$$

Table 1 Kernels $F(t)$ of the Gaussian Integral Representation for Various f_{12} Operators

f_{12}	$F(t)$
1	$\delta(t)$
r_{12}^{-1}	$2/\sqrt{\pi}$
r_{12}^{-2}	$2t$
$(r_{12}^2 + \lambda^2)^{-1/2}$	$(2/\sqrt{\pi}) \exp\left(-\lambda^2 t^2\right)$
$\exp(-\lambda\, r_{12})$	$(\lambda\, t^{-2}/\pi) \exp\left(-\lambda^2 t^{-2}/4\right)$
$r_{12}^{-1} \exp(-\lambda\, r_{12})$	$(2/\sqrt{\pi}) \exp\left(-\lambda^2 t^{-2}/4\right)$
$\exp\left(-\lambda^2 r_{12}^2\right)$	$\delta(t - \lambda)$
$r_{12}^{-1} \mathrm{erfc}(\lambda\, r_{12})$	$(2/\sqrt{\pi}) \, \theta(t - \lambda)$
$r_{12}^{-1} \mathrm{erf}(\lambda\, r_{12})$	$(2/\sqrt{\pi})[1 - \theta(t - \lambda)]$

$\delta(x)$ and $\theta(x)$ are, respectively, the Dirac delta and Heaviside step functions, and $\mathrm{erf}(x)$ and $\mathrm{erfc}(x)$ are the error function and its complement version, respectively.[51]

where $t = (t_{12}, t_{13}, t_{23}, t_{34})$ and

$$w_0(t) = \left(\frac{\pi^4}{D(t)}\right)^{3/2} \exp\left[-\frac{N(t)}{D(t)}\right]. \tag{12}$$

Defining the following polynomials

$$s_1 = t_{12}^2, \quad s_2 = t_{13}^2, \qquad\qquad s_3 = t_{23}^2, \tag{13a}$$
$$s_4 = t_{34}^2, \quad s_5 = t_{12}^2 t_{13}^2 + t_{12}^2 t_{23}^2 + t_{13}^2 t_{23}^2, \quad s_6 = t_{12}^2 t_{34}^2, \tag{13b}$$
$$s_7 = t_{13}^2 t_{34}^2, \quad s_8 = t_{23}^2 t_{34}^2, \qquad\qquad s_9 = t_{12}^2 t_{13}^2 t_{34}^2 + t_{12}^2 t_{23}^2 t_{34}^2 + t_{13}^2 t_{23}^2 t_{34}^2, \tag{13c}$$

we have

$$\begin{aligned}
D(t) &= \zeta_1\zeta_2\zeta_3\zeta_4 + (\zeta_1 + \zeta_2)\zeta_3\zeta_4 s_1 + \zeta_2\zeta_4(\zeta_1 + \zeta_3)s_2 \\
&\quad + \zeta_1\zeta_4(\zeta_2 + \zeta_3)s_3 + \zeta_1\zeta_2(\zeta_3 + \zeta_4)s_4 + \zeta_4(\zeta_1 + \zeta_2 + \zeta_3)s_5 \\
&\quad + (\zeta_1 + \zeta_2)(\zeta_3 + \zeta_4)s_6 + \zeta_2(\zeta_1 + \zeta_3 + \zeta_4)s_7 \\
&\quad + \zeta_1(\zeta_2 + \zeta_3 + \zeta_4)s_8 + (\zeta_1 + \zeta_2 + \zeta_3 + \zeta_4)s_9,
\end{aligned} \tag{14a}$$

$$\begin{aligned}
N(t) &= \zeta_3\zeta_4\kappa_{12}s_1 + \zeta_2\zeta_4\kappa_{13}s_2 + \zeta_1\zeta_4\kappa_{23}s_3 \\
&\quad + \zeta_1\zeta_2\kappa_{34}s_4 + \zeta_4(\kappa_{12} + \kappa_{13} + \kappa_{23})s_5 + [(\zeta_3 + \zeta_4)\kappa_{12} + (\zeta_1 + \zeta_2)\kappa_{34}]s_6 \\
&\quad + \zeta_2(\kappa_{13} + \kappa_{14} + \kappa_{34})s_7 + \zeta_1(\kappa_{23} + \kappa_{24} + \kappa_{34})s_8 \\
&\quad + (\kappa_{12} + \kappa_{13} + \kappa_{14} + \kappa_{23} + \kappa_{24} + \kappa_{34})s_9,
\end{aligned} \tag{14b}$$

where $\kappa_{ij} = \zeta_i\zeta_j |\mathbf{Z}_i - \mathbf{Z}_j|^2$.

Following Obara and Saika,[32,52] vertical RRs (VRRs) are obtained by differentiation of Eq. (11) with respect to the center coordinates. Therefore, one can show that (11) has to be generalized to the following form:

$$[\mathbf{0}]^m = S_1 S_2 S_3 S_4 \iiiint F(t_{12})\, G(t_{13})\, H(t_{23})\, I(t_{34})\, w_m(t)\, dt, \tag{15}$$

where $m = (m_1, m_2, m_3, m_4, m_5, m_6, m_7, m_8, m_9)$ is, for the pacman operator, a nine-dimensional auxiliary index, and

$$w_m(t) = w_0(t) \prod_{k=1}^{\dim m} \left[\frac{s_k}{D(t)}\right]^{m_k}. \tag{16}$$

As reported in Fig. 1, while the fundamental integrals of the pacman operator contains 9 auxiliary indices (i.e., $\dim m = 9$), the two interesting

four-electron operators (trident and chain) contains 7. The cyclic and chain three-electron operators have only four and three, respectively, while the two-electron chain operator has a single m component (i.e., dim $\boldsymbol{m} = 1$). These numbers are drastically reduced if one uses Gaussian geminals due to their factorization properties.[53]

4. RECURRENCE RELATIONS

In this section, we report vertical, transfer, and horizontal RRs for the computation of four-electron integrals of arbitrary angular momentum. In particular, we refer the interested readers to the appendix of Ref. 35 for more details about how to derive these VRRs following the late R. Ahlrichs.[54]

4.1 Vertical Recurrence Relations

To build angular momentum over center $\mathbf{A}_1$, we have derived the following 24-term VRR:

$$
\begin{aligned}
[a_1^+ a_2 a_3 a_4]^{\boldsymbol{m}} = {} & \mathbf{Z}_1 \mathbf{A}_1 [a_1 a_2 a_3 a_4]^{\boldsymbol{m}} - \zeta_2 \zeta_3 \zeta_4 \mathbf{Z}_{12} [a_1 a_2 a_3 a_4]^{\{1\}} \\
& - \zeta_2 \zeta_3 \zeta_4 \mathbf{Z}_{13} [a_1 a_2 a_3 a_4]^{\{2\}} - \zeta_4 (\zeta_2 \mathbf{Z}_{12} + \zeta_3 \mathbf{Z}_{13}) [a_1 a_2 a_3 a_4]^{\{5\}} \\
& - \zeta_2 (\zeta_3 + \zeta_4) \mathbf{Z}_{12} [a_1 a_2 a_3 a_4]^{\{6\}} - \zeta_2 (\zeta_3 \mathbf{Z}_{13} + \zeta_4 \mathbf{Z}_{14}) [a_1 a_2 a_3 a_4]^{\{7\}} \\
& - (\zeta_2 \mathbf{Z}_{12} + \zeta_3 \mathbf{Z}_{13} + \zeta_4 \mathbf{Z}_{14}) [a_1 a_2 a_3 a_4]^{\{9\}} \\
& + \frac{a_1}{2\zeta_1} \Big\{ [a_1^- a_2 a_3 a_4]^{\boldsymbol{m}} - \zeta_2 \zeta_3 \zeta_4 \mathbf{Z}_{12} [a_1^- a_2 a_3 a_4]^{\{1\}} \\
& - \zeta_2 \zeta_3 \zeta_4 \mathbf{Z}_{13} [a_1^- a_2 a_3 a_4]^{\{2\}} - \zeta_4 (\zeta_2 + \zeta_3) [a_1^- a_2 a_3 a_4]^{\{5\}} \\
& - \zeta_2 (\zeta_3 + \zeta_4) [a_1^- a_2 a_3 a_4]^{\{6\}} - \zeta_2 (\zeta_3 + \zeta_4) [a_1^- a_2 a_3 a_4]^{\{7\}} \\
& - (\zeta_2 + \zeta_3 + \zeta_4) [a_1^- a_2 a_3 a_4]^{\{9\}} \Big\} \\
& + \frac{a_2}{2} \Big\{ \zeta_3 \zeta_4 [a_1 a_2^- a_3 a_4]^{\{1\}} + \zeta_4 [a_1 a_2^- a_3 a_4]^{\{5\}} \\
& + (\zeta_3 + \zeta_4) [a_1 a_2^- a_3 a_4]^{\{6\}} + [a_1 a_2^- a_3 a_4]^{\{9\}} \Big\} \\
& + \frac{a_3}{2} \Big\{ \zeta_2 \zeta_4 [a_1 a_2 a_3^- a_4]^{\{2\}} + \zeta_4 [a_1 a_2 a_3^- a_4]^{\{5\}} \\
& + \zeta_2 [a_1 a_2 a_3^- a_4]^{\{7\}} + [a_1 a_2 a_3^- a_4]^{\{9\}} \Big\} \\
& + \frac{a_4}{2} \Big\{ \zeta_2 [a_1 a_2 a_3 a_4^-]^{\{7\}} + [a_1 a_2 a_3 a_4^-]^{\{9\}} \Big\},
\end{aligned}
$$

$$\tag{17}$$

where the superscript $+$ or $-$ denotes an increment or decrement of one unit of Cartesian angular momentum. (Thus, $a^{\pm}$ is analogous to $a \pm 1_i$ in the notation of Obara and Saika.) The value in the curly superscript indicates which component of the auxiliary index vector m is incremented.

Because Eq. (17) builds angular momentum over $\mathbf{A}_1$ and all four bra centers have nonzero angular momentum, we will call this expression $\mathrm{VRR}_4^{\mathbf{A}_1}$. The VRRs used to obtain $[a_1^+ a_2 a_3]^m$, $[a_1^+ a_2]^m$, and $[a_1^+]^m$ can be easily derived from Eq. (17) by setting successively $a_4 = 0$, $a_3 = 0$, and $a_2 = 0$. These are, respectively, named $\mathrm{VRR}_3^{\mathbf{A}_1}$, $\mathrm{VRR}_2^{\mathbf{A}_1}$, and $\mathrm{VRR}_1^{\mathbf{A}_1}$.

One can easily derive VRR_4 for the trident and 4-chain operators following the simple rules given in Fig. 1. We obtain the VRRs for the trident operator by removing the terms {1} and {6}. Similarly, 4-chain VRRs are obtained by removing the terms {2} and {7}. This yields an 18- and 17-term $\mathrm{VRR}_4^{\mathbf{A}_1}$ for the trident and 4-chain operators, respectively.

$\mathrm{VRR}_4^{\mathbf{A}_2}$, $\mathrm{VRR}_4^{\mathbf{A}_3}$, and $\mathrm{VRR}_4^{\mathbf{A}_4}$ are used to build angular momentum over $\mathbf{A}_2$, $\mathbf{A}_3$, and $\mathbf{A}_4$, respectively. Their expressions are

$$
\begin{aligned}
[a_1 a_2^+ a_3 a_4]^m =\ & \mathbf{Z}_2 \mathbf{A}_2 [a_1 a_2 a_3 a_4]^m + \zeta_1 \zeta_3 \zeta_4 \mathbf{Z}_{12} [a_1 a_2 a_3 a_4]^{\{1\}} \\
& - \zeta_1 \zeta_3 \zeta_4 \mathbf{Z}_{23} [a_1 a_2 a_3 a_4]^{\{3\}} + \zeta_4 (\zeta_1 \mathbf{Z}_{12} - \zeta_3 \mathbf{Z}_{23}) [a_1 a_2 a_3 a_4]^{\{5\}} \\
& + \zeta_1 (\zeta_3 + \zeta_4) \mathbf{Z}_{12} [a_1 a_2 a_3 a_4]^{\{6\}} - \zeta_1 (\zeta_3 \mathbf{Z}_{23} + \zeta_4 \mathbf{Z}_{24}) [a_1 a_2 a_3 a_4]^{\{8\}} \\
& + (\zeta_1 \mathbf{Z}_{12} - \zeta_3 \mathbf{Z}_{23} - \zeta_4 \mathbf{Z}_{24}) [a_1 a_2 a_3 a_4]^{\{9\}} \\
& + \frac{a_2}{2\zeta_2} \Big\{ [a_1 a_2^- a_3 a_4]^m - \zeta_1 \zeta_3 \zeta_4 [a_1 a_2^- a_3 a_4]^{\{1\}} - \zeta_1 \zeta_3 \zeta_4 [a_1 a_2^- a_3 a_4]^{\{3\}} \\
& \qquad - \zeta_4 (\zeta_1 - \zeta_3) [a_1 a_2^- a_3 a_4]^{\{5\}} + \zeta_1 (\zeta_3 + \zeta_4) [a_1 a_2^- a_3 a_4]^{\{6\}} \\
& \qquad - \zeta_1 (\zeta_3 + \zeta_4) [a_1 a_2^- a_3 a_4]^{\{8\}} - (\zeta_1 + \zeta_3 + \zeta_4) [a_1 a_2^- a_3 a_4]^{\{9\}} \Big\} \\
& + \frac{a_1}{2} \Big\{ \zeta_3 \zeta_4 [a_1^- a_2 a_3 a_4]^{\{1\}} + \zeta_4 [a_1^- a_2 a_3 a_4]^{\{5\}} \\
& \qquad + (\zeta_3 + \zeta_4) [a_1^- a_2 a_3 a_4]^{\{6\}} + [a_1^- a_2 a_3 a_4]^{\{9\}} \Big\} \\
& + \frac{a_3}{2} \Big\{ \zeta_1 \zeta_4 [a_1 a_2 a_3^- a_4]^{\{3\}} + \zeta_4 [a_1 a_2 a_3^- a_4]^{\{5\}} \\
& \qquad + \zeta_1 [a_1 a_2 a_3^- a_4]^{\{8\}} + [a_1 a_2 a_3^- a_4]^{\{9\}} \Big\} \\
& + \frac{a_4}{2} \Big\{ \zeta_1 [a_1 a_2 a_3 a_4^-]^{\{8\}} + [a_1 a_2 a_3 a_4^-]^{\{9\}} \Big\},
\end{aligned}
$$

(18)

$$[a_1 a_2 a_3^{+} a_4]^{m} = \mathbf{Z}_3 \mathbf{A}_3 [a_1 a_2 a_3 a_4]^{m}$$

$$+\zeta_1 \zeta_2 \zeta_4 \mathbf{Z}_{13}[a_1 a_2 a_3 a_4]^{\{2\}} + \zeta_1 \zeta_2 \zeta_4 \mathbf{Z}_{23}[a_1 a_2 a_3 a_4]^{\{3\}}$$

$$+\zeta_1 \zeta_2 \zeta_4 \mathbf{Z}_{34}[a_1 a_2 a_3 a_4]^{\{4\}} + \zeta_4(\zeta_1 \mathbf{Z}_{13} + \zeta_2 \mathbf{Z}_{23})[a_1 a_2 a_3 a_4]^{\{5\}}$$

$$-\zeta_4(\zeta_1 + \zeta_2)\mathbf{Z}_{34}[a_1 a_2 a_3 a_4]^{\{6\}} + \zeta_2(\zeta_1 \mathbf{Z}_{13} - \zeta_4 \mathbf{Z}_{34})[a_1 a_2 a_3 a_4]^{\{7\}}$$

$$+\zeta_1(\zeta_2 \mathbf{Z}_{23} - \zeta_4 \mathbf{Z}_{34})[a_1 a_2 a_3 a_4]^{\{8\}}$$

$$+(\zeta_1 \mathbf{Z}_{13} + \zeta_2 \mathbf{Z}_{23} - \zeta_4 \mathbf{Z}_{34})[a_1 a_2 a_3 a_4]^{\{9\}}$$

$$+\frac{a_3}{2\zeta_3}\Big\{[a_1 a_2 a_3^{-} a_4]^{m} - \zeta_1 \zeta_2 \zeta_4 [a_1 a_2 a_3^{-} a_4]^{\{2\}} - \zeta_1 \zeta_2 \zeta_4 [a_1 a_2 a_3^{-} a_4]^{\{3\}}$$

$$-\zeta_1 \zeta_2 \zeta_4 [a_1 a_2 a_3^{-} a_4]^{\{4\}} - \zeta_4(\zeta_1 + \zeta_2)[a_1 a_2 a_3^{-} a_4]^{\{5\}}$$

$$-\zeta_4(\zeta_1 + \zeta_2)[a_1 a_2 a_3^{-} a_4]^{\{6\}} - \zeta_2(\zeta_1 + \zeta_4)[a_1 a_2 a_3^{-} a_4]^{\{7\}}$$

$$-\zeta_1(\zeta_2 + \zeta_4)[a_1 a_2 a_3^{-} a_4]^{\{8\}} - (\zeta_1 + \zeta_2 + \zeta_4)[a_1 a_2 a_3^{-} a_4]^{\{9\}}\Big\}$$

$$+\frac{a_1}{2}\Big\{\zeta_2 \zeta_4 [a_1^{-} a_2 a_3 a_4]^{\{2\}} + \zeta_4 [a_1^{-} a_2 a_3 a_4]^{\{5\}}$$

$$+\zeta_2 [a_1^{-} a_2 a_3 a_4]^{\{7\}} + [a_1^{-} a_2 a_3 a_4]^{\{9\}}\Big\}$$

$$+\frac{a_2}{2}\Big\{\zeta_1 \zeta_4 [a_1 a_2^{-} a_3 a_4]^{\{3\}} + \zeta_4 [a_1 a_2^{-} a_3 a_4]^{\{5\}}$$

$$+\zeta_1 [a_1 a_2^{-} a_3 a_4]^{\{8\}} + [a_1 a_2^{-} a_3 a_4]^{\{9\}}\Big\}$$

$$+\frac{a_4}{2}\Big\{\zeta_1 \zeta_2 [a_1 a_2 a_3 a_4^{-}]^{\{4\}} + (\zeta_1 + \zeta_2)[a_1 a_2 a_3 a_4^{-}]^{\{6\}}$$

$$+\zeta_2 [a_1 a_2 a_3 a_4^{-}]^{\{7\}} + \zeta_1 [a_1 a_2 a_3 a_4^{-}]^{\{8\}} + [a_1 a_2 a_3 a_4^{-}]^{\{9\}}\Big\}$$

$$(19)$$

$$[a_1 a_2 a_3 a_4^{+}]^{m} = \mathbf{Z}_4 \mathbf{A}_4 [a_1 a_2 a_3 a_4]^{m} + \zeta_1 \zeta_2 \zeta_3 \mathbf{Z}_{34}[a_1 a_2 a_3 a_4]^{\{4\}}$$

$$+\zeta_3(\zeta_1 + \zeta_2)\mathbf{Z}_{34}[a_1 a_2 a_3 a_4]^{\{6\}} + \zeta_2(\zeta_1 \mathbf{Z}_{14} + \zeta_3 \mathbf{Z}_{34})[a_1 a_2 a_3 a_4]^{\{7\}}$$

$$+\zeta_1(\zeta_2 \mathbf{Z}_{24} + \zeta_3 \mathbf{Z}_{34})[a_1 a_2 a_3 a_4]^{\{8\}}$$

$$+(\zeta_1 \mathbf{Z}_{14} + \zeta_2 \mathbf{Z}_{24} + \zeta_3 \mathbf{Z}_{34})[a_1 a_2 a_3 a_4]^{\{9\}}$$

$$+\frac{a_4}{2\zeta_4}\Big\{[a_1 a_2 a_3 a_4^{-}]^{m} - \zeta_1 \zeta_2 \zeta_3 [a_1 a_2 a_3 a_4^{-}]^{\{4\}}$$

$$-\zeta_3(\zeta_1 + \zeta_2)[a_1 a_2 a_3 a_4^{-}]^{\{6\}} - \zeta_2(\zeta_1 + \zeta_3)[a_1 a_2 a_3 a_4^{-}]^{\{7\}}$$

$$-\zeta_1(\zeta_2 + \zeta_3)[a_1 a_2 a_3 a_4^{-}]^{\{8\}} - (\zeta_1 + \zeta_2 + \zeta_3)[a_1 a_2 a_3 a_4^{-}]^{\{9\}}\Big\}$$

$$+\frac{a_1}{2}\Big\{\zeta_2 [a_1^{-} a_2 a_3 a_4]^{\{7\}} + [a_1^{-} a_2 a_3 a_4]^{\{9\}}\Big\}$$

$$+\frac{a_2}{2}\Big\{\zeta_1 [a_1 a_2^{-} a_3 a_4]^{\{8\}} + [a_1 a_2^{-} a_3 a_4]^{\{9\}}\Big\}$$

$$+\frac{a_3}{2}\Big\{\zeta_1 \zeta_2 [a_1 a_2 a_3^{-} a_4]^{\{4\}} + (\zeta_1 + \zeta_2)[a_1 a_2 a_3^{-} a_4]^{\{6\}}$$

$$+\zeta_2 [a_1 a_2 a_3^{-} a_4]^{\{7\}} + \zeta_1 [a_1 a_2 a_3^{-} a_4]^{\{8\}} + [a_1 a_2 a_3^{-} a_4]^{\{9\}}\Big\}$$

$$(20)$$

Fig. 2 Graph representation of the VRRs for the 3-chain $f_{12}h_{23}$ (*top left*), cyclic $f_{12}g_{13}h_{23}$ (*top right*), 4-chain $f_{12}h_{23}i_{34}$ (*bottom left*), and trident $g_{13}h_{23}i_{34}$ (*bottom right*) operators. The *edge label* gives the number of terms in the corresponding VRR. The *red path* corresponds to the algorithm generating the smallest number of intermediates.

Again, the corresponding expressions for VRR_1, VRR_2, and VRR_3 can be easily derived from Eqs. (18), (19), and (20). The number of terms for each of these VRRs is reported in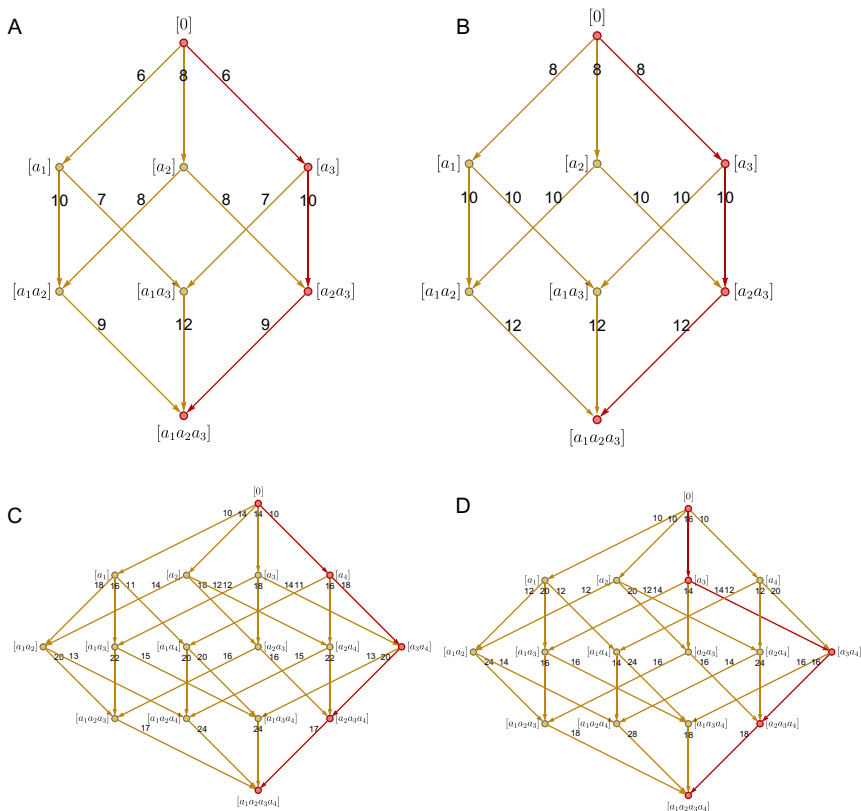 Fig. 2 for the 3-chain $f_{12}h_{23}$ (top left), cyclic $f_{12}g_{13}h_{23}$ (top right), 4-chain $f_{12}h_{23}i_{34}$ (bottom left), and trident $g_{13}h_{23}i_{34}$ (bottom right) operators.

4.2 Transfer Recurrence Relations

TRRs redistribute angular momentum between centers hosting to different electrons. Using translational invariance, one can derive

$$
\begin{aligned}
[a_1^+ a_2 a_3 a_4] =& \frac{a_1}{2\zeta_1} [a_1^- a_2 a_3 a_4] + \frac{a_2}{2\zeta_1} [a_1 a_2^- a_3 a_4] \\
&+ \frac{a_3}{2\zeta_1} [a_1 a_2 a_3^- a_4] + \frac{a_4}{2\zeta_1} [a_1 a_2 a_3 a_4^-] \\
&- \frac{\zeta_2}{\zeta_1} [a_1 a_2^+ a_3 a_4] - \frac{\zeta_3}{\zeta_1} [a_1 a_2 a_3^+ a_4] - \frac{\zeta_4}{\zeta_1} [a_1 a_2 a_3 a_4^+] \\
&- \frac{\beta_1 \, \mathbf{A}_1 \mathbf{B}_1 + \beta_2 \, \mathbf{A}_2 \mathbf{B}_2 + \beta_3 \, \mathbf{A}_3 \mathbf{B}_3 + \beta_4 \, \mathbf{A}_4 \mathbf{B}_4}{\zeta_1} [a_1 a_2 a_3 a_4].
\end{aligned}
\tag{21}
$$

4.3 Horizontal Recurrence Relations

The so-called HRRs enable to shift momentum between centers over the same electronic coordinate:

$$
\langle a_1 a_2 a_3 a_4 | b_4^+ \rangle = \langle a_1 a_2 a_3 a_4^+ | b_4 \rangle + \mathbf{A}_4 \mathbf{B}_4 \langle a_1 a_2 a_3 a_4 | b_4 \rangle,
\tag{22a}
$$

$$
\langle a_1 a_2 a_3 a_4 | b_3^+ b_4 \rangle = \langle a_1 a_2 a_3^+ a_4 | b_3 b_4 \rangle + \mathbf{A}_3 \mathbf{B}_3 \langle a_1 a_2 a_3 a_4 | b_3 b_4 \rangle,
\tag{22b}
$$

$$
\langle a_1 a_2 a_3 a_4 | b_2^+ b_3 b_4 \rangle = \langle a_1 a_2^+ a_3 a_4 | b_2 b_3 b_4 \rangle + \mathbf{A}_2 \mathbf{B}_2 \langle a_1 a_2 a_3 a_4 | b_2 b_3 b_4 \rangle,
\tag{22c}
$$

$$
\langle a_1 a_2 a_3 a_4 | b_1^+ b_2 b_3 b_4 \rangle = \langle a_1^+ a_2 a_3 a_4 | b_1 b_2 b_3 b_4 \rangle + \mathbf{A}_1 \mathbf{B}_1 \langle a_1 a_2 a_3 a_4 | b_1 b_2 b_3 b_4 \rangle.
\tag{22d}
$$

Note that HRRs can be applied to contracted integrals because they are independent of the contraction coefficients and exponents.

5. ALGORITHM

In this section, we describe a recursive scheme for the computation of three- and four-electron integrals based on the late-contraction path of the Head–Gordon–Pople (HGP) algorithm.[33] The general skeleton of the algorithm is shown in Fig. 3 for two representative examples: the 3-chain operator $f_{12}g_{23}$ (left) and the 4-chain operator $f_{12}h_{23}i_{34}$ (right). First, let us focus on the 3-chain operator.

To compute a class of three-electron integrals $\langle a_1 a_2 a_3 | b_1 b_2 b_3 \rangle$, starting from the fundamental integrals $[000]^m$, we first build up angular momentum over center $\mathbf{A}_3$ with the 6-term VRR_1 to obtain $[00a_3]$. Then, we use the 10-term VRR_2 over $\mathbf{A}_2$ to obtain $[0a_2 a_3]$. Finally, we build up momentum over the last bra center $\mathbf{A}_1$ using the 9-term VRR_3 to get $[a_1 a_2 a_3]$.
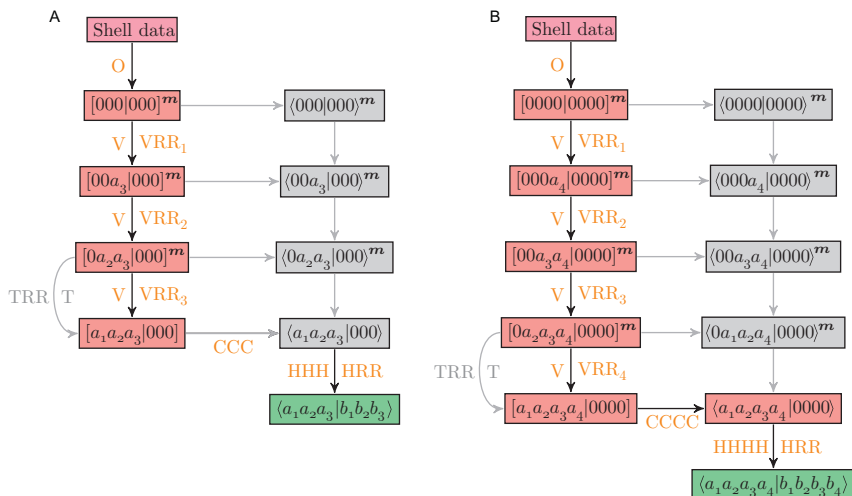
Fig. 3 Schematic representation of the algorithm used to compute three-electron integrals over the 3-chain operator $f_{12}g_{23}$ (*left*) and the four-electron integrals over the 4-chain operator $f_{12}h_{23}i_{34}$ (*right*). The three- and four-electron algorithms follow a OVVVCCCHHH and OVVVVCCCCHHHH path, respectively.

Note that, in our previous paper,[35] we claimed that it would be computationally cheaper to use the 6-term TRR instead of VRR_3 because the number of terms in the TRR is much smaller than in VRR_3. However, we have found here that the number of intermediates (i.e., the number of precomputed classes needed to calculate a given class) required by the paths involving the TRR is much larger (see Table 2). This is readily understood: note that a unit increase in momentum on the last center requires the same increase on all the other centers (as evidenced by the second term in the right–hand side of (21)). Hence, the TRR is computationally expensive for three– and four-electron integrals due to the large number of centers.

As illustrated in the top left graph of Fig. 2, other paths, corresponding to different VRRs, are possible. However, we have found that they do generate a larger number of intermediates, as reported in Table 2.

Similarly to the 3-chain operator, for the 4-chain operator, we get $[a_1a_2a_3a_4]$ by successively building up momentum over $\mathbf{A}_4$, $\mathbf{A}_3$, $\mathbf{A}_2$, and $\mathbf{A}_1$. The number of intermediates required by the other paths is gathered in Table 2. Again, the paths involving the 8-term TRR (reported in Eq. (21)) are much more expensive.

The last two steps of the algorithm are common to the three– and four-electron integral schemes. Following the HGP algorithm,[33] we contract the

Table 2 Number of Intermediates Required to Compute Various Integral Classes for Two-, Three-, and Four-Electron Operators

Integral	Type	Operator	Path	Number of Terms	Centers	Integral Class $[p...p]$	$[d...d]$	$[f...f]$
Two-electron		f_{12}	**VV**	**(4,6)**	$(\mathbf{A}_2,\mathbf{A}_1)$	**4**	**13**	**25**
			VT	(4,4)	$(\mathbf{A}_2,\mathbf{A}_1)$	7	19	37
Three-electron	Chain	$f_{12}h_{23}$	VVV	(6,7,12)	$(\mathbf{A}_3,\mathbf{A}_1,\mathbf{A}_2)$	34	230	881
			VVV	**(6,10,9)**	$(\mathbf{A}_3,\mathbf{A}_2,\mathbf{A}_1)$	**32**	**209**	**778**
			VVV	(8,8,9)	$(\mathbf{A}_2,\mathbf{A}_3,\mathbf{A}_1)$	32	212	801
			VVT	(6,7,6)	$(\mathbf{A}_3,\mathbf{A}_1,\mathbf{A}_2)$	38	246	873
			VVT	(6,10,6)	$(\mathbf{A}_3,\mathbf{A}_2,\mathbf{A}_1)$	43	314	1,256
			VVT	(8,8,6)	$(\mathbf{A}_2,\mathbf{A}_3,\mathbf{A}_1)$	40	260	923
	Cyclic	$f_{12}g_{13}h_{23}$	**VVV**	**(8,10,12)**	$(\mathbf{A}_3,\mathbf{A}_2,\mathbf{A}_1)$	**52**	**469**	**2,216**
			VVT	(8,10,6)	$(\mathbf{A}_3,\mathbf{A}_2,\mathbf{A}_1)$	61	539	2,426
Four-electron	Chain	$f_{12}h_{23}i_{34}$	VVVV	(10,11,20,24)	$(\mathbf{A}_4,\mathbf{A}_1,\mathbf{A}_3,\mathbf{A}_2)$	465	13,781	150,961
			VVVV	**(10,18,20,17)**	$(\mathbf{A}_4,\mathbf{A}_3,\mathbf{A}_2,\mathbf{A}_1)$	**436**	**12,535**	**133,891**
			VVVV	(14,14,20,17)	$(\mathbf{A}_3,\mathbf{A}_4,\mathbf{A}_2,\mathbf{A}_1)$	433	12,704	138,913
			VVVV	(14,18,16,17)	$(\mathbf{A}_3,\mathbf{A}_2,\mathbf{A}_4,\mathbf{A}_1)$	435	12,863	141,679
			VVVT	(10,11,20,8)	$(\mathbf{A}_4,\mathbf{A}_1,\mathbf{A}_3,\mathbf{A}_2)$	532	16,295	181,178

		VVVT	(10,18,20,8)	$(\mathbf{A}_4,\mathbf{A}_3,\mathbf{A}_2,\mathbf{A}_1)$	560	17,029	188,242
		VVVT	(14,14,20,8)	$(\mathbf{A}_3,\mathbf{A}_4,\mathbf{A}_2,\mathbf{A}_1)$	559	17,487	199,050
		VVVT	(14,18,16,8)	$(\mathbf{A}_3,\mathbf{A}_2,\mathbf{A}_4,\mathbf{A}_1)$	543	16,612	185,869
Trident	$g_{13}h_{23}i_{34}$	VVVV	(10,12,14,28)	$(\mathbf{A}_4,\mathbf{A}_2,\mathbf{A}_1,\mathbf{A}_3)$	445	13,139	143,619
		VVVV	(10,12,24,18)	$(\mathbf{A}_4,\mathbf{A}_2,\mathbf{A}_3,\mathbf{A}_1)$	447	13,381	148,911
		VVVV	(10,20,16,18)	$(\mathbf{A}_4,\mathbf{A}_3,\mathbf{A}_2,\mathbf{A}_1)$	418	12,447	133,853
		VVVV	**(16,14,16,18)**	$(\mathbf{A}_3,\mathbf{A}_4,\mathbf{A}_2,\mathbf{A}_1)$	**418**	**12,054**	**129,322**
		VVVT	(10,12,14,8)	$(\mathbf{A}_4,\mathbf{A}_2,\mathbf{A}_1,\mathbf{A}_3)$	470	13,306	136,584
		VVVT	(10,12,24,8)	$(\mathbf{A}_4,\mathbf{A}_2,\mathbf{A}_3,\mathbf{A}_1)$	546	16,917	191,171
		VVVT	(10,20,16,8)	$(\mathbf{A}_4,\mathbf{A}_3,\mathbf{A}_2,\mathbf{A}_1)$	521	15,515	168,958
		VVVT	(16,14,16,8)	$(\mathbf{A}_3,\mathbf{A}_4,\mathbf{A}_2,\mathbf{A}_1)$	499	13,969	142,264

The path generating the minimum number of intermediates is highlighted in bold. The number of terms in the RRs and the associated incremental center is also reported.

integrals: $[a_1a_2a_3a_4|0000]$ to form $\langle a_1a_2a_3a_4|0000\rangle$ in the four–electron case, or $[a_1a_2a_3|000]$ to form $\langle a_1a_2a_3|000\rangle$ in the three–electron case. More details about the contraction step can be found in Ref. 34. The final step of the algorithm shifts momentum to the ket centers from the bra centers with the help of the 2-term HRRs reported in Section 4.3.

6. CONCLUDING REMARKS

In this study, we have reported RRs for the efficient and accurate computation of four–electron integrals over Gaussian basis functions and a general class of multiplicative four–electron operators of the form $f_{12}g_{13}h_{23}i_{34}$. Starting from this master operator, one can easily derive the RRs for various operators arising in explicitly correlated methods following simple diagrammatic rules (see Fig. 1).

Here, we have derived three types of RRs: (i) starting from the fundamental integrals, vertical RRs (VRRs) allow to increase the angular momentum over the bra centers; (ii) the transfer RR (TRR) redistributes angular momentum between centers hosting different electrons and can be used instead of the VRR on the last bra center; (iii) the horizontal RRs (HRRs) enable to shift momentum from the bra to the ket centers corresponding to the same electronic coordinate. Importantly, HRRs can be applied to contracted integrals.

Finally, after carefully studying the different paths one can follow to build up angular momentum (see Fig. 2), we have proposed a late-contraction recursive scheme which minimizes the number of intermediates to be computed (see Fig. 3). We believe our approach represents a major step toward a fast and accurate computational scheme for three- and four–electron integrals within explicitly correlated methods. It also paves the way to contraction–effective methods for these types of integrals.[55] In particular, an early contraction scheme would have significant computational benefits.

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