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Computation of some new two-electron Gaussian integrals

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Summary. The evaluation of a new form of two-electron integrals is required if the interelectronic distance r_{12} is used as a variable in the n-electron functions of electron correlation methods. The McMurchie–Davidson algorithm for the generation of molecular integrals over Gaussian-type functions is ideally suited to this. The new Gaussian integrals are formed from Hermite integrals over r_{12} (rather than $1/r_{12}$) by standard techniques. The Hermite integrals over r_{12} itself are generated by a simple procedure with negligible computational effort. The key results are discussed in the context of general recursion formulas.

Key words: Molecular two-electron integrals – r_{12} methods – Cartesian Gaussians – Hermite functions

1 Introduction

The convergence of CI-type expansions is considerably speeded up by the inclusion of linear terms in the interelectronic distance r_{12} into n-electron wave functions. These terms address the correlation cusp problem which is closely related to the common one-particle basis set deficiencies in correlation treatments.

Our work in this field is based upon ideas of Kutzelnigg [1, 2]. The inclusion of only one single r_{12} term into the two-electron wave function of He-like atoms was investigated in Ref. [1]. The results of the study encouraged a similar approach to many-electron systems.

A computationally practicable method for n-electron systems is, of course, imperative. Concern with integral evaluation arises, in particular with regard to molecular systems. The straightforward inclusion of linear r_{12} terms into n-electron functions readily leads to three- and four-electron integrals.

It is described in Ref. [2] how "difficult integrals" can be avoided by means of certain approximations. It is ensured that the approximations become exact in

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the limit of a complete one-particle basis. On the other hand, the merits of linear r_{12} terms are maintained. The methods hence converge to the same limit as traditional CI-type calculations, but more rapidly. We will refer to our approaches as "r_{12} methods" in the following. Examples are the MP2-R12 [3] and CID-R12 [4] methods.

In this paper we describe the computation of all molecular two-electron integrals that arise in the r_{12} methods. The same integrals are required by the extended version of the MP2-R12 method which has been proposed very recently [5].

In earlier work [3, 4], two-electron integrals were calculated from the formulas of Preiskorn and Zurawski [6] for Gaussian lobes (combinations of s-type Gaussians mimic $p, d, \ldots$ etc. functions). We here report on the computer implementation of the molecular two-electron integrals over Cartesian Gaussians. This implementation is done in the context of methods which are based on the so-called auxiliary functions $F_m(W)$.

Bearpark et al. [7] have implemented the necessary integrals over Cartesian Gaussians as they investigated the MP2-R12 method. They use the Rys quadrature scheme [8] which is quite different from the present approach.

The integral formulas presented here can alternatively be deduced from the integral formulas of Preiskorn et al. [9] who in addition give formulas for three- and four-electron integrals over Cartesian Gaussians. Some remarks on the computation of the integrals in the case of one-center integrals over Slater-type functions can be found in Ref. [10].

The four types of integrals which are subject of this report are shown in Sect. 2. The computationally most demanding of them is transformed into a convenient form in Sect. 2.1. We then describe the expansion of Gaussian charge distributions in Sect. 2.2 and how we compute the required integrals over Hermite functions in Sect. 2.3. Parts of the work of Helgaker and Taylor [11] and of the work of McMurchie and Davidson [12] are briefly reviewed for this purpose.

In Sect. 3 we discuss our computational strategy in the context of more general "recursive computations". Except for the improvements described in Ref. [11], the present computer implementation strictly follows the McMurchie–Davidson scheme. We show that our results are not restricted to the specific scheme of computation, but that they are of broader validity.

2 Integral formulas

The r_{12} methods require the evaluation of four different types of two-electron integrals over Cartesian Gaussian functions:

$$(ab|\frac{1}{r_{12}}|cd) \equiv \int\int \psi_a(1)\psi_c(2)\frac{1}{r_{12}}\psi_b(1)\psi_d(2)\,d\tau_1\,d\tau_2, \tag{1}$$

$$(ab|r_{12}|cd) \equiv \int\int \psi_a(1)\psi_c(2)r_{12}\psi_b(1)\psi_d(2)\,d\tau_1\,d\tau_2, \tag{2}$$

$$(ab|[r_{12}, \hat{T}_1]|cd) \equiv \int\int \psi_a(1)\psi_c(2)[r_{12}, \hat{T}_1]\psi_b(1)\psi_d(2)\,d\tau_1\,d\tau_2, \tag{3}$$

$$(ab|[r_{12}, \hat{T}_2]|cd) \equiv \int\int \psi_a(1)\psi_c(2)[r_{12}, \hat{T}_2]\psi_b(1)\psi_d(2)\,d\tau_1\,d\tau_2. \tag{4}$$

$\hat{T} = -\frac{1}{2}\Delta$ is the kinetic energy operator, r_{12} is the interelectronic distance, and ψ_a, ψ_b, ψ_c, and ψ_d are unnormalized primitive Cartesian Gaussians:

$$\psi_a \equiv G_{ijk}(\vec{r}, a, \vec{A}) = x_A^i y_A^j z_A^k \exp(-ar_A^2). \tag{5}$$

This function is centered at $\vec{A}$ with $x_A = x - A_x$, etc. The integrals of Eqs. (3) and (4) are formally the same integrals, but since the integrals are only calculated for index quadruples:

$$(a \leqslant b) \leqslant (c \leqslant d), \tag{6}$$

i.e. in the usual canonical order, two distinct integrals are needed to form a basis for a representation of the permutational symmetry:

$$\begin{aligned}(ab|[r_{12}, \hat{T}_1]|cd) &= -(ba|[r_{12}, \hat{T}_1]|cd)\\ &= (ab|[r_{12}, \hat{T}_1]|dc) = -(ba|[r_{12}, \hat{T}_1]|dc)\\ &= (cd|[r_{12}, \hat{T}_2]|ab) = -(cd|[r_{12}, \hat{T}_2]|ba)\\ &= (dc|[r_{12}, \hat{T}_2]|ab) = -(dc|[r_{12}, \hat{T}_2]|ba).\end{aligned} \tag{7}$$

In previous formulations of the r_{12} theory [1, 2] we have used the operator:

$$\hat{U}_{12} = -\frac{1}{2}\frac{\vec{r}_{12}}{r_{12}}(\vec{\nabla}_1 - \vec{\nabla}_2) = [\hat{T}_1 + \hat{T}_2, \tfrac{1}{2}r_{12}] + \frac{1}{r_{12}}. \tag{8}$$

However, from a computational point of view the integrals (3) and (4) are more convenient to work with than the corresponding integrals over $\hat{U}_{12}$. The relations in Eq. (7) are advantageous while forming integrals over contracted functions or while performing four-index transformations in general.

We will derive a convenient expression for the integral (3) – or (4) – in Sect. 2.1. Then we will expand Gaussian charge distributions in Hermite functions in Sect. 2.2. There it will become clear that Hermite integrals over the operator r_{12} are the only new auxiliary integrals needed. In Sect. 2.3 these new Hermite integrals will be calculated.

2.1 Gaussian integrals over $[r_{12}, \hat{T}_1]$

Let us first note that:

$$(ab|[r_{12}, \hat{T}_1]|cd) = (ab|\frac{\vec{r}_{12}}{r_{12}}\vec{\nabla}_1|cd) + (ab|\frac{1}{r_{12}}|cd) \tag{9}$$

in conformity with Eq. (8), where again we use the alternative notation:

$$(ab|\frac{\vec{r}_{12}}{r_{12}}\vec{\nabla}_1|cd) \equiv \int\int \psi_a(1)\psi_c(2)\frac{\vec{r}_{12}}{r_{12}}\{\vec{\nabla}_1\psi_b(1)\}\psi_d(2)\,d\tau_1\,d\tau_2. \tag{10}$$

Since

$$\vec{\nabla}_1\psi_b(1) = -\vec{\nabla}_B\psi_b(1), \tag{11}$$

where $\vec{\nabla}_B$ denotes differentiation with respect to the coordinates of the center $\vec{B}$ of the Gaussian function ψ_b, we can also write:

$$(ab|\frac{\vec{r}_{12}}{r_{12}}\vec{\nabla}_1|cd) = -\vec{\nabla}_B(ab|\frac{\vec{r}_{12}}{r_{12}}|cd). \tag{12}$$

In a recent paper Helgaker and Taylor [11] show how the computational effort for the calculation of derivatives of Gaussian integrals can be significantly reduced by the following change of variables:

$$\vec{\nabla}_A = \frac{a}{p}\vec{\nabla}_P + \vec{\nabla}_R \tag{13}$$

and

$$\vec{\nabla}_B = \frac{b}{p}\vec{\nabla}_P - \vec{\nabla}_R. \tag{14}$$

Here

$$\vec{P} = \frac{a}{p}\vec{A} + \frac{b}{p}\vec{B}, \quad p = a + b, \tag{15}$$

and

$$\vec{R} = \vec{A} - \vec{B}. \tag{16}$$

Following this idea we write:

$$(ab|\frac{\vec{r}_{12}}{r_{12}}\vec{\nabla}_1|cd) = -\frac{b}{p}\vec{\nabla}_P(ab|\frac{\vec{r}_{12}}{r_{12}}|cd) + \vec{\nabla}_R(ab|\frac{\vec{r}_{12}}{r_{12}}|cd)\,. \tag{17}$$

Noting that:

$$\vec{\nabla}_P(ab|M_{12}|cd) = (ab|\{\vec{\nabla}_1 M_{12}\}|cd), \tag{18}$$

where M_{12} is either $\vec{r}_{12}/r_{12}$ or r_{12}, we use:

$$\vec{\nabla}_1\frac{\vec{r}_{12}}{r_{12}} = \frac{2}{r_{12}} \quad \text{and} \quad \vec{\nabla}_1 r_{12} = \frac{\vec{r}_{12}}{r_{12}} \tag{19}$$

and obtain:

$$(ab|\frac{\vec{r}_{12}}{r_{12}}\vec{\nabla}_1|cd) = -\frac{2b}{p}(ab|\frac{1}{r_{12}}|cd) + \vec{\nabla}_P\vec{\nabla}_R(ab|r_{12}|cd). \tag{20}$$

Inserting (20) into (9) yields:

$$(ab|[r_{12}, \hat{T}_1]|cd) = \left(\frac{a-b}{a+b}\right)(ab|\frac{1}{r_{12}}|cd) + \vec{\nabla}_P\vec{\nabla}_R(ab|r_{12}|cd). \tag{21}$$

Equation (18) follows from:

$$\vec{\nabla}_P\psi_a(1)\psi_b(1) = -\vec{\nabla}_1\psi_a(1)\psi_b(1) \tag{22}$$

and from integration by parts, since (for relevant M_{12}):

$$\int\int\left\{\frac{\partial}{\partial x_1}\psi_a(1)\psi_c(2)M_{12}\psi_b(1)\psi_d(2)\right\}d\tau_1\,d\tau_2 = 0, \quad \text{etc.} \tag{23}$$

Other examples of how (18) can facilitate the computation of several forms of two-electron integrals may be found in Ref. [12]. We conclude this section by noting that:

$$\Delta_1 r_{12} = \frac{2}{r_{12}} \tag{24}$$

leads to

$$\Delta_P(ab\,|r_{12}|\,cd) = 2\,(ab\,|\,\frac{1}{r_{12}}\,|cd). \tag{25}$$

2.2 Expansion of charge distributions

In Sect. 2.1 we have derived an expression for the Gaussian integral over the commutator $[r_{12}, \hat{T}_1]$. Equation (21) shows that this integral is a linear combination of integrals over $1/r_{12}$ and r_{12}. The second term on the right-hand side of Eq. (21) is an r_{12} integral over a *differentiated* Gaussian charge distribution. This is quite general and not restricted to our computational scheme.

We will proceed by expanding Gaussian charge distributions in Hermite functions, as described by McMurchie and Davidson [12] (see also a review by Saunders [13]). Differentiated charge distributions also can be expanded in Hermite functions and thus integrals over the operators $1/r_{12}$ and r_{12} are the only integrals over Hermite functions required by the r_{12} methods.

The Cartesian Gaussian function (5) factorizes into:

$$G_{ijk}(\vec{r}, a, \vec{A}) = G_i(x, a, A_x)G_j(y, a, A_y)G_k(z, a, A_z), \tag{26}$$

where

$$G_i(x, a, A_x) = x_A^i \exp(-ax_A^2), \quad \text{etc.} \tag{27}$$

and in the following we will consider only one direction, say x. An overlap distribution is expanded as:

$$\begin{aligned} G_i(x, a, A_x)G_j(x, b, B_x) &\equiv \Omega_{ij}(x, a, b, A_x, B_x) \\ &= \sum_{t=0}^{i+j} E_t^{ij;0}(a, b, R_x)\Lambda_t(x, p, P_x). \end{aligned} \tag{28}$$

The Hermite function Λ_t is defined by:

$$\Lambda_t(x, p, P_x) = (\partial/\partial P_x)^t \exp(-px_P^2) \tag{29}$$

and the expansion coefficients $E_t^{ij;n}$ (now dropping the list of arguments of both functions and coefficients) are obtained from the recursion formula (see Ref. [11]):

$$E_t^{i+1,j;n} = \frac{1}{2p} E_{t-1}^{ij;n} - \frac{b}{p}(R_x E_t^{ij;n} + nE_t^{ij;n-1}) + (t+1)E_{t+1}^{ij;n}, \tag{30}$$

with starting values:

$$E_0^{00;0} = K_{ab} \quad \text{and} \quad E_0^{00;n+1} = -\frac{2ab}{p}(R_x E_0^{00;n} + nE_0^{00,n-1}). \tag{31}$$

K_{ab} is the pre-exponential factor:

$$K_{ab} = \exp\left(-\frac{ab}{p}\overline{AB}_x^2\right) \tag{32}$$

($\overline{AB}_x = A_x - B_x$). Helgaker and Taylor [11] emphasize that the expansion coefficients depend on R_x only while the Hermite functions depend on P_x only. This supports the change of variables in Eqs. (13)–(14). Differentiation with respect to P_x is particularly simple due to the definition (29) of the Hermite functions, i.e.:

$$\frac{\partial \Lambda_t}{\partial P_x} = \Lambda_{t+1}. \tag{33}$$

Differentiating the expansion coefficients gives:

$$\frac{\partial E_t^{ij;n}}{\partial R_x} = E_t^{ij;n+1}. \tag{34}$$

Thus, the expansion of the differentiated overlap distribution as required by Eq. (21) is given by:

$$\frac{\partial^2 \Omega_{ij}}{\partial P_x \, \partial R_x} = \sum_{t=0}^{i+j} E_t^{ij;1} \Lambda_{t+1}. \tag{35}$$

Helgaker and Taylor [11] make the important observation that the range of summation in expressions of the form (35) is exactly the same as in the case of undifferentiated integrals (28). The original scheme implies a range of summation from $t = 0$ to $i + j + n$ for the nth derivative [12, 13]. The change of variables therefore leads to significant computational savings during the process where integrals over Cartesian Gaussians are formed from Hermite integrals.

We see that the range (or degree) of the Hermite functions involved in Eq. (35) is different as compared to undifferentiated integrals. However, the transformation from the Hermite function basis to the Cartesian Gaussian basis is the time-consuming step while the calculation of the Hermite integrals is fast. Note that the same Hermite integrals of higher degree are required by the original scheme of computation.

The transformation from Hermite to Cartesian Gaussian integrals is a standard technique [12–14] which we will not discuss here. Section 2.3 addresses the calculation of integrals over Hermite functions. The evaluation of the expansion coefficients (30) – and thus the differentiation with respect to R_x, etc. – is of negligible computational cost.

2.3 Hermite integrals over r_{12}

We will now evaluate the integral

$$(tuv\,|r_{12}|\,t'u'v') \equiv \int\int \Lambda_{tuv}(\vec{r}_1, p, \vec{P}) r_{12} \Lambda_{t'u'v'}(\vec{r}_2, q, \vec{Q})\, d\tau_1\, d\tau_2. \tag{36}$$

where

$$\Lambda_{tuv}(\vec{r}, p, \vec{P}) = \Lambda_t(x, p, P_x)\Lambda_u(y, p, P_y)\Lambda_v(z, p, P_z) \tag{37}$$

and where q and $\vec{Q}$ are defined analogously to p and $\vec{P}$. We write the Hermite integrals in the convenient form:

$$\begin{aligned}(tuv|\frac{1}{r_{12}}|t'u'v') &= \lambda(-1)^{t'+u'+v'}R_{TUV},\\ (tuv|r_{12}|t'u'v') &= \lambda(-1)^{t'+u'+v'}Q_{TUV},\end{aligned} \tag{38}$$

with

$$\lambda = 2\pi^{5/2}(pq)^{-1}(p+q)^{-1/2} \tag{39}$$

and

$$T = t + t', \quad U = u + u', \quad \text{and} \quad V = v + v'. \tag{40}$$

The Hermite integrals depend on the sums $t + t'$ rather than on the individual values of t and t', etc.

It would be natural to use:

$$r_{12} = \frac{x_{12}^2 + y_{12}^2 + z_{12}^2}{r_{12}}, \tag{41}$$

$$x_{12} = x_P - x_Q + \overline{PQ}_x, \tag{42}$$

$$x_P = x_1 - P_x, \quad x_Q = x_2 - Q_x, \tag{43}$$

and similar expressions for the y and z directions [7]. Preiskorn et al. [9] introduce an operator R_{ij}^{v} which generates linear combinations of integrals according to Eqs. (41)–(43). These authors thus obtain Cartesian Gaussian integrals over r_{12} as linear combinations of Cartesian Gaussian integrals over $1/r_{12}$ [7, 9]. But with the recursion relation for Hermite functions:

$$x_P \Lambda_t = t\Lambda_{t-1} + \frac{1}{2p}\Lambda_{t+1} \tag{44}$$

we find a linear combination on the level of Hermite integrals which is too complicated for practical purposes:

$$\begin{aligned}Q_{TUV} = &\left(\frac{1}{2\alpha}\right)^2 (R_{T+2,UV} + R_{T,U+2,V} + R_{TU,V+2})\\ &+ \frac{1}{\alpha}(\overline{PQ}_x R_{T+1,UV} + \overline{PQ}_y R_{T,U+1,V} + \overline{PQ}_z R_{TU,V+1})\\ &+ \left\{\overline{PQ}^2 + \frac{1}{\alpha}(T+U+V+\tfrac{3}{2})\right\} R_{TUV}\\ &+ 2(\overline{PQ}_x T R_{T-1,UV} - \overline{PQ}_y U R_{T,U-1,V} + \overline{PQ}_z V R_{TU,V-1})\\ &+ T(T-1)R_{T-2,UV} + U(U-1)R_{T,U-2,V} + V(V-1)R_{TU,V-2}.\end{aligned} \tag{45}$$

Here

$$\alpha = \frac{pq}{p+q}. \tag{46}$$

Equation (45) involves both a relatively large number of primitive floating point operations and Hermite integrals over r_{12} of high degree, for example $R_{T+2,UV}$.

Moreover, Eqs. (21) and (35) show that the formation of Cartesian Gaussian integrals over $[r_{12}, \hat{T}_1]$ increases the degree of the required r_{12} integrals once more. Thus, when we compare to the evaluation of standard electron repulsion integrals, we have to increase the degree of the Hermite integrals R_{TUV} by as much as three if we wish to use Eq. (45).

Let us instead consider the first derivative of r_{12} integrals with respect to the coordinates of $\vec{P}$. By virtue of Eq. (33) we get, e.g.

$$\frac{\partial Q_{TUV}}{\partial P_x} = Q_{T+1,UV}. \tag{47}$$

Alternatively we use Eqs. (18) and (19) and obtain:

$$\frac{\partial Q_{TUV}}{\partial P_x} = X_{TUV}, \tag{48}$$

where

$$X_{TUV} = \frac{1}{\lambda}(-1)^{(t'+u'+v')}(tuv\,|\,\frac{x_{12}}{r_{12}}\,|\,t'u'v')\,. \tag{49}$$

We rewrite (48) using (42)–(44). We get:

$$\frac{\partial Q_{TUV}}{\partial P_x} = \frac{1}{2\alpha} R_{T+1,UV} + \overline{PQ}_x R_{TUV} + T R_{T-1,UV}. \tag{50}$$

We combine Eqs. (47) and (50) and obtain:

$$Q_{T+1,UV} = \frac{1}{2\alpha} R_{T+1,UV} + \overline{PQ}_x R_{TUV} + T R_{T-1,UV}. \tag{51}$$

The number of operations in (51) is much less than in (45), while the degree of R integrals needed for a given Q integral is the same or less.

Similar formulas can be derived for the y and z directions and we finally get the following working equations for the generation of Hermite integrals over r_{12}:

$$\begin{aligned} Q_{T00} &= \frac{1}{2\alpha} R_{T00} + \overline{PQ}_x R_{T-1,00} + (T-1) R_{T-2,00}, \\ Q_{TU0} &= \frac{1}{2\alpha} R_{TU0} + \overline{PQ}_y R_{T,U-1,0} + (U-1) R_{T,U-2,0}, \\ Q_{TUV} &= \frac{1}{2\alpha} R_{TUV} + \overline{PQ}_z R_{TU,V-1} + (V-1) R_{TU,V-2}, \end{aligned} \tag{52}$$

for $T, U, V \geqslant 1$. Equation (52) can be used for all Q_{TUV} integrals except Q_{000} and we hence need a special formula for that integral:

$$Q_{000} = \left(\frac{1}{\alpha} + \overline{PQ}^2\right) R_{000} + \frac{1}{2\alpha}(\overline{PQ}_x R_{100} + \overline{PQ}_y R_{010} + \overline{PQ}_z R_{001}). \tag{53}$$

Equation (53) is derived as follows: first, it is:

$$\Delta_P Q_{000} = 2R_{000}, \tag{54}$$

as can be seen from Eqs. (24) and (25). Second, explicitly differentiating Q_{000} with respect to P_x yields:

$$\frac{\partial^2 Q_{000}}{\partial P_x^2} = Q_{200} = \frac{1}{2\alpha} R_{200} + \overline{PQ}_x R_{100} + R_{000}, \tag{55}$$

which follows from Eq. (52). We thus find:

$$\frac{1}{2\alpha}(R_{200}+R_{020}+R_{002})+\overline{PQ}_x R_{100}+\overline{PQ}_y R_{010}+\overline{PQ}_z R_{001}+R_{000}=0. \quad (56)$$

Inserting (56) into (45) gives (53).

We conclude that the working equations (52) and (53) represent efficient computational procedures for the generation of Hermite integrals over r_{12}. Except for the Q_{000} integral – which is the r_{12} integral over four s-type Gaussians – these Hermite integrals are calculated from the corresponding electron repulsion integrals without increase of the degree of the latter.

3 Computation of integrals

We will discuss the computation of r_{12} method integrals in some detail. The first step in the computation is the generation of so-called auxiliary functions (see for example Ref. [12]):

$$[\mathbf{000}\,|\,\mathbf{000}]^{(m)} \equiv R_{000m} = (-2\alpha)^m F_m(W) = (-2\alpha)^m \int_0^1 t^{2m}\exp(-Wt^2)\,dt, \quad (57)$$

with

$$0 \leqslant m \leqslant L+1 \quad \text{and} \quad W = \alpha\overline{PQ}^2. \quad (58)$$

L is the sum of the "angular momentum quantum numbers" of the four Cartesian Gaussians ψ_a, ψ_b, ψ_c, and ψ_d. For example, $L=6$ for a batch of $(sp\,|\,df)$ integrals. The integrals (3) and (4) require the range of m in (58), while for (1) and (2) the range $0 \leqslant m \leqslant L$ would suffice.

The computational steps are best pictured in a compact notation: square brackets are used for integrals over primitive Gaussians and round ones for integrals over contracted functions. Explicit reference to x, y, or z is replaced by λ. Since there are six centers involved in our formulas ($\vec{P}$, $\vec{A}$, $\vec{B}$, $\vec{Q}$, $\vec{C}$, and $\vec{D}$) we reserve six positions in our notation. Closely following the notation of Obara and Saika [15], Gaussians are represented by integer vectors, for example $\boldsymbol{pab}$. Their components denote the order N_λ of the Hermite polynomial in λ or the power N_λ of the Cartesian coordinate λ. We use $\mathbf{1}_\lambda = (\delta_{x\lambda}, \delta_{y\lambda}, \delta_{z\lambda})$ with Kronecker's deltas.

We proceed with the second step. The recursion formulas of McMurchie and Davidson are executed (i.e. the relations (4.6)–(4.8) in Ref. [12]):

$$[(\boldsymbol{p}+\mathbf{1}_\lambda)\mathbf{00}\,|\,\mathbf{000}]^{(m)} = \overline{PQ}_\lambda[\boldsymbol{p}\mathbf{00}\,|\,\mathbf{000}]^{(m+1)} + N_\lambda(\boldsymbol{p})[(\boldsymbol{p}-\mathbf{1}_\lambda)\mathbf{00}\,|\,\mathbf{000}]^{(m+1)}. \quad (59)$$

The R_{TUV} integrals are obtained as soon as $m=0$:

$$[\boldsymbol{p}\mathbf{00}\,|\,\mathbf{000}]^{(0)} \equiv [\boldsymbol{p}\mathbf{00}\,|\,\mathbf{000}] \equiv R_{TUV}, \quad (60)$$

where

$$\boldsymbol{p} = (T, U, V) \quad \text{with} \quad 0 \leqslant T+U+V \leqslant L+1. \quad (61)$$

At this point we start computing the r_{12} integrals over Hermite functions using (52) and (53). We will distinguish them from $1/r_{12}$ integrals by two vertical lines: $[\ldots \,\|\, \ldots]$. The integral $Q_{000} \equiv [\mathbf{000} \,\|\, \mathbf{000}]$ is always required. It is best computed

directly from the $F_m(W)$ integrals:

$$[\mathbf{000} \parallel \mathbf{000}] = \frac{1}{\alpha} F_0(W) + \overline{PQ}^2\{F_0(W) - F_1(W)\}. \tag{62}$$

This result is obtained by explicitly summing the x, y, z terms in (53). Other r_{12} Hermite integrals are generated by:

$$[(\boldsymbol{p} + \mathbf{1}_\lambda)\mathbf{00} \parallel \mathbf{000}] = \frac{1}{2\alpha}[(\boldsymbol{p} + \mathbf{1}_\lambda)\mathbf{00} \mid \mathbf{000}] + \overline{PQ}_\lambda[\boldsymbol{p}\mathbf{000} \mid \mathbf{000}] + N_\lambda(\boldsymbol{p})[(\boldsymbol{p} - \mathbf{1}_\lambda)\mathbf{00} \mid \mathbf{000}]. \tag{63}$$

Equations (62) and (63) represent the computer code which must be added to a computer program that starts from Hermite integrals and which has code for both integrals and their derivatives. They have been added to the HERMIT program [14, 16]. The concluding steps, i.e. the transformation to Cartesian Gaussians, are done with standard computer code.

So far we have merely rewritten well-known formulas on one hand and the working equations (52)–(53) on the other. But the choice of notation enables us to put the results of Sect. 2 in a broader perspective.

Obara and Saika [15] proposed a recursive computation of Gaussian integrals in 1986. A series of investigations have followed since then [17–19], some of them quite recently [20–25]. We conclude from the results of Lindh et al. [20] that the following computational strategy leads to an efficient generation of electron repulsion integrals: the first step is (57). The second is analogous to (59):

$$[\mathbf{0}(\boldsymbol{a} + \mathbf{1}_\lambda)\mathbf{0} \mid \mathbf{000}]^{(m)} = \overline{PA}_\lambda[\mathbf{0}\boldsymbol{a}\mathbf{0} \mid \mathbf{000}]^{(m)} + \frac{1}{2p}\overline{PQ}_\lambda[\mathbf{0}\boldsymbol{a}\mathbf{0} \mid \mathbf{000}]^{(m+1)} + \frac{N_\lambda(\boldsymbol{a})}{2p} \times \left([\mathbf{0}(\boldsymbol{a} - \mathbf{1}_\lambda)\mathbf{0} \mid \mathbf{000}]^{(m)} + \frac{1}{2p}[\mathbf{0}(\boldsymbol{a} - \mathbf{1}_\lambda)\mathbf{0} \mid \mathbf{000}]^{(m+1)} \right). \tag{64}$$

The third step moves powers of λ from center $\vec{A}$ to $\vec{C}$:

$$[\mathbf{0}\boldsymbol{a}\mathbf{0} \mid \mathbf{0}(\boldsymbol{c} + \mathbf{1}_\lambda)\mathbf{0}] = \left(\overline{QC}_\lambda + \frac{p}{q}\overline{PA}_\lambda \right)[\mathbf{0}\boldsymbol{a}\mathbf{0} \mid \mathbf{0}\boldsymbol{c}\mathbf{0}] + \frac{N_\lambda(\boldsymbol{a})}{2q}[\mathbf{0}(\boldsymbol{a} - \mathbf{1}_\lambda)\mathbf{0} \mid \mathbf{0}\boldsymbol{c}\mathbf{0}] + \frac{N_\lambda(\boldsymbol{c})}{2q}[\mathbf{0}\boldsymbol{a}\mathbf{0} \mid \mathbf{0}(\boldsymbol{c} - \mathbf{1}_\lambda)\mathbf{0}] - \frac{p}{q}[\mathbf{0}(\boldsymbol{a} + \mathbf{1}_\lambda)\mathbf{0} \mid \mathbf{0}\boldsymbol{c}\mathbf{0}]. \tag{65}$$

Lindh et al. [20] and Hamilton and Schaefer [21] independently found (65). Head-Gordon and Pople [17] recognized that the distribution of "angular momentum" from $\vec{A}$ to $\vec{B}$ (and from $\vec{C}$ to $\vec{D}$) can be carried out *after* the contraction step. Hence, the final steps are represented by:

$$(\mathbf{0}\boldsymbol{a}(\boldsymbol{b} + \mathbf{1}_\lambda) \mid \mathbf{0}\boldsymbol{cd}) = (\mathbf{0}(\boldsymbol{a} + \mathbf{1}_\lambda)\boldsymbol{b} \mid \mathbf{0}\boldsymbol{cd}) + \overline{AB}_\lambda(\mathbf{0}\boldsymbol{ab} \mid \mathbf{0}\boldsymbol{cd}). \tag{66}$$

And similar for $\boldsymbol{c}$ and $\boldsymbol{d}$. Note the round brackets in (66). The equations (57), (64), (65), and (66) constitute, say, the pure Cartesian scheme of computation.

Because of the translational invariance of the integrals:

$$\left(\frac{\partial}{\partial P_\lambda} + \frac{\partial}{\partial Q_\lambda} \right)[\mathbf{p00} \mid \mathbf{q00}] = 0, \tag{67}$$

the Hermite equivalent to (65) is:

$$[\boldsymbol{p}\mathbf{00} \mid (\boldsymbol{q} + \mathbf{1}_\lambda)\mathbf{00}] = -[(\boldsymbol{p} + \mathbf{1}_\lambda)\mathbf{00} \mid \boldsymbol{q}\mathbf{00}]. \tag{68}$$

Observe at this point that Hamilton and Schaefer [21] obtained (65) from:

$$\left(\frac{\partial}{\partial A_\lambda}+\frac{\partial}{\partial B_\lambda}+\frac{\partial}{\partial C_\lambda}+\frac{\partial}{\partial D_\lambda}\right)[\mathbf{0}\boldsymbol{ab}\mid\mathbf{0}\boldsymbol{cd}]=0. \tag{69}$$

It is obvious that (59) and (68) are computationally simpler than the corresponding steps (64) and (65). However, the final computational steps must move "angular momentum" from $\vec{P}$ to $\vec{A}$ and $\vec{B}$ and from $\vec{Q}$ to $\vec{C}$ and $\vec{D}$. This is done by means of a matrix transformation in the original scheme of McMurchie and Davidson [12] (and in our current computer implementation) using a transformation matrix of the form (30). Gill, Head-Gordon, and Pople [18, 19] have investigated an alternative scheme using the recursion relation (44) for Hermite functions:

$$\begin{aligned}[\boldsymbol{p}(\boldsymbol{a}+\mathbf{1}_\lambda)\boldsymbol{b}\mid\boldsymbol{qcd}]&=\frac{1}{2p}[(\boldsymbol{p}+\mathbf{1}_\lambda)\boldsymbol{ab}\mid\boldsymbol{qcd}]\\&\quad+N_\lambda(\boldsymbol{p})[(\boldsymbol{p}-\mathbf{1}_\lambda)\boldsymbol{ab}\mid\boldsymbol{qcd}]+\overline{PA}_\lambda[\boldsymbol{pab}\mid\boldsymbol{qcd}].\end{aligned} \tag{70}$$

Same for $\boldsymbol{b}$, same for $\boldsymbol{q}$ to $\boldsymbol{c}$ and $\boldsymbol{d}$. We may say that the steps (57), (59), (68 as a formal zero-cost step), and (70) represent the path via Hermite functions.

We do not intend to evaluate possible computational strategies. But in view of the recent progress in the field of molecular two-electron integral generation it is felt that the integral formulas of Sect. 2 should be viewed in the context of these new ways of computing integrals over Cartesian Gaussians. We therefore show that the key idea of Sect. 2 is quite general.

Obviously, the working formula (62) does not change if implemented in a pure Cartesian environment. It remains to reformulate (63). It follows from (18), (19), and an adequate form of (42) that:

$$\left(\frac{\partial}{\partial A_\lambda}+\frac{\partial}{\partial B_\lambda}\right)[\mathbf{0}\boldsymbol{a}\mathbf{0}\parallel\mathbf{000}]=[\mathbf{0}(\boldsymbol{a}+\mathbf{1}_\lambda)\mathbf{0}\mid\mathbf{000}]-[\mathbf{0}\boldsymbol{a}\mathbf{0}\mid\mathbf{01}_\lambda\mathbf{0}]+\overline{AC}_\lambda[\mathbf{0}\boldsymbol{a}\mathbf{0}\mid\mathbf{000}]. \tag{71}$$

We differentiate the left-hand side of (71) and we then push all powers of coordinates back to center $\vec{A}$ with the help of (65). We obtain:

$$\begin{aligned}[\mathbf{0}(\boldsymbol{a}+\mathbf{1}_\lambda)\mathbf{0}\parallel\mathbf{000}]&=\overline{PA}_\lambda[\mathbf{0}\boldsymbol{a}\mathbf{0}\parallel\mathbf{000}]+\frac{N_\lambda(\boldsymbol{a})}{2p}[\mathbf{0}(\boldsymbol{a}-\mathbf{1}_\lambda)\mathbf{0}\parallel\mathbf{000}]\\&\quad+\frac{1}{2\alpha}[\mathbf{0}(\boldsymbol{a}+\mathbf{1}_\lambda)\mathbf{0}\mid\mathbf{000}]-\left(\frac{1}{2p}\overline{QA}_\lambda+\frac{1}{2q}\overline{PA}_\lambda\right)[\mathbf{0}\boldsymbol{a}\mathbf{0}\mid\mathbf{000}]\\&\quad-\frac{N_\lambda(\boldsymbol{a})}{4pq}[\mathbf{0}(\boldsymbol{a}-\mathbf{1}_\lambda)\mathbf{0}\mid\mathbf{000}].\end{aligned} \tag{72}$$

We find both r_{12} and $1/r_{12}$ integrals on the right-hand side of (72). That is not the case in (63). But the result is very similar to (63) in that it allows the computation of r_{12} integrals of the type $[\mathbf{0}\boldsymbol{a}\mathbf{0}\parallel\mathbf{000}]$ from the corresponding ones over $1/r_{12}$ of same or lower degree. Equation (62) is needed as a starting value of (72).

The compact notation reveals the idea behind our computation of r_{12} integrals: obtain r_{12} integrals from integrals over $1/r_{12}$ at the stage of the computation where all "angular momentum" is at one center. This may be either $\vec{P}$, the position of the Hermite function, or $\vec{A}$, the location of the Cartesian Gaussian. Finish the calculation with computer code for standard integrals. Note that (65) and (66) hold for both $1/r_{12}$ and r_{12} integrals.

The computational cost for the generation of r_{12} integrals is not substantial at the point where they are generated. The cost is comparable to the generation of the "one-center" $1/r_{12}$ integrals (59) or (64).

The change of variables (13)–(14) is also advantageous if we do not use Hermite functions as intermediates:

$$\frac{\partial}{\partial R_\lambda}[\mathbf{0}ab \parallel \mathbf{0}cd] = 2a\overline{PA}_\lambda[\mathbf{0}ab \parallel \mathbf{0}cd]$$
$$-\frac{b}{p}N_\lambda(a)[\mathbf{0}(a-\mathbf{1}_\lambda)b \parallel \mathbf{0}cd] + \frac{a}{p}N_\lambda(b)[\mathbf{0}a(b-\mathbf{1}_\lambda) \parallel \mathbf{0}cd]. \quad (73)$$

We observe that differentiation with respect to R_λ does not increase "angular momentum quantum numbers". Therefore, evaluating the $[r_{12}, \hat{T}_1]$ integrals from (21) requires a start from $F_m(W)$ with $0 \leqslant m \leqslant L+1$. We conclude that computing (21) rather than (in the notation of Sect. 2):

$$(ab|r_{12}, \hat{T}_1]|cd) = -\tfrac{1}{2}(\Delta_B - \Delta_A)(ab|r_{12}|cd) \quad (74)$$

is economical. The computation of the integrals (3) and (4) is slightly more expensive than the generation of (1) because of the first derivatives involved. In practice we observe that the CPU-time needed for the computation of either integral (3) or (4) is roughly twice the time needed for the $1/r_{12}$ integral. The integral (2) requires the same time as (1).

Our integral formulas of Sect. 2 are tailored towards Hermite functions. In this section we have shown that they are readily translated into analogous expressions for use in pure Cartesian surroundings.

4 Conclusion

The r_{12} methods require new molecular two-electron integrals over Cartesian Gaussian functions. These integrals can readily and efficiently be obtained through minor modifications of computer programs currently in use. The requirement is that the program must be able to generate an electron repulsion integral and its first derivatives.

This becomes evident when we summarize the proposed scheme of computation: first, compute $(ss|r_{12}|ss)$ integrals from Eq. (62). Then generate integrals of the type $(xs|r_{12}|ss)$ from the corresponding integrals over $1/r_{12}$. Here x denotes either a Cartesian Gaussian higher than s or a higher order Hermite function. Equation (63) or (72) must be implemented for this purpose and existing computer code can be used from here on. Code for derivatives is required by the integral $[r_{12}, \hat{T}_1]$ which is a differentiated r_{12} integral.

The computation of $(xs|r_{12}|ss)$-type integrals is inexpensive in terms of CPU-time and requires only modest computer memory.

We have discussed so-called auxiliary function based algorithms. Methods of this kind start from a set of functions $F_m(W)$. Here we make an important observation. When certain $1/r_{12}$ integrals start from functions $F_m(W)$ with $0 \leqslant m \leqslant L$, then L is not incremented for the r_{12} integrals. The $[r_{12}, \hat{T}_1]$ integrals require a set with $0 \leqslant m \leqslant L+1$.

It has proved very valuable to integrate by parts, in other words, to use Eq. (18). Equations (18) and (19) – (24) results from (19) – link $1/r_{12}$ and r_{12} integrals. This integration by parts gives more economical links than other possible ones in the form of, for example, $r_{12} = r_{12}^2/r_{12}$.

Until now, the use of Gaussian lobes has been a restriction on applications of the r_{12} theory. The ease with which the required two-electron integrals can now be generated will allow more and larger applications of r_{12} methods in the future.

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