Molecular integrals over Gaussian-type geminal basis functions

B. Joakim Persson[1], **Peter R. Taylor**[2]

[1] Department of Chemistry and Biochemistry, University of California, San Diego La Jolla, CA 92093, USA
[2] San Diego Supercomputer Center, P.O. Box 85608, San Diego, CA 92186-9784, USA

Abstract. We present formulas for the evaluation of molecular integrals over basis functions with an explicit Gaussian dependence on interelectronic coordinates. These formulas use expansions in Hermite Gaussian functions and represent an extension to the work of McMurchie and Davidson to two-electron basis functions. Integrals that depend on the coordinates of up to four electrons are discussed explicitly. A key feature of this approach is that it allows full exploitation of the shell structure of the orbital part of the basis.

Key words: Molecular integrals – Gaussian-type geminal basis functions

1 Introduction

We have recently suggested [1] that Gaussian-type orbital (GTO) basis sets can usefully be augmented with Gaussian-type geminal (GTG) correlation factors $\exp(-\gamma r_{ij}^2)$, where r_{ij} is an interelectronic distance, to improve the description of electron correlation effects. In test calculations at the MP2 level we showed that GTGs were very effective at reducing the error in the correlation energy due to orbital basis incompleteness, even when used with rather small basis sets of double zeta plus polarization quality. The exponents of the correlation factors (typically six are included for each electron pair correlated) are not varied at all in the molecular calculation, so there is none of the nonlinear optimization required in other applications of GTGs, although we must emphasize that in these other applications the desired accuracy in the total electronic energy, compared to the complete basis result, is much greater than in our own work. This difference has a consequence in the type of basis functions that are used – in general GTG calculations (see, for example, Refs. [2] and [3] and references therein) the centres and exponents of the

GTGs are varied to optimize the energy. This usually leads to a basis set in which only a few functions are centred on the nuclei and in which different angular components of p sets, say, have different exponents. In other words, the typical shell structure of GTO basis sets, where sets of angular functions with the same exponents (and contraction coefficients in contracted basis sets) are usually centred on the nuclei in the molecule, perhaps with additional functions at bond midpoints, is completely lost.

The use of GTG basis sets on (essentially) arbitrary centres and with anisotropic angular sets is well suited to evaluating the necessary molecular integrals using formulas such as those derived by Lester and Krauss [4], in which integrals are evaluated individually. This contrasts with GTO programs, in which the shell structure that is present is heavily exploited to reduce the computational work. Our proposed addition of GTG correlation factors to GTO basis sets makes it desirable to develop formulas for the necessary integrals that exploit the shell structure of the GTO basis, and in the following sections we shall derive formulas for all the necessary integrals over the usual one- and two-electron operators. We may note here that several workers independently developed and implemented shell structure-based GTO integral programs some 20 to 25 years ago: one of these workers was Jan Almlöf [5], then a graduate student, and we dedicate this work to his memory.

We begin our presentation with a review of various definitions and useful formulas for expressions involving GTOs and GTGs. In the following section we discuss in detail the derivation of a formula for a three-electron integral over a two-electron operator involving GTOs and GTGs as an example. In Sect. 4 and Sect. 5 we then summarize the formulas for all required integrals over one- and two-electron operators, respectively. We conclude with a very brief discussion of implementation aspects.

2 Definitions and essential formulas

Our notation follows closely that of a recent review [6]. We consider GTOs of the Cartesian form

$$G_{ijk}(\mathbf{r}, a, \mathbf{A}) = x_A^i y_A^j z_A^k \exp(-a r_A^2) \ , \tag{1}$$

where $\mathbf{r}_A = (x - A_x, y - A_y, z - A_z)$ and the GTO is thus centred on a point $\mathbf{A}$ (which need not be a nucleus) and involves "angular quantum numbers" i, j, k. We note that the use of spherical harmonic angular functions and the contraction of several GTOs into a single function can be treated explicitly by the methods reviewed in [6] without adding any new features here, and in general we will consider only integrals over the primitive Cartesian GTOs.

The GTO of Eq. (1) can be factorized into three Cartesian components

$$G_{ijk}(\mathbf{r}, a, \mathbf{A}) = G_i(x, a, A_x) G_j(y, a, A_y) G_k(z, a, A_z) \tag{2}$$

where, e.g., $G_i(x, a, A_x) = x_A^i \exp(-a x_A^2)$, $x_A = x - A_x$. We shall use the differentiation properties of GTOs extensively in our exposition. The derivative of G_i with respect to either the electron or centre coordinates is given by

$$\frac{\partial G_i}{\partial A_x} = -\frac{\partial G_i}{\partial x} = 2a G_{i+1} - i G_{i-1} \ . \tag{3}$$

Introducing the notation

$$G_i^q = \frac{\partial^q G_i}{\partial A_x^q} = (-1)^q \frac{\partial^q G_i}{\partial x^q} \ , \tag{4}$$

it is straightforward to show that

$$G_i^{q+1} = 2a G_{i+1}^q - i G_{i-1}^q \ , \tag{5}$$

which provides a recursive scheme for the calculation of derivatives to any order.

GTOs commonly appear in pairs as an *overlap distribution*

$$\begin{aligned} \Omega_{il,jm,kn}(\mathbf{r}, a, b, \mathbf{A}, \mathbf{B}) &= G_{ijk}(\mathbf{r}, a, \mathbf{A}) G_{lmn}(\mathbf{r}, b, \mathbf{B}) \\ &= x_A^i y_A^j z_A^k \exp(-a r_A^2) x_B^l y_B^m z_B^n \exp(-b r_B^2) \ . \end{aligned} \tag{6}$$

The product of the two exponentials may be rewritten as a single factor using the *Gaussian product rule*:

$$\exp(-a r_A^2) \exp(-b r_B^2) = K_{AB} \exp(-p r_P^2) \ , \tag{7}$$

where $p = a + b$, $K_{AB} = \exp(-q Q^2)$, $q = ab/(a + b)$, $\mathbf{Q} = \mathbf{A} - \mathbf{B}$, and the new GTO centre $\mathbf{P}$ is given by

$$\mathbf{P} = (a + b)^{-1}(a\mathbf{A} + b\mathbf{B}) \ . \tag{8}$$

The products $x_A^i x_B^l$ etc., in Eq. (6) could be rewritten as a polynomial in x_P using the binomial theorem, but this is not the most effective way to proceed. Instead, we introduce the *Hermite Gaussian functions* Λ_{tuv} defined by

$$\Lambda_{tuv}(\mathbf{r}, p, \mathbf{P}) = \left(\frac{\partial}{\partial P_x}\right)^t \left(\frac{\partial}{\partial P_y}\right)^u \left(\frac{\partial}{\partial P_z}\right)^v \exp(-p r_P^2) \ , \tag{9}$$

which can clearly be factorized in Cartesian directions as

$$\Lambda_t(x, p, P_x) = \left(\frac{\partial}{\partial P_x}\right)^t \exp(-p x_P^2) \ , \tag{10}$$

and so forth. The operators for differentiation over the P's will be used extensively below, and in order to get a more compact notation we henceforth write these as

$$\left(\frac{\partial}{\partial P_x}\right)^t = \hat{\mathsf{P}}_x^{(t)} \tag{11}$$

and, in the three dimensional case,

$$\left(\frac{\partial}{\partial P_x}\right)^t \left(\frac{\partial}{\partial P_y}\right)^u \left(\frac{\partial}{\partial P_z}\right)^v = \hat{\mathsf{P}}_{xyz}^{(tuv)} \ . \tag{12}$$

The connections between these Hermite Gaussians and the Hermite functions of harmonic oscillator theory are discussed in detail in Ref. [6]. The Hermite Gaussians have the simple differentiation property

$$\frac{\partial \Lambda_t}{\partial P_x} = -\frac{\partial \Lambda_t}{\partial x} = \Lambda_{t+1} \ . \tag{13}$$

We now write the overlap distribution as [6]

$$\Omega_{il,jm,kn} = \sum_{t=0}^{i+l} \sum_{u=0}^{j+m} \sum_{v=0}^{k+n} E_t^{il} E_u^{jm} E_v^{kn} \Lambda_{tuv} \ , \tag{14}$$

since any polynomial in x of order M can be written as a sum of Hermite polynomials of order 0 to M. The expansion coefficients E do not depend on the electronic coordinates. The overlap distribution can also be written

$$\Omega_{il,jm,kn} = \sum_{t=0}^{i+l} \sum_{u=0}^{j+m} \sum_{v=0}^{k+n} E_t^{il} E_u^{jm} E_v^{kn} \hat{\mathsf{P}}_{xyz}^{(tuv)} \exp(-p r_P^2) \ , \tag{15}$$

emphasizing that all desired angular components can be obtained by differentiating the "spherical" Gaussian $\exp(-p r_P^2)$, which of course is Λ_{000}. We shall use this property extensively in our derivations. We also note that the expansion coefficients can be calculated by recursion from the basic $E_0^{00} = K_{AB}$ using the relations

$$E_t^{i+1,j} = \frac{1}{2p} E_{t-1}^{ij} - \frac{q Q_x}{a} E_t^{ij} + (t + 1) E_{t+1}^{ij} \ , \tag{16}$$

and

$$E_t^{i,j+1} = \frac{1}{2p} E_{t-1}^{ij} + \frac{q Q_x}{b} E_t^{ij} + (t + 1) E_{t+1}^{ij} \ . \tag{17}$$

The centre $\mathbf{Q}$ was defined after Eq. (7). We note that the expansion coefficients depend on $\mathbf{Q}$ but not $\mathbf{P}$; the reverse is true for the Hermite Gaussians Λ.

The great power of the use of Hermite Gaussians is that since any overlap distribution can be obtained by differentiation of a spherical function, integrals over general Hermite Gaussians can be obtained by differentiating an integral over spherical Gaussians. This is possible because the higher-order Hermite functions are obtained from spherical Gaussians by differentiation with respect to the spherical Gaussian centre $\mathbf{P}$, and this differentiation commutes with the integration over the electronic coordinate $\mathbf{r}$. Once the Hermite Gaussian integrals are available, integrals over Cartesian Gaussians can be formed by taking the linear combinations given in Eq. (14). We can illustrate this with a two-electron integral between two overlap distributions:

$$\iint \Omega_{il,jm,kn}(\mathbf{r}_{1P}) r_{12}^{-1} \Omega_{i'l',j'm',k'n'}(\mathbf{r}_{2P'}) d\mathbf{r}_1 \, d\mathbf{r}_2 \ , \tag{18}$$

which can be written as

$$\sum_{tuv}\sum_{t'u'v'}E_t^{il}E_u^{jm}E_v^{kn}E_{t'}^{i'l'}E_{u'}^{j'm'}E_{v'}^{k'n'}$$

$$\iint \Lambda_{tuv}(\mathbf{r}_{1P})\Lambda_{t'u'v'}(\mathbf{r}_{2P'})r_{12}^{-1}\,d\mathbf{r}_1\,d\mathbf{r}_2 \quad . \tag{19}$$

The integral over Hermite Gaussians can then be written as

$$\hat{P}_{xyz}^{(tuv)}\hat{P}_{x'y'z'}^{\prime(t'u'v')}\iint \Lambda_{000}(\mathbf{r}_{1P})\Lambda_{000}(\mathbf{r}_{2P'})r_{12}^{-1}\,d\mathbf{r}_1\,d\mathbf{r}_2 \quad . \tag{20}$$

The elementary integral to be computed is

$$\iint \Lambda_{000}(\mathbf{r}_{1P})\Lambda_{000}(\mathbf{r}_{2P'})r_{12}^{-1}\,d\mathbf{r}_1\,d\mathbf{r}_2 \quad , \tag{21}$$

which in terms of spherical Gaussians can be written as

$$\iint \exp(-pr_{1P}^2)\exp(-p'r_{2P'}^2)r_{12}^{-1}\,d\mathbf{r}_1\,d\mathbf{r}_2 \quad . \tag{22}$$

This integral was given by Boys [7] as

$$\frac{2\pi^{5/2}}{pp'\sqrt{p+p'}}F_0(\alpha R_{PP'}^2) \quad , \tag{23}$$

where

$$\alpha = \frac{pp'}{p+p'} \tag{24}$$

and

$$F_0(t) = \int_0^1 \exp(-tu^2)\,du \tag{25}$$

is one case of the general integral

$$F_n(t) = \int_0^1 \exp(-tu^2)u^{2n}\,du \quad , \tag{26}$$

usually referred to as an incomplete gamma function. We note that $F_{n+1}(t) = -dF_n/dt$, showing that the Hermite Gaussian integrals must be linear combinations of $F_n(t)$ for various values of n, since they are obtained by differentiating the elementary integral which is related to $F_0(t)$. We may also note that since Eq. (23) depends on P and P' only through the distance $R_{PP'}$, we can rewrite the integral over Hermite Gaussians as

$$\hat{P}_{xyz}^{(tuv)}\hat{P}_{x'y'z'}^{\prime(t'u'v')}\iint \Lambda_{000}(\mathbf{r}_{1P})\Lambda_{000}(\mathbf{r}_{2P'})r_{12}^{-1}\,d\mathbf{r}_1\,d\mathbf{r}_2$$

$$= (-1)^{t'+u'+v'}\hat{P}_{xyz}^{(t+t',u+u',v+v')} \tag{27}$$

$$\iint \Lambda_{000}(\mathbf{r}_{1P})\Lambda_{000}(\mathbf{r}_{2P'})r_{12}^{-1}\,d\mathbf{r}_1\,d\mathbf{r}_2 \quad .$$

As discussed for example in Ref. [6], the latter simplification is a very important one, since it reduces substantially the number of distinct Hermite Gaussian integrals that must be calculated.

So far our discussion has involved only GTOs – the introduction of Gaussian correlation factors makes things only a little more complicated in the GTG case, since there is a coupling between two electrons and their overlap distributions. For example, an integral might involve factors like

$$\Omega_{il,jm,kn}(\mathbf{r}_{1P})\Omega_{i'l',j'm',k'n'}(\mathbf{r}_{2P'})\exp(-\gamma r_{12}^2) \quad . \tag{28}$$

In this form it should be obvious that the correlation factors do not give rise to any new terms when expressing overlap distributions in terms of Hermite Gaussians, since the differentiation with respect to P does not affect the correlation factors. The greater complication when GTGs are included is the dimensionality of the integral. Even with only one- and two-electron operators in the Hamiltonian, up to four-electron integrals can appear in MP2 calculations. However, as Boys pointed out some time ago [8] the resulting formulas for GTG integrals are not much more complicated than GTO integrals. The fundamental mathematical step is a lemma proved by Boys in Ref. [8] (labelled Theorem 2 in that work) which allows us to successively eliminate electron coordinates that do not appear in the operator itself. Namely, if the dependence of an integral on electron coordinate $\mathbf{r}_1$ is completely of the form

$$\iint \ldots \ \mathscr{F}(\mathbf{r}_2,\mathbf{r}_3\ldots)\sum_i \exp(-c_i r_{1\aleph_i}^2)\,d\mathbf{r}_1\,d\mathbf{r}_2\ldots \quad , \tag{29}$$

where $\mathscr{F}(\mathbf{r}_2,\mathbf{r}_3\ldots)$ is any function of the coordinates of all the other electrons in the integral and $\aleph$ can be a fixed centre *or* another electron coordinate, then the integration over electron 1 yields the integral

$$\left(\frac{\pi}{\sum_i c_i}\right)^{\frac{3}{2}}\int\int \cdots \ \exp\left(-\sum_{i>j}c_i c_j(\aleph_i - \aleph_j)^2 \Big/ \sum_i c_i\right)$$

$$\mathscr{F}(\mathbf{r}_2,\mathbf{r}_3\ldots)\,d\mathbf{r}_2\ldots \quad . \tag{30}$$

Thus Boys' lemma allows us to integrate out all of the electron coordinates except those that appear in the operator. Eventually this will yield a one- or two-electron integral, depending on the operator. For example, in reducing integrals over the two-electron Coulomb repulsion operator, we obtain the following integral over spherical Gaussians [8]:

$$\iint \exp(-pr_{1P}^2)\exp(-p'r_{2P'}^2)\exp(-\gamma r_{12}^2)r_{12}^{-1}\,d\mathbf{r}_1\,d\mathbf{r}_2$$

$$= \frac{2\pi^{5/2}}{(pp'+p\gamma+p'\gamma)\sqrt{p+p'}}\exp\left(\frac{-pp'\gamma R_{PP'}^2}{pp'+p\gamma+p'\gamma}\right) \tag{31}$$

$$\times F_0\left(\frac{p^2 p'^2 R_{PP'}^2}{(pp'+p\gamma+p'\gamma)(p+p')}\right) \quad .$$

This integral is more complicated than the case of Eq. (23), where there was no Gaussian factor multiplying the incomplete gamma function. Since this Gaussian factor depends on the centres appearing in the original overlap distributions, it follows that the differentiation of the integral over spherical Gaussians to give integrals over Hermite Gaussians will involve more terms than appear in GTO integrals. With this observation we conclude our presentation of the basic formulas and discuss in detail an example of a three-electron integral.

3 Case study: a three-electron integral

Consider the so-called "cyclic" three-electron integral:

$$\iiint \chi_\mu(1)\chi_\nu(2)\chi_\lambda(3)\exp(-\gamma_v r_{13}^2)r_{12}^{-1}\chi_\theta(1)\chi_\varphi(2)$$
$$\times \chi_\kappa(3)\exp(-\gamma_w r_{23}^2)d\mathbf{r}_1\,d\mathbf{r}_2\,d\mathbf{r}_3 \quad . \tag{32}$$

We first construct three overlap distributions:

$$\chi_\mu(1)\chi_\theta(1) = \Omega_{il,jm,kn}$$
$$= \sum_{t=0}^{i+l}\sum_{u=0}^{j+m}\sum_{v=0}^{k+n} E_t^{il}E_u^{jm}E_v^{kn}\hat{\mathsf{P}}_{xyz}^{(tuv)}\exp(-pr_{1P}^2)$$
$$\chi_\nu(2)\chi_\varphi(2) = \Omega_{i'l',j'm',k'n'}$$
$$= \sum_{t'=0}^{i'+l'}\sum_{u'=0}^{j'+m'}\sum_{v'=0}^{k'+n'} E_{t'}^{i'l'}E_{u'}^{j'm'}E_{v'}^{k'n'}\hat{\mathsf{P}}_{xyz}'^{(t'u'v')}\exp(-p'r_{2P'}^2)$$
$$\chi_\lambda(3)\chi_\kappa(3) = \Omega_{i''l'',j''m'',k''n''}$$
$$= \sum_{t''=0}^{i''+l''}\sum_{u''=0}^{j''+m''}\sum_{v''=0}^{k''+n''} E_{t''}^{i''l''}E_{u''}^{j''m''}E_{v''}^{k''n''}\hat{\mathsf{P}}_{xyz}''^{(t''u''v'')}$$
$$\times \exp(-p''r_{3P''}^2) \quad . \tag{33}$$

The three-electron integral of Eq. (32) can now be written as

$$\sum_{t=0}^{i+l}\sum_{u=0}^{j+m}\sum_{v=0}^{k+n}\sum_{t'=0}^{i'+l'}\sum_{u'=0}^{j'+m'}\sum_{v'=0}^{k'+n'}\sum_{t''=0}^{i''+l''}\sum_{u''=0}^{j''+m''}\sum_{v''=0}^{k''+n''}$$
$$E_t^{il}E_u^{jm}E_v^{kn}E_{t'}^{i'l'}E_{u'}^{j'm'}E_{v'}^{k'n'}E_{t''}^{i''l''}E_{u''}^{j''m''}E_{v''}^{k''n''}\hat{\mathsf{P}}_{xyz}^{(tuv)}\hat{\mathsf{P}}_{xyz}'^{(t'u'v')}\hat{\mathsf{P}}_{xyz}''^{(t''u''v'')}$$
$$\times \iiint r_{12}^{-1}\exp(-pr_{1P}^2)\exp(-p'r_{2P'}^2)\exp(-p''r_{3P''}^2)$$
$$\times \exp(-\gamma_v r_{13}^2)\exp(-\gamma_w r_{23}^2)d\mathbf{r}_1\,d\mathbf{r}_2\,d\mathbf{r}_3 \quad , \tag{34}$$

which gives the desired integral as the derivative of an integral over spherical Gaussians. We can now integrate over the coordinates of electron 3 using Boys' Lemma, leading to

$$\left(\frac{\pi}{p''+\gamma_v+\gamma_w}\right)^{3/2}\iint r_{12}^{-1}\exp(-pr_{1P}^2)\exp(-p'r_{2P'}^2)\cdot$$
$$\exp\left(-\frac{p''\gamma_v r_{1P''}^2}{p''+\gamma_v+\gamma_w}\right)\exp\left(-\frac{p''\gamma_w r_{2P''}^2}{p''+\gamma_v+\gamma_w}\right)$$
$$\times \exp\left(-\frac{\gamma_v\gamma_w r_{12}^2}{p''+\gamma_v+\gamma_w}\right)d\mathbf{r}_1\,d\mathbf{r}_2 \quad . \tag{35}$$

Using the Gaussian product rule we can write this as

$$\left(\frac{\pi}{p''+\gamma_v+\gamma_w}\right)^{3/2}K_{PP''}K_{P'P''}$$
$$\iint r_{12}^{-1}\exp(-sr_{1S}^2)\exp(-tr_{2T}^2) \tag{36}$$
$$\times \exp\left(-\frac{\gamma_v\gamma_w r_{12}^2}{p''+\gamma_v+\gamma_w}\right)d\mathbf{r}_1\,d\mathbf{r}_2 \quad ,$$

where

$$K_{PP''} = \exp\left(-\frac{pp''\gamma_v R_{PP''}^2}{p\gamma_v+p\gamma_w+p''\gamma_w+pp''}\right) \tag{37}$$

$$\mathbf{R}_{PP''} = \mathbf{P} - \mathbf{P}'' \tag{38}$$

$$s = p + \frac{p''\gamma_v}{p''+\gamma_v+\gamma_w} \tag{39}$$

$$\mathbf{S} = \frac{1}{s}\left(p\mathbf{P} + \frac{p''\gamma_v}{p''+\gamma_v+\gamma_w}\mathbf{P}''\right) \tag{40}$$

$$K_{P'P''} = \exp\left(-\frac{p'p''\gamma_w R_{P'P''}^2}{p'\gamma_v+p'\gamma_w+p''\gamma_w+p'p''}\right) \tag{41}$$

$$\mathbf{R}_{P'P''} = \mathbf{P}' - \mathbf{P}'' \tag{42}$$

$$t = p' + \frac{p''\gamma_w}{p''+\gamma_v+\gamma_w} \tag{43}$$

$$\mathbf{T} = \frac{1}{t}\left(p'\mathbf{P}' + \frac{p''\gamma_w}{p''+\gamma_v+\gamma_w}\mathbf{P}''\right) \quad . \tag{44}$$

According to Boys [8] (see Eq. 31) the integral of Eq. (36) is

$$2\pi^4(p''+\gamma_v+\gamma_w)^{-3/2}\left(\frac{\gamma_v\gamma_w(s+t)}{p''+\gamma_v+\gamma_w}+st\right)^{-1}$$
$$\times (s+t)^{-1/2}K_{PP''}K_{P'P''}$$
$$\times \exp\left(-\left[\frac{st\gamma_v\gamma_w}{p''+\gamma_v+\gamma_w}\right]\left[\frac{\gamma_v\gamma_w(s+t)}{p''+\gamma_v+\gamma_w}+st\right]^{-1}R_{ST}^2\right)$$
$$\times F_0\left(\left[\frac{\gamma_v\gamma_w(s+t)}{p''+\gamma_v+\gamma_w}+st\right]^{-1}\frac{s^2t^2}{s+t}R_{ST}^2\right) \quad , \tag{45}$$

where F_0 is the zeroth-order incomplete gamma function of Eq. (25). Using an obvious short-hand notation, we can write the three-electron integral over spherical Gaussians as a four-factor product

$$K_{PP''}K_{P'P''}\exp(-\alpha R_{ST}^2)F_0(\beta R_{ST}^2) \quad , \tag{46}$$

on which we must operate with $\hat{\mathsf{P}}_{xyz}^{(tuv)}\hat{\mathsf{P}}_{xyz}'^{(t'u'v')}\hat{\mathsf{P}}_{xyz}''^{(t''u''v'')}$. We write Eq. (46) as a product of two functions, gf, of $\mathbf{P}$, $\mathbf{P}'$ and $\mathbf{P}''$, where we identify f with F_0 and g with the product of the other three factors, i.e. we have the expression

$$\hat{\mathsf{P}}_{xyz}^{(tuv)}\hat{\mathsf{P}}_{xyz}'^{(t'u'v')}\hat{\mathsf{P}}_{xyz}''^{(t''u''v'')}gf \quad . \tag{47}$$

Using the rule for differentiation of a product,

$$D^n(g\cdot f) = \sum_{k=0}^n \binom{n}{k}g^{(k)}f^{(n-k)} \tag{48}$$

we can write Eq. (47) as (note that barred indices are dummy summation indices and not Cartesian coordinates)

$$\sum_{\bar{x}=0}^t\sum_{\bar{y}=0}^u\sum_{\bar{z}=0}^v\sum_{\bar{x}'=0}^{t'}\sum_{\bar{y}'=0}^{u'}\sum_{\bar{z}'=0}^{v'}\sum_{\bar{x}''=0}^{t''}\sum_{\bar{y}''=0}^{u''}\sum_{\bar{z}''=0}^{v''}\binom{t}{\bar{x}}\binom{u}{\bar{y}}\binom{v}{\bar{z}}\binom{t'}{\bar{x}'}$$
$$\binom{u'}{\bar{y}'}\binom{v'}{\bar{z}'}\binom{t''}{\bar{x}''}\binom{u''}{\bar{y}''}\binom{v''}{\bar{z}''}$$
$$\times \hat{\mathsf{P}}_{xyz}^{(\bar{x},\bar{y},\bar{z})}\hat{\mathsf{P}}_{xyz}'^{(\bar{x}',\bar{y}',\bar{z}')}\hat{\mathsf{P}}_{xyz}''^{(\bar{x}'',\bar{y}'',\bar{z}'')}g$$
$$\times \hat{\mathsf{P}}_{xyz}^{(t-\bar{x},u-\bar{y},v-\bar{z})}\hat{\mathsf{P}}_{xyz}'^{(t'-\bar{x}',u'-\bar{y}',v'-\bar{z}')}\hat{\mathsf{P}}_{xyz}''^{(t''-\bar{x}'',u''-\bar{y}'',v''-\bar{z}'')}f \quad . \tag{49}$$

In order to further shorten the notation we write the derivatives as strings of superscript indices, i.e.

$$\hat{\mathsf{P}}_{xyz}^{(t-\bar{x},u-\bar{y},v-\bar{z})}\hat{\mathsf{P}}_{xyz}'^{(t'-\bar{x}',u'-\bar{y}',v'-\bar{z}')}\hat{\mathsf{P}}_{xyz}''^{(t''-\bar{x}'',u''-\bar{y}'',v''-\bar{z}'')}f$$
$$= f^{(t-\bar{x},u-\bar{y},v-\bar{z},t'-\bar{x}',u'-\bar{y}',v'-\bar{z}',t''-\bar{x}'',u''-\bar{y}'',v''-\bar{z}'')} \quad (50)$$

and

$$\hat{\mathsf{P}}_{xyz}^{(\bar{x},\bar{y},\bar{z})}\hat{\mathsf{P}}_{xyz}'^{(\bar{x}',\bar{y}',\bar{z}')}\hat{\mathsf{P}}_{xyz}''^{(\bar{x}'',\bar{y}'',\bar{z}'')}g = g^{(\bar{x},\bar{y},\bar{z},\bar{x}',\bar{y}',\bar{z}',\bar{x}'',\bar{y}'',\bar{z}'')} \quad (51)$$

The derivatives of f with respect to $\mathbf{P}$, $\mathbf{P}'$ and $\mathbf{P}''$ are not independent, they differ from each other only by some numerical factor. For instance, in the x-direction we have:

$$\hat{\mathsf{P}}_x f = \beta \frac{\partial F_0(\beta R_{ST}^2)}{\partial R_{ST}^2} \times \hat{\mathsf{P}}_x R_{ST}^2$$
$$\hat{\mathsf{P}}_x' f = \beta \frac{\partial F_0(\beta R_{ST}^2)}{\partial R_{ST}^2} \times \hat{\mathsf{P}}_x' R_{ST}^2 \quad (52)$$
$$\hat{\mathsf{P}}_x'' f = \beta \frac{\partial F_0(\beta R_{ST}^2)}{\partial R_{ST}^2} \times \hat{\mathsf{P}}_x'' R_{ST}^2 \quad,$$

where the only difference is in the derivatives of R_{ST}^2. From Eq. (44) we can express $\mathbf{R}_{ST}$ directly in terms of $\mathbf{P}$, $\mathbf{P}'$, and $\mathbf{P}''$:

$$\mathbf{R}_{ST} = (\mathbf{S} - \mathbf{T}) = a\mathbf{P} + b\mathbf{P}' + c\mathbf{P}'' \quad, \quad (53)$$

where we have defined

$$a = \frac{p}{s}$$
$$b = -\frac{p'}{t} \quad (54)$$
$$c = \frac{p''\gamma_v}{(p'' + \gamma_v + \gamma_w)s} - \frac{p''\gamma_w}{(p'' + \gamma_v + \gamma_w)t} \quad.$$

The derivatives of R_{ST}^2 are then

$$\hat{\mathsf{P}}_x R_{ST}^2 = 2aX_{ST},$$
$$\hat{\mathsf{P}}_x' R_{ST}^2 = 2bX_{ST}, \quad (55)$$
$$\hat{\mathsf{P}}_x'' R_{ST}^2 = 2cX_{ST}$$

and the relations between the derivatives of f are:

$$\hat{\mathsf{P}}_x' f = \left(\frac{b}{a}\right)\hat{\mathsf{P}}_x f,$$
$$\hat{\mathsf{P}}_x'' f = \left(\frac{c}{a}\right)\hat{\mathsf{P}}_x f \quad. \quad (56)$$

Thus, the differentiation of f with respect to $\mathbf{P}'$ and $\mathbf{P}''$ can be replaced by differentiation with respect to $\mathbf{P}$ and the appropriate numerical factors, which we write as a "shift" in the differentiation indices

$$f^{(t-\bar{x},u-\bar{y},v-\bar{z},t'-\bar{x}',u'-\bar{y}',v'-\bar{z}',t''-\bar{x}'',u''-\bar{y}'',v''-\bar{z}'')}$$
$$= \left(\frac{b}{a}\right)^{t'+u'+v'-\bar{x}'-\bar{y}'-\bar{z}'} \left(\frac{c}{a}\right)^{t''+u''+v''-\bar{x}''-\bar{y}''-\bar{z}''}$$
$$\times f^{(t+t'+t''-\bar{x}-\bar{x}'-\bar{x}'',u+u'+u''-\bar{y}-\bar{y}'-\bar{y}'',v+v'+v''-\bar{z}-\bar{z}'-\bar{z}'',0,0,0,0,0,0)} \quad.$$
$$(57)$$

This is the three-electron analogue of the differentiation index shift for the two-electron GTO integral employed in Eq. (27). We may note that the calculation of these

derivatives of the incomplete gamma function is already required for the evaluation of GTO integrals, as discussed in Ref. [6] where these quantities are denoted R_{tuv}. Recursive methods for their calculation are already available from the work of McMurchie and Davidson [9], for example, and it is unnecessary to discuss this further here.

As defined in Eq. (46), g is the product of three functions,

$$g = K_{PP''}K_{P'P''}\exp(-\alpha R_{ST}^2) \quad. \quad (58)$$

Differentiation of these functions is most conveniently carried out by developing recursion relations, using the recursion for differentiating a single Gaussian (Eq. 13) as a basis. These relations are straightforward to derive and we omit details of the derivation here. The final recursion relations are

$$\hat{\mathsf{P}}_x^{(q+1)}K_{P_xP_x''}^i K_{P_x'P_x''}^j K_{P_xP_x'P_x''}^k$$
$$= i\hat{\mathsf{P}}_x^{(q)}K_{P_xP_x''}^{i-1}K_{P_x'P_x''}^j K_{P_xP_x'P_x''}^k - 2\epsilon\hat{\mathsf{P}}_x^{(q)}K_{P_xP_x''}^{i+1}K_{P_x'P_x''}^j K_{P_xP_x'P_x''}^k$$
$$+ ak\hat{\mathsf{P}}_x^{(q)}K_{P_xP_x''}^i K_{P_x'P_x''}^j K_{P_xP_x'P_x''}^{k-1} - 2a\alpha\hat{\mathsf{P}}_x^{(q)}K_{P_xP_x''}^i K_{P_x'P_x''}^j K_{P_xP_x'P_x''}^{k+1} \quad,$$
$$(59)$$

$$\hat{\mathsf{P}}_x'^{(q+1)}K_{P_xP_x''}^i K_{P_x'P_x''}^j K_{P_xP_x'P_x''}^k$$
$$= j\hat{\mathsf{P}}_x'^{(q)}K_{P_xP_x''}^i K_{P_x'P_x''}^{j-1}K_{P_xP_x'P_x''}^k - 2\zeta\hat{\mathsf{P}}_x'^{(q)}K_{P_xP_x''}^i K_{P_x'P_x''}^{j+1}K_{P_xP_x'P_x''}^k$$
$$+ bk\hat{\mathsf{P}}_x'^{(q)}K_{P_xP_x''}^i K_{P_x'P_x''}^j K_{P_xP_x'P_x''}^{k-1} - 2b\alpha\hat{\mathsf{P}}_x'^{(q)}K_{P_xP_x''}^i K_{P_x'P_x''}^j K_{P_xP_x'P_x''}^{k+1} \quad,$$
$$(60)$$

$$\hat{\mathsf{P}}_x''^{(q+1)}K_{P_xP_x''}^i K_{P_x'P_x''}^j K_{P_xP_x'P_x''}^k =$$
$$- i\hat{\mathsf{P}}_x''^{(q)}K_{P_xP_x''}^{i-1}K_{P_x'P_x''}^j K_{P_xP_x'P_x''}^k + 2\epsilon\hat{\mathsf{P}}_x''^{(q)}K_{P_xP_x''}^{i+1}K_{P_x'P_x''}^j K_{P_xP_x'P_x''}^k$$
$$- j\hat{\mathsf{P}}_x''^{(q)}K_{P_xP_x''}^i K_{P_x'P_x''}^{j-1}K_{P_xP_x'P_x''}^k + 2\zeta\hat{\mathsf{P}}_x''^{(q)}K_{P_xP_x''}^i K_{P_x'P_x''}^{j+1}K_{P_xP_x'P_x''}^k$$
$$+ ck\hat{\mathsf{P}}_x''^{(q)}K_{P_xP_x''}^i K_{P_x'P_x''}^j K_{P_xP_x'P_x''}^{k-1} - 2c\alpha\hat{\mathsf{P}}_x''^{(q)}K_{P_xP_x''}^i K_{P_x'P_x''}^j K_{P_xP_x'P_x''}^{k+1} \quad,$$
$$(61)$$

where

$$K_{P_xP_x''}^i = (P_x - P_x'')^i \exp\left(-\epsilon(P_x - P_x'')^2\right) \quad, \quad (62)$$
$$K_{P_x'P_x''}^j = (P_x' - P_x'')^j \exp\left(-\zeta(P_x' - P_x'')^2\right) \quad, \quad (63)$$
$$K_{P_xP_x'P_x''}^k = (aP_x + bP_x' + cP_x'')^k$$
$$\exp\left(-\alpha(aP_x + bP_x' + cP_x'')^2\right) \quad, \quad (64)$$

$K_{PP''} \equiv K_{PP''}^0$ etc., the constants a, b and c are those given in Eq. (54), and we have collapsed the constants in the exponentials of Eqs. (37) and (41) into ϵ and ζ. Note that since the Cartesian directions are separable, the recursion relations for the y and z directions will be identical to those for the x direction. Further, the derivatives for one particular direction are not independent either, since for instance,

$$\hat{\mathsf{P}}_x K_{PP''}^i = -\hat{\mathsf{P}}_x'' K_{PP''}^i,$$
$$\hat{\mathsf{P}}_x' K_{P'P''}^j = -\hat{\mathsf{P}}_x'' K_{P'P''}^i,$$
$$\hat{\mathsf{P}}_x K_{PP'P''}^k = \left(\frac{a}{c}\right)\hat{\mathsf{P}}_x'' K_{PP'P''}^k,$$
$$\hat{\mathsf{P}}_x' K_{PP'P''}^k = \left(\frac{b}{c}\right)\hat{\mathsf{P}}_x'' K_{PP'P''}^k \quad. \quad (65)$$

The derivatives with respect to **P** and **P′** can thus in principle be expressed in terms of derivatives with respect to **P″**, etc. However, a simpler technique to obtain the derivatives with respect to all three coordinates P_x, P'_x and P''_x may be to apply the recursions of Eqs. (59–61) successively, as in

$$
\begin{aligned}
\hat{\mathsf{P}}_x^{\prime(q+1)}&\hat{\mathsf{P}}_x^{\prime\prime(r)}K_{P_x P''_x}^i K_{P'_x P''_x}^j K_{P_x P'_x}^k \\
&= j\hat{\mathsf{P}}_x^{\prime(q)}\hat{\mathsf{P}}_x^{\prime\prime(r)}K_{P_x P''_x}^i K_{P'_x P''_x}^{j-1} K_{P_x P'_x}^k \\
&\quad - 2\zeta\hat{\mathsf{P}}_x^{\prime(q)}\hat{\mathsf{P}}_x^{\prime\prime(r)}K_{P_x P''_x}^i K_{P'_x P''_x}^{j+1} K_{P_x P'_x}^k \\
&\quad + bk\hat{\mathsf{P}}_x^{\prime(q)}\hat{\mathsf{P}}_x^{\prime\prime(r)}K_{P_x P''_x}^i K_{P'_x P''_x}^j K_{P_x P'_x}^{k-1} \\
&\quad - 2b\alpha\hat{\mathsf{P}}_x^{\prime(q)}\hat{\mathsf{P}}_x^{\prime\prime(r)}K_{P_x P''_x}^i K_{P'_x P''_x}^j K_{P_x P'_x}^{k+1}
\end{aligned}
\tag{66}
$$

and so forth. This allows us to recursively calculate all the required derivatives of g. These can then be combined with the derivatives of f in the binomial expansion of Eq. (48) to obtain the integrals over Hermite Gaussians. Finally, the Hermite Gaussian integrals can then be combined with expansion coefficients to obtain the three-electron integral over Cartesian or spherical harmonic GTOs, as in Eq. (34).

In what follows we shall present the formulas necessary for the evaluation of various two-, three- and four-electron integrals over GTGs. For brevity, we have eliminated most of the derivation (the detailed case study given in Sect. 3 covered a more complicated case than any required for the integrals that follow, so deriving the formulas given should not be difficult) and discuss primarily the key integrals over spherical Gaussians. The differentiation of these integrals to give integrals over Hermite functions is again given by the procedures developed in our case study. In fact, all of the integrals we now discuss are simpler than the cyclic three-electron integral in that the spherical Gaussian integrals consist of no more than two Gaussian factors multiplying the incomplete gamma function. This makes our function g simpler, and for completeness we give here the recursion relations for derivatives of g when it comprises only two terms, rather than the three of Eq. (58):

$$
\begin{aligned}
\hat{\mathsf{P}}_x^{(q+1)}K_{P_x P''_x}^i K_{P_x P'_x P''_x}^k &= i\hat{\mathsf{P}}_x^{(q)}K_{P_x P''_x}^{i-1} K_{P_x P'_x P''_x}^k \\
&\quad - 2\epsilon\hat{\mathsf{P}}_x^{(q)}K_{P_x P''_x}^{i+1} K_{P_x P'_x P''_x}^k \\
&\quad + ak\hat{\mathsf{P}}_x^{(q)}K_{P_x P''_x}^i K_{P_x P'_x P''_x}^{k-1} \\
&\quad - 2a\alpha\hat{\mathsf{P}}_x^{(q)}K_{P_x P''_x}^i K_{P_x P'_x P''_x}^{k+1}, \\
\hat{\mathsf{P}}_x^{\prime(q+1)}K_{P_x P''_x}^i K_{P_x P'_x P''_x}^k &= bk\hat{\mathsf{P}}_x^{\prime(q)}K_{P_x P''_x}^i K_{P_x P'_x P''_x}^{k-1} \\
&\quad - 2b\alpha\hat{\mathsf{P}}_x^{\prime(q)}K_{P_x P''_x}^i K_{P_x P'_x P''_x}^{k+1}, \\
\hat{\mathsf{P}}_x^{\prime\prime(q+1)}K_{P_x P''_x}^i K_{P_x P'_x P''_x}^k &= i\hat{\mathsf{P}}_x^{\prime\prime(q)}K_{P_x P''_x}^{i-1} K_{P_x P'_x P''_x}^k \\
&\quad - 2\epsilon\hat{\mathsf{P}}_x^{\prime\prime(q)}K_{P_x P''_x}^{i+1} K_{P_x P'_x P''_x}^k \\
&\quad + ck\hat{\mathsf{P}}_x^{\prime\prime(q)}K_{P_x P''_x}^i K_{P_x P'_x P''_x}^{k-1} \\
&\quad - 2c\alpha\hat{\mathsf{P}}_x^{\prime\prime(q)}K_{P_x P''_x}^i K_{P_x P'_x P''_x}^{k+1} .
\end{aligned}
\tag{67}
$$

The case of a single-term g reduces to the Gaussian differentiation formula of Eq. (5).

We may also note here that some of the "many-electron" integrals that arise in calculations using GTGs (or other two-electron basis functions) can be written as simple products of lower-order integrals. It is not necessary to consider such products explicitly and we ignore all such possibilities here.

4 One-electron operator matrix elements

There are no GTG one-electron integrals over one-electron operators, except for the degenerate case of zero exponents for the correlation factors, i.e. GTO integrals. The simplest GTG integrals over one-electron operators are two-electron integrals.

4.1 Two-electron integrals

The simplest integral involving GTGs is the overlap integral

$$
\iint \chi_\mu(1)\chi_\nu(2)\chi_\theta(1)\chi_\varphi(2)\exp(-\gamma_v r_{12}^2)d\mathbf{r}_1\,d\mathbf{r}_2 \ ,
\tag{68}
$$

which requires the following integral over spherical Gaussians:

$$
\iint \exp(-p r_{1P}^2)\exp(-p' r_{2P'}^2)\exp(-\gamma_v r_{12}^2)d\mathbf{r}_1\,d\mathbf{r}_2 \ .
\tag{69}
$$

This integral was shown by Boys [8] to be

$$
\left(\frac{\pi^2}{pp'+p\gamma_v+p'\gamma_v}\right)^{\frac{3}{2}}K_{PP'} \ ,
\tag{70}
$$

where

$$
K_{PP'} = \exp(-q R_{PP'}^2)
\tag{71}
$$

and $q = pp'\gamma_v/(pp'+p\gamma_v+p'\gamma_v)$. Differentiation of Eq. (70), which is given directly by Eq. (5), then gives the final overlap integrals. Formulas for integrals over the multipole-moment operators can be obtained trivially as overlap integrals that involve overlap distributions with modified angular quantum numbers, just as is done for GTOs.

Calculation of kinetic energy matrix elements follows directly from the calculation of overlap integrals. The only modification is that the kinetic-energy operator produces differentiated GTGs in the original integral, which in turn leads to different terms appearing in the spherical Gaussian integrals. We illustrate this for the contribution to the kinetic energy from the operator $\partial^2/\partial x^2$ operating on the x part of a GTG (not on an overlap distribution!):

$$
\begin{aligned}
\frac{\partial^2}{\partial x^2} &x_{1A}^l x_{2B}^m \exp(-a x_{1A}^2)\exp(-b x_{2B}^2)\exp(-\gamma_v x_{12}^2) \\
&= \big\{ l(l-1)x_{1A}^{l-2} - (2a-2b)x_{1A}^l + 4a^2 x_{1A}^{l+2} \\
&\quad - 4bl x_{12}x_{1A}^{l-1} + 6ab x_{12}x_{1A}^{l+1} + 4b^2 x_{12}^2 x_{1A}^l \big\} \\
&\quad \times \big[x_{2B}^m \exp(-a x_{1A}^2)\exp(-b x_{2B}^2)\exp(-\gamma_v x_{12}^2) \big] \ .
\end{aligned}
\tag{72}
$$

The first three terms in braces in Eq. (72) are similar to the shifted angular quantum number terms that appear in GTO kinetic-energy integrals. They can be handled either by considering them as modified overlap integrals, or by deriving new expansion coefficients for expressing differentiated overlap distributions as combinations of Hermite functions. It is the last three terms in braces that give new contributions, because of the appearance of the factors in x_{12}. Our approach is to rewrite x_{12} using the identity

$$
\begin{aligned}
x_{12} &= x_1 - x_2 - A_x + B_x + (A_x - B_x) \\
&= x_{1A} - x_{2B} + X_{AB} \quad ,
\end{aligned}
\tag{73}
$$

where we have again used X_{AB} to denote $(A_x - B_x)$. Using this identity we can rewrite the last three terms in the braces in Eq. (72) as

$$
\begin{aligned}
&- 4blx_{12}x_{1A}^{l-1}x_{2B}^{m} + 6abx_{12}x_{1A}^{l+1}x_{2B}^{m} - 4b^2x_{12}^2x_{1A}^lx_{2B}^m \\
&= -4blx_{1A}^l + 4blx_{1A}^{l-1}x_{2B} - 4blX_{AB}x_{1A}^{l-1} \\
&\quad + (6ab + 2b^2)x_{1A}^{l+2} - (6ab + 8b^2)x_{1A}^{l+1}x_{2B} \\
&\quad + (6ab + 8b^2)X_{AB}x_{1A}^{l+1} \\
&\quad + 4b^2x_{1A}^lx_{2B}^2 - 8b^2X_{AB}x_{1A}^{l-1}x_{2B} + 4b^2X_{AB}^2x_{1A}^l \quad .
\end{aligned}
\tag{74}
$$

We may thus write the differentiated GTG of Eq. (72) as a linear combination of undifferentiated GTGs (with modified angular quantum numbers). The kinetic-energy integrals then become a linear combination of overlap integrals and can be evaluated using that formula. We note in passing that in practice it may be more convenient to evaluate the integrals over the operators ∇_1^2 and ∇_2^2 together.

The remaining one-electron operator we consider is the nuclear attraction. Multicentre integrals over this operator involve the incomplete gamma function and are thus more complicated than overlap, multipole, or kinetic-energy integrals. A typical two-electron integral over the nuclear-attraction operator is

$$
\sum_C Z_C \iint \chi_\mu(1)\chi_\nu(2) \exp(-\gamma_v r_{12}^2) r_{1C}^{-1} \chi_\theta(1)\chi_\varphi(2) \, d\mathbf{r}_1 \, d\mathbf{r}_2 \quad ,
\tag{75}
$$

where the sum runs over nuclei C with respective charges Z_C. The necessary integral over spherical Gaussians is

$$
\iint r_{1C}^{-1} \exp(-pr_{1P}^2) \exp(-p'r_{2P'}^2) \exp(-\gamma_v r_{12}^2) \, d\mathbf{r}_1 \, d\mathbf{r}_2 \quad ,
\tag{76}
$$

which after applying Boys' Lemma to electron 2 becomes

$$
\left(\frac{\pi}{p' + \gamma_v}\right)^{\frac{3}{2}} \int r_{1C}^{-1} \exp(-pr_{1P}^2) \exp\left(-\frac{p'\gamma_v}{p' + \gamma_v}r_{1P'}^2\right) d\mathbf{r}_1 \quad .
\tag{77}
$$

We use the Gaussian product rule as usual to rewrite the integral as

$$
\left(\frac{\pi}{p' + \gamma_v}\right)^{\frac{3}{2}} K_{PP'} \int r_{1C}^{-1} \exp(-sr_{1S}^2) \, d\mathbf{r}_1 \quad ,
\tag{78}
$$

which can be written in terms of the incomplete gamma function as

$$
\left(\frac{\pi}{p' + \gamma_v}\right)^{\frac{3}{2}} \left(\frac{2\pi}{s}\right) K_{PP'} F_0(sR_{CS}^2) \quad .
\tag{79}
$$

Here again

$$
K_{PP'} = \exp(-qR_{PP'}^2) \quad ,
\tag{80}
$$

$$
q = pp'\gamma_v/(pp' + p\gamma_v + p'\gamma_v) \quad ,
\tag{81}
$$

and now

$$
\mathbf{S} = \frac{(pp' + p\gamma_v)\mathbf{P} + p'\gamma_v\mathbf{P}'}{pp' + p\gamma_v + p'\gamma_v} \quad ,
\tag{82}
$$

$$
s = (pp' + p\gamma_v + p'\gamma_v)/(p' + \gamma_v) \quad .
\tag{83}
$$

Differentiation of the final integral (Eq. 79) over spherical Gaussians yields the desired two-electron integrals over Hermite functions.

4.2 Three-electron integrals

A typical three-electron integral over a one-electron operator would be

$$
\begin{aligned}
\iiint &\chi_\mu(1)\chi_\nu(2)\chi_\lambda(3) \exp(-\gamma_v r_{12}^2) \\
&\times O(\mathbf{r}_1)\chi_\theta(1)\chi_\varphi(2)\chi_\kappa(3) \exp(-\gamma_w r_{13}^2) \, d\mathbf{r}_1 \, d\mathbf{r}_2 \, d\mathbf{r}_3 \quad .
\end{aligned}
\tag{84}
$$

In the case of the overlap integral (which includes kinetic-energy and multipole integrals as special cases, just as discussed above for two-electron integrals) we need to evaluate the following integral over spherical Gaussians:

$$
\begin{aligned}
\iiint &\exp(-pr_{1P}^2) \exp(-p'r_{2P'}^2) \exp(-p''r_{3P''}^2) \\
&\times \exp(-\gamma_v r_{12}^2) \exp(-\gamma_w r_{13}^2) \, d\mathbf{r}_1 \, d\mathbf{r}_2 \, d\mathbf{r}_3 \quad .
\end{aligned}
\tag{85}
$$

Applying Boys' Lemma to electron 3 gives

$$
\begin{aligned}
\left(\frac{\pi}{p'' + \gamma_w}\right)^{\frac{3}{2}} K_{PP''} \int &\exp(-sr_{1S}^2) \exp(-p'r_{2P'}^2) \\
&\times \exp(-\gamma_v r_{12}^2) \, d\mathbf{r}_1 \, d\mathbf{r}_2 \quad ,
\end{aligned}
\tag{86}
$$

where

$$
K_{PP''} = \exp(-qR_{PP''}^2) \quad ,
\tag{87}
$$

$$
q = pp''\gamma_w/(pp'' + p\gamma_w + p''\gamma_w) \quad ,
\tag{88}
$$

$$
\mathbf{S} = \frac{(pp'' + p\gamma_w)\mathbf{P} + p'\gamma_w\mathbf{P}''}{pp'' + p\gamma_w + p''\gamma_w} \quad ,
\tag{89}
$$

$$
s = (pp'' + p\gamma_w + p''\gamma_w)/(p'' + \gamma_w) \quad .
\tag{90}
$$

The remaining two-electron overlap integral in Eq. (86) is then given by Eq. (70), so the final three-electron overlap integral becomes

$$\left(\frac{\pi}{p''+\gamma_w}\right)^{\frac{3}{2}}\left(\frac{\pi^2}{sp'+s\gamma_v+p'\gamma_v}\right)^{\frac{3}{2}}K_{PP''}\,K_{P'S}\ . \tag{91}$$

Hence all the required three-electron overlap and overlap-related integrals over Hermite functions can be obtained by differentiating this key integral, or a linear combination of such integrals. This differentiation can be accomplished using the recursion relation in Eq. (67).

Evaluation of the three-electron nuclear attraction integral, where $O(\mathbf{r}_1) = r_{1C}^{-1}$, follows the same procedure, yielding for the integral over spherical Gaussians

$$\iiint r_{1C}^{-1}\exp(-pr_{1P}^2)\exp(-p'r_{2P'}^2)\exp(-p''r_{3P''}^2)$$
$$\times \exp(-\gamma_v r_{12}^2)\exp(-\gamma_w r_{13}^2)\,d\mathbf{r}_1\,d\mathbf{r}_2\,d\mathbf{r}_3$$
$$= \left(\frac{\pi}{p''+\gamma_w}\right)^{\frac{3}{2}}\left(\frac{\pi}{p'+\gamma_v}\right)^{\frac{3}{2}}K_{PP''}K_{P'S}$$
$$\times \left(\frac{2\pi}{t}\right)F_0(tR_{CT}^2)\ , \tag{92}$$

where we have used the same definitions as in the three-electron overlap integral, and additionally introduced

$$\mathbf{T} = \frac{(sp'+s\gamma_v)\mathbf{P}+p'\gamma_v\mathbf{P}'}{sp'+s\gamma_v+p'\gamma_v}\ , \tag{93}$$

$$t = (sp'+s\gamma_v+p'\gamma_v)/(p'+\gamma_v)\ . \tag{94}$$

5 Two-electron operator matrix elements

5.1 Two-electron integrals

The only new integral involving the coordinates of two electrons introduced by the GTG correlation factors is

$$\iint \chi_\mu(1)\chi_v(2)\exp(-\gamma_v r_{12}^2)r_{12}^{-1}\chi_\theta(1)\chi_\varphi(2)\,d\mathbf{r}_1\,d\mathbf{r}_2\ . \tag{95}$$

This involves the following integral over spherical Gaussians:

$$\iint r_{12}^{-1}\exp(-pr_{1P}^2)\exp(-p'r_{2P'}^2)\exp(-\gamma_v r_{12}^2)\,d\mathbf{r}_1\,d\mathbf{r}_2\ , \tag{96}$$

which is the same as the form treated by Boys and is given by Eq. (31). Differentiation of the integral over spherical Gaussians is straightforward, since only one Gaussian factor multiplies the incomplete gamma function.

5.2 Three-electron integrals

We have already discussed the "cyclic" three-electron integral

$$\iiint \chi_\mu(1)\chi_v(2)\chi_\lambda(3)$$
$$\times \exp(-\gamma_v r_{13}^2)r_{12}^{-1}\chi_\theta(1)\chi_\varphi(2)\chi_\kappa(3)$$
$$\times \exp(-\gamma_w r_{23}^2)\,d\mathbf{r}_1\,d\mathbf{r}_2\,d\mathbf{r}_3 \tag{97}$$

in our case study in Sect. 3. There are two other three-electron integrals over the interelectronic repulsion we need to consider. The first is

$$\iiint \chi_\mu(1)\chi_v(2)\chi_\lambda(3)$$
$$\times \exp(-\gamma_v r_{12}^2)r_{12}^{-1}\chi_\theta(1)\chi_\varphi(2)\chi_\kappa(3)$$
$$\times \exp(-\gamma_w r_{13}^2)\,d\mathbf{r}_1\,d\mathbf{r}_2\,d\mathbf{r}_3\ , \tag{98}$$

which requires the following integral over spherical Gaussians:

$$\iiint r_{12}^{-1}\exp(-pr_{1P}^2)$$
$$\times \exp(-p'r_{2P'}^2)\exp(-p''r_{3P''}^2)\exp(-\gamma_v r_{12}^2)$$
$$\times \exp(-\gamma_w r_{13}^2)\,d\mathbf{r}_1\,d\mathbf{r}_2\,d\mathbf{r}_3\ . \tag{99}$$

This integral can be written as

$$\left(\frac{\pi}{p''+\gamma_w}\right)^{\frac{3}{2}}\frac{2\pi^{5/2}}{(sp'+s\gamma_v+p'\gamma_v)\sqrt{s+p'}}K_{PP''}$$
$$\times \exp\left(\frac{-sp'\gamma_v R_{P'S}^2}{sp'+s\gamma_v+p'\gamma_v}\right)F_0\left(\frac{s^2 p'^2 R_{P'S}^2}{(sp'+s\gamma_v+p'\gamma_v)(s+p')}\right)\ , \tag{100}$$

where

$$K_{PP''} = \exp(-qR_{PP''}^2)\ , \tag{101}$$

$$q = pp''\gamma_w/(pp''+p\gamma_w+p''\gamma_w)\ , \tag{102}$$

$$\mathbf{S} = \frac{(pp''+p\gamma_w)\mathbf{P}+p'\gamma_w\mathbf{P}''}{pp''+p\gamma_w+p''\gamma_w}\ , \tag{103}$$

$$s = (pp''+p\gamma_w+p''\gamma_w)/(p''+\gamma_w)\ . \tag{104}$$

Here the incomplete gamma function is multiplied by only two Gaussian factors. Hence, the recursion formula for the differentiation of the exponential factors in generating integrals over Hermite Gaussians is the simpler two-term formula of Eq. (67).

The final three-electron integral is

$$\iiint \chi_\mu(1)\chi_v(2)\chi_\lambda(3)$$
$$\times \exp(-\gamma_v r_{13}^2)r_{12}^{-1}\chi_\theta(1)\chi_\varphi(2)\chi_\kappa(3)\,d\mathbf{r}_1\,d\mathbf{r}_2\,d\mathbf{r}_3\ , \tag{105}$$

which requires the following integral over spherical Gaussians:

$$\iiint r_{12}^{-1}\exp(-pr_{1P}^2)\exp(-p'r_{2P'}^2)$$
$$\times \exp(-p''r_{3P''}^2)\exp(-\gamma_v r_{13}^2)\,d\mathbf{r}_1\,d\mathbf{r}_2\,d\mathbf{r}_3\ . \tag{106}$$

This integral can be written as

$$\left(\frac{\pi}{p''+\gamma_v}\right)^{\frac{3}{2}}\frac{2\pi^{5/2}}{(sp')\sqrt{s+p'}}K_{PP''}F_0\left(\frac{sp'R_{P'S}^2}{s+p'}\right)\ , \tag{107}$$

where

$$K_{PP''} = \exp(-qR_{PP''}^2)\ , \tag{108}$$

$$q = pp''\gamma_v/(pp'' + p\gamma_v + p''\gamma_v) \ , \tag{109}$$

$$\mathbf{S} = \frac{(pp'' + p\gamma_v)\mathbf{P} + p'\gamma_v\mathbf{P}''}{pp'' + p\gamma_v + p''\gamma_v} \ , \tag{110}$$

$$s = (pp'' + p\gamma_v + p''\gamma_v)/(p'' + \gamma_v) \ . \tag{111}$$

This is the simplest of the three-electron integral cases, since the incomplete gamma function is multiplied by only a single Gaussian factor. The differentiation of this single factor is the usual rule for differentiation of a Gaussian, Eq. (5).

5.3 Four-electron integrals

There are three four-electron integrals over the two-electron operator. The first yields the following integral over spherical Gaussians:

$$\iiiint r_{12}^{-1} \exp(-pr_{1P}^2) \exp(-p'r_{2P'}^2) \exp(-p''r_{3P''}^2)$$
$$\exp(-p'''r_{4P'''}^2) \times \exp(-\gamma_v r_{13}^2) \exp(-\gamma_w r_{24}^2) d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4 \ . \tag{112}$$

The course of action here is obvious: we apply Boys' Lemma twice, first to electron four to obtain

$$\left(\frac{\pi}{p''' + \gamma_w}\right)^{\frac{3}{2}} \iiint r_{12}^{-1} \exp(-pr_{1P}^2) \exp(-p'r_{2P'}^2)$$
$$\times \exp(-p''r_{3P''}^2) \exp(-\gamma_v r_{13}^2)$$
$$\times \exp\left(-\frac{p'''\gamma_w}{p''' + \gamma_w}r_{2P'''}^2\right) d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \ , \tag{113}$$

and then to electron 3, yielding

$$\left(\frac{\pi}{p''' + \gamma_w}\right)^{\frac{3}{2}}\left(\frac{\pi}{p'' + \gamma_v}\right)^{\frac{3}{2}}$$
$$\times \iint r_{12}^{-1} \exp(-pr_{1P}^2) \exp(-p'r_{2P'}^2)$$
$$\times \exp\left(-\frac{p''\gamma_v}{p'' + \gamma_v}r_{1P''}^2\right) \exp\left(-\frac{p'''\gamma_w}{p''' + \gamma_w}r_{2P'''}^2\right) d\mathbf{r}_1 d\mathbf{r}_2 \ . \tag{114}$$

Note that this integral contains no geminal correlation factors and must thus be expressible as a GTO two-electron integral. Using the Gaussian product rule twice we can rewrite it as

$$\left(\frac{\pi}{p''' + \gamma_w}\right)^{\frac{3}{2}}\left(\frac{\pi}{p'' + \gamma_v}\right)^{\frac{3}{2}} K_{PP''}K_{P'PP'''}$$
$$\times \iint r_{12}^{-1} \exp(-sr_{1S}^2) \exp(-tr_{2T}^2) d\mathbf{r}_1 d\mathbf{r}_2$$
$$= \left(\frac{\pi}{p''' + \gamma_w}\right)^{\frac{3}{2}}\left(\frac{\pi}{p'' + \gamma_v}\right)^{\frac{3}{2}} \frac{2\pi^{5/2}}{st\sqrt{s + t}}$$
$$K_{PP''}K_{P'P'''}F_0\left(\frac{stR_{ST}^2}{s + t}\right) \ , \tag{115}$$

where

$$K_{PP''} = \exp(-qR_{PP''}^2) \ , \tag{116}$$

$$q = \frac{pp''\gamma_v}{pp'' + p\gamma_v + p''\gamma_v} \ , \tag{117}$$

$$\mathbf{R}_{PP''} = \mathbf{P} - \mathbf{P}'' \ , \tag{118}$$

$$s = \frac{pp'' + p\gamma_v + p''\gamma_v}{p'' + \gamma_v} \ , \tag{119}$$

$$\mathbf{S} = \frac{(pp'' + p\gamma_v)\mathbf{P} + p''\gamma_v\mathbf{P}''}{pp'' + p\gamma_v + p''\gamma_v} \ , \tag{120}$$

$$K_{P'P'''} = \exp(-mR_{P'P'''}^2) \ , \tag{121}$$

$$m = \frac{p'p'''\gamma_w}{p'p''' + p'\gamma_w + p'''\gamma_w} \ , \tag{122}$$

$$\mathbf{R}_{P'P'''} = \mathbf{P}' - \mathbf{P}''' \ , \tag{123}$$

$$t = \frac{p'p''' + p'\gamma_w + p'''\gamma_w}{p''' + \gamma_w} \ , \tag{124}$$

$$\mathbf{T} = \frac{(p'p''' + p'\gamma_w)\mathbf{P} + p'''\gamma_w\mathbf{P}'''}{p'p''' + p'\gamma_w + p'''\gamma_w} \ , \tag{125}$$

The second four-electron integral is

$$\iiiint r_{12}^{-1} \exp(-pr_{1P}^2) \exp(-p'r_{2P'}^2)$$
$$\times \exp(-p''r_{3P''}^2) \exp(-p'''r_{4P'''}^2)$$
$$\times \exp(-\gamma_v r_{13}^2) \exp(-\gamma_w r_{14}^2) d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4 \ . \tag{126}$$

Again, applying Boys' Lemma twice yields a GTO two-electron integral:

$$\left(\frac{\pi}{p'' + \gamma_w}\right)^{\frac{3}{2}}\left(\frac{\pi}{p'' + \gamma_v}\right)^{\frac{3}{2}} K_{P''S}K_{P'P'''}$$
$$\times \iint r_{12}^{-1} \exp(-tr_{1T}^2) \exp(-p'r_{2P'}^2) d\mathbf{r}_1 d\mathbf{r}_2$$
$$= \left(\frac{\pi}{p''' + \gamma_w}\right)^{\frac{3}{2}}\left(\frac{\pi}{p'' + \gamma_v}\right)^{\frac{3}{2}} \frac{2\pi^{5/2}}{p't\sqrt{p' + t}}$$
$$K_{PP'''}K_{P''S}F_0\left(\frac{p'tR_{ST}^2}{p' + t}\right) \ . \tag{127}$$

where

$$K_{PP'''} = \exp(-qR_{PP'''}^2) \ , \tag{128}$$

$$q = \frac{pp'''\gamma_w}{pp''' + p\gamma_w + p'''\gamma_w} \ , \tag{129}$$

$$\mathbf{R}_{PP'''} = \mathbf{P} - \mathbf{P}''' \ , \tag{130}$$

$$s = \frac{pp''' + p\gamma_w + p'''\gamma_w}{p''' + \gamma_w} \ , \tag{131}$$

$$\mathbf{S} = \frac{(pp''' + p\gamma_w)\mathbf{P} + p'''\gamma_w\mathbf{P}'''}{pp''' + p\gamma_w + p'''\gamma_w} \ , \tag{132}$$

$$K_{P''S} = \exp(-mR_{P''S}^2) \quad , \tag{133}$$

$$m = \frac{sp''\gamma_v}{sp'' + s\gamma_v + p''\gamma_v} \quad , \tag{134}$$

$$\mathbf{R}_{P''S} = \mathbf{P}'' - \mathbf{S} \quad , \tag{135}$$

$$t = \frac{sp'' + s\gamma_v + p''\gamma_v}{p'' + \gamma_v} \quad , \tag{136}$$

$$\mathbf{T} = \frac{(sp'' + s\gamma_v)\mathbf{P} + p''\gamma_v\mathbf{P}''}{sp'' + s\gamma_v + p''\gamma_v} \quad . \tag{137}$$

The final four-electron integral over spherical Gaussians is

$$\int\int\int\int r_{12}^{-1} \exp(-pr_{1P}^2) \exp(-p'r_{2P'}^2)$$
$$\times \exp(-p''r_{3P''}^2) \exp(-p'''r_{4P'''}^2) \tag{138}$$
$$\times \exp(-\gamma_v r_{13}^2) \exp(-\gamma_w r_{34}^2) \, d\mathbf{r}_1 \, d\mathbf{r}_2 \, d\mathbf{r}_3 \, d\mathbf{r}_4 \quad .$$

Applying Boys' Lemma twice yields

$$\left(\frac{\pi}{p''' + \gamma_w}\right)^{\frac{3}{2}} \left(\frac{\pi}{s + \gamma_v}\right)^{\frac{3}{2}} K_{P''P'''} K_{P'S}$$
$$\int\int r_{12}^{-1} \exp(-tr_{1T}^2) \exp(-p'r_{2P'}^2) \, d\mathbf{r}_1 \, d\mathbf{r}_2$$
$$= \left(\frac{\pi}{p''' + \gamma_w}\right)^{\frac{3}{2}} \left(\frac{\pi}{s + \gamma_v}\right)^{\frac{3}{2}} \frac{2\pi^{5/2}}{p't\sqrt{p' + t}} \tag{139}$$
$$K_{PS} K_{P''P'''} F_0\left(\frac{p'tR_{ST}^2}{p' + t}\right) \quad .$$

where

$$K_{P''P'''} = \exp(-qR_{P''P'''}^2) \quad , \tag{140}$$

$$q = \frac{p''p'''\gamma_w}{p''p''' + p''\gamma_w + p'''\gamma_w} \quad , \tag{141}$$

$$\mathbf{R}_{P''P'''} = \mathbf{P}'' - \mathbf{P}''' \quad , \tag{142}$$

$$s = \frac{p''p''' + p''\gamma_w + p'''\gamma_w}{p''' + \gamma_w} \quad , \tag{143}$$

$$\mathbf{S} = \frac{(p''p''' + p''\gamma_w)\mathbf{P}'' + p'''\gamma_w\mathbf{P}'''}{p''p''' + p''\gamma_w + p'''\gamma_w} \quad , \tag{144}$$

$$K_{PS} = \exp(-mR_{PS}^2) \quad , \tag{145}$$

$$m = \frac{ps\gamma_v}{ps + p\gamma_v + s\gamma_v} \quad , \tag{146}$$

$$\mathbf{R}_{PS} = \mathbf{P} - \mathbf{S} \quad , \tag{147}$$

$$t = \frac{ps + p\gamma_v + s\gamma_v}{s + \gamma_v} \quad , \tag{148}$$

$$\mathbf{T} = \frac{(ps + p\gamma_v)\mathbf{P} + s\gamma_v\mathbf{S}}{ps + p\gamma_v + s\gamma_v} \quad . \tag{149}$$

We note that in all these four-electron integrals we have only two Gaussian factors multiplying the in-complete gamma function. Our calculation of Hermite integrals by differentiation of the spherical Gaussian integrals therefore involves only the recursion formula of Eq. (67): the four-electron integrals are simpler than the cyclic three-electron integral in this respect.

6 Discussion and conclusions

Our presentation here has used exclusively the expansion of Gaussian overlap distributions in Hermite functions commonly referred to in the context of GTO integrals as the McMurchie-Davidson approach [9]. Just as this is not the only way to compute GTO integrals, there is no reason to suppose it is the only way to compute GTG integrals. In very recent work Komornicki and King (to be published) have developed a scheme for GTG integrals built on the Rys quadrature approach [10] to calculating GTO integrals. Their scheme also involves recursion to obtain the final integrals, but the recursion relations are quite different from the scheme suggested here. Like the McMurchie-Davidson approach, Rys quadrature is also a very efficient method for computing GTO integrals, and we may expect that efficient evaluation of GTG integrals can also be accomplished in this way.

We have said little about computational implementation here, in part because a detailed discussion would lengthen the paper excessively. Nevertheless, the gross features of an implementation of the approach we have developed are clear: the calculation of derivatives of the incomplete gamma function are already required for GTO integrals and are thus available for GTG integrals. The new feature is the recursive calculation of derivatives of the Gaussian factors that multiply the incomplete gamma function. Once these are available the Hermite Gaussian integrals can be computed, and then combined with the expansion coefficients to give final Cartesian or spherical harmonic integrals. The program loop structure that drives this calculation must be generalized to handle three overlap distributions (for three-electron integrals) or even four distributions, compared to the two distributions required for GTO integrals. This increases the complexity of the program but does not add materially to the computational effort required, which will be completely dominated by the calculation of the Hermite Gaussian and then the Cartesian or spherical harmonic integrals. We note also that the many-electron integrals are used immediately in partial trace operations (see, for example, Ref. [11], to give matrix elements over Coulomb or exchange operators, or matrix elements of projection operators. Hence it is never necessary to store three- or four-electron integrals on disk. We are currently incorporating the formulas we have derived in this work into the DALTON program [12] for use in calculations with the GTG-augmented basis sets suggested in Ref. [1].

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