A unified scheme for the calculation of differentiated and undifferentiated molecular integrals over solid-harmonic Gaussians

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Utilizing the fact that solid-harmonic combinations of Cartesian and Hermite Gaussian atomic orbitals are identical, a new scheme for the evaluation of molecular integrals over solid-harmonic atomic orbitals is presented, where the integration is carried out over Hermite rather than Cartesian atomic orbitals. Since Hermite Gaussians are defined as derivatives of spherical Gaussians, the corresponding molecular integrals become the derivatives of integrals over spherical Gaussians, whose transformation to the solid-harmonic basis is performed in the same manner as for integrals over Cartesian Gaussians, using the same expansion coefficients. The presented solid-harmonic Hermite scheme simplifies the evaluation of derivative molecular integrals, since differentiation by nuclear coordinates merely increments the Hermite quantum numbers, thereby providing a unified scheme for undifferentiated and differentiated four-center molecular integrals. For two- and three-center two-electron integrals, the solid-harmonic Hermite scheme is particularly efficient, significantly reducing the cost relative to the Cartesian scheme.

1. Introduction

In molecular electronic-structure theory, an essential step is the evaluation of molecular one- and two-electron integrals over one-electron basis functions, which are typically taken to be linear combinations of solid-harmonic Gaussians. Over the years, several efficient schemes have been developed for the evaluation of such integrals: the Rys scheme,[1] the McMurchie–Davidson scheme,[2] the Obara–Saika scheme,[3] as well as modifications to these schemes.[4,5] In all these schemes, the integration is carried out over Cartesian Gaussians, followed by a transformation to the solid-harmonic basis (or by a series of partial transformations to this basis, in the course of the integration). A disadvantage of this approach is that derivatives of Cartesian Gaussians with respect to the orbital centers are linear combinations of undifferentiated Gaussians, making the evaluation of derivative integrals cumbersome.

In the present paper, we observe that solid-harmonic combinations of Cartesian Gaussian atomic orbitals are in fact identical to the corresponding combinations of Hermite Gaussians, generated by differentiation of spherical Gaussians with respect to the orbital center. Based on this observation, we propose to evaluate molecular integrals over Hermite rather than Cartesian Gaussians or, equivalently, to generate molecular integrals by differentiation of integrals over spherical Gaussians. In this manner, we obtain derivative integrals (as needed for the evaluation of molecular gradients and Hessians) and integrals involving the momentum operator (as needed for the kinetic energy and for kinetically-balanced small components in relativistic theory) by a simple modification of the scheme for undifferentiated integrals, consisting only in the raising of the Hermite quantum numbers. As a bonus, the use of Hermite rather than Cartesian Gaussians simplifies the evaluation of two- and three-center integrals significantly, relative to the scheme based on Cartesian Gaussians.[6] Živković and Maksić have considered the use of Hermite Gaussian basis functions but not in solid-harmonic form.[7]

The remainder of this paper consists of four sections. First, in Section 2, we demonstrate that solid-harmonic Gaussians may be expanded in Hermite Gaussians, using the same expansion coefficients as for the Cartesian Gaussians. Next, in Section 3, we expand molecular integrals over solid-harmonic Gaussians in terms of two-, three- and four-center Hermite integrals, whose evaluation by the Obara–Saika and McMurchie–Davidson schemes is described in Section 4. Section 5 contains some concluding remarks.

2. Solid-harmonic Gaussians

In the present section, we discuss solid-harmonic Gaussian functions, noting that these may be constructed equally well from Cartesian and Hermite Gaussians, using the same solid-harmonic expansion coefficients. The properties of the Cartesian and Hermite Gaussians are compared and it is pointed out that Hermite Gaussians, defined as (scaled) derivatives of spherical Gaussians, are better suited than Cartesian Gaussians in applications where orbital derivatives are needed—for example, in calculations of molecular gradients and Hessians and in relativistic calculations where the small-component

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functions are obtained from the large-component ones by differentiation.

2.1 Solid-harmonic Gaussians expanded in Cartesian Gaussians

In this paper, we consider the evaluation of molecular integrals over solid-harmonic Gaussians of the form

$$G_{lm}(\mathbf{r}, a, \mathbf{A}) = S_{lm}(\mathbf{r}_A) \exp(-ar_A^2) \qquad (1)$$

where $a > 0$ is the Gaussian exponent, $\mathbf{r}_A = \mathbf{r} - \mathbf{A}$ is the position of the electron $\mathbf{r}$ relative to the center of the Gaussian $\mathbf{A}$, and $S_{lm}(\mathbf{r}_A)$ with $0 \leq |m| \leq l$ is a real-valued solid-harmonic function of $\mathbf{r}_A$. The real-valued solid-harmonic functions satisfy Laplace's equation and are eigenfunctions of the total angular momentum and (when linearly combined) of the projected angular momentum:[8]

$$\nabla^2 S_{lm}(\mathbf{r}_A) = 0 \qquad (2)$$

$$L^2 S_{lm}(\mathbf{r}_A) = l(l+1) S_{lm}(\mathbf{r}_A) \qquad (3)$$

$$L_z[S_{lm}(\mathbf{r}_A) + \mathrm{i}S_{l,-m}(\mathbf{r}_A)] = m[S_{lm}(\mathbf{r}_A) + \mathrm{i}S_{l,-m}(\mathbf{r}_A)] \qquad (4)$$

In atomic units, the angular-momentum operators about $\mathbf{A}$ are as usual given by

$$L^2 = L_x^2 + L_y^2 + L_z^2 \qquad (5)$$

$$L_z = -\mathrm{i}\left(x_A \frac{\mathrm{d}}{\mathrm{d}y_A} - y_A \frac{\mathrm{d}}{\mathrm{d}x_A}\right) \qquad (6)$$

and similarly for L_x and L_y. Rewriting the operator for the total angular momentum about $\mathbf{A}$ in the form

$$L^2 = -r_A^2 \nabla^2 + (\mathbf{r}_A \cdot \boldsymbol{\nabla})^2 + \mathbf{r}_A \cdot \boldsymbol{\nabla} \qquad (7)$$

and invoking eqn (2), we find that the solid harmonics satisfy the eigenvalue equation

$$(\mathbf{r}_A \cdot \boldsymbol{\nabla}) S_{lm}(\mathbf{r}_A) = l S_{lm}(\mathbf{r}_A) \qquad (8)$$

Since the eigenfunctions of $\mathbf{r}_A \cdot \boldsymbol{\nabla}$ belonging to the eigenvalue l are the set of homogeneous polynomials of degree l in $\mathbf{r}_A$, we conclude that the solid harmonics $S_{lm}(\mathbf{r}_A)$ are homogeneous polynomials of degree l in $\mathbf{r}_A$:

$$S_{lm}(\zeta \mathbf{r}_A) = \zeta^l S_{lm}(\mathbf{r}_A) \qquad (9)$$

Consequently, we may expand the solid harmonics in Cartesian monomials in the form

$$S_{lm}(\mathbf{r}_A) = \sum_{i+j+k=l} S_{ijk}^{lm} x_A^i y_A^j z_A^k \qquad (10)$$

where all terms vanish except those for which $i + j + k = l$. An explicit expression for this expansion is given in ref. 8 and 9 but is not needed for the present development.

In the calculation of one- and two-electron molecular integrals over solid-harmonic Gaussians eqn (1), the integration is commonly performed over Cartesian Gaussians

$$G_{ijk}(\mathbf{r}, a, \mathbf{A}) = x_A^i y_A^j z_A^k \exp(-ar_A^2), \qquad (11)$$

with "quantum numbers" $i \geq 0$, $j \geq 0$, $k \geq 0$, using for example the Rys scheme,[1] the McMurchie–Davidson scheme,[2]

or the Obara–Saika scheme[3] followed by a transformation to solid-harmonic form

$$G_{lm}(\mathbf{r}, a, \mathbf{A}) = \sum_{i+j+k=l} S_{ijk}^{lm} G_{ijk}(\mathbf{r}, a, \mathbf{A}) \qquad (12)$$

Here, we shall consider an alternative approach, where the integration is first performed over the Hermite Gaussians

$$H_{ijk}(\mathbf{r}, a, \mathbf{A}) = \frac{\partial^{i+j+k} \exp(-ar_A^2)}{(2a)^{i+j+k} \partial A_x^i \partial A_y^j \partial A_z^k} \qquad (13)$$

followed by the transformation

$$G_{lm}(\mathbf{r}, a, \mathbf{A}) = \sum_{i+j+k=l} S_{ijk}^{lm} H_{ijk}(\mathbf{r}, a, \mathbf{A}) \qquad (14)$$

using the same coefficients as in eqn (12). In Subsection 2.2, we shall demonstrate that the resulting functions eqn (14) are in fact identical to the standard solid-harmonic Gaussians eqn (12). Consequently, we may choose for our integration those functions that are best suited to the task: the Cartesian Gaussians eqn (11) or the Hermite Gaussians eqn (13).

Let us briefly compare the properties of the Cartesian and Hermite Gaussians eqns (11) and (13). Both functions may be factorized in the Cartesian directions

$$G_{ijk}(\mathbf{r}, a, \mathbf{A}) = G_i(x, a, A_x) G_j(y, a, A_y) G_k(z, a, A_z) \qquad (15)$$

$$H_{ijk}(\mathbf{r}, a, \mathbf{A}) = H_i(x, a, A_x) H_j(y, a, A_y) H_k(z, a, A_z) \qquad (16)$$

where the x components are given by

$$G_i(x, a, A_x) = x_A^i \exp(-ax_A^2) \qquad (17)$$

$$H_i(x, a, A_x) = \frac{\mathrm{d}^i \exp(-ax_A^2)}{(2a)^i \mathrm{d}A_x^i} \qquad (18)$$

and likewise for the other components. We also note that the Cartesian Gaussians satisfy the recurrence relations

$$x_A G_i(x, a, A_x) = G_{i+1}(x, a, A_x) \qquad (19)$$

$$\frac{\mathrm{d}G_i(x, a, A_x)}{\mathrm{d}A_x} = 2aG_{i+1}(x, a, A_x) - iG_{i-1}(x, a, A_x) \qquad (20)$$

whereas the corresponding relations for the Hermite Gaussians are given by

$$x_A H_i(x, a, A_x) = H_{i+1}(x, a, A_x) + \frac{i}{2a} H_{i-1}(x, a, A_x) \qquad (21)$$

$$\frac{\mathrm{d}H_i(x, a, A_x)}{\mathrm{d}A_x} = 2aH_{i+1}(x, a, A_x) \qquad (22)$$

where eqn (21) follows from $[(\mathrm{d}/\mathrm{d}A_x)^i, x_A] = -i(\mathrm{d}/\mathrm{d}x_A)^{i-1}$. Note that the first (incremented) term is the same in the Cartesian and Hermite recurrence relations eqns (19)–(22). The only difference occurs in the second (decremented) term, which vanishes upon multiplication by x_A in the Cartesian Gaussian and upon differentiation by A_x in the Hermite Gaussian.

Because of eqn (22), the Hermite Gaussians are particularly well suited to integration over differentiated solid-harmonic functions since differentiation of eqn (14) merely raises the

quantum numbers of the Hermite Gaussians:

$$\frac{\partial^{I+J+K} G_{lm}(\mathbf{r}, a, \mathbf{A})}{\partial A_x^I \partial A_y^J \partial A_z^K} = (2a)^{I+J+K} \sum_{i+j+k=l} S_{ijk}^{lm} H_{i+I,j+J,k+K}(\mathbf{r}, a, \mathbf{A})$$

(23)

whereas differentiation of the Cartesian Gaussians produces linear combinations of Gaussians eqn (20). Thus, provided the solid-harmonic Gaussians are expanded in Hermite Gaussians, there is no need for a special derivative code, to any order in differentiation. We shall also see that Hermite Gaussians are better suited than Cartesian Gaussians to integration over charge distributions consisting of linear combinations of single Gaussians rather than product Gaussians, as occur, for example, in the evaluation of Coulomb energies by density fitting.[10, 11] Special methods for two- and three-center Coulomb integrals have previously been considered by Köster[6] (for Hermite functions) and by Ahlrichs.[12]

2.2 Solid-harmonic Gaussians expanded in Hermite Gaussians

In Subsection 2.1, we expressed the solid-harmonic function $S_{lm}(\mathbf{r}_A)$ as a homogeneous polynomial of degree l in x_A, y_A, and z_A, see eqn (10). We shall now establish the equivalence of the real solid-harmonic functions expressed as linear combinations of either Hermite or Cartesian Gaussians. For this purpose, consider the transformed solid harmonics

$$\mathcal{S}_{lm}(\mathbf{r}_A) = \sum_{i+j+k=l} S_{ijk}^{lm} \mathcal{H}_i(x_A) \mathcal{H}_j(y_A) \mathcal{H}_k(z_A) \quad (24)$$

where the coefficients S_{ijk}^{lm} are the same as in eqn (10) but where the monomial x_A^i of degree i has been replaced by the Hermite polynomial of the same degree:

$$\mathcal{H}_i(x_A) = (-2)^{-i} \exp(x_A^2) \frac{\mathrm{d}^i}{\mathrm{d}x_A^i} \exp(-x_A^2) \quad (25)$$

and likewise for y_A^j and z_A^k. As seen by induction on the Rodrigues expression eqn (25), the Hermite polynomials may be generated recursively as

$$\mathcal{H}_{i+1}(x_A) = x_A \mathcal{H}_i(x_A) - \frac{i}{2} \mathcal{H}_{i-1}(x_A) \quad (26)$$

beginning with $\mathcal{H}_0(x_A) = 1$. Note that we have normalized the Hermite polynomials such that the leading term is equal to x_A^i: 1, x_A, $x_A^2 - \frac{1}{2}$, $x_A^3 - \frac{3}{2}x_A$, and so on.

Clearly, the transformed solid harmonics eqn (24) have the same leading terms as the standard solid harmonics eqn (10). Therefore, since the standard solid harmonics are homogeneous eqn (9) (which means that all terms are leading terms), the equivalence of the standard and transformed solid harmonics eqns (10) and (24) is established if we can show that the transformed solid harmonics eqn (24) are also homogeneous. For this purpose, we introduce the differential operator

$$D_x = \exp\left(-\frac{1}{4}\frac{\mathrm{d}^2}{\mathrm{d}x_A^2}\right) = \sum_{k=0}^{\infty} \frac{1}{(-4)^k k!} \frac{\mathrm{d}^{2k}}{\mathrm{d}x_A^{2k}} \quad (27)$$

which commutes with $\mathrm{d}/\mathrm{d}x_A$ and satisfies the commutator relation

$$[x_A, D_x] = \frac{1}{2}\frac{\mathrm{d}}{\mathrm{d}x_A} D_x \quad (28)$$

Using this relation, we find that

$$\begin{aligned} D_x x_A^{i+1} &= x_A D_x x_A^i - [x_A, D_x] x_A^i \\ &= x_A D_x x_A^i - \frac{i}{2} D_x x_A^{i-1} \end{aligned} \quad (29)$$

Comparing with eqn (26) and noting that $D_x 1 = 1$, we conclude that the operator D_x, when applied to x_A^i, generates the Hermite polynomial $\mathcal{H}_i(x_A)$ of eqn (25):

$$\mathcal{H}_i(x_A) = D_x x_A^i \quad (30)$$

Next, introducing this relation and the corresponding relations for y_A^j and z_A^k in eqn (24), we find that the transformed and standard solid harmonics are related in the following manner:

$$\begin{aligned} \mathcal{S}_{lm}(\mathbf{r}_A) &= \sum_{i+j+k=l} S_{ijk}^{lm} D_x x_A^i D_y y_A^j D_z z_A^k \\ &= D_x D_y D_z S_{lm}(\mathbf{r}_A) \end{aligned} \quad (31)$$

Finally, applying $\mathbf{r}_A \cdot \nabla$ to the transformed solid harmonics eqn (31), we obtain

$$\begin{aligned} (\mathbf{r}_A \cdot \nabla) \mathcal{S}_{lm}(\mathbf{r}_A) &= (\mathbf{r}_A \cdot \nabla) D_x D_y D_z S_{lm}(\mathbf{r}_A) \\ &= D_x D_y D_z (\mathbf{r}_A \cdot \nabla) S_{lm}(\mathbf{r}_A) + [\mathbf{r}_A \cdot \nabla, D_x D_y D_z] S_{lm}(\mathbf{r}_A) \\ &= D_x D_y D_z l S_{lm}(\mathbf{r}_A) + \tfrac{1}{2} D_x D_y D_z \nabla^2 S_{lm}(\mathbf{r}_A) \\ &= l D_x D_y D_z S_{lm}(\mathbf{r}_A) = l \mathcal{S}_{lm}(\mathbf{r}_A) \end{aligned} \quad (32)$$

where we have used the homogeneity of the solid harmonics eqn (8), the commutator relation eqn (28), and Laplace's equation eqn (2), thereby demonstrating that the $\mathcal{S}_{lm}(\mathbf{r}_A)$ are homogeneous polynomials of degree l. Since the standard and transformed solid harmonics are homogeneous polynomials with the same leading terms, they must be identical. We may therefore write the solid harmonics in the form

$$S_{lm}(\mathbf{r}_A) = \sum_{i+j+k=l} S_{ijk}^{lm} \mathcal{H}_i(x_A) \mathcal{H}_j(y_A) \mathcal{H}_k(z_A) \quad (33)$$

which differs from the standard expression eqn (10) in the replacement of x_A^i, y_A^j, and z_A^k by $\mathcal{H}_i(x_A)$, $\mathcal{H}_j(y_A)$, and $\mathcal{H}_k(z_A)$, respectively.

Combining eqns (1) and (33), we may now express the solid-harmonic Gaussians as

$$G_{lm}(\mathbf{r}, a, \mathbf{A}) = a^{-l/2} \sum_{i+j+k=l} S_{ijk}^{lm} \mathcal{H}_i(\sqrt{a}x_A) \mathcal{H}_j(\sqrt{a}y_A) \mathcal{H}_k(\sqrt{a}z_A)$$

$$\times \exp(-ar_A^2) \quad (34)$$

where the homogeneity of the solid harmonics ensures that the coordinate scaling is canceled by the prefactor $a^{-l/2} = a^{(-i-j-k)/2}$. Substituting x_A by $\sqrt{a}x_A$ in eqn (25) and multiplying the resulting equation from the left by $\exp(-ax_A^2)$, we obtain:[2]

$$\mathcal{H}_i(\sqrt{a}x_A) \exp(-ax_A^2) = (2\sqrt{a})^{-i} \left(\frac{\mathrm{d}}{\mathrm{d}A_x}\right)^i \exp(-ax_A^2) \quad (35)$$

Using this result in eqn (34), we arrive at eqn (14), where we have introduced the Hermite Gaussians eqn (13). Thus, we may globally replace the Cartesian Gaussians eqn (11) by the Hermite Gaussians eqn (13) in the expansion of the solid harmonics eqn (12).

3. Molecular integrals over solid-harmonic Gaussians

In this section, we demonstrate how integrals over solid-harmonic Gaussians can be expanded in integrals over Hermite Gaussians, expressed as scaled derivatives of integrals over spherical Gaussians. The evaluation of these Hermite integrals is discussed in Section 4.

3.1 Overlap and multipole-moment integrals

Consider the multipole-moment integrals about M between two solid-harmonic Gaussians at A and B expanded in Hermite Gaussians eqn (14):

$$M_{ab}^{k} = \int G_{l_a m_a}(\mathbf{r}, a, \mathbf{A}) \, G_{l_b m_b}(\mathbf{r}, b, \mathbf{B}) \, x_M^{k_x} y_M^{k_y} z_M^{k_z} \, d\mathbf{r}$$
$$= \sum_{ij} S_{i}^{l_a m_a} S_{j}^{l_b m_b} m_{ijk}^{ab} \qquad (36)$$

An important special case is the overlap integral $S_{ab} = M_{ab}^{0}$. The Hermite multipole-moment integrals m_{ijk}^{ab} are given by

$$m_{ijk}^{ab} = \int H_{i}(\mathbf{r}, a, \mathbf{A}) \, H_{j}(\mathbf{r}, b, \mathbf{B}) \, x_M^{k_x} y_M^{k_y} z_M^{k_z} \, d\mathbf{r}$$
$$= \frac{\partial^{i+j} \int \exp(-a r_A^2) \exp(-b r_B^2) x_M^{k_x} y_M^{k_y} z_M^{k_z} \, d\mathbf{r}}{(2a \partial A_x)^{i_x} \cdots (2b \partial B_z)^{j_z}} \qquad (37)$$

We have here inserted the Hermite Gaussians eqn (13) and used the Leibniz integral rule to take the differential operators outside the integration sign, noting that the integration limits are independent of the Gaussian coordinates.[2,7] For brevity, we have introduced the notation $\mathbf{i} = (i_x, i_y, i_z)$ and $i = i_x + i_y + i_z$ (and likewise for $\mathbf{j}$ and $\mathbf{k}$); we also adopt the convention of denoting integrals over solid-harmonic Gaussians eqn (36) by uppercase letters M_{ab}^{k} and the corresponding Hermite integrals eqn (37) by lowercase letters m_{ijk}^{ab}. Invoking the Gaussian product rule[13]

$$\exp(-a r_A^2) \exp(-b r_B^2) = \exp(-\mu R_{AB}^2) \exp(-p r_P^2) \qquad (38)$$

with

$$p = a + b, \quad \mu = \frac{ab}{p}, \quad \mathbf{R}_{AB} = \mathbf{A} - \mathbf{B},$$
$$\mathbf{P} = \frac{a\mathbf{A} + b\mathbf{B}}{p} \qquad (39)$$

we find that the integral over the product of spherical Gaussians eqn (38) is given by

$$\int \exp(-a r_A^2) \exp(-b r_B^2) x_M^{k_x} y_M^{k_y} z_M^{k_z} \, d\mathbf{r} = \exp(-\mu R_{AB}^2) \, M_k(p, \mathbf{R}_{PM}) \qquad (40)$$

We have here introduced the multipole-moment integral

$$M_k(p, \mathbf{R}_{PM}) = \int x_M^{k_x} y_M^{k_y} z_M^{k_z} \exp(-p r_P^2) \, d\mathbf{r} \qquad (41)$$

which depends on p and $\mathbf{R}_{PM} = \mathbf{P} - \mathbf{M}$, with the special value $M_0(p, \mathbf{R}_{PM}) = (\pi/p)^{3/2}$. Inserting this result into eqn (37), we obtain the following Hermite multipole-moment integral

$$m_{ijk}^{ab} = \frac{\partial^{i+j} \exp(-\mu R_{AB}^2) \, M_k(p, \mathbf{R}_{PM})}{(2a \partial A_x)^{i_x} \cdots (2b \partial B_z)^{j_z}} \qquad (42)$$

whose recursive evaluation is discussed in Section 4. However, we note here that the overlap integral may be expressed as a scaled Hermite Gaussian eqn (13) in $\mathbf{R}_{AB}$ with exponent μ:[7]

$$s_{ij}^{ab} = m_{ij0}^{ab} = (-1)^i \left(\frac{\pi}{p}\right)^{3/2} \left(\frac{b}{p}\right)^i \left(\frac{a}{p}\right)^j H_{i+j}(\mathbf{R}_{AB}, \mu, \mathbf{0}) \quad (43)$$

Since odd-order Hermite Gaussians vanish at the origin, the overlap integrals vanish for odd $i_x + j_x$ if $A_x = B_x$ (and likewise for the y and z directions).

The integrals discussed above were evaluated over a two-center overlap distribution, generated by a product of two Gaussians. Sometimes, we are interested in integrals over one-center overlap distributions—in particular, in density-fitting methods. Let us therefore consider the one-center overlap integrals

$$S_p = \int G_{l_p m_p}(\mathbf{r}, p, \mathbf{P}) \, d\mathbf{r} = \sum_t S_t^{l_p m_p} s_t^p \qquad (44)$$

where, by convention, we use p and $\mathbf{P}$ for one-center overlap distributions, with the Hermite quantum numbers $\mathbf{t} = (t_x, t_y, t_z)$. Proceeding as for two-center overlap distributions eqn (37), we find that

$$s_t^p = \left(\frac{\pi}{p}\right)^{3/2} \delta_{t0} \qquad (45)$$

where $t = t_x + t_y + t_z$, in agreement with the fact that integration over a single solid-harmonic Gaussian gives zero except in the totally symmetric case $l_p = m_p = 0$.

3.2 Integrals over differential operators

In the Hermite scheme, one-electron integrals over differential operators are easily obtained from the overlap integrals:

$$D_{ab}^{k} = \int G_{l_a m_a}(\mathbf{r}, a, \mathbf{A}) \left(\frac{\partial^{k_x}}{\partial x^{k_x}}\right) \left(\frac{\partial^{k_y}}{\partial y^{k_y}}\right) \left(\frac{\partial^{k_z}}{\partial z^{k_z}}\right) G_{l_b m_b}(\mathbf{r}, b, \mathbf{B}) \, d\mathbf{r}$$
$$= \sum_{ij} S_i^{l_a m_a} S_j^{l_b m_b} d_{ijk}^{ab} \qquad (46)$$

where the Hermite integrals may be calculated in a variety of equivalent ways, such as

$$d_{ijk}^{ab} = (2a)^k s_{i+k,j}^{ab} = (-2b)^k s_{i,j+k}^{ab} \qquad (47)$$

As an important special case, the kinetic-energy integral is given by

$$T_{ab} = -\tfrac{1}{2} (D_{ab}^{200} + D_{ab}^{020} + D_{ab}^{002}) \qquad (48)$$

and is thus easily obtained from overlap integrals with incremented quantum numbers.

3.3 One-electron Coulomb integrals

For the one-electron Coulomb integrals, we follow the same approach as for the multipole-moment integrals in Subsection

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3.1, expanding in Hermite integrals

$$V_{ab} = \iint \frac{G_{l_a m_a}(\boldsymbol{r}, a, \boldsymbol{A})\, G_{l_b m_b}(\boldsymbol{r}, b, \boldsymbol{B})}{r_C}\, \mathrm{d}\boldsymbol{r} = \sum_{ij} S_i^{l_a m_a} S_j^{l_b m_b} v_{ij}^{ab}$$ (49)

where the Leibniz rule gives

$$v_{ij}^{ab} = \iint \frac{H_i(\boldsymbol{r}, a, \boldsymbol{A}) H_j(\boldsymbol{r}, b, \boldsymbol{B})}{r_C}\, \mathrm{d}\boldsymbol{r} = \frac{\partial^{i+j} \int \exp(-a r_A^2) \exp(-b r_B^2)\, r_C^{-1}\, \mathrm{d}\boldsymbol{r}}{(2a\partial A_x)^{i_x} \cdots (2b\partial B_z)^{j_z}}$$ (50)

Following Boys, we next invoke the Gaussian product rule eqn (38), obtaining

$$\int \frac{\exp(-a r_A^2) \exp(-b r_B^2)}{r_C}\, \mathrm{d}\boldsymbol{r} = \frac{2\pi}{p} \exp(-\mu R_{AB}^2)\, F_0(p R_{PC}^2)$$ (51)

where we have introduced the Boys function[13]

$$F_n(x) = \int_0^1 \exp(-x t^2) t^{2n}\, \mathrm{d}t$$ (52)

Inserting eqn (51) in eqn (50), we find that the two-center one-electron Coulomb integrals are scaled derivatives of $\exp(-\mu R_{AB}^2) F_0(p R_{PC}^2)$ with respect to $\boldsymbol{A}$ and $\boldsymbol{B}$:

$$v_{ij}^{ab} = \frac{2\pi}{p} \frac{\partial^{i+j} \exp(-\mu R_{AB}^2)\, F_0(p R_{PC}^2)}{(2a\partial A_x)^{i_x} \cdots (2b\partial B_z)^{j_z}}$$ (53)

Unlike the multipole-moment integral eqn (42), it cannot be factorized in the Cartesian directions. For the corresponding one-center Coulomb integrals, we obtain

$$V_p = \int \frac{G_{l_p m_p}(\boldsymbol{r}, p, \boldsymbol{P})}{r_C}\, \mathrm{d}\boldsymbol{r} = \sum_t S_t^{l_p m_p} v_t^p$$ (54)

$$v_t^p = \int \frac{H_t(\boldsymbol{r}, p, \boldsymbol{P})}{r_C}\, \mathrm{d}\boldsymbol{r} = \frac{2\pi}{p} \frac{\partial^t F_0(p R_{PC}^2)}{(2p\partial P_x)^{t_x} \cdots (2p\partial P_z)^{t_z}}$$ (55)

Comparing with the two-center case eqn (53), we note the expected absence of the exponential $\exp(-\mu R_{AB}^2)$, greatly simplifying its evaluation, as discussed in Section 4.

3.4 Two-electron Coulomb integrals

The four-center two-electron repulsion integrals over solid-harmonic Gaussians

$$G_{abcd} = \iint \frac{G_{l_a m_a}(\boldsymbol{r}_1, a, \boldsymbol{A})\, G_{l_b m_b}(\boldsymbol{r}_1, b, \boldsymbol{B})\, G_{l_c m_c}(\boldsymbol{r}_2, c, \boldsymbol{C})\, G_{l_d m_d}(\boldsymbol{r}_2, d, \boldsymbol{D})}{r_{12}}\, \mathrm{d}\boldsymbol{r}_1\, \mathrm{d}\boldsymbol{r}_2$$ (56)

and the corresponding two- and three-center integrals G_{pq}, $G_{ab,q}$ and $G_{p,cd}$ may be treated in the same way as the one-electron integrals in Subsection 3.3. Substituting the expansions of the solid-harmonic functions eqn (14) in Hermite

Gaussians, we obtain

$$G_{abcd} = \sum_{ijkl} S_i^{l_a m_a} S_j^{l_b m_b} S_k^{l_c m_c} S_l^{l_d m_d} g_{ijkl}^{abcd}$$ (57)

$$G_{ab,q} = \sum_{iju} S_i^{l_a m_a} S_j^{l_b m_b} S_u^{l_q m_q} g_{ij,u}^{ab,q}$$ (58)

$$G_{p,cd} = \sum_{tkl} S_t^{l_p m_p} S_k^{l_c m_c} S_l^{l_d m_d} g_{t,kl}^{p,cd}$$ (59)

$$G_{pq} = \sum_{tu} S_t^{l_p m_p} S_u^{l_q m_q} g_{tu}^{pq}$$ (60)

where the Hermite integrals are denoted by g_{ijkl}^{abcd}, $g_{ij,u}^{ab,q}$, $g_{t,kl}^{p,cd}$, and g_{tu}^{pq}. As for the one-electron integrals, we substitute the Hermite Gaussians eqn (13) in the Hermite integrals, invoke the Leibniz rule and apply the Gaussian product rule eqn (38), introducing the exponents and coordinates eqn (39) for the first electron and

$$q = c + d, \quad \nu = \frac{cd}{q}, \quad \boldsymbol{R}_{CD} = \boldsymbol{C} - \boldsymbol{D},$$
$$\boldsymbol{Q} = \frac{c\boldsymbol{C} + d\boldsymbol{D}}{q}$$ (61)

for the second one. Finally, using the result of Boys[13]

$$\iint \frac{\exp(-p r_{1P}^2) \exp(-q r_{2Q}^2)}{r_{12}}\, \mathrm{d}\boldsymbol{r}_1\, \mathrm{d}\boldsymbol{r}_2 = \frac{2\pi^{5/2}}{pq\sqrt{p+q}} F_0(\alpha R_{PQ}^2)$$ (62)

with

$$\alpha = \frac{pq}{p+q}, \quad \boldsymbol{R}_{PQ} = \boldsymbol{P} - \boldsymbol{Q}$$ (63)

we find that the two-electron Hermite integrals are given by

$$g_{ijkl}^{abcd} = \frac{2\pi^{5/2}}{pq\sqrt{p+q}} \frac{\partial^{i+j+k+l} \exp(-\mu R_{AB}^2) \exp(-\nu R_{CD}^2)\, F_0(\alpha R_{PQ}^2)}{(2a\partial A_x)^{i_x} \cdots (2d\partial D_z)^{l_z}}$$ (64)

$$g_{ij,u}^{ab,q} = \frac{2\pi^{5/2}}{pq\sqrt{p+q}} \frac{\partial^{i+j+u} \exp(-\mu R_{AB}^2)\, F_0(\alpha R_{PQ}^2)}{(2a\partial A_x)^{i_x} \cdots (2q\partial Q_z)^{u_z}}$$ (65)

$$g_{t,kl}^{p,cd} = \frac{2\pi^{5/2}}{pq\sqrt{p+q}} \frac{\partial^{t+k+l} \exp(-\nu R_{CD}^2)\, F_0(\alpha R_{PQ}^2)}{(2p\partial P_x)^{t_x} \cdots (2d\partial D_z)^{l_z}}$$ (66)

$$g_{tu}^{pq} = \frac{2\pi^{5/2}}{pq\sqrt{p+q}} \frac{\partial^{t+u} F_0(\alpha R_{PQ}^2)}{(2p\partial P_x)^{t_x} \cdots (2q\partial Q_z)^{u_z}}$$ (67)

to be compared with the multipole-moment integrals eqn (42) and the one-electron Coulomb integrals eqns (53) and (55). The two- and three-center two-electron integrals are easier to calculate than the four-center integrals, not only because there are fewer differentiations to be carried out but also since the functions to be differentiated are simpler. In Section 4, we shall consider the evaluation of the Hermite Coulomb integrals.

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3.5 Differentiated molecular integrals

Let us consider the evaluation of integrals over the differentiated solid-harmonic Gaussians

$$G_{l_a m_a}^{I_x I_y I_z}(\boldsymbol{r}, a, \boldsymbol{A}) = \frac{\partial^{I_x + I_y + I_z} G_{l_a m_a}(\boldsymbol{r}, a, \boldsymbol{A})}{\partial A_x^{I_x} \partial A_y^{I_y} \partial A_z^{I_z}} \quad (68)$$

Substituting here the expansion of solid-harmonic Gaussians in Hermite Gaussians eqn (14) and noting that the expansion coefficients are independent of $\boldsymbol{A}$, we obtain

$$G_{l_a m_a}^{\boldsymbol{I}}(\boldsymbol{r}, a, \boldsymbol{A}) = (2a)^I \sum_{\boldsymbol{i}} S_{\boldsymbol{i}}^{lm} H_{\boldsymbol{i}+\boldsymbol{I}}(\boldsymbol{r}, a, \boldsymbol{A}) \quad (69)$$

where $\boldsymbol{I} = (I_x, I_y, I_z)$ and $I = I_x + I_y + I_z$. Letting $G_{abcd}^{\boldsymbol{IJKL}}$ denote the two-electron integral evaluated over such functions, we obtain

$$\begin{aligned} G_{abcd}^{\boldsymbol{IJKL}} =& (2a)^I (2b)^J (2c)^K (2d)^L \\ & \times \sum_{\boldsymbol{ijkl}} S_{\boldsymbol{i}}^{l_a m_a} S_{\boldsymbol{j}}^{l_b m_b} S_{\boldsymbol{k}}^{l_c m_c} S_{\boldsymbol{l}}^{l_d m_d} g_{\boldsymbol{i}+\boldsymbol{I},\boldsymbol{j}+\boldsymbol{J},\boldsymbol{k}+\boldsymbol{K},\boldsymbol{l}+\boldsymbol{L}}^{abcd} \end{aligned} \quad (70)$$

as a generalization of eqn (57). The same result applies to all other integrals evaluated in terms of Hermite Gaussians. Molecular integrals over differentiated solid-harmonic Gaussians are thus obtained in the same manner as undifferentiated integrals, by incrementing the quantum numbers of the Hermite Gaussians eqn (69). A code written for general angular momentum is therefore also a code for general geometrical derivatives.

Assume that we wish to calculate the nth-order Cartesian derivatives arising from of an orbital shell of angular momentum l_0 (which we may take to be the first of four orbital shells in a two-electron integral). There are $(n + 1)(n + 2)/2$ independent Cartesian derivatives of each of the $2l_0 + 1$ solid-harmonic Gaussians in this shell. In the Hermite scheme, we begin by calculating all integrals arising from this shell with the angular momentum increased from l_0 to $l_0 + n$. Next, the resulting $(l_0 + n + 1)(l_0 + n + 2)/2$ Hermite components are combined to differentiated solid harmonics, using eqn (69). By contrast, in the Cartesian scheme, we first calculate all integrals with angular momentum $\max(0, l_0 - n) \le l \le l_0 + n$ on the first orbital. The number of such components is proportional to $l_0^2 n + n^3/3$. Subsequently, these Cartesian integrals are transformed to the derivative solid-harmonic basis, each transformation of which is more expensive than that from the Hermite basis.[14] Clearly, in this case, it is advantageous to use Hermite rather than Cartesian integrals as intermediates, as their number depends quadratically rather than cubically on n.

The advantages of the Hermite scheme become less pronounced when all derivatives in a given range $0 \le n \le n_{max}$ are needed—we then need Hermite integrals with $l_0 \le l \le l_0 + n_{max}$, compared with $\max(0, l_0 - n_{max}) \le l \le l_0 + n_{max}$ in the Cartesian case. The Hermite scheme is still preferable, however, since the subsequent transformation to the derivative solid harmonics is simpler, the same number of Hermite Gaussians contributing to each solid-harmonic function, for all orders of differentiation n.

4. Evaluation of Hermite integrals

In Section 3, we expanded molecular integrals over solid-harmonic Gaussians in integrals over Hermite Gaussians, expressed as derivatives of a generating function—see eqn (42) for multipole-moment integrals, eqns (53) and (55) for one-electron Coulomb integrals, and eqns (64)–(67) for two-electron Coulomb integrals. In the present section, we consider the evaluation of these Hermite integrals, using the Obara–Saika scheme[3] in Subsection 4.1 and the McMurchie–Davidson scheme[2] in Subsection 4.2. Živković and Maksić have given expressions for integrals over Hermite functions, without the use of recurrence relations.[7]

4.1 The Obara–Saika scheme for Hermite integrals

In the Obara–Saika scheme, the integrals are calculated from recurrence relations between integrals of different Hermite quantum numbers. Consider first the multipole-moment integrals eqn (42), which may be factorized in the three Cartesian directions, yielding the x component:

$$m_{ijk}^{ab} = \frac{\partial^{i+j} \exp(-\mu X_{AB}^2) M_k(p, X_{PM})}{(2a\partial A_x)^i (2b\partial B_x)^j} \quad (71)$$

in the short-hand notation i, j and k for i_x, j_x and k_x, respectively. The function $M_k(p, X_{PC})$, which is the x factor of eqn (41), satisfies the relations

$$M_0(p, X_{PM}) = \sqrt{\frac{\pi}{p}} \quad (72)$$

$$M_{k+1}(p, X_{PM}) = X_{PM} M_k(p, X_{PM}) + \frac{k}{2p} M_{k-1}(p, X_{PM}) \quad (73)$$

$$\frac{\partial M_k(p, X_{PM})}{\partial P_x} = k M_{k-1}(p, X_{PM}) \quad (74)$$

Incrementing the three indices, we obtain after a little algebra

$$m_{i+1,j,k}^{ab} = X_{PA} m_{ijk}^{ab} + \frac{1}{2p}(i w_{ab} m_{i-1,j,k}^{ab} + j m_{i,j-1,k}^{ab} + k m_{i,j,k-1}^{ab}) \quad (75)$$

$$m_{i,j+1,k}^{ab} = X_{PB} m_{ijk}^{ab} + \frac{1}{2p}(i m_{i-1,j,k}^{ab} + j w_{ba} m_{i,j-1,k}^{ab} + k m_{i,j,k-1}^{ab}) \quad (76)$$

$$m_{i,j,k+1}^{ab} = X_{PM} m_{ijk}^{ab} + \frac{1}{2p}(i m_{i-1,j,k}^{ab} + j m_{i,j-1,k}^{ab} + k m_{i,j,k-1}^{ab}) \quad (77)$$

where we have introduced the factor

$$w_{ab} = -\frac{b}{a} \quad (78)$$

From these "vertical" recurrence relations (which increment the highest $i + j + k$), we may generate the full set of integrals, beginning with m_{000}^{ab}. For example, we may first generate the overlap integrals using the first two recurrences eqns (75) and (76), followed by the generation of the multipole-moment integrals from the overlap integrals using eqn (77). We also note the "horizontal" recurrence relation

$$2a m_{i+1,j,k}^{ab} + 2b m_{i,j+1,k}^{ab} = k m_{i,j,k-1}^{ab} \quad (79)$$

which follows from translational invariance and conserves the highest $i + j + k$.

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The same approach can be applied to the Coulomb integrals. Because of the presence of the Boys function, the integrals can no longer be factorized into Cartesian factors, although the recurrence relations in the three Cartesian directions are still independent. In the following, we therefore consider only increments in the x direction. Introducing the auxiliary functions

$$\Theta_{ij}^n = \frac{2\pi}{p} \frac{\partial^{i+j} \exp(-\mu R_{AB}^2) \, (-2p)^n F_n(p R_{PC}^2)}{(2a\partial A_x)^i (2b\partial B_x)^j} \qquad (80)$$

$$\Theta_{ijkl}^n = \frac{2\pi^{5/2}}{pq\sqrt{p+q}} \times$$
$$\frac{\partial^{i+j+k+l} \exp(-\mu R_{AB}^2) \exp(-\nu R_{CD}^2)(-2\alpha)^n F_n(\alpha R_{PQ}^2)}{(2a\partial A_x)^i (2b\partial B_x)^j (2c\partial C_x)^k (2d\partial D_x)^l} \qquad (81)$$

and using $F_n'(x) = -F_{n+1}(x)$, we obtain the following vertical recurrence relations

$$\Theta_{i+1,j}^n = X_{PA}\Theta_{ij}^n + \frac{1}{2p}(iw_{ab}\Theta_{i-1,j}^n + j\Theta_{i,j-1}^n)$$
$$+ \frac{1}{2p}X_{PC}\Theta_{ij}^{n+1} + \frac{1}{4p^2}(i\Theta_{i-1,j}^{n+1} + j\Theta_{i,j-1}^{n+1}) \qquad (82)$$

$$\Theta_{i+1,j,k,l}^n = X_{PA}\Theta_{ijkl}^n + \frac{1}{2p}(iw_{ab}\Theta_{i-1,j,k,l}^n + j\Theta_{i,j-1,k,l}^n)$$
$$+ \frac{1}{2p}X_{PQ}\Theta_{ijkl}^{n+1} + \frac{1}{4p^2}(i\Theta_{i-1,j,k,l}^{n+1} + j\Theta_{i,j-1,k,l}^{n+1})$$
$$- \frac{1}{4pq}(k\Theta_{i,j,k-1,l}^{n+1} + l\Theta_{i,j,k,l-1}^{n+1}) \qquad (83)$$

and likewise for increments in j, k and l. Beginning from Θ_{00}^n with $0 \leq n \leq \max(i+j)$ or Θ_{0000}^n with $0 \leq n \leq \max(i+j+k+l)$, we may thus generate the full set of Hermite Coulomb integrals $\nu_{i00,j00}^{ab} = \Theta_{ij}^0$ and $g_{i00,j00,k00,l00}^{abcd} = \Theta_{ijkl}^0$. Note that the one-electron Coulomb recurrence relations eqn (82) are identical to the two-electron relations eqn (83) except for the replacement of X_{PQ} by X_{PC} and the absence of the last two terms; also, the first three terms in eqns (82) and (83) are the same as for the multipole-moment integral eqn (75).

The Obara–Saika recurrence relations for Hermite Coulomb integrals eqns (82) and (83) resemble closely those for Cartesian integrals,[3,8] to which they reduce if we arbitrarily set $w_{ab} = 1$. As in the Cartesian case, it may be advantageous to use additional recurrence relations. From eqn (21), we obtain the horizontal recurrence relations

$$\Theta_{i,j+1,k,l}^n = \Theta_{i+1,j,k,l}^n + X_{AB}\Theta_{ijkl}^n + \frac{i}{2a}\Theta_{i-1,j,k,l}^n$$
$$- \frac{j}{2b}\Theta_{i,j-1,k,l}^n \qquad (84)$$

which differ from the Cartesian recurrences[4] by the presence of the two last terms. Finally, from the translational invariance of the integrals, we obtain the electron-transfer relations

$$\Theta_{i,0,k+1,0}^n = -\frac{bX_{AB} + dX_{CD}}{q}\Theta_{i0k0}^n + \frac{iw_{ab}}{2q}\Theta_{i-1,0,k,0}^n$$
$$+ \frac{kw_{cd}}{2q}\Theta_{i,0,k-1,0}^n - \frac{p}{q}\Theta_{i+1,0,k,0}^n \qquad (85)$$

which differ from to the corresponding relations for Cartesian Gaussians[15,16] only in the presence of the w_{ab} and w_{cd} factors. Using these relations, we may simplify the evaluation of integrals by using a reduced Obara–Saika recurrence eqn (83) to generate all $\Theta_{i+j+k+l,0,0,0}^n$, followed by use of the electron-transfer relation eqn (85) to generate all $\Theta_{i+j,0,k+l,0}$. In the final step, we use the horizontal recurrences eqn (84) to generate the final integrals Θ_{ijkl}.

The Coulomb recurrence relations given above eqns (82) and (83) are for two-center overlap distributions. The corresponding relations for integrals with one-center distributions eqn (55) and eqns (65)–(67) are obtained by setting $a = b = p$, $\boldsymbol{A} = \boldsymbol{B} = \boldsymbol{P}$, and $i + j = t$ for the first electron and $c = d = q$, $\boldsymbol{C} = \boldsymbol{D} = \boldsymbol{Q}$, and $k + l = u$ for the second electron. For example, for two-center two-electron Coulomb integrals, we obtain from eqn (83) the recursion

$$\Theta_{t+1,u}^n = \frac{1}{2p}X_{PQ}\Theta_{tu}^{n+1} + \frac{t}{4p^2}\Theta_{t-1,u}^{n+1} - \frac{u}{4pq}\Theta_{t,u-1}^{n+1} \qquad (86)$$

where the first three terms of eqn (83) vanish and the pairs of terms in parentheses collapse into single terms, reducing the total number of terms from eight to three. By further rewriting the intermediate integrals in the form

$$\Theta_{tu}^n = (2p)^{-t}(-2q)^{-u}\theta_{t+u}^n \qquad (87)$$

$$\theta_t^n = (-2\alpha)^n \frac{2\pi^{5/2}}{pq\sqrt{p+q}} \frac{\partial^t F_n(\alpha R_{PQ}^2)}{\partial P_x^t} \qquad (88)$$

we obtain the even simpler McMurchie–Davidson recursion:[2]

$$\theta_{t+1}^n = X_{PQ}\theta_t^{n+1} + t\theta_{t-1}^{n+1} \qquad (89)$$

and similarly for the y and z directions. We have thus reduced the Obara–Saika recurrence relations from eight to two terms. No such reduction is possible in the Cartesian basis.

Finally, we note that it is possible to set up a scheme for the Hermite integrals eqn (64), where we first calculate the derivatives of the three factors $F_n^{ab} = \partial^n \exp(-\mu R_{AB}^2)/\partial A_x^n$, $F_n^{cd} = \partial^n \exp(-\nu R_{CD}^2)/\partial C_x^n$, and $R_n^{pq} = \partial^n F_0(\alpha R_{PQ}^2)/\partial P_x^n$, after which the Hermite integrals are assembled by binomial expansion, as done by Živković and Maksić.[7]

4.2 The McMurchie–Davidson scheme for Hermite integrals

In the Obara–Saika scheme, molecular integrals are generated recursively, using different sets of recurrence relations for one- and two-center overlap distributions, as discussed in Subsection 4.1. In the McMurchie–Davidson scheme, we take a different approach, expanding two-center overlap distributions in one-center overlap distributions. In this way, all four-center two-electron Coulomb integrals are reduced to two-center Coulomb integrals, which are evaluated using the same recurrence relations as in the Obara–Saika scheme.

Consider the overlap distribution generated by the Hermite Gaussians $H_i(\boldsymbol{r}_1, a, \boldsymbol{A})$ and $H_j(\boldsymbol{r}_1, b, \boldsymbol{B})$:

$$\Omega_{ij}(\boldsymbol{r}, a, \boldsymbol{A}, b, \boldsymbol{B}) = H_i(\boldsymbol{r}, a, \boldsymbol{A}) H_j(\boldsymbol{r}, b, \boldsymbol{B}) \qquad (90)$$

In the McMurchie–Davidson scheme, this two-center distribution is expanded in Hermite Gaussians about the product

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center P:

$$\Omega_{ij}(\boldsymbol{r}, a, \boldsymbol{A}, b, \boldsymbol{B}) = \sum_{t=0}^{i+j} F_t^{ij}(a, b, \boldsymbol{R}_{AB}) H_t(\boldsymbol{r}, p, \boldsymbol{P}) \qquad (91)$$

noting that the expansion coefficients depend only on the relative positions of the Gaussians. Substituting eqn (91) in eqn (37) and using eqn (45), we obtain for the overlap integrals

$$s_{ij}^{ab} = \sum_t F_t^{ij} s_t^p = F_0^{ij} s_0^p \qquad (92)$$

For the two-center one-electron Coulomb integrals eqn (50), substitution of eqn (91) yields

$$v_{ij}^{ab} = \sum_t F_t^{ij} v_t^p \qquad (93)$$

where the one-center integral is given by eqn (55). Finally, for the two-electron Coulomb integrals of Subsection 3.4, eqn (91) and a similar expansion of $\Omega_{kl}(\boldsymbol{r}, c, \boldsymbol{C}, d, \boldsymbol{D})$ yield

$$g_{ij,\boldsymbol{u}}^{ab,q} = \sum_t F_t^{ij} g_{tu}^{pq} \qquad (94)$$

$$g_{t,kl}^{p,cd} = \sum_u g_{tu}^{pq} F_u^{kl} \qquad (95)$$

$$g_{ijkl}^{abcd} = \sum_{tu} F_t^{ij} g_{tu}^{pq} F_u^{kl} \qquad (96)$$

where the basic two-center integrals g_{tu}^{pq} are given by eqn (67). In the original Cartesian-based McMurchie–Davidson scheme,[2] also one-center overlap distributions are expanded in Hermite orbitals according to eqn (96). In the purely Hermite scheme presented here, only two-center distributions are expanded, greatly simplifying the evaluation of few-center integrals. The Hermite integrals v_t^p and g_{tu}^{pq} are evaluated using eqns (87)–(89).[2]

It only remains to discuss the evaluation of the expansion coefficients of eqn (91). Factorizing the expansion in the Cartesian directions and introducing the following short-hand notation for the x direction

$$\Omega_{ij} = \sum_t F_t^{ij} H_t \qquad (97)$$

we obtain

$$2a\Omega_{i+1,j} + 2b\Omega_{i,j+1} = 2p \sum_t F_t^{ij} H_{t+1} \qquad (98)$$

where we have applied $\partial/\partial A_x + \partial/\partial B_x = \partial/\partial P_x$ and then eqn (22) on both sides of the equation. Inserting eqn (97) on the left-hand side and collecting terms, we arrive at the horizontal recurrence relation

$$aF_t^{i+1,j} + bF_t^{i,j+1} = pF_{t-1}^{ij} \qquad (99)$$

Next, we rewrite each term in eqn (98) using eqn (21), yielding

$$2px_P\Omega_{ij} - i\Omega_{i-1,j} - j\Omega_{i,j-1} = 2px_P \sum_t F_t^{ij} H_t$$
$$- \sum_t F_t^{ij} t H_{t-1} \qquad (100)$$

where we have used the relation $ax_A + ax_B = px_P$ on the left-hand side. Canceling the first term on each side and rearran-

ging, we obtain the vertical recurrence relation

$$iF_t^{i-1,j} + jF_t^{i,j-1} = (t+1)F_{t+1}^{ij} \qquad (101)$$

However, this relation can only be used to increment the upper indices ij for F_t^{ij} with $t > 0$. Different vertical recurrences are obtained by incrementing the first index of Ω_{ij}, yielding

$$\Omega_{i+1,j} = x_A\Omega_{ij} - \frac{i}{2a}\Omega_{i-1,j}$$
$$= X_{PA}\Omega_{ij} + \sum_t F_t^{ij} x_P H_t - \frac{i}{2a}\Omega_{i-1,j}$$
$$= X_{PA}\Omega_{ij} + \sum_t F_t^{ij} H_{t+1} + \sum_t F_t^{ij} \frac{t}{2p} H_{t-1} - \frac{i}{2a}\Omega_{i-1,j}$$
$$\qquad (102)$$

where we have first used eqn (21) for orbital a, then expanded $x_A = x_P + X_{PA}$, followed by the application of eqn (21) for orbital p. Collecting terms, we obtain

$$F_t^{i+1,j} = F_{t-1}^{ij} + X_{PA}F_t^{ij} + \frac{t+1}{2p}F_{t+1}^{ij} - \frac{i}{2a}F_t^{i-1,j} \qquad (103)$$

A similar set of recurrence relations may be derived for increments in the second index j. However, the most efficient scheme for the evaluation of the full set of expansion coefficients is to use the following combination of eqns (99), (101) and (103):

$$F_0^{i+1,0} = X_{PA}F_0^{i0} + \frac{1}{2p}F_1^{i0} - \frac{i}{2a}F_0^{i-1,0} \qquad (104)$$

$$F_0^{i,j+1} = -\frac{a}{b}F_0^{i+1,j} \qquad (105)$$

$$F_t^{ij} = \frac{i}{t}F_{t-1}^{i-1,j} + \frac{j}{t}F_{t-1}^{i,j-1}, \quad t > 0 \qquad (106)$$

beginning with $F_0^{00} = \exp(-\mu X_{AB}^2)$. The recurrence relations of the Hermite Gaussians are therefore no more complicated than those for the Cartesian Gaussians.[2,8] We note, however, that our definition of Hermite Gaussians eqn (13) differs from that of McMurchie and Davidson,[2] who use $\Lambda_t(\boldsymbol{r}, p, \boldsymbol{P}) = (2p)^{t_x+t_y+t_z} H_t(\boldsymbol{r}, p, \boldsymbol{P})$. We have therefore here denoted the expansion coefficients in eqn (91) by F_t^{ij} rather than by E_t^{ij} as in ref. 2.

5. Conclusions

We have presented a scheme for the evaluation of molecular integrals over solid-harmonic Gaussians, in which the integration is carried out over Hermite Gaussians rather than over Cartesian Gaussians, based on the observation that solid-harmonic Hermite Gaussians are identical to the corresponding solid-harmonic Cartesian Gaussians. The presented scheme simplifies the evaluation of derivative integrals (needed for energy derivatives and in relativistic theory) since differentiation with respect to nuclear coordinates merely increments the quantum numbers of the Hermite integrals, in the same way as when the angular momentum is increased. Consequently, the differentiation can be carried out to arbitrary order using the same code as for undifferentiated

integrals. Moreover, the presented Hermite-based scheme simplifies the evaluation of two- and three-center two-electron integrals, of importance in density-fitting schemes, bypassing the traditional time-consuming transformation to Cartesian basis.

Note added in proof

After this article had been accepted for publication, we became aware of the general theory of spherical tensor gradient operators, as reviewed by Weniger.[17] From this theory, the equivalence of the expansions of solid-harmonic Gaussians in Cartesian and Hermite Gaussians follows as a special result. For further details and references, we refer the reader to this work. However, it is proper here to mention the work of Dunlap[18–20] and of Ishida,[21] who have used spherical tensor gradient theory to develop integration techniques based on angular-momentum recoupling, bypassing the evaluation of integrals over Cartesian and Hermite Gaussians entirely. We would also like to draw attention to the work of Fortunelli and Salvetti,[22] where two-electron integrals over Hermite functions are considered within the Obara–Saika scheme.

Acknowledgements

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