



Multi-electron integrals

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This review presents techniques for the computation of multi-electron integrals over Cartesian and solid-harmonic Gaussian-type orbitals as used in standard electronic-structure investigations. The review goes through the basics for one- and two-electron integrals, discuss details of various two-electron integral evaluation schemes, approximative methods, techniques to compute multi-electron integrals for explicitly correlated methods, and property integrals. © 2011 John Wiley & Sons, Ltd.

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INTRODUCTION

In the standard electronic-structure methods of quantum chemistry, the electronic wave function is expressed in terms of Slater determinants, either to describe the real interacting system or to describe the fictitious noninteracting reference system of Kohn–Sham theory. Given that the electronic Hamiltonian contains only one- and two-body interactions, the many-body integration over the Hamiltonian reduces to one- and two-electron integrals over spin-orbital products. More elaborate treatments of the electronic structure, in which the wave function depends explicitly on the separation between the electrons (explicitly correlated methods), lead to Hamiltonian integrals containing three and more electrons. However, by invoking the resolution of the identity (RI), the resulting many-electron integrals may also in this case be expressed in terms of one- and two-electron integrals. In practice, therefore, only one- and two-electron Hamiltonian integrals are needed for nearly all electronic-structure calculations.

In this review, we discuss the techniques that have been developed for the efficient evaluation of all one- and two-electron integrals needed for electronic-structure studies, including highly accurate studies of small systems by explicitly correlated methods and more qualitative studies of large systems using Kohn–Sham theory. However, we restrict ourselves to integration over *Gaussian-type orbitals* (GTOs), used in

most molecular studies of electronic structure. Specifically, we do not consider the less versatile *Slater-type orbitals* (STOs), used in some atomic and diatomic studies and in Kohn–Sham theory. Also, we do not consider plane-wave basis sets, commonly used in calculations with periodic boundary conditions. Moreover, we limit our discussion to nonrelativistic Hamiltonian integrals.

The review is organized as follows. First, in section *Integrals over Spherical Gaussians*, we consider two-electron repulsion integrals between two (spherical) Gaussian orbitals, outlining the modifications needed for the evaluation of integrals involving various other operators in quantum chemistry. Then, in section *Integrals over Real Solid-Harmonic GTOs*, we give an overview of the various integrals needed in quantum chemistry. In section *Integral Evaluation Schemes*, we review the integral evaluation methods, followed in section *Approximate Integral Schemes* by the approximations, most commonly used in quantum chemistry today. In section *Explicitly Correlated Methods*, we give a brief overview of recent explicitly correlated methods and outline how to evaluate the integrals appearing here. Then, in section *Property Integrals*, we look into the evaluation of differentiated integrals, including geometrical and magnetic variations. Finally, in section *Concluding Remarks* we give a few closing remarks.

INTEGRALS OVER SPHERICAL GAUSSIANS

An important breakthrough in quantum chemistry was the proposal of Boys¹ in the early 1950s to expand the molecular orbitals in GTOs rather than STOs. Although two to three times more GTOs are

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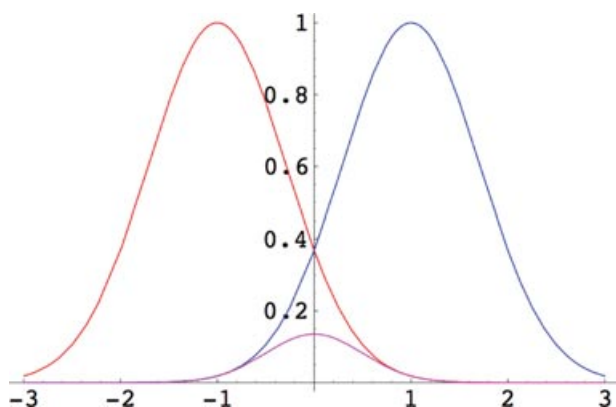


FIGURE 1 | Illustration of the Gaussian product rule.

needed than STOs to achieve a given level of accuracy in the calculations, many-center integrals over GTOs can be computed much more efficiently than those over STOs, owing to the simple analytical properties of the GTOs. First, unlike STOs, GTOs are separable in the Cartesian directions. Next, according to the *Gaussian product rule*, the product of two spherical Gaussians $\exp(-ar_A^2)$ and $\exp(-br_B^2)$ centered on **A** and **B** and with exponents a and b , respectively, is itself a spherical Gaussian:

$$\exp(-ar_A^2)\exp(-br_B^2) = \kappa_{ab}\exp(-pr_P^2), \quad (1)$$

with exponent p and centered at a point **P** on the line connecting **A** and **B**:

$$\begin{aligned} p &= a + b, \\ \mathbf{P} &= \frac{a\mathbf{A} + b\mathbf{B}}{p}. \end{aligned} \quad (2)$$

The prefactor $\kappa_{ab} = \exp(-\mu R_{AB}^2)$ in Eq. (1) depends on the reduced exponent $\mu = ab/(a + b)$ and decays exponentially with the square of the distance R_{AB} between the original Gaussians. The Gaussian product rule is illustrated in Figure 1.

The Gaussian product rule and the separability of Gaussians in the Cartesian directions greatly simplify the integration over such functions. For example, from the standard integral $\int_{-\infty}^{\infty} \exp(-x^2)dx = \sqrt{\pi}$, we obtain directly the integral over all space of a product of two Gaussians:

$$\int \exp(-ar_A^2)\exp(-br_B^2) d\mathbf{r} = \left(\frac{\pi}{p}\right)^{3/2} \kappa_{ab}. \quad (3)$$

Less trivially, six-dimensional four-center two-electron integrals over spherical Gaussians with exponents a and b for the first electron and c and d for the second electron may be expressed as two-center integrals over Gaussians with exponents $p = a + b$

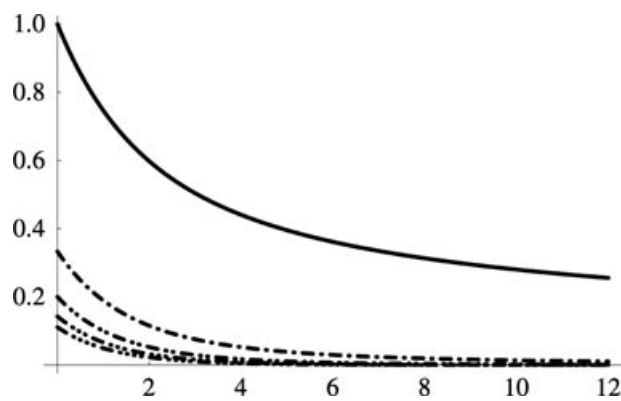


FIGURE 2 | The Boys function $F_n(x)$ for $n \geq 0$. Functions of different n may be distinguished by noting that $F_n(0) = 1/(2n + 1)$.

and $q = c + d$:

$$V_{pq} = \iint \exp(-pr_{1P}^2) \frac{1}{r_{12}} \exp(-qr_{2Q}^2) d\mathbf{r}_1 d\mathbf{r}_2, \quad (4)$$

which by means of the Laplace-like transformation,

$$\frac{1}{r_{12}} = \frac{1}{\pi} \int_{-\infty}^{\infty} \exp(-r_{12}^2 u^2) du, \quad (5)$$

can be reduced to the following one-dimensional integral over a finite interval:

$$V_{pq} = \frac{2\pi^{5/2}}{pq\sqrt{p+q}} F_0(\alpha R_{PQ}^2), \quad (6)$$

where we have introduced the reduced exponent $\alpha = pq/(p + q)$, the separation between the two centers R_{PQ} , and the n th-order *Boys function* n^1

$$F_n(x) = \int_0^1 \exp(-xt^2) t^{2n} dt. \quad (7)$$

For a detailed derivation of Eq. (6) see, for example, Ref 2. The Boys function $F_n(x)$ with $n > 0$ is needed for integrals over the nonspherical solid-harmonic Gaussians, as discussed in section *Integral Evaluation Schemes*.

The Boys function $F_n(x)$ is illustrated in Figure 2. It is a strictly positive, decreasing, and convex function, as follows from the observation that its integrand is positive and from the relation

$$F'_n(x) = -F_{n+1}(x). \quad (8)$$

The Boys function is a special case of the Kummer confluent hypergeometric function $M(a, b, x) = {}_1F_1(a, b, x)$, available in many software packages and libraries:

$$\begin{aligned} F_n(x) &= \frac{M(n + 1/2, n + 3/2, -x)}{2n + 1}, \\ M(a, b, x) &= \sum_{k=0}^{\infty} \frac{(a)_k}{k!(b)_k} x^k, \end{aligned} \quad (9)$$

where $(a)_k = a(a+1)(a+2)\dots(a+k-1)$. Given that the zero-order Boys function is related to the error function

$$F_0(x) = \sqrt{\frac{\pi}{4x}} \operatorname{erf}(\sqrt{x}), \quad (10)$$

the two-electron integral V_{pq} in Eq. (6) can be written in the instructive form

$$V_{pq} = \left(\frac{\pi}{p}\right)^{3/2} \left(\frac{\pi}{q}\right)^{3/2} \frac{\operatorname{erf}(\sqrt{\alpha} R_{PQ})}{R_{PQ}}, \quad (11)$$

which represents the Coulomb interaction between two point charges $(\pi/p)^{3/2}$ and $(\pi/q)^{3/2}$ at separation R_{PQ} and damped by the error function $0 \leq \operatorname{erf}(\sqrt{\alpha} R_{PQ}) < 1$. For large separations or large reduced exponents, the error function tends to unity and the interaction between the Gaussians approaches that of two point charges.

In some cases, we are interested in Gaussians multiplied by plane-wave function:

$$\omega_{\mathbf{k},a}(\mathbf{r}_A) = \exp(i\mathbf{k} \cdot \mathbf{r}) \exp(-ar_A^2),$$

where \mathbf{k} is the wave vector. Such *plane-wave Gaussians* (PWGs) have several uses. They may serve as mixed basis functions for calculations with periodic boundary conditions and for scattering studies; more importantly, they are used for gauge-origin-independent calculations on molecules in external magnetic fields. For PWGs, the Gaussian product rule still holds

$$\omega_{\mathbf{k},a}(\mathbf{r}_A)^* \omega_{\mathbf{l},b}(\mathbf{r}_B) = \kappa_{ab} \omega_{-\mathbf{k}+\mathbf{l},p}(\mathbf{r}_P). \quad (12)$$

Integration over all space yields

$$\int \omega_{\mathbf{k},a}(\mathbf{r}_A)^* \omega_{\mathbf{l},b}(\mathbf{r}_B) d\mathbf{r} = \exp\left[-\frac{(\mathbf{k}-\mathbf{l}) \cdot (\mathbf{k}-\mathbf{l})}{4p}\right] + i(\mathbf{k}-\mathbf{l}) \cdot \mathbf{P} \left[\left(\frac{\pi}{p}\right)^{3/2} \kappa_{ab},\right.$$

which differs from the GTO integral in Eq. (3) in the presence of a prefactor that depends on the wave vectors \mathbf{k} and \mathbf{l} . As for standard Gaussians, Coulomb integrals reduce to the Boys function³

$$\iint \frac{\exp(-i\mathbf{k} \cdot \mathbf{r}_1) \exp(-pr_{1P}^2) \exp(i\mathbf{l} \cdot \mathbf{r}_2) \exp(-qr_{2Q}^2)}{r_{12}} \times d\mathbf{r}_1 d\mathbf{r}_2 = \exp\left(-\frac{k^2}{4p} - \frac{l^2}{4q} - i\mathbf{k} \cdot \mathbf{P} - i\mathbf{l} \cdot \mathbf{Q}\right) \times \frac{2\pi^{5/2}}{pq\sqrt{p+q}} F_0(\alpha R_{PQ}^2),$$

which differs from the standard expression of Eq. (6) in that the prefactor is different and in that R'_{PQ} is the

distance between the complex vectors $\mathbf{P}' = \mathbf{P} - i\mathbf{k}/2p$ and $\mathbf{Q}' = \mathbf{Q} - i\mathbf{l}/2q$.

INTEGRALS OVER REAL SOLID-HARMONIC GTOs

The complex-valued *solid-harmonic Gaussians* $\mathcal{G}_{lm}(\mathbf{r}, a, \mathbf{A})$ are products of a spherical Gaussian $\exp(-ar_A^2)$ with a solid-harmonic function $\mathcal{Y}_{lm}(\mathbf{r}_A)$:

$$\mathcal{G}_{lm}(\mathbf{r}, a, \mathbf{A}) = \mathcal{Y}_{lm}(\mathbf{r}_A) \exp(-ar_A^2). \quad (13)$$

The *solid-harmonic* functions $\mathcal{Y}_{lm}(\mathbf{r})$ are related to the *spherical-harmonic functions* $Y_{lm}(\theta, \phi)$ (which are the simultaneous eigenfunctions of the operators for the total squared angular momentum \hat{L}^2 and the projected angular momentum \hat{L}_z) as

$$\mathcal{Y}_{lm}(\mathbf{r}) = r^l Y_{lm}(\mathbf{r}), \quad (14)$$

where l and m are the quantum numbers for the total and projected angular momenta, respectively. In molecules without spherical or axial symmetries, nothing is gained by expanding the wave function in eigenfunctions of the angular-momentum operators. Instead, real-valued *solid-harmonic polynomials* $S_{lm}(\mathbf{r})$ are employed. Thus, the real-valued *solid-harmonic Gaussians* $G_{lm}(\mathbf{r}, a, \mathbf{A})$ are products of a solid-harmonic polynomial and a Gaussian function:

$$G_{lm}(\mathbf{r}, a, \mathbf{A}) = S_{lm}(\mathbf{r}_A) \exp(-ar_A^2). \quad (15)$$

In practice, the GTOs used in quantum chemistry are fixed linear combinations of primitive real solid-harmonic Gaussian functions,

$$\chi_a(\mathbf{r}) = \sum_k c_k G_{lm}(\mathbf{r}, a_k, \mathbf{A}), \quad (16)$$

with contraction coefficients c_k and exponents a_k . Such combinations of primitive GTOs are known as *contracted GTOs*. In this review, we refer to these contracted GTOs as *atomic orbitals* (AOs).

Cartesian and Hermite GTOs

When evaluating integrals over real solid-harmonic GTOs, it is convenient to expand the primitive real solid-harmonic GTOs in primitive *Cartesian Gaussians* $G_i(\mathbf{r}, a, \mathbf{A})$ or in *Hermite Gaussians* $H_i(\mathbf{r}, a, \mathbf{A})$ according to

$$G_{lm}(\mathbf{r}, a, \mathbf{A}) = \sum_{|i|=l} S_{lm}^i G_i(\mathbf{r}, a, \mathbf{A}) = \sum_{|i|=l} S_{lm}^i H_i(\mathbf{r}, a, \mathbf{A}), \quad (17)$$

where we have introduced the *multi-index* $\mathbf{i} = (i_x, i_y, i_z)^T$ with $|\mathbf{i}| = i_x + i_y + i_z$. The motivation for making either of these expansions is that the Cartesian and Hermite GTOs (unlike the solid-harmonic GTOs) are separable in the Cartesian directions and may be written in the product form

$$\begin{aligned} G_i(\mathbf{r}, a, \mathbf{A}) &= G_{i_x}(a, x_A) G_{i_y}(a, y_A) G_{i_z}(a, z_A), \\ H_i(\mathbf{r}, a, \mathbf{A}) &= H_{i_x}(a, x_A) H_{i_y}(a, y_A) H_{i_z}(a, z_A), \end{aligned} \quad (18)$$

given by

$$\begin{aligned} G_i(\mathbf{r}, a, \mathbf{A}) &= \mathbf{r}_A^i \exp(-a r_A^2), \\ H_i(\mathbf{r}, a, \mathbf{A}) &= \frac{\partial_A^i \exp(-a r_A^2)}{(2a)^{|\mathbf{i}|}} \end{aligned} \quad (19)$$

in the standard multi-index notation $\mathbf{r}_A^i = x_A^{i_x} y_A^{i_y} z_A^{i_z}$ and $\partial_A^i = \partial^{i_x} / \partial x_A^{i_x} \partial^{i_y} / \partial y_A^{i_y} \partial^{i_z} / \partial z_A^{i_z}$. The equivalence of the Cartesian and Hermite expansions in Eq. (17) follows by noting that the leading polynomial terms of $G_i(\mathbf{r}, a, \mathbf{A})$ and $H_i(\mathbf{r}, a, \mathbf{A})$ are identical and that only these terms contribute to the S_m^i transformation.⁴ The properties of the Cartesian and Hermite Gaussians are summarized by the relations (omitting arguments for brevity):

$$\begin{aligned} \mathbf{r}_A^\lambda G_i &= G_{i+\lambda}, & \mathbf{r}_A^\lambda H_i &= H_{i+\lambda} + \frac{i^\lambda}{2a} H_{i-\lambda}, \\ \frac{\partial_A^\lambda H_i}{2a} &= H_{i+\lambda}, & \frac{\partial_A^\lambda G_i}{2a} &= G_{i+\lambda} - \frac{i^\lambda}{2a} G_{i-\lambda}, \end{aligned} \quad (20)$$

where λ is a multi-index of unit length, $(1, 0, 0)^T$, $(0, 1, 0)^T$, or $(0, 0, 1)^T$, corresponding to the x , y , or z components, respectively. Traditionally, Cartesian Gaussians have been used in quantum-chemistry software. However, the use of Hermite Gaussians simplifies the calculation of derivatives of integrals with respect to nuclear displacements and is preferable whenever molecular forces and force constants are to be evaluated. Furthermore, the use of Hermite Gaussians simplify the calculation of two- and three-center Coulomb integrals such as those needed for density fitting (see example in section *The McMurchie–Davidson Scheme*). Finally, the use of Hermite Gaussians reduces all integration to differentiation of integrals over spherical Gaussians, thereby simplifying the development of integration techniques for integrals over new operators. It is here worth mentioning the efficient approach of Ahlrichs⁵ for the evaluation of two- and three-center integrals and the work of Köster⁶ for which Hermite, rather than solid-harmonic Gaussians, are used for the auxiliary density-fitting basis.

One-Electron Integrals

Many different types of *one-electron integrals* appear in quantum chemistry, some of the most common being (integration over all space \mathbb{R}^3 being understood)

$$\begin{aligned} S_{ab} &= \langle ab \rangle = \int \chi_a(\mathbf{r}) \chi_b(\mathbf{r}) \, d\mathbf{r}, \\ T_{ab} &= -\frac{1}{2} \langle a | \nabla^2 | b \rangle = -\frac{1}{2} \int \chi_a(\mathbf{r}) \nabla^2 \chi_b(\mathbf{r}) \, d\mathbf{r}, \\ M_{ab}^{e,C} &= \langle a | \mathbf{r}_C^e | b \rangle = \int \chi_a(\mathbf{r}) \chi_b(\mathbf{r}) \mathbf{r}_C^e \, d\mathbf{r}, \\ \langle a | r_{1C}^{-1} | b \rangle &= \int \frac{\chi_a(\mathbf{r}) \chi_b(\mathbf{r})}{r_C} \, d\mathbf{r}, \end{aligned} \quad (21)$$

where S_{ab} is an *overlap integral*, T_{ab} is a *kinetic-energy integral*, $M_{ab}^{e,C}$ is a *multipole-moment integral* about C , and $\langle a | r_{1C}^{-1} | b \rangle$ is a *nuclear–electron attraction integral* between the orbital product $\chi_a(\mathbf{r}) \chi_b(\mathbf{r})$ and a point-charge nucleus of unit charge at C . These integrals are first calculated in terms of primitive Cartesian or Hermite Gaussians, followed by the transformation to the contracted basis in a *contraction step* and the transformation to the real solid-harmonic basis in a final *spherical-transformation step*. For example, the contracted solid-harmonic overlap integrals S_{ab} are given by

$$S_{ab} = \sum_{ij} S_{l_a m_a}^i S_{l_b m_b}^j \sum_{kl} c_k c_l S_{ij}^{kl}, \quad (22)$$

where the primitive overlap integrals S_{ij}^{kl} may be evaluated in the Cartesian or Hermite basis:

$$S_{ij}^{kl} = \begin{cases} \int G_i(\mathbf{r}, a_k, \mathbf{A}) G_j(\mathbf{r}, b_l, \mathbf{B}) \, d\mathbf{r} & \text{(Cartesian basis),} \\ \int H_i(\mathbf{r}, a_k, \mathbf{A}) H_j(\mathbf{r}, b_l, \mathbf{B}) \, d\mathbf{r} & \text{(Hermite basis).} \end{cases} \quad (23)$$

We emphasize that, even though the intermediate integrals in Eq. (23) are different in the two cases, the final solid-harmonic integrals in Eq. (22) are identical.

Before proceeding with the two-electron integrals, we note some features that are important for an efficient integral evaluation in general. First, we are free to choose the order of the contraction and the spherical-transformation steps, the two steps being independent of each other. For efficiency, we choose the order that gives the greatest reduction in intermediates. Second, integrals are calculated simultaneously over AO shells rather than over individual AOs, an *AO shell* consisting of all AOs at the same center and with the same exponent and angular-momentum quantum number l . This approach is taken since integrals of AOs in the same shell share many intermediate integrals; it can be generalized to *family basis sets*,

whose shells consist of AOs of the same center and same exponents but different quantum numbers.⁷

Two-Electron Integrals

In quantum chemistry, a variety of two-electron integrals of the general form (integration over \mathbb{R}^6 being understood)

$$(f|w|g) = \iint f(\mathbf{r}_1)w(\mathbf{r}_1, \mathbf{r}_2)g(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (24)$$

are of interest, with different operators $w(\mathbf{r}_1, \mathbf{r}_2)$ and different functions f and g , which may be either single AOs or products of AOs. Among these integrals, the four-center electron-repulsion integrals (ERIs) $(ab|cd) \equiv (ab|r_{12}^{-1}|cd)$ between the AO products $\chi_a(\mathbf{r}_1)\chi_b(\mathbf{r}_1)$ and $\chi_c(\mathbf{r}_2)\chi_d(\mathbf{r}_2)$ are the most important. In the density-fitting approximation, two- and three-center ERIs are also needed, for example, three-center ERIs $(ab|\alpha)$ between AO products $\chi_a(\mathbf{r}_1)\chi_b(\mathbf{r}_1)$ and single AOs $\chi_\alpha(\mathbf{r}_2)$.

Integrals where the Coulomb operator is replaced by the corresponding attenuated operator $\text{erf}(\mu r_{12})/r_{12}$ are also encountered, in particular, in the range-separated Kohn–Sham methods such the CAM-B3LYP method of Yanai et al.⁸ and in certain density-fitting approaches.^{9, 10} Similarly, the Yukawa potential $\exp(-\mu r_{12}^2)/r_{12}$ and Gaussian-damped operator $\exp(-\mu r_{12}^2)/r_{12}$ is sometimes used.^{10–12} Moreover, in the explicitly correlated methods discussed in section *Explicitly Correlated Methods*, a variety of operators $w(\mathbf{r}_1, \mathbf{r}_2)$ occur.

INTEGRAL EVALUATION SCHEMES

Integral evaluation central to any quantum-chemistry calculation and its efficiency is of paramount importance. In this section, we outline the strategies for integral evaluation, with emphasis on the popular McMurchie–Davidson, Obara–Saika, and Dupuis–King–Rys schemes. Although these schemes follow different strategies for integral evaluation, the real solid-harmonic GTOs are in all cases expanded in Cartesian (or Hermite) GTOs. Moreover, in all cases, some auxiliary integrals in a reduced dimension are first calculated, from which the full integrals in a Cartesian or partially Cartesian basis are assembled before contraction and transformation to the solid-harmonic basis. The order of the steps and the choice of auxiliary integrals give different flavors to the different schemes.

The efficiency of the integral evaluation depends not only on the choice of integration scheme, but also on how this scheme is translated into computer code.

An important measure of efficiency is the *flop count* (the number of floating-point operations needed) for the computation of integrals of various types. This is a useful way to compare methods and a low flop count is always desirable. However, an equally important parameter is the efficiency of the computer implementation—its efficient use and reuse of intermediate quantities, memory management, and so on. Moreover, over time, the usefulness of any code also depends on its flexibility, that is, on the ease with which it may be modified and adapted to new integral types, to new computational requirements, and to new computer hardware and platforms. Therefore, a compromise between efficiency and flexibility is typically sought rather than selecting the ‘best’ integral evaluation scheme.

Before considering the various integral evaluation schemes, we review our notation. The Mulliken-like notation (ab) and $[ab]$ is used for Coulomb-repulsion integrals over contracted and primitive solid-harmonic GTOs, respectively, whereas $(i|j)$ and $[i|j]$ denote integrals over contracted and primitive Cartesian (or Hermite) GTOs. A combined notation such as $[i|b]$ is used to denote mixed integrals as needed.

The McMurchie–Davidson Scheme

In the McMurchie–Davidson scheme,¹³ the product $\Omega_{ab}(\mathbf{r})$ of two primitive solid-harmonic Gaussians $G_{l_a m_a}(\mathbf{r}, a, \mathbf{A})$ and $G_{l_b m_b}(\mathbf{r}, b, \mathbf{B})$ is expanded in Hermite GTOs according to

$$\begin{aligned} \Omega_{ab}(\mathbf{r}) &= G_{l_a m_a}(\mathbf{r}, a, \mathbf{A})G_{l_b m_b}(\mathbf{r}, b, \mathbf{B}) \\ &= \sum_{|t|=0}^{l_a+l_b} E_t^{ab} \Lambda_t(\mathbf{r}, p, \mathbf{P}), \end{aligned} \quad (25)$$

where p and \mathbf{P} are defined in Eq. (2), l_a and l_b are the angular-momentum quantum numbers of the two solid-harmonic GTOs, and the Hermite GTOs are defined as

$$\Lambda_t(\mathbf{r}, p, \mathbf{P}) = (2p)^{|t|} H_t(\mathbf{r}, p, \mathbf{P}). \quad (26)$$

The Hermite expansion coefficients E_t^{ab} are obtained from $E_0^{00} = \kappa_{ab}$ in the Cartesian¹³ or Hermite⁴ basis for the three Cartesian components by recursion

$$\begin{aligned} E_t^{i+\lambda, j} &= \frac{1}{2p} E_{t-1}^{ij} + \mathbf{R}_{pA}^\lambda E_t^{ij} + (t+\lambda) E_{t+\lambda}^{ij} - \left[\frac{i^\lambda}{2a} E_t^{i-\lambda, j} \right]_{\text{H}}, \\ E_t^{i, j+\lambda} &= \frac{1}{2p} E_{t-1}^{ij} + \mathbf{R}_{pB}^\lambda E_t^{ij} + (t+\lambda) E_{t+\lambda}^{ij} - \left[\frac{j^\lambda}{2b} E_t^{i, j-\lambda} \right]_{\text{H}}, \end{aligned} \quad (27)$$

Set $p, \mathbf{P}, E_{\mathbf{t}}^{ab}$ for all shell pairs	$\mathcal{O}(p^2 l^3)$
Loop over ab shell pairs	
Loop over cd shell pairs	
Set α, \mathbf{R}_{PQ} for all primitive products between the two shell pairs	$\mathcal{O}(p^4)$
Build $F_n(\alpha, \mathbf{R}_{PQ})$	$\mathcal{O}(p^4 l)$
Build $R_{\mathbf{t}+\mathbf{u}}(\alpha, \mathbf{R}_{PQ})$	$\mathcal{O}(p^4 l^4)$
Contract $[\mathbf{t} cd] = \sum_{\mathbf{u}} (-1)^{ \mathbf{u} } E_{\mathbf{u}}^{cd} R_{\mathbf{t}+\mathbf{u}}(\alpha, \mathbf{R}_{PQ})$	$\mathcal{O}(p^4 l^8)$
Contract from primitive to contracted basis to form $[\mathbf{t} cd]$	$\mathcal{O}(p^4 l^5 c)$
Contract $[ab cd] = \sum_{\mathbf{t}} E_{\mathbf{t}}^{ab} [\mathbf{t} cd]$	$\mathcal{O}(p^2 l^7 c^2)$
Contract from primitive to contracted basis to form $(ab cd)$	$\mathcal{O}(p^2 l^4 c^3)$
End loop cd	
End loop ab	

FIGURE 3 | The McMurchie–Davidson algorithm for four-center two-electron integrals. The computational costs of the steps are given to the right, p and c being the numbers of primitive and contracted functions of a given AO shell and l , the angular-momentum quantum number (assuming that these are the same for all orbitals).

and then transformed to the real solid-harmonic basis according to

$$E_{\mathbf{t}}^{ab} = \sum_{ij} S_{l_a m_a}^i S_{l_b m_b}^j E_{\mathbf{t}}^{ij}. \quad (28)$$

The bracketed terms of Eq. (27) are included for Hermite GTOs but omitted for Cartesian GTOs. To justify Eq. (25), we note from Eq. (15) that the product of the two solid-harmonic GTOs in Eq. (25) is simply the product of two solid-harmonic polynomials $S_{l_a m_a}(\mathbf{r}_A)$ and $S_{l_b m_b}(\mathbf{r}_B)$ multiplied by the product Gaussian $\exp(-ar_A^2) \exp(-br_B^2)$. From the relations $\mathbf{r}_A = \mathbf{r}_P - \mathbf{R}_{PA}$ and $\mathbf{r}_B = \mathbf{r}_P - \mathbf{R}_{PB}$ with $\mathbf{R}_{PA} = \mathbf{P} - \mathbf{A}$ and $\mathbf{R}_{PB} = \mathbf{P} - \mathbf{B}$, it follows that $S_{l_a m_a}(\mathbf{r}_A) S_{l_b m_b}(\mathbf{r}_B)$ can be written as a polynomial of degree $l_p = l_a + l_b$ in \mathbf{r}_P .

The expansion of Eq. (25) in Hermite Gaussians greatly simplifies integral evaluation, enabling us to take advantage of the Leibniz integration rule

$$\frac{d}{dx} \int f(x, y) dy = \int \frac{\partial f(x, y)}{\partial x} dy, \quad (29)$$

given that the integration limits are independent of x . In particular, by applying the Leibniz integration rule to the four-center integral $[ab|cd]$ over primitive solid-harmonic GTOs (note here the square-bracketed Mulliken-like notation for primitive basis functions), we obtain

$$[ab|cd] = \sum_{|\mathbf{t}|=0}^{l_a+l_b} E_{\mathbf{t}}^{ab} \sum_{|\mathbf{u}|=0}^{l_c+l_d} (-1)^{|\mathbf{u}|} E_{\mathbf{u}}^{cd} R_{\mathbf{t}+\mathbf{u}}(\alpha, \mathbf{R}_{PQ}) \quad (30)$$

with the Hermite ERIs $R_{\mathbf{t}+\mathbf{u}}(\alpha, \mathbf{R}_{PQ})$ given by

$$\begin{aligned} R_{\mathbf{t}+\mathbf{u}}(\alpha, \mathbf{R}_{PQ}) &= (-1)^{|\mathbf{u}|} [\mathbf{t}|\mathbf{u}] \\ &= (-1)^{|\mathbf{u}|} \frac{\partial^{\mathbf{t}+\mathbf{u}} V_{pq}}{\partial_{\mathbf{P}}^{\mathbf{t}} \partial_{\mathbf{Q}}^{\mathbf{u}}} = \frac{\partial^{\mathbf{t}+\mathbf{u}} V_{pq}}{\partial_{\mathbf{P}}^{\mathbf{t}+\mathbf{u}}}, \end{aligned} \quad (31)$$

where V_{pq} is given by Eq. (6). Combining Eqs (6) and (8), we arrive at the recurrence relations for the Hermite ERIs

$$R_{\mathbf{t}+\lambda}^n = \mathbf{t}^\lambda R_{\mathbf{t}-\lambda}^{n+1} + R_{PQ}^\lambda R_{\mathbf{t}}^{n+1}, \quad (32)$$

starting from

$$R_0^n = (-2\alpha)^n \frac{2\pi^{5/2}}{pq\sqrt{p+q}} F_n(\alpha R_{PQ}^2). \quad (33)$$

The McMurchie–Davidson scheme for four-center two-electron integrals is outlined in Figure 3. For integrals of high angular momentum, this scheme is dominated by the contraction of the Hermite integrals $R_{\mathbf{t}+\mathbf{u}}(\alpha, \mathbf{R}_{PQ})$ with the coefficients $E_{\mathbf{u}}^{cd}$, which scales as $\mathcal{O}(p^4 l^8)$, where p is the number of primitives and l is the angular-momentum quantum number.

To illustrate the benefits of using Hermite GTOs for the two- and three-center two-electron integrals, we consider the two-center integrals $[\alpha|\beta]$ between two primitive solid-harmonic functions $G_{l_a m_a}(\mathbf{r}, \alpha, \mathbf{P})$ and $G_{l_b m_b}(\mathbf{r}, \beta, \mathbf{Q})$. Expanding the GTOs in Cartesian and Hermite Gaussians, respectively, we need to evaluate the intermediate integrals

$$[\alpha|\beta]_C = \sum_{|\mathbf{t}|=0}^{l_\alpha} {}^C E_{\mathbf{t}}^\alpha \sum_{|\mathbf{u}|=0}^{l_\beta} (-1)^{|\mathbf{u}|} E_{\mathbf{u}}^\beta R_{\mathbf{t}+\mathbf{u}}(\alpha, \mathbf{R}_{PQ}), \quad (34)$$

$$[\alpha|\beta]_{\text{H}} = \sum_{|\mathbf{t}|=l_{\alpha}}^{\text{H}} E_{\mathbf{t}}^{\alpha} \sum_{|\mathbf{u}|=l_{\beta}} (-1)^{|\mathbf{u}|} E_{\mathbf{u}}^{\beta} R_{\mathbf{t}+\mathbf{u}}(\alpha, \mathbf{R}_{PQ}), \quad (35)$$

with ${}^{\text{H}}E_{\mathbf{t}}^{\alpha}$ and ${}^{\text{H}}E_{\mathbf{u}}^{\beta}$ combining the prefactors $(2\alpha)^{-l_{\alpha}}$ and $(2\beta)^{-l_{\beta}}$ with the respective spherical-transformation coefficients from the Hermite to solid-harmonic basis. In the Cartesian case, all $|\mathbf{t}| \leq l_{\alpha}$ and $|\mathbf{u}| \leq l_{\beta}$ contribute, whereas only $|\mathbf{t}| = l_{\alpha}$ and $|\mathbf{u}| = l_{\beta}$ are needed in the Hermite case, reducing the scaling from $\mathcal{O}(l^7 p^2)$ to $\mathcal{O}(l^5 p^2)$. In the same fashion, the cost of primitive three-center integral evaluation is reduced from $\mathcal{O}(l^7 p^3)$ to $\mathcal{O}(l^6 p^3)$ by the use of Hermite Gaussians.

The Obara–Saika Scheme

In the *Obara–Saika scheme* for four-center two-electron ERIs, the auxiliary integrals

$$[\mathbf{ij}|\mathbf{kl}]^m = \frac{2}{\pi^{1/2}} \int_0^{\infty} \left(\frac{u^2}{\alpha + u^2} \right)^m \times [\mathbf{ij}|\exp(-u^2 \mathbf{r}_{12}^2)|\mathbf{kl}] du \quad (36)$$

are introduced,¹⁴ where the innermost integral, over the spatial coordinates \mathbf{r}_1 and \mathbf{r}_2 , can be factorized in the three Cartesian directions. These auxiliary integrals contain the two special cases $[\mathbf{ij}|\mathbf{kl}]^0$ and $[\mathbf{00}|\mathbf{00}]^m$, where the former is a standard ERI and the latter a standard Boys function. From the generalized Boys function, the following Obara–Saika recurrence relation may be set up:

$$\begin{aligned} [\mathbf{i} + \lambda, \mathbf{j}|\mathbf{kl}]^m &= \mathbf{R}_{PA}^{\lambda} [\mathbf{ij}|\mathbf{kl}]^m - \frac{\alpha}{q} \mathbf{R}_{PQ}^{\lambda} [\mathbf{ij}|\mathbf{kl}]^{m+1} \\ &+ \frac{i^{\lambda}}{2p} [\mathbf{i} - \lambda, \mathbf{j}|\mathbf{kl}]^m - \frac{i^{\lambda}\alpha}{2p^2} [\mathbf{i} - \lambda, \mathbf{j}|\mathbf{kl}]^{m+1} \\ &+ \frac{j^{\lambda}}{2p} [\mathbf{i}, \mathbf{j} - \lambda|\mathbf{kl}]^m - \frac{j^{\lambda}\alpha}{2p^2} [\mathbf{i}, \mathbf{j} - \lambda|\mathbf{kl}]^{m+1} \\ &+ \frac{k^{\lambda}}{2\alpha} [\mathbf{ij}|\mathbf{k} - \lambda, \mathbf{l}]^{m+1} + \frac{l^{\lambda}}{2\alpha} [\mathbf{ij}|\mathbf{k}, \mathbf{l} - \lambda]^{m+1}, \quad (37) \end{aligned}$$

allowing us to generate the standard ERIs $[\mathbf{ij}|\mathbf{kl}]^0$ from $[\mathbf{00}|\mathbf{00}]^m$ recursively.

Although conceptually attractive, the cost of the eight-term Obara–Saika recursion is high. As suggested by Head-Gordon and Pople,¹⁵ the cost of integral evaluation may be significantly reduced by exploiting the recurrence relation of the Cartesian GTOs in Eq. (20):

$$\begin{aligned} G_{\mathbf{i}+\lambda}(\mathbf{r}, a, \mathbf{A}) G_{\mathbf{j}}(\mathbf{r}, b, \mathbf{B}) &= G_{\mathbf{i}}(\mathbf{r}, a, \mathbf{A}) G_{\mathbf{j}+\lambda}(\mathbf{r}, b, \mathbf{B}) \\ &+ \mathbf{R}_{BA}^{\lambda} G_{\mathbf{i}}(\mathbf{r}, a, \mathbf{A}) G_{\mathbf{j}}(\mathbf{r}, b, \mathbf{B}). \quad (38) \end{aligned}$$

Since this relation does not depend on the Gaussian exponents, it can be applied to contracted integrals, yielding the following *horizontal recurrence relation*:

$$(\mathbf{i} + \lambda, \mathbf{j}|\mathbf{kl})^m = (\mathbf{i}, \mathbf{j} + \lambda|\mathbf{kl})^m + \mathbf{R}_{BA}^{\lambda} (\mathbf{ij}|\mathbf{kl})^m. \quad (39)$$

In combination with this recursion, we may use a simplified five-term version of the Obara–Saika recurrence relation known as the *vertical recurrence relation*:

$$\begin{aligned} [\mathbf{e} + \lambda, \mathbf{0}|\mathbf{f0}]^m &= -\frac{\alpha}{q} \mathbf{R}_{PA}^{\lambda} [\mathbf{e0}|\mathbf{f0}]^m + \mathbf{R}_{PQ}^{\lambda} [\mathbf{e0}|\mathbf{f0}]^{m+1} \\ &+ \frac{e^{\lambda}}{2p} [\mathbf{e} - \lambda, \mathbf{0}|\mathbf{f0}]^m \\ &- \frac{e^{\lambda}\alpha}{2p^2} [\mathbf{e} - \lambda, \mathbf{0}|\mathbf{f0}]^{m+1} \\ &+ \frac{f^{\lambda}}{2\alpha} [\mathbf{e0}|\mathbf{f} - \lambda, \mathbf{0}]^{m+1}. \quad (40) \end{aligned}$$

In the resulting *Head-Gordon–Pople* scheme, we first generate $[\mathbf{e0}|\mathbf{f0}]$ from $[\mathbf{00}|\mathbf{00}]^m$ by vertical recursion followed by contraction to $(\mathbf{e0}|\mathbf{f0})$, from which the integrals $(\mathbf{ij}|\mathbf{kl})$ are obtained by horizontal recursion. The final integrals (\mathbf{abcd}) are obtained by separate spherical transformation steps for each Cartesian or Hermite GTO index i, j, k , or l , according to Eq. (17). There are many ways to make these contractions. One possibility is to perform the horizontal recursion and spherical transformations first for the second electron and then for the first electron, generating in succession $(\mathbf{e0}|\mathbf{f0})$, $(\mathbf{e0}|\mathbf{kl})$, $(\mathbf{e0}|\mathbf{cd})$, $(\mathbf{ij}|\mathbf{cd})$, and (\mathbf{abcd}) .

The Dupuis–King–Rys Scheme

The *Dupuis–King–Rys* (DKR) scheme for two-electron integrals is based on Gaussian-quadrature techniques and the use of orthonormal polynomials.^{16–19} Unlike the McMurchie–Davidson and Obara–Saika schemes, the DKR scheme avoids the evaluation of the Boys function, computing instead the roots and weights for quadrature. For a detailed review the DKR method, see Ref 20.

In the DKR scheme, an integral is computed as a weighted sum of the integrand, evaluated at the roots x_k of an orthonormal polynomial $P_n(x)$ of degree n . The integral over the polynomial $P_n(x)$ and a weight function $w(x)$ is now evaluated as

$$\int P_n(x) w(x) dx = \sum_k^n W_k P_n(x_k), \quad (41)$$

where the W_k are the weights associated with the roots x_k . In the evaluation of the two-electron

integrals, the weight function is given by

$$w(t) = \exp(-\alpha R_{PQ}^2 t^2), \quad (42)$$

which we recognize as the integrand of the Boys functions in Eq. (7). These weights define the set of orthonormal polynomials, the *Rys–Gauss polynomials*, in the DRK scheme.

Given that the primitive two-electron integral $[abcd]$ is symmetric (the integral vanishes for polynomials P_m of odd degree), we can express the integral in the form

$$[abcd] = \int_0^1 P_{2n}(t)w(t) dt. \quad (43)$$

In the auxiliary-function-based techniques, the same integral is expressed as

$$[abcd] = \sum_{k=0}^n C_k^n(\mathbf{R}_{PQ}, \alpha) F_k(\alpha R_{PQ}^2), \quad (44)$$

and leading to the coefficients $C_k^n(\mathbf{R}_{PQ}, \alpha)$ of the polynomial $P_{2n}(t)$ being evaluated and combined with the Boys functions, either directly or indirectly via recurrence relations. The *Rys–Gauss* quadrature avoids the explicit evaluation of these coefficients; instead, they are indirectly and exactly assessed from the roots and weights of the orthonormal polynomials. The roots are derived from the *Rys–Gauss* polynomials and the weights are derived in association with the Lagrange form of interpolation polynomials (see Ref 20). From the symmetry of the two-electron integrals, it follows that, for a polynomial $P_{2n}(x)$ with $n = l_a + l_b + l_c + l_d$, the roots and weights of the *Rys–Gauss* polynomial of degree $n_{\text{Rys}} = \lfloor (n+2)/2 \rfloor$ are sufficient for an exact representation. The major difference from the auxiliary-function schemes is that the recurrence relations are different, being dictated by the properties of the integrand rather than the integral.

Following Lindh et al.,¹⁹ we calculate six-dimensional two-electron primitive integrals as a sum over products of two-dimensional integrands $I_{\lambda}^{e_x, f_x}$ according to

$$[e0|f0] = 2 \left(\frac{\alpha}{\pi}\right)^{1/2} \kappa_{ab} \kappa_{cd} \left(\frac{\pi^2}{pq}\right)^{3/2} \times \sum_{k=1}^{n_{\text{Rys}}} W(t_k) I^{ef} \quad (45)$$

with $I^{ef} = I_x^{e_x, f_x} I_y^{e_y, f_y} I_z^{e_z, f_z}$, evaluated at the roots t_k of the *Rys–Gauss* polynomial $Q_{n_{\text{Rys}}}(\alpha R_{PQ}^2)$ using the

recurrence relations

$$I^{e+\lambda, f} = \left(\mathbf{R}_{PA}^{\lambda} + \frac{\alpha t^2}{p} \mathbf{R}_{QP}^{\lambda} \right) I^{ef} + \frac{e^{\lambda}}{2p} \left(1 - \frac{\alpha t^2}{p} \right) I^{e-\lambda, f} + \frac{f^{\lambda} \alpha t^2}{2pq} I^{e, f-\lambda} \quad (46)$$

beginning with $I^{00} = 1$. The recurrence relations given here are for Cartesian GTOs; similar relations hold for Hermite GTOs. Following contraction of the integrals in Eq. (45), the horizontal recurrence relation in Eq. (39) is used to produce the final integrals in the Cartesian basis, subsequently transformed to the real solid-harmonic basis.

APPROXIMATE INTEGRAL SCHEMES

The integration schemes discussed so far are exact (to within the numerical errors in the Boys functions and in the *Rys–Gauss* roots of weights) and efficient. However, even with the most efficient molecular integral codes, such an exact integral evaluation would be the computational bottleneck in nearly all molecular studies. To speed up integral evaluation, efficient screening and approximation methods have been developed, to which we now turn our attention. We begin by considering techniques for integral screening in section *Integral Screening* and then discuss multipole-moment methods in section *Multipole-Moment Methods*. In section *Density Fitting*, we review density-fitting methods and conclude with discussion of Cholesky decomposition methods in section *Cholesky Decomposition*.

Integral Screening

For large molecular systems, most integrals are negligible and can be omitted from the calculation by efficient integral screening techniques without affecting the overall result. Such screening techniques should exploit two separate effects—first, that the product between two (or more) basis functions decreases rapidly with increasing separation between the functions; second, that the interaction between the electrons decreases with increasing separation between the electrons.

For ERIs, the first effect is by far most important, given that the Coulomb operator decays only as $1/r_{12}$, whereas Ω_{ab} decreases as a Gaussian $\exp(-\mu R_{AB}^2)$ according to the Gaussian product rule of Eq. (1). The removal of small products Ω_{ab} can be achieved by the technique proposed by Häser and Ahlrichs,²¹ which relies on the application of the

Cauchy–Schwarz inequality:

$$|(f|g)| \leq \sqrt{(f|f)}\sqrt{(g|g)}. \quad (47)$$

By precalculating integrals of the type $G_{ab} = \sqrt{(ab|ab)}$, we may in this manner generate an inexpensive upper bound to all two-electron integrals. When applied to four-center two-electron integrals over N basis functions with a given tolerance τ , the scaling is reduced from $\mathcal{O}(N^4)$ to $\mathcal{O}(N^2)$ by removal of all integrals $(ab|cd)$ for which $G_{ab}G_{cd} < \tau$.

The Cauchy–Schwarz screening does not account for the $1/R_{PQ}$ (or faster) decay between centers of two (nonoverlapping) charge distributions $f(\mathbf{r}_1)$ and $g(\mathbf{r}_2)$. This distance decay can be screened for by using the multipole-based integral estimate of Lambrecht and Ochsenfeld.²² Such screening becomes important when dealing with electron correlation or orbitals of high angular momentum because the interactions then decay asymptotically as R_{PQ}^{-k} for some positive integer k , for instance, two-center ERIs over f orbitals decay as R_{PQ}^{-7} .

Multipole-Moment Methods

The interaction between well-separated charge distributions can be accurately represented by the corresponding multipole-moment interactions from the expression

$$(ab|cd) = \sum_{l,l'=0}^{l_{\max}} \sum_{m=-l}^{m=l} \sum_{m'=-l'}^{m'=l'} q_{lm}^{ab}(\mathbf{P}) \times T_{lm,l'm'}(\mathbf{R}_{QP}) q_{l'm'}^{cd}(\mathbf{Q}) \quad (48)$$

for sufficiently large l_{\max} . The (complex) solid harmonic multipole moments $q_{lm}(\mathbf{P})$ are given as the integrals over the product between $\Omega_{ab}(\mathbf{r})$ and the *regular solid harmonics* $R_{lm}(\mathbf{r}_P)$ with centers \mathbf{P} according to

$$q_{lm}(\mathbf{P}) = \int \Omega_{ab}(\mathbf{r}) R_{lm}(\mathbf{r}_P) d\mathbf{r}, \quad (49)$$

where the zero-, first-, second-, and higher-order terms are the charge, dipole, quadrupole, and higher-order moments. The regular solid harmonics $R_{lm}(\mathbf{r}_P)$ are scaled versions of the *complex solid harmonics* $C_{lm}(\mathbf{r})$, related to the real solid harmonics $S_{lm}(\mathbf{r})$ by a linear combination (of $+m$ and $-m$ pairs). The interaction matrix $T_{lm,l'm'}$ is given in terms of the *irregular solid harmonics*, again related to the regular solid harmonics (see Ref 2 for details).

The expansion of Eq. (48) gives no computational gain when applied individually to each integral, even when the multipole moments can be calculated for each electron before evaluating the integrals. In

fact, when applicable, the expression in Eq. (48) is typically slower than standard techniques because of the large l_{\max} values (10–20) needed for convergence. The advantage of the multipole expansion arises when the multipole moments of several charge distributions are combined into one multipole moment with a single (shared) center, as can be accomplished by translation of the various multipole moments. Decomposing the two-electron Coulomb contribution to the Fock or Kohn–Sham matrix into a classical part (to be treated by multipole expansion) and a nonclassical part (to be treated by explicit integration), we obtain

$$J_{ab} = \sum_{cd} (ab|cd) D_{cd} = J_{ab}^{\text{cls}} + J_{ab}^{\text{non}},$$

$$J_{ab}^{\text{cls}} = \sum_{l,l'=0}^{l_{\max}} \sum_{m=-l}^{m=l} \sum_{m'=-l'}^{m'=l'} q_{lm}^{ab}(\mathbf{P}) \sum_{\mathbf{Q}} T_{lm,l'm'}(\mathbf{R}_{QP}) q_{l'm'}^{\mathbf{Q}},$$

$$q_{l'm'}^{\mathbf{Q}} = \sum_{cd \in \mathbf{Q}} q_{l'm'}^{cd}(\mathbf{Q}) D_{cd}, \quad (50)$$

where the notation $cd \in \mathbf{Q}$ indicates pairs cd sharing the same expansion center \mathbf{Q} . The nonclassical part J_{ab}^{non} is treated by regular integral evaluation methods, leading to linear scaling by screening. The classical part J_{ab}^{cls} may be evaluated by treating multipole moments of larger and larger charge distributions at increasing distances, reducing the complexity to $\mathcal{O}(N \log N)$.

Linear complexity $\mathcal{O}(N)$ of the classical contribution in Eq. (50) may be achieved by the *fast multipole method* (FMM) of Greengard and Rokhlin,²³ originally designed for gravitational interactions in astrophysics. In the FMM, all particles are contained in a parent box, which is recursively bisected in each Cartesian direction into smaller and smaller *children boxes* of a family tree. The interactions between the particles are then calculated from the lowest level up, introducing interactions over larger and larger separations until all have been accounted for. For the Coulomb systems encountered in quantum chemistry, the FMM was generalized by White and Head-Gordon²⁴ to treat interactions between continuous, overlapping charge distributions. In their *continuous fast-multipole method* (CFMM), the extent (effective size) of each charge distribution is determined. Distributions of similar extent are classified into branches of the family tree, based on the number of boxes that must separate two distributions for the interaction to be treated classically.

In the method described above, each Coulomb contribution $(ab|cd)D_{cd}$ is treated either fully classically (by the CFMM) or fully nonclassically (by

explicit integration). Alternatively, each contribution $(ab|cd)D_{cd}$ may be decomposed into a classical (point-charge) part and a nonclassical (finite-size) part, treating all classical parts by the traditional FMM and all nonclassical parts by explicit integration, as advocated in Ref 25.

Density Fitting

In the *density-fitting approximation*, the four-center two-electron integrals $(ab|cd)$ are approximated in terms of two- and three-center integrals. In this way, significant computational speedups are obtained, typically by one to two orders of magnitude.

Following Dunlap,²⁶ a *robust* fit $(\widetilde{ab|cd})$ to $(ab|cd)$ is obtained according to

$$(\widetilde{ab|cd}) = (ab|\widetilde{cd}) + (\widetilde{ab}|\Delta cd), \quad (51)$$

where $|\widetilde{ab})$ and $|\widetilde{cd})$ are fitted approximations to $|ab)$ and $|cd)$, respectively, and with $|\Delta cd) = |cd) - |\widetilde{cd})$. The approximation is robust in the sense that the error in the fitted integral is bilinear in the errors in the fitted densities:

$$(\Delta ab|\Delta cd) = (ab|cd) - (\widetilde{ab|cd}), \quad (52)$$

with $|\Delta ab) = |ab) - |\widetilde{ab})$. In Eq. (51), $(\widetilde{ab}|\Delta cd)$ provides a first-order correction to $(ab|cd)$, making the approximation robust; without this *Dunlap correction*, the error in the fitted integral would be linear in $|\Delta cd)$.

There are several ways to obtain the fitted distributions $|\widetilde{ab})$ and $|\widetilde{cd})$. If these distributions are expanded in atom-centered auxiliary basis functions, only two- and three-center integrals need to be evaluated. Usually, both distributions are expanded in the full set of atom-centered auxiliary basis functions $\alpha \in \mathcal{M}$, with \mathcal{M} denoting all atoms in the molecule, according to

$$\begin{aligned} |ab) &\approx |\widetilde{ab}) = \sum_{\alpha \in \mathcal{M}} c_{\alpha}^{ab} |\alpha), \\ |cd) &\approx |\widetilde{cd}) = \sum_{\alpha \in \mathcal{M}} c_{\alpha}^{cd} |\alpha). \end{aligned} \quad (53)$$

The fitting coefficients c_{α}^{ab} and c_{α}^{cd} are obtained by minimizing the residual Coulomb-repulsion interactions $(\Delta ab|\Delta cd)$ of Eq. (52) with respect to these coefficients, yielding the following set of linear equations:

$$\begin{aligned} (\alpha|\widetilde{ab}) &= \sum_{\beta \in \mathcal{M}} (\alpha|\beta) c_{\beta}^{ab} = (\alpha|ab), \\ (\alpha|\widetilde{cd}) &= \sum_{\beta \in \mathcal{M}} (\alpha|\beta) c_{\beta}^{cd} = (\alpha|cd). \end{aligned} \quad (54)$$

In this manner, the last term of Eq. (51) vanishes according to Eq. (54), giving the following RI approximation (in a nonorthogonal basis) to the fitted integrals:

$$(\widetilde{ab|cd}) = \sum_{\alpha\beta} (ab|\alpha)(\alpha|\beta)^{-1}(\beta|cd). \quad (55)$$

Furthermore, substitution of the four-center two-electron integrals $(ab|cd)$ by $(\widetilde{ab|cd})$ in any energy expression $E[(ab|cd)]$ yields a stable quantity:

$$\frac{\partial E[(\widetilde{ab|cd})]}{\partial c_{\alpha}^{ab}} = \frac{\partial E[(\widetilde{ab|cd})]}{\partial (\widetilde{ab|cd})} \frac{\partial (\widetilde{ab|cd})}{\partial c_{\alpha}^{ab}} = 0, \quad (56)$$

as from Eq. (54) it follows that

$$\frac{\partial (\widetilde{ab|cd})}{\partial c_{\alpha}^{ab}} = 0. \quad (57)$$

This result is important for response theory since $E[(\widetilde{ab|cd})]$ then follows the $2n + 1$ rule, according to which the response to order n determines the energy to order $2n + 1$. For improved efficiency of integral fitting, the Poisson approach of Manby and Knowles may be used.²⁷

Cholesky Decomposition

The *Cholesky decomposition* (CD) method has recently been introduced as an alternative to conventional integral fitting. As pointed out in Ref 28, Cholesky decomposition of the two-electron integral supermatrix²⁹ corresponds to integral fitting in a particular auxiliary basis, the Cholesky basis. Relying on a single error-control threshold τ , the CD method may be used to set up a hierarchy of approximations connecting conventional integral treatments with integral-fitting techniques.

Applied to the two-electron integral supermatrix, the CD method is nothing but a truncated Gram-Schmidt (GS) orthonormalization procedure, controlled by τ . This is the source of the rank reduction, which is the key to the efficiency of the method. We begin by defining the two-electron supermatrix as

$$(ab|cd) = (I|J), \quad (58)$$

where the bra and ket indices ab and cd have been compounded together into the superindices I and J , respectively, representing elements of the parent product basis. The auxiliary basis generated by the decomposition are denoted a GS or CD basis, depending the details of the procedure.

In the GS procedure, the lower-triangular transformation matrix between the parent basis set and the GS auxiliary basis set is expressed for the diagonal

$$(ab|\alpha) = \left[(ab|ab) - \sum_{\beta < \alpha} (ab|\beta)^2 \right]^{1/2} \quad (59)$$

and off-diagonal elements as

$$(cd|\alpha) = \frac{(ab|cd) - \sum_{\beta < \alpha} (ab|\beta)(\beta|cd)}{(ab|\alpha)}, \quad (60)$$

respectively. If the GS procedure is applied to the full set of parent basis functions, then the GS basis spans the same space as the parent basis and no approximations are introduced. In the GS basis, any matrix in the parent basis can be expressed as

$$(ab|cd) = \sum_{\alpha} (ab|\alpha)(\alpha|cd). \quad (61)$$

In practice, however, this expression is not used directly. Instead, for optimal cost reduction, the index α is used to reorder summations of the equations for energies, Fock and Kohn–Sham matrix contributions, molecular gradients, and so on.

The CD method differs from the GS method in imposing a particular order on the processing of the parent basis, thereby generating a unique auxiliary basis (in the absence of degeneracies) that is truncated in a controlled fashion for rank reduction. The order is defined by forming an error vector that represents the difference between diagonal elements expressed exactly and approximately, in the auxiliary basis:

$$D_{ab}(\alpha) = (ab|ab) - \sum_{\alpha} (ab|\alpha)^2, \quad (62)$$

where α is the index of the currently last included parent basis function, corresponding to the pair cd . Note that, for $ab \leq cd$, $D_{ab}(\alpha) = 0$. The order is defined as the α th GS function is the one for which the element of $\mathbf{D}(\alpha - 1)$ has the largest value. This ordered set of GS basis functions defines the Cholesky auxiliary basis set. For the parent basis functions included so far in the GS procedure, this error is zero and the representation is exact; for the remaining parent functions, there is a residual error which is an upper bound by $\max(\mathbf{D}(\alpha)) = \tau(\alpha)$. Considering the Cauchy–Schwarz inequality, it is found that $\tau(\alpha)$ also is the upper bound of error of any integral approximated with the CD auxiliary basis set. This provides for a single-parameter control of when to terminate the generation of the CD auxiliary basis, given a desired accuracy of the integrals in the parent basis sets which the auxiliary basis set is to

reproduce. Typically, the size of a CD auxiliary basis, given a standard error of 10^{-4} , is $3n - 5n$, whereas the size of the parent basis set is n^2 , where n is the size of the original orbital basis set. To conclude, note that, in the complete GS/CD procedure, the whole super matrix in the parent basis would be needed, whereas a much smaller subset is needed in the truncated CD approach. In this respect, the truncated CD procedure is the optimal integral prescreening based on the integral values only.

EXPLICITLY CORRELATED METHODS

Many-electron wave functions expanded in Slater determinants exhibit a slow convergence of the energy with respect to the number of orbitals in the basis set. In explicitly correlated methods, this slow basis-set convergence is overcome by introducing an explicit dependence on the interelectronic distances r_{ij} into the wave function. These methods have a long history, beginning already with the work of Hylleraas in the 1920s, whose method was not immediately successful for general many-electron systems because of the presence of many-electron integrals. In the transcurred method of Boys³⁰ and the weak orthogonality functional of Szalewicz et al.,^{31–33} the need to compute integrals involving more than three electrons is avoided.

The development of explicitly correlated methods into general many-electron methods applicable to large molecules goes back to the work of Kutzelnigg in 1985,³⁴ who proposed to modify orbital pair correlation functions by including also functions of the form (properly symmetrized) $\hat{Q}_{12} r_{12} \phi_i(\mathbf{r}_1) \phi_j(\mathbf{r}_2)$ where $\phi_i(\mathbf{r}_1)$ and $\phi_j(\mathbf{r}_2)$ are occupied spin orbitals and the projector \hat{Q}_{12} ensures orthogonality to the traditional spin-orbital products. Importantly, all integrals involving more than two electrons (generated by the projection operator) are avoided by the RI techniques, thereby making the R12 method practical for many-electron systems.³⁵ The R12 ansatz has been extensively used for small molecules but exhibits the wrong long-range behavior. Recently, the more general F12 ansatz $\hat{Q}_{12} f_{12} \phi_i(\mathbf{r}_1) \phi_j(\mathbf{r}_2)$ has become popular. In this ansatz, the pair function depends in a more general manner on the interelectronic distance as in the damped forms $f_{12} = r_{12} e^{-\gamma r_{12}}$ and $f_{12} = r_{12} \operatorname{erfc}(\gamma r_{12})$ and in the Slater-type geminals $f_{12} = e^{-\gamma r_{12}}$ introduced into F12 theory by Ten-no,³⁶ sometimes expanded in (typically, five or six) Gaussian geminals $e^{-\omega r_{12}^2}$. For recent reviews of explicitly correlated methods, see Refs 37 and 38.

TABLE 1 | One-Electron n th-Order Auxiliary Integrals Appearing in R12 Theory when Using Gaussian-Type Geminals $g_{12} = \exp(-\omega r_{12}^2)$ and $g'_{12} = \exp(-\omega' r_{12}^2)$

Operator	One-Electron auxiliary integral
r_{12}^{-1}	$F_n(\alpha R_{PQ}^2)$
g_{12}	$\frac{\alpha}{2\pi} \left(\frac{\pi}{\alpha+\omega}\right)^{3/2} \exp\left(-\frac{\alpha\omega}{\alpha+\omega} R_{PQ}^2\right)$
$g_{12} r_{12}^{-1}$	$\frac{\alpha}{\alpha+\omega} \exp\left(-\frac{\alpha\omega}{\alpha+\omega} R_{PQ}^2\right) \sum_m \binom{n}{m} \left(\frac{\omega}{\alpha+\omega}\right)^{n-m} \left(\frac{\alpha}{\alpha+\omega}\right)^m F_n\left(\frac{\alpha}{\alpha+\omega} \alpha R_{PQ}^2\right)$
$[[\hat{T}_{12}, g_{12}], g'_{12}]$	$-\frac{\sqrt{\pi\omega\omega'}}{(\alpha+\omega\omega')^{5/2}} \left(\frac{3\omega\omega'}{\alpha+\omega\omega'} + \frac{\alpha\omega\omega'}{(\alpha+\omega\omega')^2} - n \frac{\omega\omega'}{\alpha+\omega\omega'}\right) \exp\left(-\frac{\alpha\omega\omega'}{\alpha+\omega\omega'} R_{PQ}^2\right)$

A thorough discussion of integration techniques in F12 theory is beyond the scope of this review. Instead, we restrict our discussion to integrals involving Gaussian geminals and where the RI approximation have been taken. To give an example of the RI approximation, let us consider how this approximation is taken for one of the three-electron integrals appearing in F12 theory:

$$\langle ikm | r_{13}^{-1} f_{23} | jlm \rangle = \iiint \chi_i(\mathbf{r}_1) \chi_j(\mathbf{r}_1) r_{13}^{-1} \chi_m(\mathbf{r}_3)^2 \times f_{23} \chi_k(\mathbf{r}_2) \chi_l(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3. \quad (63)$$

By introducing the RI-like expansion $P' = \sum |p'\rangle \langle p'|$ for the third electron, we arrive at

$$\langle ikm | r_{13}^{-1} f_{23} | jlm \rangle \approx \langle ikm | r_{13}^{-1} P' f_{23} | jlm \rangle = \sum_{p'} \langle ij | p'm \rangle \langle p'm | f_{12} | kl \rangle, \quad (64)$$

involving only the regular two-electron ERIs $\langle ij | p'm \rangle$ and the Gaussian-geminals overlap integrals $\langle p'm | f_{12} | kl \rangle$. The Gaussian-geminal overlap integrals can be evaluated straightforwardly using the standard integral evaluation schemes, by a simple replacement of the n th-order Boys function $F_n(x)$. Such replacements are possible for the other two-electron operators³⁹ (see Table 1), except for integrals over the commutator $[\hat{T}_{12}, f_{12}]$, which is more involved and can be written in terms of expressions involving derivatives with respect to the nuclear coordinate. Simplification using the RI approximation is also possible for this term.⁴⁰

PROPERTY INTEGRALS

To determine various chemical properties, we need to calculate property integrals and, in particular, differentiated integrals. We here restrict ourselves to differentiation with respect to nuclear coordinates and external magnetic fields.

Geometrical Derivatives

For chemistry, the most important molecular properties are those involving geometrical derivatives. Geometrical derivatives are needed for the determination of equilibrium structures and transition states, for trajectories in molecular dynamics studies, for the determination of harmonic and anharmonic vibrational frequencies, for relativistic calculations, and so on. The calculation of geometrical derivatives of molecular integrals is therefore an important task.

By expanding the real solid-harmonic Gaussians in Hermite rather than Cartesian Gaussians according to Eq. (17), the calculation of differentiated integrals becomes equivalent to the calculation of scaled undifferentiated integrals with incremented quantum numbers.⁴ In particular, from the relation $\partial_A^\lambda H_i = 2a H_{i+\lambda}$ in Eq. (20), we obtain for the two-electron integrals:

$$\frac{\partial^{JKL} [ij|kl]}{\partial_A^I \partial_B^J \partial_C^K \partial_D^L} = (2a)^{|I|} (2b)^{|J|} (2c)^{|K|} (2c)^{|L|} \times [i + I, j + J | k + K, l + L]. \quad (65)$$

Similar relations hold for the one-electron Hamiltonian and overlap integrals.

Magnetic Derivatives

When studying molecules in the presence of a magnetic field, we typically Taylor expand the energy in terms of the energy derivatives with respect to the magnetic field. The magnetic properties (for finite field strengths) can in this way be expressed in terms of the energy derivatives of different orders (at zero field strength).

One well-known problem affecting the convergence of finite-basis *ab initio* calculations of magnetic properties is the gauge-origin dependence of the results and the associated slow basis-set convergence of the calculated properties. The most efficient

technique for solving this problem is to use London orbitals.^{41–43}

The external magnetic field is represented by a vector potential

$$\pi = -i\hbar\nabla + e\mathbf{A}(\mathbf{r}), \quad \mathbf{A}(\mathbf{r}) = \frac{1}{2}\mathbf{B} \times (\mathbf{r} - \mathbf{O}),$$

$$\mathbf{B}(\mathbf{r}) = \nabla \times \mathbf{A}(\mathbf{r}),$$

and because the position of the gauge origin \mathbf{O} is not unique, approximate calculations may suffer from spurious gauge-origin dependence. Gauge-origin invariance may be enforced by using London atomic orbitals:

$$\omega_{lm} = \exp[i\mathbf{A}_{\mathbf{K}}(\mathbf{O}) \cdot \mathbf{r}] \chi_{lm}(\mathbf{r}_{\mathbf{K}}).$$

Standard atomic orbitals equipped with a complex phase factor, so-called London orbitals, exhibit the correct behavior to first order with respect to changes in the external magnetic field.

CONCLUDING REMARKS

We have in this brief review described the status of contemporary methods in evaluating integrals over GTOs used in nonrelativistic molecular *ab initio* theory. Since their introduction by Boys in the 1950s, the GTOs have proved to be highly flexible basis functions, easily adapted to new computational situations and requirements, being used in highly accurate explicitly correlated calculations on small molecules and in Kohn–Sham calculations on very large molecules using FMM and density-fitting techniques, for the calculation of molecular properties as well as energies. Over the last 60 years, GTO integration techniques have been continuously refined and improved. It is a safe prediction that this development will continue in the future, further refining the integration techniques described in the present review.

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