Generalized Gaunt coefficients

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Solid-harmonic derivatives of solid-harmonic-Gaussian integrals are evaluated. Cross differentiation and the *n-j* generalized Gaunt coefficients are defined. The generalized Gaunt coefficients ensure that cross differentiation in uncoupled, *n*-center, solid-harmonic derivatives of rotationally invariant Gaussian matrix elements subtracts zero total angular momentum. This preserves the spherical-tensor properties of quantum-chemical matrix elements. The generalized Gaunt coefficients are $(n-1)$-dimensional objects because the sum of the azimuthal quantum numbers is zero, which facilitates their use in computer programs. The 4-*j* and higher number of centers generalized Gaunt coefficients are characterized by quantum numbers k_{ij}, the angular momentum lost directly by cross differentiation from solid harmonics of differential operators about centers *i* and *j*. The generalized Gaunt coefficients vanish if the absolute value of the sum of the *i* and *j* azimuthal quantum numbers is greater than the sum of the two total angular momenta minus twice k_{ij}. This constraint further limits the number of coefficients that must be processed at one time. All coefficients for any given number of centers satisfy the same recurrence relations but differ, because different terms in any given recurrence relation vanish according to the various azimuthal-quantum-number bounds. Direct and recursive FORTRAN-90 code has been written for the 3-*j* to 6-*j* generalized Gaunt coefficients.

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I. INTRODUCTION

Analytic Gaussian integral evaluation is the foundation of the quantum-chemical software industry. Currently that industry is based on global recursive Gaussian integral evaluation using the Cartesian Gaussian basis [1–3]. Gaussian integrals may be thought of as large matrices having many indices, where each index can represent an azimuthal quantum number, primitive exponent, contraction number, Cartesian derivative, etc. If, for example, three-index integrals are computed using global recursion, then three-index quantities are combined to generate higher three-indexed quantities that yield the required three-index integrals. Other codes using the solid-harmonic Gaussian basis are being developed [4–6]. Two of those codes use global recursion [5,6]. Ultimately such codes can at best be marginally more efficient because a simple basis set transformation connects the solid harmonic basis and a subset of the Cartesian basis. Nevertheless, a solid-harmonic Gaussian code that had earlier incorporated efficient use of symmetry-adapted solid-harmonic atomic orbitals [7] enabled the largest-basis-set *ab initio* calculation of that time [8]. That same technology, now parallelized, is apparently still setting records [9], 14,000 contracted orbital basis functions, which is three times the size of the basis in Ref. [8]. The state of the art using solid-harmonic Gaussians is not completely satisfactory, however. Analytic normal-mode analysis, which requires second derivatives of the energy with respect to nuclear motion, is standard in commercial Cartesian Gaussian codes [10]. There is obvious need for efficiently computed first and second derivatives of solid-harmonic Gaussian integrals. This problem is challenging because the solid-harmonic basis (and all of its derivatives) is the Cartesian basis in momentum space. On the other hand, once one has written a general Cartesian Gaussian integral code it can be directly used to get derivatives of those integrals. The solid-harmonic basis, however, is the unique basis that diagonalizes angular momentum about its center. It facilitates analysis of chemical bonding because the Gaussian basis sets of quantum chemistry [11] are eigenfunctions of angular momentum. Furthermore, a very large number of different and exclusive recurrence relations for Cartesian Gaussian integral evaluation have been published and are used in very complex sorting algorithms. Currently speed is gained by increasing the number of different ways any given integral can be computed [1,2]. On the other hand, recurrence on the solid harmonics either alters the angular momentum or else is unlikely to be useful. In this work only solid harmonics are used; these methods are not directly appropriate for bases larger than the solid harmonics [12].

The first solid-harmonic Gaussian derivative codes have begun to appear [13–17]. Our original code [14–16] for computing first derivatives in the solid-harmonic Gaussian basis set is based on reusing the list of cross derivatives over and over again for each *n*-tuple of Gaussian exponents that result if up to four solid harmonics of differential operators act on a Gaussian. Unfortunately, that method of derivative integral evaluation when coded in FORTRAN-90 is remarkably slow, and puts significant calculations out of reach. Another approach to solid-harmonic derivative integral evaluation is to compute the first and second derivatives of all factors that go into the computation of the derivatives of solid-harmonic integrals. That method is practical [18]; however, the code requires that an array, of length 28 for second derivatives of three-center integrals, be associated with every quantity. The approach of Saunders to multicenter solid-harmonic integrals is to expand each product of solid-harmonic Gaussians in terms of Hermite Gaussians about its center [4]. Computer algebra is probably essential for optimizing that approach [19]. Such an approach, however, is unlikely to be significantly faster than the equivalent Cartesian Gaussian based approach. Rösch and co-workers use spherical-tensor meth-

ods to compute first derivatives of two-center solid-harmonic Gaussian integrals [20], i.e., first derivatives were evaluated using spherical-harmonic technology relevant to *p*-type orbital basis functions [5]. Toward generalizing that approach to more centers and higher derivatives, code for generating the generalized Gaunt coefficients is developed in this work. Closed-form expressions for solid harmonics of differential operators acting on three- to five-center Gaussians of scalar arguments have appeared [5,18,21]. For three centers the angular factor that arises is proportional to the Gaunt coefficient. The corresponding angular factors for four and five centers have been shown to be invariants [21]. It might be possible to use these factors effectively to compute two-center (second) derivatives of solid-harmonic Gaussian integrals. As a first step toward that goal FORTRAN-90 code has been written to recursively generate these 3-*j* to 6-*j* generalized Gaunt coefficients, which are necessary for closed-form evaluation of, e.g., two-center solid-harmonic derivatives of two- to four-center Coulomb integrals.

II. THE *n-j* GENERALIZED GAUNT COEFFICIENTS

The solid-harmonics Gaussians may be written $[\mathbf{r}]_M^L \exp(-\alpha r^2)$, where square brackets have been used to avoid the $\mathcal{Y}$ of conventional notation for the solid harmonics [22]. The unnormalized solid harmonic

$$[\mathbf{r}]_M^L = (-1)^m r^L Y_{LM}(\theta,\phi)\sqrt{4\pi/(2L+1)(L+M)!(L-M)!}$$
$$= \sum_k \frac{(-1)^k (x+iy)^{M+k}(x-iy)^k z^{L-M-2k}}{2^{2k+M}(M+k)!k!(L-M-2k)!}, \quad (1)$$

contains the spherical harmonic $Y_{LM}(\theta,\phi)$, of Edmonds [23], and the second equality is Eq. (3.153) of Ref. [24]. In practice these solid harmonics are generated recursively,

$$(L-M)[\mathbf{r}]_M^L = z[\mathbf{r}]_M^{L-1} + 2[\mathbf{r}]_{-1}^1[\mathbf{r}]_{M+1}^{L-1}, \quad (2)$$

from $[\mathbf{r}]_{-1}^1 = (x+iy)/2$ and the corresponding equation generated by taking the complex conjugate of this equation and then using the spherical-tensor identity $[\mathbf{r}]_M^{L*} = (-1)^M [\mathbf{r}]_{-M}^L$. Using these unnormalized solid harmonics avoids all square-root factors and streamlines the working equations. The factors that normalize these solid harmonics vary by as much as $\sqrt{(2L)!/L!}$ but are not large enough to be problematical through $L=6$ in double-precision arithmetic.

The simplest two-center Gaussian function may be written,

$$G = \exp[-\alpha(\mathbf{a}-\mathbf{b})^2]. \quad (3)$$

This Gaussian matrix element has Gaussian exponent α and centers **a** and **b**. Such a Gaussian is called an *s*-type matrix element because it is invariant under rotation of the entire coordinate system. The product or overlap of any number of Gaussians is such a Gaussian function. The argument is a function of centers, which will be labeled by lower case letters **a**, **b**, **c**,... . The derivatives of the argument of the Gaussian with respect to each of these centers must be a vector. Each such vector divided by the original Gaussian will be indicated by upper-case letters **A**, **B**, **C**,... . Thus the gradient with respect to the sixth center defines the sixth vector, $\boldsymbol{\nabla}_\mathbf{f} G = \mathbf{F}G$.

Eigenfunctions of definite angular momentum are generated by a solid harmonic of the gradient with respect to a center operating on an *s*-type Gaussian matrix element. For our simple two-center matrix element a solid-harmonic Gaussian is generated through differentiation:

$$[\boldsymbol{\nabla}_\mathbf{a}]_{M_1}^{L_1} G = [2\alpha(\mathbf{b}-\mathbf{a})]_{M_1}^{L_1} G \equiv [\mathbf{A}]_{M_1}^{L_1} G. \quad (4)$$

Angular momentum can also be generated from the second center using the product rule of differentiation via the solid-harmonic addition theorem

$$([\boldsymbol{\nabla}_\mathbf{b}]_{M_2}^{L_2})^* [\boldsymbol{\nabla}_\mathbf{a}]_{M_1}^{L_1} G$$
$$= \sum_{jm} ([\mathbf{B}]_{M_2-m}^{L_2-j})^* G([\boldsymbol{\nabla}_\mathbf{b}]_m^j)^* [\mathbf{A}]_{M_1}^{L_1}$$
$$= \sum_{jm} (2j-1)!!([\mathbf{B}]_{M_2-m}^{L_2-j})^* [\mathbf{A}]_{M_1-m}^{L_1-j} \alpha_{12}^j G /$$
$$(j+m)!(j-m)! \quad (5)$$

where $\alpha_{12} = \boldsymbol{\nabla}_\mathbf{a} \cdot \mathbf{B}/3 = 2\alpha$, the expression for the solid-harmonic gradient of a solid harmonic [25] has been used, and the sum is over all values of j and m for which the angular momenta of the two solid harmonics are physical. One can say that the first term in the summation after the second equality is simplest because if $j=m=0$ then both solid harmonics act only on the Gaussian. That first term involves no cross differentiation. Each other term involves cross differentiation. The same amount of angular momentum is lost from each solid harmonic of the two vectors because part of the solid harmonic of one gradient acted on the other solid harmonic, not on the Gaussian. The terms involving cross differentiation are simpler, however, in the sense that each solid-harmonic differentiation of a solid harmonic reduces the total angular momentum by two units. In fact, if and only if the two initial solid harmonics are the same, $M_1 = M_2$ and $L_1 = L_2 = L$, then the final term on the right-hand side of Eq. (4) is $(2L-1)!!\alpha_{12}^L G/(L+M_1)!(L-M_1!$, and there is no angular momentum left. If both initial angular momenta are *p* type then the right-hand side has one or two terms depending on whether the two azimuthal quantum numbers match.

The derivatives of the *n*-center Gaussian matrix element can be expressed in uncoupled form [21],

$$[\boldsymbol{\nabla}_\mathbf{a}]_{M_1}^{L_1} [\boldsymbol{\nabla}_\mathbf{b}]_{M_2}^{L_2} \cdots [\boldsymbol{\nabla}_\mathbf{n}]_{M_n}^{L_n} G$$
$$= \sum_{\mathbf{k},\mathbf{m}} [\mathbf{A}]_{M_1-m_1}^{L_1-j_1} [\mathbf{B}]_{M_2-m_2}^{L_2-j_2} \cdots [\mathbf{N}]_{M_n-m_n}^{L_n-j_n} G_\mathbf{m}^\mathbf{k}, \quad (6)$$

where $j_i = \sum_{j\neq i, j=1}^n k_{ij}$, $\mathbf{k}$ is symmetric (the diagonal elements can be considered zero), and the sum over a boldface quantity means a sum over all unique, allowed *n*-tuples for that set of integers. The *n* equations defining $\mathbf{j}$ can be used to

eliminate the variables k_{in} and k_{n-1n-2} [18,21]. Note that the as yet undefined coefficient $G^{\mathbf{k}}_{\mathbf{m}}$ is independent of all initial quantum numbers **L**. The initial quantum numbers occur only in the quantum numbers of the solid harmonics on the right-hand side of Eq. (6). The sums over **k** and **m** stand for the sum over each of their components and are limited to those values for which all resultant quantum numbers are physical and every component of **k** is nonnegative.

The Gaussian transform of the Coulomb operator is the integral of a Gaussian, $1/r=2\int_0^\infty \exp(-u^2r^2)du/\sqrt{\pi}$. Therefore, for *n*-center Coulomb integrals these exponents will contain the final integration variable, and the relevant spherical tensors should be expanded into a higher-dimensional object [18] $[\mathbf{C}_1+u^2\mathbf{C}_2]^L_M=\Sigma_{jm}u^{2j}[\mathbf{C}_1]^{L-j}_{M-m}[\mathbf{C}_2]^j_m$ via the solid-harmonic addition theorem. The extra dimension is indicated by j and has length $L+1$. The molecular-orientation-independent factors may be expressed as

$$G^{\mathbf{k}}_{\mathbf{m}}/G=\delta(m_1+m_2+\cdots+m_n)V^{\mathbf{jk}}_{m_1m_2\cdots m_{n-1}}\prod_{i<j=2}^{n}\alpha_{ij}^{k_{ij}}. \tag{7}$$

As the argument of a Gaussian is quadratic in distances, the gradients of the vectors that result from operating on a Gaussian with a gradient are combinations of Gaussian exponents, which are represented as an α that has two subscripts corresponding to the two centers in Eq. (7), $\boldsymbol{\nabla}_{\mathbf{a}}\cdot\mathbf{F}=\boldsymbol{\nabla}_{\mathbf{f}}\cdot\mathbf{A}=3\alpha_{16}$. Explicit evaluation of the remaining numerical factors, which are called generalized Gaunt coefficients, involves an antisymmetric matrix **n**, which gives the azimuthal quantum numbers $m_i=\Sigma_{j=1}^{n}n_{ij}$. This set of $n-1$ independent equations can be used to substitute for the highest row of **n**. Thus in the following **n** represents an antisymmetric matrix of rank $n-1$. The weights associated with the elements of **n** are easily obtained using the product rule for differentiation via the solid-harmonic addition theorem and then using the known expression [25] for the solid-harmonic derivative of a solid harmonic [5,18,21]. The relative weights are expressed as

$$p_{ij}(n_{ij})=\frac{(-1)^{n_{ij}}(2k_{ij}-1)!!}{(k_{ij}+n_{ij})!(k_{ij}-n_{ji})!}=\frac{(-1)^{n_{ij}}(2k_{ij}-1)!!}{(k_{ij}+n_{ij})!(k_{ij}-n_{ij})!}. \tag{8}$$

The allowed values for the elements of **n** are those for which the factorials have nonnegative arguments. It is convenient to shift the allowed values of **n** to be nonnegative,

$$f_{ij}=\frac{(2k_{ij}-1)!!}{(2k_{ij}-n_{ij})!n_{ij}!}. \tag{9}$$

Note the phase change between this and the previous equation, which is accumulated in an overall phase later. A weight of the same form holds for the last row of **n**, which can be transformed to introduce the important quantum numbers

$$f_{in}=\frac{\left(2j_i-2\sum_{j\neq i}^{n-1}k_{ij}-1\right)!!}{\left(j_i+m_i-2\sum_{j<i}k_{ij}-\sum_{j\neq i}^{n-1}n_{ij}\right)!\left(j_i-m_i-2\sum_{j>i}^{n-1}k_{ij}+\sum_{j\neq i}^{n-1}n_{ij}\right)!}. \tag{10}$$

These definitions simplify the general expression for the *n-j* generalized Gaunt coefficient,

$$V^{\mathbf{jk}}_{m_1m_2\cdots m_{n-1}}=(-1)^{\Lambda+j_n+m_n}\sum_{\mathbf{n}}\prod_{i<j=2}^{n}f_{ij}, \tag{11}$$

where $\Lambda=(j_1+j_2+\cdots+j_n)/2$ is integral and the summation over **n** indicates a summation over the independent elements of the $(n-1)$-dimensional antisymmetric matrix. Thus the generalized Gaunt coefficient in three, four, five, and six centers involves, respectively, one-, three-, six-, and tenfold summations; specifically for six centers,

$$\begin{aligned}V^{j_1j_2j_3j_4j_5j_6k_{12}k_{13}k_{23}k_{14}k_{24}k_{34}k_{15}k_{25}k_{35}}_{m_1m_2m_3m_4m_5}=&\frac{(-1)^{j_n+m_n}}{(-2)^{\Lambda}\mathbf{k}!}\sum_{\mathbf{n}}\left[\prod_{i<j=2}^{5}\binom{2k_{ij}}{n_{ij}}\right]\times\binom{2j_1-2k_{12}-2k_{13}-2k_{14}-2k_{15}}{j_1+m_1-n_{12}-n_{13}-n_{14}-n_{15}}\\&\times\binom{2j_2-2k_{12}-2k_{23}-2k_{24}-2k_{25}}{j_2+m_2+n_{12}-n_{23}-n_{24}-n_{25}}\times\binom{2j_3-2k_{13}-2k_{23}-2k_{34}-2k_{35}}{j_3+m_3+n_{13}+n_{23}-n_{34}-n_{35}}\\&\times\binom{2j_4-2k_{14}-2k_{24}-2k_{34}-2k_{45}}{j_4+m_4+n_{14}+n_{24}+n_{34}-n_{45}}\times\binom{2j_5-2k_{15}-2k_{25}-2k_{35}-2k_{45}}{j_5+m_5+n_{15}+n_{25}+n_{35}+n_{45}},\end{aligned} \tag{12}$$

where $k_{45}=\Lambda-j_6-k_{12}-k_{13}-k_{23}-k_{14}-k_{24}-k_{34}-k_{15}-k_{25}-k_{35}$ and $\mathbf{k}!\equiv\Pi_{i<j=2}^{6}k_{ij}!$. The summations are over the standard range for binomial coefficients $0\leqslant n_{ij}\leqslant 2k_{ij}$.

For more than three centers, the generalized Gaunt coefficients can be expanded in more than one way as a product of 3-*j* symbols to explicitly demonstrate that Eq. (11) couples all the angular momenta to zero. The expansion coefficients in any such expression can be obtained by projecting out each of the 3-*j* symbols using a free azimuthal quantum number. Then the methods of Racah can be used to simplify the resulting expressions [21]. That affords one route to nonrecursive solid-harmonic Gaussian integral evaluation, but the reduced matrix elements remain rather complicated—a fivefold summation for 5-*j* generalized Gaunt coefficients in contrast to the in general sixfold summation involved in a direct evaluation of Eq. (11).

The generalized Gaunt coefficients are independent of all original angular momenta. Thus they can be reused for all basis sets about each center. The following examines using azimuthal recursion to evaluate, at least partially, the generalized Gaunt coefficients for four to six coupled angular momenta.

III. RECURSION

FORTRAN-90 code exists to evaluate Eq. (11) directly for up to six centers. The generalized Gaunt coefficients can also be evaluated semirecursively. The three-center recurrence relations are given in Ref. [21]. In Ref. [18] that code was used repeatedly in the innermost loop, where the entire set of nonzero Gaunt coefficients were recomputed again and again rather than stored, with insignificant computational cost. A way to develop recurrence relations for higher dimension in number of angular-momentum quantum numbers is to consider special cases of Eq. (11). If $m_1=-j_1$ then $n_{1i}=0$ for $i=2$ to $n-1$. If in addition $m_{n-1}=j_{n-1}$ then $n_{in-1}=0$ for $i=1$ to $n-2$. Then standard methods raise an azimuthal quantum number if all the generalized Gaunt coefficients are known that result from raising every other azimuthal quantum number,

$$\begin{aligned}0=&(j_1+m_1+1)V^{\mathbf{jk}}_{m_1+1m_2\cdots m_{n-1}}\\&+(j_2+m_2+1)V^{\mathbf{jk}}_{m_1m_2+1\cdots m_{n-1}}+\cdots\\&+(j_n-m_1-m_2-\cdots-m_{n-1})V^{\mathbf{jk}}_{m_1m_2\cdots m_{n-1}},\end{aligned}\quad(13)$$

or lower an azimuthal quantum number if the others are known,

$$\begin{aligned}0=&(j_1-m_1+1)V^{\mathbf{jk}}_{m_1-1m_2\cdots m_{n-1}}\\&+(j_2-m_2+1)V^{\mathbf{jk}}_{m_1m_2-1\cdots m_{n-1}}+\cdots\\&+(j_n+m_1+m_2+\cdots+m_{n-1})V^{\mathbf{jk}}_{m_1m_2\cdots m_{n-1}}\end{aligned}\quad(14)$$

In these equations the **jk** superscripts can be taken to represent the entire matrix **k** or all the angular momenta and the remaining linearly independent part of **k**. Care must be taken in these equations either to zero each coefficient with out-of-range azimuthal quantum numbers or else not to use those coefficients.

IV. 4-*j* GENERALIZED GAUNT COEFFICIENTS

The 4-*j* generalized Gaunt coefficients have three azimuthal quantum numbers that are treated explicitly (because all four sum to zero). The unfamiliar bounds are $|m_i+m_j|\leqslant j_i+j_j-2k_{ij}$. For three centers $2k_{ij}=j_i+j_j-j_k$ and this bound reduces to $|m_k|\leqslant j_k$. No bounds involving the fourth angular momentum are used because, e.g., the bounds $|m_2+m_3|\leqslant j_2+j_3-2k_{23}$ and $|m_1+m_4|=|m_2+m_3|\leqslant j_1+j_4-2k_{14}$ are identical given $k_{23}=\Lambda-j_4-k_{12}-k_{13}$ and $k_{14}=j_1-k_{12}-k_{13}$ [18]. Table I is a measure of the tightness of these unusual bounds. It gives the ratio of the number of potentially nonzero 4-*j* generalized Gaunt coefficients, because they satisfy all bounds, to the number of coefficients that satisfy only $|m_i|\leqslant j_i$ and $m_4=-m_1-m_2-m_3$. All coefficients are examined in the range $j_{\max}\geqslant j_4\geqslant j_3\geqslant j_2\geqslant j_1\geqslant 1$. Roughly a quarter of all 4-*j* generalized Gaunt coefficients are affected by these unusual bounds.

Direct examination of Eq. (11) shows that for $m_1=j_1$ and $m_3=-j_3$ nonzero 4-*j* generalized Gaunt coefficients are proportional to a binomial coefficient,

$$V^{j_1j_2j_3j_4k_{12}k_{23}}_{j_1m_2-j_3}=(-1)^{j_2+m_2}\binom{2k_{24}}{j_2+m_2-2k_{23}}\Big/(-2)^{\Lambda}\mathbf{k}!,\quad(15)$$

and thus have m_2 values bounded between $m_2^-=-j_2+2k_{23}$ and j_2-2k_{12}. These Gaunt coefficients are generated recursively from the lower bound on the second azimuthal quantum number, $V^{j_1j_2j_3j_4k_{12}k_{23}}_{j_1m_2^--j_3}=1/(-2)^{\Lambda}\mathbf{k}!$, by including an additional phase in the standard recursion for binomial coefficients,

$$\begin{aligned}V^{j_1j_2j_3j_4k_{12}k_{23}}_{j_1m_2-j_3}=&(2k_{24}+m_2^--m_2+1)\\&\times V^{j_1j_2j_3j_4k_{12}k_{23}}_{j_1m_2-1-j_3}/(m_2^--m_2).\end{aligned}\quad(16)$$

Next Eq. (14) is used to lower m_1, and finally Eq. (13) is used to raise m_3.

TABLE I. The fraction of *n*-*j* generalized Gaunt coefficients that satisfy the bounds on sums of azimuthal quantum numbers $|m_i+m_j|\leqslant j_i+j_j-k_{ij}$, etc., out of all the potentially nonzero coefficients satisfying $|m_i|\leqslant j_i$, as a function of the number of angular momenta *n* and $j_{\max}\geqslant j_n\geqslant\cdots\geqslant j_1\geqslant 1$.

$j_{\max}$	4-*j*	5-*j*	6-*j*
1	0.82		0.19
2	0.80	0.47	0.34
3	0.76	0.52	0.42
4	0.75	0.56	0.47
5	0.73	0.58	0.50
6	0.73	0.60	0.53

V. 5-*j* GENERALIZED GAUNT COEFFICIENTS

The independent physical variables for five angular momenta are taken to be j_1-j_5, m_1-m_4, and k_{12}, k_{13}, k_{23}, k_{14}, and k_{24}. The 5-*j* generalized Gaunt coefficients can be nonzero only if $|m_1+m_2+m_3+m_4|\leqslant j_5$ because the sum of the azimuthal quantum numbers must be zero in order for the angular momenta to be coupled to a scalar by the 5-*j* generalized Gaunt coefficients. There are nine more, unusual constraints on the nonzero 5-*j* generalized Gaunt coefficients: $|m_1+m_2|\leqslant j_1+j_2-2k_{12}$, $|m_1+m_3|\leqslant j_1+j_3-2k_{13}$, $|m_1+m_4|\leqslant j_1+j_4-2k_{14}$, $|m_2+m_3|\leqslant j_2+j_3-2k_{23}$, $|m_2+m_4|\leqslant j_2+j_4-2k_{24}$, $|m_1+m_2+m_3|\leqslant j_4+j_5-2k_{45}$, $|m_1+m_2+m_4|\leqslant j_3+j_5-2k_{35}$, $|m_1+m_3+m_4|\leqslant j_2+j_5-2k_{25}$, and $|m_2+m_3+m_4|\leqslant j_1+j_5-2k_{25}$. None of these constraints are redundant. Table I measures the tightness of these unusual bounds. It gives the ratio of the number of potentially nonzero 5-*j* generalized Gaunt coefficients to the number of coefficients that satisfy only $|m_i|\leqslant j_i$ and $m_5=-m_1-m_2-m_3-m_4$. All coefficients are examined in the range $j_{\max}\geqslant j_5\geqslant j_4\geqslant j_3\geqslant j_2\geqslant j_1\geqslant 1$. There is no entry for $j_{\max}=1$ because the sum of the angular momenta is even for nonzero generalized Gaunt coefficients. Roughly half of all 5-*j* generalized Gaunt coefficients are affected by these unusual bounds. A way to easily handle this sparsity is to set up a logical array that is true if all the screens are passed.

A recursive generation of all the 5-*j* generalized Gaunt coefficients can proceed via raising and lowering all azimuthal quantum numbers, respectively, through Eqs. (13) and (14) if the coefficients have all been evaluated except for two azimuthal quantum numbers,

$$V^{\mathbf{k}}_{m_1m_2-j_3j_4}=\sum_u (-1)^{\Lambda+j_3+j_4+j_5+m_1+m_2+u}\binom{2k_{12}}{u}\binom{2k_{15}}{j_1+m_1-2k_{13}-u}\binom{2k_{25}}{j_2-m_2-2k_{24}-u}\Big/ 2^{\Lambda}\mathbf{k}!$$
$$\equiv f_{125}(j_1+m_1-2k_{13},j_2-m_2-2k_{24})/(-2)^{\Lambda}\mathbf{k}!. \tag{17}$$

These special 5-*j* generalized Gaunt coefficients have limited range due to the selection rules on $\mathbf{k}$,

$$\begin{aligned} -j_1+2k_{13}\leqslant m_1\leqslant j_1-2k_{14},\\ -j_2+2k_{23}\leqslant m_2\leqslant j_2-2k_{24}, \end{aligned} \tag{18}$$

and are invariant under the symmetry of the three binomial coefficients,

$$\begin{aligned} m_1\rightarrow 2k_{13}-2k_{14}-m_1,\\ m_2\rightarrow 2k_{23}-2k_{24}-m_2. \end{aligned} \tag{19}$$

Thus only half of the coefficients must be computed directly.

VI. 6-*j* GENERALIZED GAUNT COEFFICIENTS

For six angular momenta the independent physical variables are taken to be j_1-j_6, m_1-m_5, and k_{12}, k_{13}, k_{23}, k_{14}, k_{24}, k_{34}, k_{15}, k_{25}, and k_{35}. The 6-*j* generalized Gaunt coefficients can be nonzero only if $|m_1+m_2+m_3+m_4+m_5|\leqslant j_6$ because the sum of the azimuthal quantum numbers must be zero in order for the angular momenta to be coupled to a scalar by the 6-*j* generalized Gaunt coefficients. There are ten unusual constraints on the sum of two azimuthal quantum number for nonzero 6-*j* generalized Gaunt coefficients: $|m_i+m_j|\leqslant j_i+j_j-2k_{ij}$ for $i<j<6$, and five more involving four azimuthal quantum numbers $|m_1+m_2+m_3+m_4|\leqslant j_5+j_6-2k_{56}$, $|m_1+m_2+m_3+m_5|\leqslant j_4+j_6-2k_{46}$, $|m_1+m_2+m_4+m_5|\leqslant j_3+j_6-2k_{36}$, $|m_1+m_3+m_4+m_5|\leqslant j_2+j_6-2k_{26}$, and $|m_2+m_3+m_4+m_5|\leqslant j_1+j_6-2k_{26}$. Table I measures the sparsity of the 6-*j* generalized Gaunt coefficients. For low values of the maximum angular momentum they are rather sparse. For high angular momenta approximately one-half are nonzero.

Again, one way to start the 6-*j* generalized Gaunt coefficient recursion is to use binomial coefficients,

$$V^{\mathbf{k}}_{m_1m_2m_3-j_4j_5}=\sum_{u,v,w}(-1)^{\Lambda+j_4+j_5+j_6+m_1+m_2+m_3+u+v+w}\binom{2k_{12}}{u}\binom{2k_{13}}{v}\binom{2k_{23}}{w}\binom{2k_{16}}{j_1+m_1-2k_{14}-u-v}$$
$$\times\binom{2k_{26}}{j_2+m_2-2k_{12}-2k_{24}+u-w}\binom{2k_{36}}{j_3-m_3-2k_{35}-v-w}\Big/ 2^{\Lambda}\mathbf{k}!$$
$$=\sum_{v,w}(-1)^{\Lambda+j_3+m_3}\binom{2k_{13}}{v}\binom{2k_{23}}{w}\binom{2k_{36}}{j_3-m_3-2k_{35}-v-w}f_{126}(j_1+m_1-2k_{14}-v,j_2-m_2-2k_{23}-2k_{25}+w), \tag{20}$$

where the second equality gives a computational simplification that is repeated for the summation over v. In coding this it is convenient to evaluate the binomial coefficients by recursion while at the same time alternating the signs of each coefficient starting from either end, $\binom{2n}{0}=\binom{2n}{2n}=+1$. That accounts for all the phase in this equation except $(-1)^{\Lambda}$. Even for these special generalized Gaunt coefficients, all the other unusual **k** constraints must be tested. The most important are related to the two extreme azimuthal quantum numbers,

$$\begin{aligned} -j_1+2k_{14} &\leqslant m_1 \leqslant j_1-2k_{15}, \\ -j_2+2k_{24} &\leqslant m_2 \leqslant j_2-2k_{25}, \\ -j_3+2k_{34} &\leqslant m_3 \leqslant j_3-2k_{35}. \end{aligned} \tag{21}$$

The rest of these coefficients are generated using Eqs. (13) and (14).

VII. DISCUSSION

This work has stressed the similarity of n-center solid-harmonic derivatives of Gaussian functions. For four and more centers, however, no common matrix element appears to be completely general. The Coulomb matrix elements of quantum chemistry are often called two-electron integrals because they are the Coulomb interaction of two charge distributions. If in a four-center Coulomb integral centers 1 and 2 contribute one charge distribution, then the matrix element is independent of k_{13}. Thus in filling out the extreme 4-j generalized Gaunt coefficient matrix the unused quantum number can and therefore should be summed [18],

$$W^{j_1 j_2 j_3 j_4 k_{12}}_{m_1 - j_2 j_3} = \sum_{k_{13}} V^{j_1 j_2 j_3 j_4 k_{12} k_{13}}_{m_1 - j_2 j_3}. \tag{22}$$

Each of the V's satisfy the same recurrence relations. Therefore W satisfies the same recurrence relations (but has fewer zeros). First derivatives of three-center integrals are also simpler than the general four-center solid-harmonic Gaussian integral. If one is taking a solid-harmonic derivative of a three-center integral with respect to the first center, then there are only four Gaussian exponent combinations, α_{11}, α_{12}, α_{13}, and α_{23}. In general there are six such exponent combinations. Thus for higher numbers of centers and solid-harmonic derivatives each individual code can gain significant performance through customization.

The n-j generalized Gaunt coefficients have been defined. Two ways to compute them have been given for four through six angular momenta. They couple the n angular momenta to zero [21]. It is possible that they can be used to advantage in Gaussian integral evaluation. Their properties are unusual, however, and are explored toward writing efficient solid-harmonic Gaussian integral and gradient code. No finished integral or gradient code exists, however, but REAL*8 FORTRAN-90 code for generating these generalized Gaunt coefficient is available from the author upon request. Sometimes authors of Gaussian integral codes quote flop (floating-point operation) counts. All equations in this work involve integers, apart from arbitrary normalization. If the generalized Gaunt coefficients were redefined to include an addition factor of $2^{\Lambda}\mathbf{k!}$, then they would all be integral, specifically products of binomial coefficients as suggested by Eqs. (12), (17), and (20), and could be evaluated with no flops. The azimuthal quantum numbers of the n-j generalized Gaunt coefficient sum to zero because they couple total angular momentum to zero. Thus they are really $(n-1)$-dimensional objects. If they are used to compute n-index integrals, then only the final step need involve n-index quantities (if one is working with the complex solid harmonics).

It is possible that these or similar coefficients are useful with exponential-type orbitals. In any event, using these coefficients to evaluate an extremely large number of different solid-harmonic Gaussian integrals is straightforward. Apart from the (3-j) Gaunt coefficients, no conventional vector coupling coefficients have appeared in this work. That is because all angular-momentum coupling in the **kn** basis is maximal, and this primitive angular-momentum coupling defines the generalized Gaunt coefficients.

Preliminary work shows that these methods in one of many possible implementations are at least competitive [18]. It is likely that quantum chemistry can become significantly more powerful by abandoning global recursion for integral evaluation, particularly for calculations involving many heavy atoms. The simplest generalized Gaunt coefficient, which generates rotational invariants from four solid harmonics, is being incorporated into our analytic approach [26] to density-functional chemical dynamics [14–16]. To extend this methodology to hybrid functionals [27] requires the 5-j generalized Gaunt coefficients. Ultimately, any direct, nonrecursive approach to second derivatives within solid-harmonic Gaussian quantum chemistry would require one of the generalized Gaunt coefficients discussed above. The code that has been developed for the generalized Gaunt coefficients might best serve as a template. It will be best to sum over as many components of **k** as is possible before beginning the recursion process, which will affect the input and short sections of these subroutines, which accordingly compute the n-j coefficients for a single **k** at a time. How a customized code can accumulate as much of the calculation as possible, of course, will depend on the specific integral or solid-harmonic derivative in question.

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