Three-center Gaussian-type-orbital integral evaluation using solid spherical harmonics

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An analysis of various approaches to evaluating overlap and Coulomb matrix elements involving Gaussian-type-orbital primitive functions whose angular parts are solid spherical harmonics is given. Direct (angular momentum) coupled, direct uncoupled, and recursive evaluations are considered. The direct uncoupled evaluation involves some remarkably simple and transparent expressions. Using *n-j* symbols on a computer requires enough intermediate summations that uncoupled methods are best, particularly for higher angular momentum. Recursive methods may be competitive for low angular momenta.

I. INTRODUCTION

The Gaussian-type-orbital (GTO) approach to the calculation of the electronic structure of molecules within local-density-functional (LDF) theory is well established.[1-6] Because the one-electron potential is fitted to a single-center GTO expansion in these approaches, they require only three-center integrals, a considerable simplification over *ab initio* approaches, which require four-center integrals. (The electron-nuclear term is already three-centered and neglected in the following.) Furthermore, these methods are simpler than hybrid GTO methods in which only the LDF approximations to the exchange and correlation functionals are fit,[7] because the electron-electron Coulomb repulsion problem itself is four-centered.

Two reasons drive three-center GTO LDF methods toward routinely including higher angular-momentum basis functions than are routinely included in GTO *ab initio* methods. First, fitting the entire potential greatly reduces the number of integrals to be processed. This allows larger atomic basis sets of each angular momentum, but relatively early in the process of augmenting these basis sets for the molecular environment it becomes more efficient to add polarization functions, which typically have one unit higher angular momentum. Second, fitting the potential can involve basis functions having twice the angular momentum of orbital basis functions, unless off-center functions are used.

To see the second point, consider the linear-combination-of-atomic-orbitals (LCAO) philosophy itself. In the LCAO approach the optimal orbital angular dependences are the spherical harmonics of orbital angular momentum appropriate to each electronic subshell. Because a central potential is required for atomic orbitals to be eigenstates of angular momentum, a philosophically consistent LCAO approach to fitting the potential would yield a superposition of spherically symmetric atomic central-field potentials. As implemented in either the muffin-tin[8] or self-consistent-charge[9] approximations, such an approach yields a simple and quite reliable description of molecules. An exact solution, however, requires either more centers or nonzero-angular-momentum functions.

To get some idea of the range of nonzero-angular-momentum functions that might be necessary to fit molecular potentials accurately, consider the treatment of atoms beyond the central-field approximation. The most important and difficult term in the potential to fit is the electron-electron Coulomb potential because it is the largest and the most rapidly varying part of the electron-electron potential. The highest angular variation of the charge density is easily established. The charge density, being the sum of the magnitudes squared of the orbitals, has components having twice the angular momentum of the open-shell molecular orbital of highest angular momentum L. The angular variations of the charge density are preserved upon integration of Poisson's equation; therefore, the Coulomb potential also has components up to this same limit $2L$. Either fit must be variational in the high accuracy limit.[2] Although it is possible to variationally fit the electron-electron Coulomb potential directly,[10,11] the most efficient calculations at high accuracy fit the charge density instead, because it is easier to determine an appropriate radial GTO basis.

In other words, given this increased simplicity of three-centered GTO methods, it is natural to consider larger and higher-angular-momentum basis sets. Using these larger and more complex basis sets leads to increased accuracy in the one-electron orbitals. In order to ensure that this increased accuracy manifests itself in an equally accurate total energy (apart from questions of overcompleteness which are not addressed here) one must have the possibility of using high-angular-momentum fitting functions in the charge-density fitting basis. A reasonable upper limit on fitting-function angular momentum is twice the maximum orbital angular momentum on each center.

In considering higher angular momentum, it is beneficial to switch from Cartesian Gaussians[12,13] to solid spherical harmonic Gaussians.[14,15] The first advantage in doing so is to eliminate unwanted basis functions such as r^2 from the d shell and xr^2, yr^2, and zr^2 from the f shell. But there are additional advantages. First, the basis

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functions have the same angular dependences in both position and momentum space, in contrast to the Cartesian-Gaussian—Hermite-Gaussian[12] Fourier transformation pairs. Second, the recursion relations yielding all solid spherical harmonics are essentially as simple as those relating Hermite-Gaussian functions. Finally, vector-coupling coefficients can be used to write compact expression for matrix elements.[15]

While vector-coupling coefficients enable compact expressions for matrix elements such expressions are not necessarily optimal for machine computation. This is because in efficient quantum chemical calculations one needs to minimize the number of machine operations per usable integral. If vector-coupling coefficients are computed individually as they are needed, then their computation on average requires too many machine cycles. So they must be precomputed as a transforming array,[16,17] which rapidly becomes large. For f electrons and four centers the number of distinct matrix elements and thus the transforming array dimension, N, is $7^4=2401$. (For three centers, one of which has twice the angular momentum of the other two f centers, N is only a factor of 4 smaller.) The transformation to the coupled space costs several N^2 operations after which (for scalar matrix elements) one faces a computation that is simplified by at most the modest factor of the ratio of the number of ways four angular momenta can be coupled to zero total angular momentum to the number of all possible angular couplings.

There is another reason to consider an uncoupled approach, beyond the fact that the computational saving due to an angular momentum coupling is not overwhelming. Coupling two solid spherical harmonics to a specific final angular momentum yields a result that is proportional to the result of coupling two spherical harmonics with different angular momentum quantum numbers but the same sum of L and M quantum numbers to the same final total angular momentum. Thus the order in which the angular momenta are coupled becomes unimportant. This special feature of the spherical harmonics lies outside a direct application of angular momentum theory and affords numerous relationships between special n-j symbols.[18] Such simplifications are easier to see in an uncoupled or partially coupled approach. This work explores efficient means to evaluate the uncoupled high-angular-momentum three-center integrals that might be used in self-consistent-field (SCF) LDF molecular calculations.

II. PRELIMINARY DETAILS

A practical Gaussian basis set for three-center GTO LDF calculations is Gaussians multiplied by a solid spherical harmonic[15] to give the appropriate angular dependence. Including an extra factor of $(-1)^M$ in the definition of the solid spherical harmonics,

$$\{\mathbf{r}\}_M^L=(-1)^M\left[\frac{4\pi}{2L+1}\right]^{1/2}r^L Y_{LM}(\theta,\phi)$$

$$=(-1)^M r^L C_M^{(L)}(\theta,\phi)\ , \tag{1}$$

where $Y_{LM}(\theta,\phi)$ is the spherical harmonic of Edmonds[19] and $C_M^{(L)}(\theta,\phi)$ is the corresponding spherical tensor, yields p-like real solid harmonics having a familiar form, $+x$, $+y$, and $+z$, for $L=1$. Conventionally[14] the complex solid harmonics are denoted by an italic Y. Primarily to have more compact equations, they will be denoted by curly braces, $\{\mathbf{r}\}_M^L$, and the corresponding real solid harmonics by angular braces, $\langle\mathbf{r}\rangle_M^L$, herein. The real solid spherical harmonics corresponding to the complex harmonics of Eq. (1) are given in Table I. In the table $m=1$ corresponds to complex $M=0$ in Eq. (1); otherwise $m=2M$ and $m=2M+1$ give $\sqrt{2}$ times the real and imaginary parts, respectively, of the complex $M>0$ solid harmonics. The $\{\mathbf{r}\}_M^L$ for all M form a complete set of linearly independent homogeneous polynomials of rank L in three dimensions.

The (unnormalized) complex basis functions under consideration can be written in two ways:

$$\{\mathbf{r}-\mathbf{c}\}_M^L\exp[-\alpha(\mathbf{r}-\mathbf{c})^2]$$

$$=\{\nabla_c\}_M^L\exp[-\alpha(\mathbf{r}-\mathbf{c})^2]/(2\alpha)^L\ , \tag{2}$$

where ∇_c is the gradient with respect to the center at $\mathbf{c}$. A related equality holds for any rotationally invariant function of $\mathbf{r}-\mathbf{c}$. This equality is a consequence of the fact that $\{\mathbf{r}\}_\cdot^L$, where the dot stands for any magnetic quantum number, is proportional to $\mathbf{r}$ multiplied by itself $L-1$ times, each time coupling to highest angular momentum. If any one of the powers of ∇_c on the right-hand side (rhs) acted on other than the exponential term, then two powers of r would be lost and maximum coupling could not be achieved. Using differential operators and interchanging differentiation and integration allows all higher-angular-momentum matrix elements to be written as derivatives of s-type matrix elements. (This approach and much of the work herein can be extended to any type of basis function.[20–22]). In general, two-, three-, and four-center integrals become, respectively, products of two, three, and four solid spherical harmonics of ∇ about the various centers operating on an s-type integral.

A few simple formulas are all that are necessary in order to compute the general three-center matrix elements in the uncoupled approach. Most important is the addition theorem for solid spherical harmonics,[14]

$$\{\alpha\mathbf{A}+\beta\mathbf{B}\}_M^L=\sum_{\lambda,\mu}\left[\binom{L+M}{\lambda+\mu}\binom{L-M}{\lambda-\mu}\right]^{1/2}$$

$$\times\alpha^\lambda\beta^{L-\lambda}\{\mathbf{A}\}_\mu^\lambda\{\mathbf{B}\}_{M-\mu}^{L-\lambda}\ . \tag{3}$$

This expression, written in its simplest form, does not obviously display the fact that both sides of the equation transform like $Y_{LM}(\theta,\phi)$ under rotations of the coordinate system. The coefficient,

$$\binom{L\ \ M}{\lambda\ \ \mu}=\left[\binom{L+M}{\lambda+\mu}\binom{L-M}{\lambda-\mu}\right]^{1/2}\ , \tag{4}$$

however, contains precisely the magnetic quantum number dependence of the appropriate vector-coupling coefficient,[19]

TABLE I. The real solid harmonics $\langle \mathbf{r} \rangle_m^l$ are defined in Eq. (1).

l	m	$\langle \mathbf{r} \rangle_m^l$	l	m	$\langle \mathbf{r} \rangle_m^l$
0	1	1	4	1	$\frac{1}{8}(35z^4-30r^2z^2+3r^4)$
			4	2	$\sqrt{5/8}xz(7z^2-3r^2)$
1	1	z	4	3	$\sqrt{5/8}yz(7z^2-3r^2)$
1	2	x	4	4	$\sqrt{5/16}(x^2-y^2)(7z^2-r^2)$
1	3	y	4	5	$\sqrt{5/4}xy(7z^2-r^2)$
			4	6	$\sqrt{35/8}xz(x^2-3y^2)$
2	1	$\frac{1}{2}(3z^2-r^2)$	4	7	$\sqrt{35/8}yz(3x^2-y^2)$
2	2	$\sqrt{3}xz$	4	8	$\sqrt{35/64}(x^4-6x^2y^2+y^4)$
2	3	$\sqrt{3}yz$	4	9	$\sqrt{35/4}xy(x^2-y^2)$
2	4	$\sqrt{3/4}(x^2-y^2)$			
2	5	$\sqrt{3}xy$	5	1	$\frac{1}{8}z(63z^4-70r^2z^2+15r^4)$
			5	2	$\sqrt{15/64}x(21z^4-14z^2r^2+r^4)$
3	1	$\frac{1}{2}z(5z^2-3r^2)$	5	3	$\sqrt{15/64}y(21z^4-14z^2r^2+r^4)$
3	2	$\sqrt{3/8}x(5z^2-r^2)$	5	4	$\sqrt{105/16}z(x^2-y^2)(3z^2-r^2)$
3	3	$\sqrt{3/8}y(5z^2-r^2)$	5	5	$\sqrt{105/4}xyx(3z^2-r^2)$
3	4	$\sqrt{15/4}z(x^2-y^2)$	5	6	$\sqrt{35/128}z(x^2-3y^2)(9z^2-r^2)$
3	5	$\sqrt{15}xyz$	5	7	$\sqrt{35/128}z(3x^2-y^2)(9z^2-r^2)$
3	6	$\sqrt{5/8}x(x^2-3y^2)$	5	8	$\sqrt{315/64}z(x^4-6x^2y^2+y^4)$
3	7	$\sqrt{5/8}y(3x^2-y^2)$	5	9	$\sqrt{315/4}xyz(x^2-y^2)$
			5	10	$\sqrt{63/128}x(x^4-10x^2y^2+5y^4)$
			5	11	$\sqrt{63/128}x(5x^4-10x^2y^2+y^4)$

$$\begin{pmatrix} L & M \\ \lambda & \mu \end{pmatrix} = \begin{bmatrix} 2L \\ 2\lambda \end{bmatrix}^{1/2} (\lambda\mu \;\; (L-\lambda)(M-\mu)|\lambda(L-\lambda) \;\; LM) , \tag{5}$$

that is needed to make Eq. (3) transform properly. The symbol defined by Eq. (4) can be distinguished from the binomial coefficient by its four, not two, arguments. The special vector-coupling coefficients encountered in this work are particularly simple—a single-term expression—because they describe maximal angular momentum coupling. Proving Eq. (3) is simplified by using the fact that both sides transform as spherical tensors under rotation of the entire coordinate system. Writing the appropriate coupled equations is aided by additional notation,

$$(\{\mathbf{A}\}_{\cdot}^{L_1}\{\mathbf{B}\}_{\cdot}^{L_2})_M^J = \sum_{M_1,M_2} (L_1M_1 \;\; L_2M_2|L_1L_2 \;\; JM)\{\mathbf{A}\}_{M_1}^{L_1}\{\mathbf{B}\}_{M_2}^{L_2} , \tag{6}$$

where dots have been used to unobtrusively indicate the summation over magnetic quantum numbers of the right hand side of this equation. If its left-hand side (lhs) is desired in uncoupled form, as will generally be the case in integral evaluation, the well-known orthonormality properties of the vector-coupling coefficients can be used,[19]

$$\{\mathbf{A}\}_{M_1}^{L_1}\{\mathbf{B}\}_{M_2}^{L_2} = \sum_{J,M} (L_1M_1 \;\; L_2M_2|L_1L_2 \;\; JM)(\{\mathbf{A}\}_{\cdot}^{L_1}\{\mathbf{B}\}_{\cdot}^{L_2})_M^J . \tag{7}$$

Using these definitions Eq. (3) can be written in coupled form,

$$\{\alpha\mathbf{A}+\beta\mathbf{B}\}_M^L = \sum_{\lambda} \alpha^{\lambda}\beta^{L-\lambda} \begin{bmatrix} 2L \\ 2\lambda \end{bmatrix}^{1/2} (\{\mathbf{A}\}_{\cdot}^{\lambda}\{\mathbf{B}\}_{\cdot}^{L-\lambda})_M^J . \tag{8}$$

Equation (8) appears slightly more complicated when written in coupled form, because of the vector-coupling coefficient implicitly required here, which in general would require a summation for its evaluation. This difference indicates that it is worth investigating whether or not it is more advantageous to evaluate high-angular-momentum matrix elements without coupling their angular momenta.

One need only establish Eq. (3) or Eq. (8) for a particular value of M. For $M=L$ the solid spherical harmonics are simplest,

$$\{\mathbf{r}\}_L^L = (x+iy)^L\sqrt{(2L)!}/(2L)!! , \tag{9}$$

and for such solid harmonics the rhs of Eq. (3) only involves such solid harmonics.

As a special case, Eq. (3) gives the result of a solid harmonic of ∇ operating on a product of functions,

$$\begin{aligned} \{\nabla\}_M^L f_1(\mathbf{r})f_2(\mathbf{r}) &= \{\nabla_1+\nabla_2\}_M^L f_1(\mathbf{r})f_2(\mathbf{r}) \\ &= \sum_{\lambda,\mu} \begin{pmatrix} L & M \\ \lambda & \mu \end{pmatrix} \{\nabla_1\}_{\mu}^{\lambda}\{\nabla_2\}_{M-\mu}^{L-\lambda} f_1(\mathbf{r})f_2(\mathbf{r}) \\ &= \sum_{\lambda} \begin{bmatrix} 2L \\ 2\lambda \end{bmatrix}^{1/2} (\{\nabla_1\}_{\cdot}^{\lambda}\{\nabla_2\}_{\cdot}^{L-\lambda})_M^J f_1(\mathbf{r})f_2(\mathbf{r}) , \end{aligned} \tag{10}$$

where the subscripts 1 and 2 indicate which of the two functions is to be operated upon. The convention for the rest of this section will be to express each equation in two ways, a coupled version and an uncoupled version. The uncoupled version of each pair will appear above its coupled counterpart.

Using the uncoupled version of Eq. (10) for d, f, and g solid harmonics of ∇ is aided by Tables II and III. Operating with a single $L>0$ spherical harmonic on a product of two functions of $\mathbf{r}$ yields two trivial terms at least. The first trivial term is to operate on the first factor alone, and the second trivial term is to operate on the second factor alone. These trivial terms are omitted from the tables. For $L>1$ nontrivial, cross terms arise. An entry in Table II means that the corresponding d or f solid harmonic of ∇ from the left-hand column of the table acting on a product of functions includes a cross term in which a p function from across the top of the table acts on one of the two product functions while the entry in the table acts on the other. Unless the two spherical harmonics in the decomposition are identical, a second term must be included in which the two factors of the original spherical harmonic each act on the opposite function of the original product. For the g solid harmonics of Table III, two types of cross terms arise that are distinguished by the two separate parts of the table. The first three columns include the terms in which harmonics having three units of angular momentum act on one function while harmonics having one unit of angular momentum act on the other. The last five columns include terms in which the angular momenta are divided equally. A use of these tables is to evaluate the action of $\langle\nabla\rangle_8^4$ on the product $f_1(\mathbf{r})f_2(\mathbf{r})$,

$$\begin{aligned}\langle\nabla\rangle_8^4 f_1(\mathbf{r})f_2(\mathbf{r})=&\langle\nabla_1\rangle_8^4 f_1(\mathbf{r})\langle\nabla_2\rangle_0^0 f_2(\mathbf{r})+\langle\nabla_1\rangle_0^0 f_1(\mathbf{r})\langle\nabla_2\rangle_8^4 f_2(\mathbf{r})\\&+\sqrt{14}[\langle\nabla_1\rangle_6^3 f_1(\mathbf{r})\langle\nabla_2\rangle_2^1 f_2(\mathbf{r})+\langle\nabla_1\rangle_2^1 f_1(\mathbf{r})\langle\nabla_2\rangle_6^3 f_2(\mathbf{r})]\\&-\sqrt{14}[\langle\nabla_1\rangle_7^3 f_1(\mathbf{r})\langle\nabla_2\rangle_3^1 f_2(\mathbf{r})+\langle\nabla_1\rangle_3^1 f_1(\mathbf{r})\langle\nabla_2\rangle_7^3 f_2(\mathbf{r})]\\&+\sqrt{35}[\langle\nabla_1\rangle_4^2 f_1(\mathbf{r})\langle\nabla_2\rangle_4^2 f_2(\mathbf{r})+\langle\nabla_1\rangle_5^2 f_1(\mathbf{r})\langle\nabla_2\rangle_5^2 f_2(\mathbf{r})]\ .\end{aligned}\tag{11}$$

The two complex solid spherical harmonics corresponding to the real $\langle\nabla\rangle_8^4$ and $\langle\nabla\rangle_9^4$ are $\langle\nabla\rangle_{\pm4}^4$. For both of these Eq. (10) gives five terms rather than the eight terms of Eq. (11).

The final two basic relationships used in this work involve differentiation of the solid harmonics. The first is the solid harmonics of ∇ operating on the solid harmonics of $\mathbf{r}$,

$$\begin{aligned}(\{\nabla\}_\mu^\lambda)^*\{\mathbf{r}\}_M^L&=(2\lambda-1)!!\begin{bmatrix}L & M\\ \lambda & \mu\end{bmatrix}\{\mathbf{r}\}_{M-\mu}^{L-\lambda}\ ,\\(\{\nabla\}^\lambda\cdot\{\mathbf{r}\}^L)_M^L&=(-1)^\lambda(2\lambda-1)!!\\&\quad\times\begin{bmatrix}2L+1\\ 2\lambda\end{bmatrix}^{1/2}\{\mathbf{r}\}_M^{L-\lambda}\delta_{JL-\lambda}\ ,\end{aligned}\tag{12}$$

where δ_{IJ} is one if $I=J$ and zero otherwise. Apart from the double factorial the coefficients of the uncoupled versions of Eqs. (3) and (12) involve the same coefficients. The final relationship,

$$\begin{aligned}\frac{\partial^\lambda}{\partial\alpha^\lambda}\{\alpha\mathbf{A}+\beta\mathbf{B}\}_M^L&=\lambda!\sum_\mu\begin{bmatrix}L & M\\ \lambda & \mu\end{bmatrix}\{\mathbf{A}\}_\mu^\lambda\{\alpha\mathbf{A}+\beta\mathbf{B}\}_{M-\mu}^{L-\lambda}\\&=\lambda!\begin{bmatrix}2L\\ 2\lambda\end{bmatrix}^{1/2}(\{\mathbf{A}\}^\lambda\cdot\{\alpha\mathbf{A}+\beta\mathbf{B}\}^{L-\lambda})_M^L\ ,\end{aligned}\tag{13}$$

is particularly important in the GTO LDF approach,[2] where integrals of the total electron density are fit. Atomic charge densities have shoulders in the radial direction caused by the electrons in filled inner shells.

TABLE II. Nontrivial terms in differentiation of a product of functions with respect to the d and f real solid harmonics of ∇ from Eq. (10).

	$\langle\nabla\rangle_1^1$	$\langle\nabla\rangle_2^1$	$\langle\nabla\rangle_3^1$
$\langle\nabla\rangle_1^2$	$2\langle\nabla\rangle_1^1$	$-\langle\nabla\rangle_2^1$	$-\langle\nabla\rangle_3^1$
$\langle\nabla\rangle_2^2$	$\sqrt{3}\langle\nabla\rangle_2^1$		
$\langle\nabla\rangle_3^2$	$\sqrt{3}\langle\nabla\rangle_3^1$		
$\langle\nabla\rangle_4^2$		$\sqrt{3}\langle\nabla\rangle_2^1$	$-\sqrt{3}\langle\nabla\rangle_3^1$
$\langle\nabla\rangle_5^2$		$\sqrt{3}\langle\nabla\rangle_3^1$	
$\langle\nabla\rangle_1^3$	$3\langle\nabla\rangle_1^2$	$-\sqrt{3}\langle\nabla\rangle_2^2$	$-\sqrt{3}\langle\nabla\rangle_3^2$
$\langle\nabla\rangle_2^3$	$\sqrt{8}\langle\nabla\rangle_2^2$	$\sqrt{6}\langle\nabla\rangle_1^2-\sqrt{1/2}\langle\nabla\rangle_4^2$	$-\sqrt{1/2}\langle\nabla\rangle_5^2$
$\langle\nabla\rangle_3^3$	$\sqrt{8}\langle\nabla\rangle_3^2$	$-\sqrt{1/2}\langle\nabla\rangle_5^2$	$\sqrt{6}\langle\nabla\rangle_1^2+\sqrt{1/2}\langle\nabla\rangle_4^2$
$\langle\nabla\rangle_4^3$	$\sqrt{5}\langle\nabla\rangle_4^2$	$\sqrt{5}\langle\nabla\rangle_2^2$	$-\sqrt{5}\langle\nabla\rangle_3^2$
$\langle\nabla\rangle_5^3$	$\sqrt{5}\langle\nabla\rangle_5^2$	$\sqrt{5}\langle\nabla\rangle_3^2$	$\sqrt{5}\langle\nabla\rangle_2^2$
$\langle\nabla\rangle_6^3$		$\sqrt{15/2}\langle\nabla\rangle_4^2$	$-\sqrt{15/2}\langle\nabla\rangle_5^2$
$\langle\nabla\rangle_7^3$		$\sqrt{15/2}\langle\nabla\rangle_5^2$	$\sqrt{15/2}\langle\nabla\rangle_4^2$

TABLE III. Nontrivial terms in differentiation of a product of functions with respect to the g real solid harmonics of ∇ from Eq. (10).

	$\langle\nabla\rangle_1^1$	$\langle\nabla\rangle_2^1$	$\langle\nabla\rangle_3^1$	$\langle\nabla\rangle_1^2$	$\langle\nabla\rangle_2^2$	$\langle\nabla\rangle_3^2$	$\langle\nabla\rangle_4^2$	$\langle\nabla\rangle_5^2$
$\langle\nabla\rangle_1^4$	$4\langle\nabla\rangle_1^3$	$-\sqrt{6}\langle\nabla\rangle_2^3$	$-\sqrt{6}\langle\nabla\rangle_3^3$	$6\langle\nabla\rangle_1^2$	$-4\langle\nabla\rangle_2^2$	$-4\langle\nabla\rangle_3^2$	$\langle\nabla\rangle_4^2$	$\langle\nabla\rangle_5^2$
$\langle\nabla\rangle_1^4$	$\sqrt{15}\langle\nabla\rangle_1^3$	$\sqrt{10}\langle\nabla\rangle_1^3-\sqrt{3/2}\langle\nabla\rangle_4^3$	$-\sqrt{3/2}\langle\nabla\rangle_5^3$	$\sqrt{30}\langle\nabla\rangle_1^2$	$-\sqrt{5/2}\langle\nabla\rangle_4^2$	$-\sqrt{5/2}\langle\nabla\rangle_5^2$		
$\langle\nabla\rangle_2^4$	$\sqrt{15}\langle\nabla\rangle_2^3$	$-\sqrt{3/2}\langle\nabla\rangle_5^3$	$\sqrt{10}\langle\nabla\rangle_1^3+\sqrt{3/2}\langle\nabla\rangle_4^3$	$\sqrt{30}\langle\nabla\rangle_2^2$	$-\sqrt{5/2}\langle\nabla\rangle_5^2$	$\sqrt{5/2}\langle\nabla\rangle_4^2$		
$\langle\nabla\rangle_3^4$	$\sqrt{15}\langle\nabla\rangle_3^3$	$\sqrt{15/2}\langle\nabla\rangle_1^3-\sqrt{1/2}\langle\nabla\rangle_6^3$	$-\sqrt{15/2}\langle\nabla\rangle_3^3-\sqrt{1/2}\langle\nabla\rangle_7^3$	$\sqrt{15}\langle\nabla\rangle_3^2$	$\sqrt{20}\langle\nabla\rangle_2^2$	$-\sqrt{20}\langle\nabla\rangle_3^2$		
$\langle\nabla\rangle_4^4$	$\sqrt{12}\langle\nabla\rangle_4^3$	$\sqrt{15/2}\langle\nabla\rangle_2^3-\sqrt{1/2}\langle\nabla\rangle_6^3$	$\sqrt{15/2}\langle\nabla\rangle_2^3+\sqrt{1/2}\langle\nabla\rangle_6^3$	$\sqrt{15}\langle\nabla\rangle_4^2$	$\sqrt{20}\langle\nabla\rangle_3^2$	$\sqrt{20}\langle\nabla\rangle_2^2$		
$\langle\nabla\rangle_5^4$	$\sqrt{12}\langle\nabla\rangle_5^3$	$\sqrt{15/2}\langle\nabla\rangle_3^3-\sqrt{1/2}\langle\nabla\rangle_7^3$	$\sqrt{15/2}\langle\nabla\rangle_3^3+\sqrt{1/2}\langle\nabla\rangle_7^3$	$\sqrt{15}\langle\nabla\rangle_5^2$	$\sqrt{20}\langle\nabla\rangle_4^2$	$\sqrt{20}\langle\nabla\rangle_3^2$		
$\langle\nabla\rangle_6^4$	$\sqrt{7}\langle\nabla\rangle_6^3$	$\sqrt{21/2}\langle\nabla\rangle_4^3$	$-\sqrt{21/2}\langle\nabla\rangle_5^3$		$\sqrt{35/2}\langle\nabla\rangle_5^2$	$-\sqrt{35/2}\langle\nabla\rangle_5^2$		
$\langle\nabla\rangle_7^4$	$\sqrt{7}\langle\nabla\rangle_7^3$	$\sqrt{21/2}\langle\nabla\rangle_5^3$	$\sqrt{21/2}\langle\nabla\rangle_4^3$		$\sqrt{35/2}\langle\nabla\rangle_4^2$	$\sqrt{35/2}\langle\nabla\rangle_4^2$		
$\langle\nabla\rangle_8^4$		$\sqrt{14}\langle\nabla\rangle_6^3$	$-\sqrt{14}\langle\nabla\rangle_7^3$				$\sqrt{35}\langle\nabla\rangle_4^2$	$-\sqrt{35}\langle\nabla\rangle_5^2$
$\langle\nabla\rangle_9^4$		$\sqrt{14}\langle\nabla\rangle_7^3$	$\sqrt{14}\langle\nabla\rangle_6^3$				$\sqrt{35}\langle\nabla\rangle_5^2$	

Fitting such densities to a sum of simple s-type Gaussians results in sign alternation among the coefficients and less numerical stability than adding enough r^2 fitting functions,

$$(\mathbf{r}-\mathbf{c})^2\exp[-\alpha(\mathbf{r}-\mathbf{c})^2]=-\frac{\partial}{\partial\alpha}\exp[-\alpha(\mathbf{r}-\mathbf{c})^2]\ , \tag{14}$$

to give s-type fitting coefficients that are all positive, at least for the large exponents that dominate the core regions of the atoms.

Equation (13) does not trivially follow from Eq. (8). The fact that the coefficients are the same apart from λ factorial is the result of the fact that

$$(\{\mathbf{r}\}^{\lambda}_{\cdot}\{\mathbf{r}\}^{L-\lambda}_{\cdot})^{L}_{M}=\{\mathbf{r}\}^{L}_{M}\begin{bmatrix}L\\ \lambda\end{bmatrix}\Big/\begin{bmatrix}2L\\ 2\lambda\end{bmatrix}^{1/2}\ , \tag{15}$$

which in turn is a special case of spherical harmonic product formula,

$$\begin{aligned}\{\mathbf{r}\}^{L_1}_{M_1}\{\mathbf{r}\}^{L_2}_{M_2}&=\sum_{J,M}(-1)^M[J]\begin{pmatrix}L_1 & L_2 & J\\ 0 & 0 & 0\end{pmatrix}\\&\quad\times\begin{pmatrix}L_1 & L_2 & J\\ M_1 & M_2 & M\end{pmatrix}r^{2n}\{\mathbf{r}\}^{J}_{M}\\ (\{\mathbf{r}\}^{L_1}_{\cdot}\{\mathbf{r}\}^{L_2}_{\cdot})^{J}_{M}&=(-1)^J\sqrt{[J]}\begin{pmatrix}L_1 & L_2 & J\\ 0 & 0 & 0\end{pmatrix}r^{2n}\{\mathbf{r}\}^{J}_{M}\ ,\end{aligned} \tag{16}$$

where $[L_1,L_2,\ldots]=(2L_1+1)(2L_2+1)\cdots$. Unless J equals L_1+L_2-2n where n is some integer, the 3-j symbol[19] that is common to both equations vanishes. In that case the lower of these two equations is trivial.

Equations (3), (10), (12), and (13) are all that are necessary in a direct (uncoupled) computation of all higher-angular-momentum matrix elements from s-type matrix elements involving any number of centers. No limits on the summations are given in these equations because the angular momentum triangular conditions of angular momentum theory are preserved through the binomial coefficients of Eq. (4) that obviously vanish outside the allowed ranges.

Because the magnetic quantum number dependences in the uncoupled versions of the equations to follow will occur only in the combination,

$${}^{L}_{M}\{\mathbf{r}\}^{\lambda}_{\mu}=\begin{bmatrix}L & M\\ \lambda & \mu\end{bmatrix}\{\mathbf{r}\}^{L-\lambda}_{M-\mu}\ , \tag{17}$$

this special symbol is conveniently defined. The right superscript is the subtrahend angular momentum λ, rather than the resultant angular momentum $L-\lambda$. This choice makes apparent the scalar (under rotation of the coordinate system) nature of the various products of the subtrahend angular momenta that will occur. The scalar coupling occurs even though the equations are written in uncoupled form.

The principal advantage of the uncoupled approach is now immediately obvious. The final magnetic quantum number dependence of any matrix element will be given simply by the multiplication of an intermediate quantity

by this matrix, Eq. (17). The disadvantage of the uncoupled approach is the proliferation of solid harmonics, e.g., Eq. (10), which grows rapidly with the number of centers. The uncoupled approach is clearly better for up to three centers, even without the simplifications that are described in the following sections.

III. TWO-CENTER OVERLAP INTEGRAL

It is most convenient to begin a study of the relative merits of computing GTO LDF matrix elements in their coupled or in their uncoupled forms with the simplest such integral, the two-center overlap integral. Apart from a position-independent factor, the two-center s-type overlap integral is another Gaussian,

$$\int \exp[-\alpha(\mathbf{r}-\mathbf{a})^2]\exp[-\beta(\mathbf{r}-\mathbf{b})^2]d\mathbf{r} = \left[\frac{\pi}{\alpha+\beta}\right]^{3/2}\exp\left[-\frac{\alpha\beta}{\alpha+\beta}(\mathbf{a}-\mathbf{b})^2\right] . \quad (18)$$

Therefore, the two-center overlap integral of arbitrary angular momentum can be expressed in uncoupled form, using the uncoupled forms of Eqs. (10) and (12),

$$\{\nabla_a\}^{L_1}_{M_1}\{\nabla_b\}^{L_2}_{M_2}\exp\left[-\frac{\alpha\beta}{\alpha+\beta}(\mathbf{a}-\mathbf{b})^2\right] = \exp\left[-\frac{\alpha\beta}{\alpha+\beta}(\mathbf{a}-\mathbf{b})^2\right]\sum_{\lambda,\mu}(-1)^{L_1-\lambda+\mu}(2\lambda-1)!!\left[\frac{2\alpha\beta}{\alpha+\beta}\right]^{L_1+L_2-\lambda} \times {}^{L_1}_{M_1}\{\mathbf{a}-\mathbf{b}\}^{\lambda}_{\mu}\,{}^{L_2}_{M_2}\{\mathbf{a}-\mathbf{b}\}^{\lambda}_{-\mu} , \quad (19)$$

where ∇_a is the gradient with respect to $\mathbf{a}$. For each subtrahend angular momentum, λ, the summation over μ yields a coupled quantity that is invariant under rotation, as must be the case for this overlap integral to be consistently calculated in any coordinate system. Note that this equation factors into a product of the matrices of Eq. (17).

Equation (19) can be extended to other functional forms,

$$\{\nabla\}^{L_1}_{M_1}\{\nabla\}^{L_2}_{M_2}F(|\mathbf{r}+\mathbf{a}|^2) = \sum_{\lambda,\mu}(-1)^{\mu}(2\lambda-1)!!\,{}^{L_1}_{M_1}\{\mathbf{r}+\mathbf{a}\}^{\lambda}_{\mu}\,{}^{L_2}_{M_2}\{\mathbf{r}+\mathbf{a}\}^{\lambda}_{-\mu}2^{L_1+L_2-\lambda}F^{L_1+L_2-\lambda}(|\mathbf{r}+\mathbf{a}|^2) , \quad (20)$$

where

$$F^N(|\mathbf{r}+\mathbf{a}|^2) = \left[\frac{\partial}{\partial|\mathbf{r}+\mathbf{a}|^2}\right]^N F(|\mathbf{r}+\mathbf{a}|^2) . \quad (21)$$

Now the phase factor is simplified because the two ∇ operators are the same in Eq. (21), but equal to the negative of each other in their effect in Eq. (20). Although this expression is valid for any function $F(|\mathbf{r}+\mathbf{a}|^2)$ that is invariant under rotation of the entire coordinate system (including the coordinates of every atom), it is simplest for Gaussians. For Gaussians, $F(r^2)=\exp(-r^2)$, and

$$F^N=(-1)^N\exp(-r^2) , \quad (22)$$

thus for the products of Gaussians and indefinite integrals of products of Gaussians that are met in the GTO methods, no inverse powers of r or other singularities arise from the operation of Eq. (21).

The other approach to the two-center overlap integral is to couple the angular momenta of the two solid harmonics of ∇, using Eq. (16),

$$(\{\nabla\}^{L_1}\{\nabla\}^{L_2})^J_M F(\alpha r^2) = (-1)^J\sqrt{[J]}\begin{bmatrix} L_1 & L_2 & J \\ 0 & 0 & 0\end{bmatrix}\nabla^{2n}\{\nabla\}^J_M F(\alpha r^2)$$

$$= (-1)^J 2^n(2\alpha)^{J+n}\sqrt{[J]}\begin{bmatrix} L_1 & L_2 & J \\ 0 & 0 & 0\end{bmatrix}\sum_{\tau}\begin{bmatrix} n \\ \tau\end{bmatrix}\frac{(J+n-\frac{1}{2})!}{(J+\tau-\frac{1}{2})!}(2\alpha r^2)^{\tau}\{\mathbf{r}\}^J_M F^{L_1+L_2-n}(\alpha r^2) , \quad (23)$$

where

$$(n-\tfrac{1}{2})! = \Gamma(n+\tfrac{1}{2})/\Gamma(\tfrac{1}{2}) ,$$

and n is defined as before. This expression appears quite different from Eq. (20). Compared to the former, it has a single advantage, which is that one, rather than two, solid spherical harmonics appear in the RHS. Counterbalancing this advantage are three disadvantages. First, and most importantly, the magnetic quantum number dependence of Eq. (23) cannot be factored after uncoupling the two angular momenta using Eq. (6). Second, in general the latter equation requires a summation over τ. Third, the solid spherical harmonics of this equation have larger angular momenta, because J ranges up to L_1+L_2.

The relative advantage of Eq. (19) over Eq. (23) is not so strong as to rule out a hybrid approach. The $\lambda=0$ term of Eq. (19) is trivial and should always be computed separately and used to initialize the matrix-element arrays in the computer. The $\lambda\neq 0$ terms of Eq. (19) could then be coupled to yield highest angular momentum L_1+L_2-2, which is two units less than would have to be evaluated in the direct coupled approach, Eq. (23).

IV. THE SYMMETRIC THREE-CENTER OVERLAP INTEGRAL

The three-center overlap integral,

$$I_{ABC}=\int \exp[-\alpha(\mathbf{r}-\mathbf{a})^2]\exp[-\beta(\mathbf{r}-\mathbf{b})^2] \times\exp[-\gamma(\mathbf{r}-\mathbf{c})^2]d\mathbf{r}\ , \tag{24}$$

is necessary for fitting LDF expressions for exchange and correlation. This integral is most often expressed as a product of two Gaussians,

$$I_{ABC}=\left[\frac{\pi}{\alpha+\beta+\gamma}\right]^{3/2}\exp\left[-\frac{\alpha\beta}{\alpha+\beta}(\mathbf{a}-\mathbf{b})^2\right] \times\exp\left[-\frac{\gamma(\alpha+\beta)}{\alpha+\beta+\gamma}\left[\mathbf{c}-\frac{\alpha\mathbf{a}+\beta\mathbf{b}}{\alpha+\beta}\right]^2\right]. \tag{25}$$

The exponential factors of this equation can be symmetrically expressed,

$$\exp\left[-\frac{\alpha\beta}{\alpha+\beta}(\mathbf{a}-\mathbf{b})^2\right]\exp\left[-\frac{\gamma(\alpha+\beta)}{\alpha+\beta+\gamma}\left[\mathbf{c}-\frac{\alpha\mathbf{a}+\beta\mathbf{b}}{\alpha+\beta}\right]^2\right] =\exp\left[-\frac{\alpha\beta}{\alpha+\beta+\gamma}(\mathbf{a}-\mathbf{b})^2-\frac{\alpha\gamma}{\alpha+\beta+\gamma}(\mathbf{a}-\mathbf{c})^2-\frac{\beta\gamma}{\alpha+\beta+\gamma}(\mathbf{b}-\mathbf{c})^2\right], \tag{26}$$

only as a product of three Gaussians. Differentiating either expression extends Eq. (19) to the three-center overlap integral for the case in which one of the centers has zero angular momentum associated with it,

$$\{\nabla_a\}^{L_1}_{M_1}\{\nabla_b\}^{L_2}_{M_2}I_{ABC}=I_{ABC}\left[-\frac{2\alpha(\beta+\gamma)}{\alpha+\beta+\gamma}\right]^{L_1}\left[-\frac{2\beta(\alpha+\gamma)}{\alpha+\beta+\gamma}\right]^{L_2} \times\sum_{\lambda,\mu}(-1)^{\mu}(2\lambda-1)!!\left[\frac{\alpha+\beta+\gamma}{2(\beta+\gamma)(\alpha+\gamma)}\right]^{\lambda}\begin{matrix}L_1\\ M_1\end{matrix}\left\{\mathbf{a}-\frac{\beta\mathbf{b}+\gamma\mathbf{c}}{\beta+\gamma}\right\}^{\lambda}_{\mu}\begin{matrix}L_2\\ M_2\end{matrix}\left\{\mathbf{b}-\frac{\alpha\mathbf{a}+\gamma\mathbf{c}}{\alpha+\gamma}\right\}^{\lambda}_{-\mu}. \tag{27}$$

Equation (27) is not as important in practical calculations as one might expect, however. The problem is that the arguments of the two solid spherical harmonics are different. The first is only independent of α, and the second is only independent of β. Therefore, two sets of solid spherical harmonics must be computed for each triplet of exponents.

A coupled version of Eq. (27) follows from the coupled forms of Eqs. (10) and (12), together with the evaluation of the special 6-j symbol,[19]

$$\begin{Bmatrix}L_1 & L_2 & J\\ L_2-\lambda & L_1-\lambda & \lambda\end{Bmatrix}=\frac{(-1)^{L_1+L_2+J}}{\left[[L_1,L_2]\begin{bmatrix}2L_1\\ 2\lambda\end{bmatrix}\begin{bmatrix}2L_2\\ 2\lambda\end{bmatrix}\right]^{1/2}}\left[\begin{bmatrix}L_1+L_2+J+1\\ 2\lambda\end{bmatrix}\begin{bmatrix}L_1+L_2-J\\ 2\lambda\end{bmatrix}\right]^{1/2}. \tag{28}$$

The coupled form of Eq. (27) is

$$(\{\nabla_a\}^{L_1}_{\cdot}\{\nabla_b\}^{L_2}_{\cdot})^{J}_{M}I_{ABC}=I_{ABC}\left[-\frac{2\alpha(\beta+\gamma)}{\alpha+\beta+\gamma}\right]^{L_1}\left[-\frac{2\beta(\alpha+\gamma)}{\alpha+\beta+\gamma}\right]^{L_2} \times\sum_{\lambda}(2\lambda-1)!!\left[\frac{\alpha+\beta+\gamma}{2(\beta+\gamma)(\alpha+\gamma)}\right]^{\lambda} \times\left[\begin{bmatrix}L_1+L_2+J+1\\ 2\lambda\end{bmatrix}\begin{bmatrix}L_1+L_2-J\\ 2\lambda\end{bmatrix}\right]^{1/2} \times\left[\left\{\mathbf{a}-\frac{\beta\mathbf{b}+\gamma\mathbf{c}}{\beta+\gamma}\right\}^{L_1-\lambda}_{\cdot}\left\{\mathbf{b}-\frac{\alpha\mathbf{a}+\gamma\mathbf{c}}{\alpha+\gamma}\right\}^{L_2-\lambda}_{\cdot}\right]^{J}_{M}. \tag{29}$$

To complete this analysis of symmetric three-center matrix elements, one must consider the effect of operating on the matrix elements of this section with $\{\nabla_c\}^{L_3}_{M_3}$. Coupling the angular momentum of this third operator to the lhs of Eq. (29) leads to a very complicated expression. In fact, the uncoupled approach is required if one wants to display the symmetry of the three-center overlap integral, under permutation of the various solid spherical harmonics of ∇. That approach first requires extending Eq. (20) to three ∇ operators,

$$\{\nabla\}^{L_1}_{M_1}\{\nabla\}^{L_2}_{M_2}\{\nabla\}^{L_3}_{M_3}F(|\mathbf{r}+\mathbf{a}|^2)=\sum_{\substack{\lambda_1,\lambda_2,\lambda_3\\ \mu_1,\mu_2,\mu_3}}(2)^{L_1+L_2+L_3-\Lambda/2}(\Lambda+1)!!\begin{bmatrix}\lambda_1&\lambda_2&\lambda_3\\ \mu_1&\mu_2&\mu_3\end{bmatrix}\begin{bmatrix}\lambda_1&\lambda_2&\lambda_3\\ 0&0&0\end{bmatrix}\{\mathbf{r}+\mathbf{a}\}^{L_1}_{M_1}\{\mathbf{r}+\mathbf{a}\}^{\lambda_1}_{\mu_1}$$
$$\times\{\mathbf{r}+\mathbf{a}\}^{L_2}_{M_2}\{\mathbf{r}+\mathbf{a}\}^{\lambda_2}_{\mu_2}\{\mathbf{r}+\mathbf{a}\}^{L_3}_{M_3}\{\mathbf{r}+\mathbf{a}\}^{\lambda_3}_{\mu_3}F^{L_1+L_2+L_3-\Lambda/2}(|\mathbf{r}+\mathbf{a}|^2)\ , \tag{30}$$

where $\Lambda=\lambda_1+\lambda_2+\lambda_3$ and $\Lambda/2$ must be integral or the second 3-j symbol vanishes. The first 3-j symbol imposes the constraint that the subtrahend angular momenta must couple up to be a scalar under rotation of the coordinate system.

Equation (30) is easily extended to give the general three-center overlap integral in symmetric form,

$$\{\nabla\}^{L_1}_{M_1}\{\nabla\}^{L_2}_{M_2}\{\nabla\}^{L_3}_{M_3}I_{ABC}=I_{ABC}\left[-\frac{2\alpha(\beta+\gamma)}{\alpha+\beta+\gamma}\right]^{L_1}\left[-\frac{2\beta(\alpha+\gamma)}{\alpha+\beta+\gamma}\right]^{L_2}\left[-\frac{2\gamma(\alpha+\beta)}{\alpha+\beta+\gamma}\right]^{L_3}$$
$$\times\sum_{\substack{\lambda_1,\lambda_2,\lambda_3,\\ \mu_1,\mu_2,\mu_3}}\begin{bmatrix}\lambda_1&\lambda_2&\lambda_3\\ \mu_1&\mu_2&\mu_3\end{bmatrix}\begin{bmatrix}\lambda_1&\lambda_2&\lambda_3\\ 0&0&0\end{bmatrix}$$
$$\times\frac{(\Lambda+1)!!}{(\beta+\gamma)^{\lambda_1}(\alpha+\gamma)^{\lambda_2}(\alpha+\beta)^{\lambda_3}}\left[\frac{\alpha+\beta+\gamma}{2}\right]^{\Lambda/2}\{\}^{L_1}_{M_1}\left\{\mathbf{a}-\frac{\beta\mathbf{b}+\gamma\mathbf{c}}{\beta+\gamma}\right\}^{\lambda_1}_{\mu_1}$$
$$\times\{\}^{L_2}_{M_2}\left\{\mathbf{b}-\frac{\alpha\mathbf{a}+\gamma\mathbf{c}}{\alpha+\gamma}\right\}^{\lambda_2}_{\mu_2}\{\}^{L_3}_{M_3}\left\{\mathbf{c}-\frac{\alpha\mathbf{a}+\beta\mathbf{b}}{\alpha+\beta}\right\}^{\lambda_3}_{\mu_3}\ . \tag{31}$$

Note that the L_i and M_i dependences of this equation can be factored into a separate matrix multiplication for each i. Unfortunately this expression can only be used for the three-center overlap integral. Including one or two r^2 functions, Eq. (14), makes an unsymmetric expression for the three-center overlap integral. For these, and intrinsically unsymmetric three-center integrals, such as the Coulomb matrix element, another approach is required.

V. NONSYMMETRIC THREE-CENTER INTEGRALS

The alternative approach to the three-center overlap integral does not treat the three centers a, b, and c symmetrically. This second approach is necessary in treating the unsymmetric Coulomb repulsion integrals. It is convenient to define symbols for the two important distance vectors,

$$\mathbf{p}=\mathbf{a}-\mathbf{b},\quad \mathbf{q}=\mathbf{c}-\frac{\alpha\mathbf{a}+\beta\mathbf{b}}{\alpha+\beta}$$

$$P=\frac{\alpha\beta}{\alpha+\beta}p^2,\quad Q=\frac{\gamma(\alpha+\beta)}{\alpha+\beta+\gamma}q^2\ .$$

With these definitions, the Coulomb repulsion integral of a product of two s-type Gaussians on centers **a** and **b** with exponents α and β, respectively, repelling a single s-type Gaussian on center **c** with exponent γ,

$$\int\exp[-\alpha(\mathbf{r}_1-\mathbf{a})^2]\exp[-\beta(\mathbf{r}_1-\mathbf{b})^2]\exp[-\gamma(\mathbf{r}_2-\mathbf{c})^2]d\mathbf{r}_1d\mathbf{r}_2/r_{12}\ , \tag{32}$$

becomes the simple product, $\exp(-P)F(Q)$, where

$$F(Q)=\frac{2\pi^{5/2}}{(\alpha+\beta)\gamma[(\alpha+\beta+\gamma)]^{1/2}}\int_0^1\exp(-Qu^2)du\ . \tag{33}$$

Such integrals are not symmetric in the three exponents, precluding a functional form similar to Eq. (31).

The coupled approach to differentiating $\exp(-P)F(Q)$ is quite complicated and it will be pursued only so far as to suggest the results of Ref. 15. Each ∇ operator acts on both factors,

$$(\{\nabla_a\}^{L_1}_{\cdot}\{\nabla_b\}^{L_2}_{\cdot})^J_M\exp(-P)F(Q)=\left[\left\{\nabla_p-\frac{\alpha}{\alpha+\beta}\nabla_q\right\}^{L_1}_{\cdot}\left\{-\nabla_p-\frac{\beta}{\alpha+\beta}\nabla_q\right\}^{L_2}_{\cdot}\right]^J_M\exp(-P)F(Q)\ . \tag{34}$$

The rhs of this expression can be expanded using Eq. (8), and the operators can be regrouped according to which factor they operate on using the 9-j symbols,[15]

$$(\{\nabla_a\}^{L_1}\{\nabla_b\}^{L_2})^J_M \exp(-P)F(Q)=\sum_{\lambda_1,\lambda_2,J_1,J_2}(-1)^{L_1+L_2-\lambda_1}$$
$$\times\left[\frac{\alpha}{\alpha+\beta}\right]^{\lambda_1}\left[\frac{\beta}{\alpha+\beta}\right]^{\lambda_2}\begin{bmatrix}L_1\\ \lambda_1\end{bmatrix}\begin{bmatrix}L_2\\ \lambda_2\end{bmatrix}\left[\begin{bmatrix}2L_1\\ 2\lambda_1\end{bmatrix}\begin{bmatrix}2L_2\\ 2\lambda_2\end{bmatrix}\right]^{1/2}$$
$$\times[L_1,L_2,J_1,J_2]^{1/2}\begin{Bmatrix}L_1-\lambda_1 & \lambda_1 & L_1\\ L_2-\lambda_2 & \lambda_2 & L_2\\ J_1 & J_2 & J\end{Bmatrix}$$
$$\times((\{\nabla_p\}^{L_1-\lambda_1}\{\nabla_p\}^{L_2-\lambda_2})^{J_1}\exp(-P)(\{\nabla_q\}^{\lambda_1}\{\nabla_q\}^{\lambda_2})^{J_2}F(Q))^J_M \ . \quad (35)$$

Within the J_1 and J_2 couplings, the spherical harmonic product formula, Eq. (16), can be used to simplify this expression a little further. But the appearance of the 9-j symbol alone severely complicates machine computation of coupled matrix elements. For f electrons ($L_1=L_2=3$) the number of 9-j symbols needed to compute the matrix elements is already so large (J_1 and J_2 can range up to 6), on the one hand, that they cannot conveniently be stored in current computers. On the other hand, explicit calculation of the 9-j symbol requires a summation to reduce it to a product of three 6-j symbols and then a further summation to evaluate each 6-j symbol. In this case, despite the two maximal couplings that appear in the 9-j symbol of Eq. (35), few of these summations are limited to one term.

It is much easier to proceed in the uncoupled approach, using Eqs. (10) and (12) as well as Eq. (A1.1) of Ref. 19 to perform a summation over a magnetic quantum number,

$$\{\nabla_a\}^{L_1}_{M_1}\{\nabla_b\}^{L_2}_{M_2}\exp(-P)F(Q)=(-1)^{L_1}\left[\frac{2\alpha\beta}{\alpha+\beta}\right]^{L_1+L_2}\exp(-P)$$
$$\times\sum_{l_1,l_2,m_1,m_2}\left[\frac{1}{2\beta}\right]^{l_1}\left[-\frac{1}{2\alpha}\right]^{l_2}{}^{L_1}_{M_1}\{\mathbf{p}\}^{l_1}_{m_1}{}^{L_2}_{M_2}\{\mathbf{p}\}^{l_2}_{m_2}$$
$$\times\sum_{\lambda_1,\mu_1}(-1)^{\mu_1}(2\lambda_1-1)!!\,{}^{l_1}_{m_1}\{\mathbf{q}\}^{\lambda_1}_{\mu_1}{}^{l_2}_{m_2}\{\mathbf{q}\}^{\lambda_1}_{-\mu_1}$$
$$\times\left[\frac{2\gamma(\alpha+\beta)}{\alpha+\beta+\gamma}\right]^{l_1+l_2-\lambda_1}\left[\frac{d}{dQ}+\frac{\alpha+\beta+\gamma}{\gamma}\right]^{\lambda_1}F^{l_1+l_2-2\lambda_1}(Q) \ . \quad (36)$$

This expression confines the exponent of the third center, γ, in the final summation. Thus the majority of the evaluation can be precomputed on a computer. The full three-center overlap problem requires only the following relationship,

$$\{\nabla_c\}^{L_3}_{M_3}\sum_{\lambda_1,\mu_1}(-1)^{\mu_1}{}^{l_1}_{m_1}\{\mathbf{q}\}^{\lambda_1}_{\mu_1}{}^{l_2}_{m_2}\{\mathbf{q}\}^{\lambda_1}_{-\mu_1}(2\lambda_1-1)!!\left[\frac{2\gamma(\alpha+\beta)}{\alpha+\beta+\gamma}\right]^{l_1+l_2-\lambda_1}\left[\frac{d}{dQ}+\frac{\alpha+\beta+\gamma}{\gamma}\right]^{\lambda_1}F^{l_1+l_2-2\lambda_1}(Q)$$
$$=\sum_{\lambda_1-\lambda_3,\mu_1-\mu_3}(\Lambda+1)!!\,{}^{l_1}_{m_1}\{\mathbf{q}\}^{\lambda_1}_{\mu_1}{}^{l_2}_{m_2}\{\mathbf{q}\}^{\lambda}_{\mu_2}{}^{L_3}_{M_3}\{\mathbf{q}\}^{\lambda_3}_{\mu_3}\begin{bmatrix}\lambda_1 & \lambda_2 & \lambda_3\\ \mu_1 & \mu_2 & \mu_3\end{bmatrix}\begin{bmatrix}\lambda_1 & \lambda_2 & \lambda_3\\ 0 & 0 & 0\end{bmatrix}\left[\frac{2\gamma(\alpha+\beta)}{\alpha+\beta+\gamma}\right]^{l_1+l_2+L_3-\Lambda/2}$$
$$\times\left[\frac{d}{dQ}+\frac{\alpha+\beta+\gamma}{\gamma}\right]^{\Lambda/2-\lambda_3}F^{l_1+l_2+L_3-\Lambda+\lambda_3}(Q) \ . \quad (37)$$

For the three-center overlap integral, Eq. (31) is an alternative to Eqs. (36) and (37). For this special integral Eq. (31) requires summing over one less magnetic quantum number and two less angular momentum quantum numbers. On the other hand, solid spherical harmonic computation can be taken outside the loop over exponents γ in Eqs. (36) and (37).

VI. RECURSION

Recursive methods involving solid spherical harmonics and Gaussians are quite simple because a spherical harmonic of ∇ operating on a Gaussian is the same spherical harmonic of some distance vector. A strategy then is to factor out one power of that distance and commute it through all other ∇ operators. To that end a single solid spherical harmonic must be factorized,

$$\{\mathbf{r}\}^L_M=\left[\frac{L^2-M^2}{L^2}\right]^{1/2}\{\mathbf{r}\}^1_0\{\mathbf{r}\}^{L-1}_M$$
$$+\left[\frac{(L+M)(L+M-1)}{2L^2}\right]^{1/2}\{\mathbf{r}\}^1_1\{\mathbf{r}\}^{L-1}_{M-1}$$
$$+\left[\frac{(L-M)(L-M-1)}{2L^2}\right]^{1/2}\{\mathbf{r}\}^1_{-1}\{\mathbf{r}\}^{L-1}_{M+1} \ . \quad (38)$$

For the real solid harmonics of Table I, this factorization has three different cases,

$$\langle \mathbf{r}\rangle_1^L = z\langle \mathbf{r}\rangle_1^{L-1} - \left[\frac{L-1}{2L}\right]^{1/2}(x\langle \mathbf{r}\rangle_2^{L-1} + y\langle \mathbf{r}\rangle_3^{L-1}) ,$$

$$\begin{aligned}\langle \mathbf{r}\rangle_{2M}^L &= LM^0 z\langle \mathbf{r}\rangle_{2M}^{L-1} + LM^-(x\langle \mathbf{r}\rangle_{2M-2}^{L-1} - y\langle \mathbf{r}\rangle_{2M-1}^{L-1}) \\ &\quad + LM^+(-x\langle \mathbf{r}\rangle_{2M+2}^{L-1} - y\langle \mathbf{r}\rangle_{2M+3}^{L-1}) ,\end{aligned} \tag{39}$$

$$\begin{aligned}\langle \mathbf{r}\rangle_{2M+1}^L &= LM^0 z\langle \mathbf{r}\rangle_{2M+1}^{L-1} \\ &\quad + LM^-(x\langle \mathbf{r}\rangle_{2M-1}^{L-1} + y\langle \mathbf{r}\rangle_{2M-2}^{L-1}) \\ &\quad + LM^+(-x\langle \mathbf{r}\rangle_{2M+3}^{L-1} + y\langle \mathbf{r}\rangle_{2M+2}^{L-1}) ,\end{aligned}$$

where

$$LM^0 = \frac{\sqrt{(L^2-M^2)}}{L}$$

and

$$LM^{\mp} = \frac{[(L\pm M)(L\pm M-1)]^{1/2}}{2L} .$$

These equations could be used to generate the solid spherical harmonics themselves, but more efficient methods (requiring fewer terms than the five that in general are required here) can be found if one allows equations that include spherical harmonics of three different, rather than just two different, total angular momenta, although computer times are quite similar if the LM^0 and $LM^{\mp}$ are precomputed and stored in a short array.

Equation (38) or (39) alone can be used to recursively generate single-center integrals. Multicenter integrals also require the commutator,

$$[\{\nabla_b\}_{M_2}^{L_2}, (\{\mathbf{a}+\beta\mathbf{b}\}^1\{\nabla_a\}^{L_1-1})_{M_1}^{L_1}] ,$$

which, apart from a spherically symmetric factor, is the general result of operating with a single factor of ∇_a on a some s-type Gaussian matrix element involving centers **a** and **b**. For the complex spherical harmonics this commutator has three terms,

$$\begin{aligned}[\{\nabla_b\}_{M_2}^{L_2}, (\{\mathbf{a}+\beta\mathbf{b}\}^1\{\nabla_a\}^{L_1-1})_{M_1}^{L_1}]/L_2 &= \beta L_2 M_2^0 L_1 M_1^0 \{\nabla_b\}_{M_2}^{L_2-1}\{\nabla_a\}_{M_1}^{L_1-1} \\ &\quad - 2\beta L_2 M_2^+ L_1 M_1^- \{\nabla_b\}_{M_2+1}^{L_2-1}\{\nabla_a\}_{M_1-1}^{L_1-1} - 2\beta L_2 M_2^- L_1 M_1^+ \{\nabla_b\}_{M_2-1}^{L_2-1}\{\nabla_a\}_{M_1+1}^{L_1-1} ,\end{aligned} \tag{40}$$

where Eq. (38) and $\lambda = 1$ in Eq. (10) have been used. The right-hand side of this expression contains solid spherical harmonics of the ∇ operators that are both one unit of angular momentum lower than those that appear on the left-hand side. Thus, if one is willing to compute all matrix elements up to some highest angular momentum, then this expression can be used to move the result of operating with ∇_a, $\mathbf{a}+\beta\mathbf{b}$, through each ∇ operator to the left, one power and one ∇ operator at a time,

$$\begin{aligned}[\{\nabla_c\}_{M_3}^{L_3}\{\nabla_b\}_{M_2}^{L_2}, (\{\mathbf{a}+\beta\mathbf{b}+\gamma\mathbf{c}\}^1\{\nabla_a\}^{L_1-1})_{M_1}^{L_1}] &= \beta[\{\nabla_b\}_{M_2}^{L_2}, (\{\mathbf{b}\}^1\{\nabla_a\}^{L_1-1})_{M_1}^{L_1}]\{\nabla_c\}_{M_3}^{L_3} \\ &\quad + \gamma[\{\nabla_c\}_{M_3}^{L_3}, (\{\mathbf{c}\}^1\{\nabla_a\}^{L_1-1})_{M_1}^{L_1}]\{\nabla_b\}_{M_2}^{L_2} .\end{aligned} \tag{41}$$

Applying recursion to the three-center Coulomb repulsion matrix element, or using the r^2 functions of Eq. (14), requires additional complete sets of integrals where the s-type integral includes differentiation with respect to Q. The simplest equations result from using recursion involving the simplest ∇ first. This is accomplished by making it the rightmost operation,

$$\{\nabla_a\}_{M_1}^{L_1}\{\nabla_b\}_{M_2}^{L_2}\{\nabla_c\}_{M_3}^{L_3}\exp(-P)F^n(Q) = \frac{2\gamma(\alpha+\beta)}{\alpha+\beta+\gamma}\{\nabla_a\}_{M_1}^{L_1}\{\nabla_b\}_{M_2}^{L_2}(\{\mathbf{q}\}^1\{\nabla_c\}^{L_3-1})_{M_3}^{L_3}\exp(-P)F^{n+1}(Q) , \tag{42}$$

and using commutators to move the effect of operating with a single ∇_c all the way to the left,

$$\begin{aligned}&\{\nabla_a\}_{M_1}^{L_1}\{\nabla_b\}_{M_2}^{L_2}(\{\mathbf{q}\}^1\{\nabla_c\}^{L_3-1})_{M_3}^{L_3}\exp(-P)F^{n+1}(Q) \\ &\quad = (\{\mathbf{q}\}^1\{\nabla_c\}^{L_3-1})_{M_3}^{L_3}\{\nabla_a\}_{M_1}^{L_1}\{\nabla_b\}_{M_2}^{L_2}\exp(-P)F^{n+1}(Q) \\ &\quad\quad + [\{\nabla_a\}_{M_1}^{L_1}\{\nabla_b\}_{M_2}^{L_2}, (\{\mathbf{q}\}^1\{\nabla_c\}^{L_3-1})_{M_3}^{L_3}]\exp(-P)F^{n+1}(Q) .\end{aligned} \tag{43}$$

It is tedious, but straightforward, to extend this approach to four centers, thereby extending the method of Ref. 13 from Cartesian Gaussians to spherical harmonic Gaussians.

VII. CONCLUSION

This work has considered various ways of approaching the GTO LDF problem using an orbital basis of solid spherical harmonics. In general, this problem involves

solid harmonics about three centers, one of which may involve high angular momentum. Coupling the angular momenta of all harmonics involved in order to evaluate each matrix element appears impractical at the moment, because of the high dimension of the matrix needed to transform back from the coupled representation in which the matrix elements are computed to the uncoupled form in which they are used in existing self-consistent-field methods. Recursion has the advantage of using simple formulas. Recursion has the disadvantage of requiring the evaluation of unwanted low angular momentum matrix elements of the type considered, as well as completely different matrix elements in the case of the Coulomb repulsion.

In the current version of the LCGTO-LDF computer code recursion is used sparingly—only when matrix elements of all lower angular momenta are used. Tables II and III are heavily used in nonvectorizable computer code. The use of these tables, however, can be pulled out of the innermost loop over the primitive exponents of a given angular momentum about a given center. The computer code allows g orbital functions and can use up to $L=6$ functions for fitting the local potential.

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