Contracted auxiliary Gaussian basis integral and derivative evaluation

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The rapid evaluation of two-center Coulomb and overlap integrals between contracted auxiliary solid harmonic Gaussian functions is examined. Integral expressions are derived from the application of Hobson's theorem and Dunlap's product and differentiation rules of the spherical tensor gradient operator. It is shown that inclusion of the primitive normalization constants greatly simplifies the calculation of contracted functions corresponding to a Gaussian multipole expansion of a diffuse charge density. Derivative expressions are presented and it is shown that chain rules are avoided by expressing the derivatives as a linear combination of auxiliary integrals involving no more than five terms. Calculation of integrals and derivatives requires the contraction of a single vector corresponding to the monopolar result and its scalar derivatives. Implementation of the method is discussed and comparison is made with a Cartesian Gaussian-based method. The current method is superior for the evaluation of both integrals and derivatives using either primitive or contracted functions. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2821745]

I. INTRODUCTION

The development of accurate multiscale models for simulations of complex biochemical processes is an area of growing interest and importance. To this end, recent advancements in molecular mechanical (MM),[1–11] semiempirical quantum mechanical (QM),[12] and hybrid QM/MM (Ref. 13) methods have emphasized the use of auxiliary basis functions to treat the diffuse and multipolar character of electron density, and their incorporation within energetic models requiring the calculation of two-center Coulomb and overlap integrals. The purpose of this work is to present a new method for the rapid evaluation of these integrals and their derivatives using an auxiliary basis of contracted solid harmonic Gaussian (SHG) functions. Gaussian functions are a convenient choice for an auxiliary basis;[2] unlike integral pretabulation methods,[14,15] the spatial extent of Gaussians can be varied by adjusting their exponents, and they can be more readily generalized to high angular momentum. In addition, many *ab initio* methods use Gaussian functions as an orbital basis and, therefore, new methods employing auxiliary Gaussian functions can be seamlessly incorporated with existing methods[16–19] to facilitate the development of new multiscale models.

The primitive auxiliary SHG's considered here are

$$\chi_{l,\mu}(\mathbf{r};\zeta_\gamma) = N_{\gamma,l}C_{l,\mu}(\mathbf{r})e^{-\zeta_\gamma r^2}, \tag{1}$$

where $C_{l,\mu}(\mathbf{r})$ is a regular solid harmonic and $N_{\gamma,l}$ is the normalization constant

$$N_{\gamma,l} = \left(\frac{\zeta_\gamma}{\pi}\right)^{3/2}\frac{(2\zeta_\gamma)^l}{(2l-1)!!}, \tag{2}$$

which is chosen to reproduce unit multipole moment. Contracted auxiliary SHG's are constructed as a linear combination of primitive functions, i.e.,

$$\varphi_{l,\mu}(\mathbf{r}) = \sum_\gamma c_\gamma \chi_{l,\mu}(\mathbf{r};\zeta_\gamma). \tag{3}$$

The formulation presented herein is applicable to *any* two-center auxiliary SHG integral whose monopole result can be expressed in terms of the norm-squared separation between the two Gaussian centers, $|\mathbf{R}_a-\mathbf{R}_b|^2$, thus including: The two-center auxiliary SHG Coulomb

$$\begin{pmatrix} l_a & & l_b \\ \mu_a & |J| & \mu_b \end{pmatrix} = \int\int \frac{\varphi_{l_a,\mu_a}(\mathbf{r})\varphi_{l_b,\mu_b}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d^3rd^3r' \tag{4}$$

Gaussian multipole-point multipole Coulomb

$$\begin{pmatrix} l_a & & l_b \\ \mu_a & |V| & \mu_b \end{pmatrix} = \sum_{\alpha\in a} c_\alpha \lim_{\zeta_\beta\to\infty}\begin{bmatrix} l_a & & l_b \\ \mu_a & |J| & \mu_b \end{bmatrix} \tag{5}$$

and overlap integrals

$$\begin{pmatrix} l_a & & l_b \\ \mu_a & |S| & \mu_b \end{pmatrix} = \int \varphi_{l_a,\mu_a}(\mathbf{r})\varphi_{l_b,\mu_b}(\mathbf{r})d^3r, \tag{6}$$

where square and round brackets denote primitive and contracted integrals, respectively. The formulation of these integrals is based on the application of the spherical tensor gradient operator (STGO) theorem of Hobson,[20–26] and results in a method that does not require the calculation of intermediary integrals involving Cartesian[27] or Hermite[28] Gaussian functions. The resulting expressions can be used for segmented SHG's; however, in the interest of representing electron density with diffuse functions applicable to molecular dynamics simulations, we consider the more general case of treating all $(l_{max}+1)^2$ functions from $0\leq l\leq l_{max}$ *simultaneously*. One can consider this approach as being a Gaussian multipole expansion of a diffuse charge density.

There have been a number of articles describing Gaussian integral evaluation[16–19,23,29–44] in the context of *ab initio* theory.[45] The integrals examined herein are extraordinarily simple with respect to the four-center electron repulsion integrals found in *ab initio* methods; however, their efficient

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evaluation becomes very important when large systems are considered with new MM models. In this paper, we show that the inclusion of the normalization constants [Eq. (2)] within the construction of the present method has significant algorithmic consequences for both integral and derivative evaluation. For example, it is shown that the expressions for the contracted Coulomb integrals [Eq. (4)] and their derivatives require contraction of the Boys function *only*.

Section II develops the equations used for auxiliary SHG integral and derivative evaluation. Section III discusses the implementation of the method, and compares the performance with a Cartesian Gaussian-based method as a function of angular momentum and contraction length. The paper concludes in Sec. IV with a summary of the key results.

II. METHODS

Sections II A and II B derive the equations necessary to compute the integrals described in Sec. I. The notation used herein closely follows Ref. 46, which contains the definition and recurrence relations of the real regular scaled solid harmonics $R_{l,\mu}(\mathbf{r})$, their symmetry properties, and expressions for the translation matrix $\mathbf{W}(\mathbf{r})$. Reference 47 provides the Cartesian derivatives of $R_{l,\mu}(\mathbf{r})$. The relationship between the regular solid harmonics $C_{l,\mu}$ and the regular scaled solid harmonics is

$$C_{l,m}^{c/s}(\mathbf{r}) = A_{l,m} R_{l,m}^{c/s}(\mathbf{r}), \tag{7}$$

where

$$A_{l,m} = (-1)^m \sqrt{(2 - \delta_{m,0})(l+m)!(l-m)!}. \tag{8}$$

We adopt Watson and Helgaker's use of the cosine/sine decomposition of the complex harmonics and their usage of Greek subscripts [see Eq. (51) of Ref. 46].

A. Integral evaluation

In this section, we derive the expression for the integral

$$\begin{pmatrix} l_a \\ \mu_a \end{pmatrix} |O| \begin{pmatrix} l_b \\ \mu_b \end{pmatrix} = \int \int \varphi_{l_a,\mu_a}(\mathbf{r}) \varphi_{l_b,\mu_b}(\mathbf{r}') O(\mathbf{r} - \mathbf{r}') d^3r d^3r', \tag{9}$$

whose monopole result is a function of the square separation R_{ab}^2. In the case where $O(\mathbf{r} - \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}')$, Eq. (9) becomes the overlap integral, and when $O(\mathbf{r} - \mathbf{r}') = |\mathbf{r} - \mathbf{r}'|^{-1}$, the integral corresponds to the two-center Coulomb integral.

The derivation begins by first noting,

$$\chi_{l,\mu}(\mathbf{r} - \mathbf{R}_a) = \frac{1}{(2l-1)!!} C_{l,\mu}(\nabla_a) \chi_{0,0}(\mathbf{r} - \mathbf{R}_a), \tag{10}$$

where $C_{l,\mu}(\nabla_a)$ is the STGO (Refs. 20 and 21) acting on $\mathbf{R}_a$. Equation (9) becomes

$$\begin{pmatrix} l_a \\ \mu_a \end{pmatrix} |O| \begin{pmatrix} l_b \\ \mu_b \end{pmatrix} = \frac{C_{l_a,\mu_a}(\nabla_a) C_{l_b,\mu_b}(\nabla_b)}{(2l_a - 1)!!(2l_b - 1)!!} \begin{pmatrix} 0 \\ 0 \end{pmatrix} |O| \begin{pmatrix} 0 \\ 0 \end{pmatrix}. \tag{11}$$

Application of the Dunlap's product and differentiation rules of the STGO (Refs. 16–18 and 48) yields

$$\begin{pmatrix} l_a \\ \mu_a \end{pmatrix} |O| \begin{pmatrix} l_b \\ \mu_b \end{pmatrix}$$
$$= (-1)^{l_b} \sum_{j=0}^{\min(l_a,l_b)} \begin{pmatrix} 0 \\ 0 \end{pmatrix} |O| \begin{pmatrix} 0 \\ 0 \end{pmatrix}^{(l_a+l_b-j)}$$
$$\times \frac{2^{l_a+l_b-j}(2j-1)!!}{(2l_a-1)!!(2l_b-1)!!} \sum_{\kappa=-j}^{j} \widetilde{W}_{(l_a,\mu_a),(j,\kappa)}(\mathbf{R}_{ab})$$
$$\times \widetilde{W}_{(l_b,\mu_b),(j,\kappa)}(\mathbf{R}_{ab}), \tag{12}$$

where

$$\widetilde{W}_{(l,\mu),(j,\kappa)}(\mathbf{r}) = \frac{A_{l,\mu}}{A_{j,\kappa}} W_{(l,\mu),(j,\kappa)}(-\mathbf{r}) \tag{13}$$

is a type of translation matrix, and

$$\begin{pmatrix} 0 \\ 0 \end{pmatrix} |O| \begin{pmatrix} 0 \\ 0 \end{pmatrix}^{(n)} = \sum_{\alpha \in a} \sum_{\beta \in b} c_\alpha c_\beta \left(\frac{d}{dR_{ab}^2} \right)^n \begin{bmatrix} 0 \\ 0 \end{bmatrix} |O| \begin{bmatrix} 0 \\ 0 \end{bmatrix} \tag{14}$$

is a scalar derivative of the monopole integral, which we refer to as the *auxiliary vector*. By developing an analogous expression for the matrix transpose, one can show

$$\begin{pmatrix} l_a \\ \mu_a \end{pmatrix} |O| \begin{pmatrix} l_b \\ \mu_b \end{pmatrix} = (-1)^{l_b-l_a} \begin{pmatrix} l_b \\ \mu_b \end{pmatrix} |O| \begin{pmatrix} l_a \\ \mu_a \end{pmatrix}. \tag{15}$$

B. Derivative evaluation

In this section, we develop expressions for the Cartesian derivatives. Implementation of a naive chain-rule derivative of Eq. (12) would require nine to ten times more effort than computing the integrals alone. The derivative method described in this section circumvents this problem by reexpressing the product rule in terms of auxiliary integrals. The resulting expressions involve at most five terms, and the derivatives in each Cartesian direction reuse a *single* set of auxiliary integrals. The formation of the auxiliary integrals requires the same effort as that used to form the integrals and, therefore, using the method described herein, the effort used to evaluate the integrals and derivatives is only two to three times more than evaluation of the integrals alone.

The auxiliary integrals are constructed from a higher-order auxiliary vector, e.g., the first order auxiliary integrals are

$$\begin{pmatrix} l_a \\ \mu_a \end{pmatrix} |O| \begin{pmatrix} l_b \\ \mu_b \end{pmatrix}^{(1)}$$
$$= (-1)^{l_b} \sum_{j=0}^{\min(l_a,l_b)} \begin{pmatrix} 0 \\ 0 \end{pmatrix} |O| \begin{pmatrix} 0 \\ 0 \end{pmatrix}^{(l_a+l_b-j+1)}$$
$$\times \frac{2^{l_a+l_b-j}(2j-1)!!}{(2l_a-1)!!(2l_b-1)!!} \sum_{\kappa=-j}^{j} \widetilde{W}_{(l_a,\mu_a),(j,\kappa)}(\mathbf{R}_{ab})$$
$$\times \widetilde{W}_{(l_b,\mu_b),(j,\kappa)}(\mathbf{R}_{ab}). \tag{16}$$

The derivatives of $R_{l,\mu}(\mathbf{r})$ can be shown to be linear combinations of lower order (i.e., $l-1$) harmonics[47] and, therefore,

the derivatives of the translation matrix[46] are linear combinations of lower order translation matrix elements. By applying this property to the chain-rule derivative of Eq. (12), one can rewrite the derivatives as linear combinations of auxiliary integrals:

$$
\frac{d}{dx_a}\begin{pmatrix} c/s & c/s \\ l_a\ |O|\ l_b \\ m_a & m_b \end{pmatrix} = 2(x_a - x_b)\begin{pmatrix} c/s & c/s \\ l_a\ |O|\ l_b \\ m_a & m_b \end{pmatrix}^{(1)}
$$

$$
+ \frac{1}{2l_a - 1}\frac{A_{l_a,m_a}}{A_{l_a-1,m_a+1}}\begin{pmatrix} c/s & c/s \\ l_a-1\ |O|\ l_b \\ m_a+1 & m_b \end{pmatrix}^{(1)}
$$

$$
- \frac{1}{2l_a - 1}\frac{A_{l_a,m_a}}{A_{l_a-1,m_a-1}}\begin{pmatrix} c/s & c/s \\ l_a-1\ |O|\ l_b \\ m_a-1 & m_b \end{pmatrix}^{(1)}
$$

$$
- \frac{1}{2l_b - 1}\frac{A_{l_b,m_b}}{A_{l_b-1,m_b+1}}\begin{pmatrix} c/s & c/s \\ l_a\ |O|\ l_b-1 \\ m_a & m_b+1 \end{pmatrix}^{(1)}
$$

$$
+ \frac{1}{2l_b - 1}\frac{A_{l_b,m_b}}{A_{l_b-1,m_b-1}}\begin{pmatrix} c/s & c/s \\ l_a\ |O|\ l_b-1 \\ m_a & m_b-1 \end{pmatrix}^{(1)},
$$

$$(17)$$

$$
\frac{d}{dy_a}\begin{pmatrix} c/s & c/s \\ l_a\ |O|\ l_b \\ m_a & m_b \end{pmatrix} = 2(y_a - y_b)\begin{pmatrix} c/s & c/s \\ l_a\ |O|\ l_b \\ m_a & m_b \end{pmatrix}^{(1)}
$$

$$
+ \frac{(\pm)_{m_a}}{2l_a - 1}\frac{A_{l_a,m_a}}{A_{l_a-1,m_a+1}}\begin{pmatrix} s/c & c/s \\ l_a-1\ |O|\ l_b \\ m_a+1 & m_b \end{pmatrix}^{(1)}
$$

$$
+ \frac{(\pm)_{m_a}}{2l_a - 1}\frac{A_{l_a,m_a}}{A_{l_a-1,m_a-1}}\begin{pmatrix} s/c & c/s \\ l_a-1\ |O|\ l_b \\ m_a-1 & m_b \end{pmatrix}^{(1)}
$$

$$
- \frac{(\pm)_{m_b}}{2l_b - 1}\frac{A_{l_b,m_b}}{A_{l_b-1,m_b+1}}\begin{pmatrix} c/s & s/c \\ l_a\ |O|\ l_b-1 \\ m_a & m_b+1 \end{pmatrix}^{(1)}
$$

$$
- \frac{(\pm)_{m_b}}{2l_b - 1}\frac{A_{l_b,m_b}}{A_{l_b-1,m_b-1}}\begin{pmatrix} c/s & s/c \\ l_a\ |O|\ l_b-1 \\ m_a & m_b-1 \end{pmatrix}^{(1)},
$$

$$(18)$$

$$
\frac{d}{dz_a}\begin{pmatrix} c/s & c/s \\ l_a\ |O|\ l_b \\ m_a & m_b \end{pmatrix} = 2(z_a - z_b)\begin{pmatrix} c/s & c/s \\ l_a\ |O|\ l_b \\ m_a & m_b \end{pmatrix}^{(1)}
$$

$$
+ \frac{2}{2l_a - 1}\frac{A_{l_a,m_a}}{A_{l_a-1,m_a}}\begin{pmatrix} c/s & c/s \\ l_a-1\ |O|\ l_b \\ m_a & m_b \end{pmatrix}^{(1)}
$$

$$
- \frac{2}{2l_b - 1}\frac{A_{l_b,m_b}}{A_{l_b-1,m_b}}\begin{pmatrix} c/s & c/s \\ l_a\ |O|l_b-1 \\ m_a & m_b \end{pmatrix}^{(1)},
$$

$$(19)$$

where $(\pm)_m = +$ when m references a cosine component, i.e., $c/s = c$. It is worthwhile to briefly discuss the consequences of having included the normalization constants within the formulation in order to better understand the benefits of the method. Equations (17)–(19) are independent of primitive exponents and, therefore, these operations can be computed outside of the contraction loops; however, also note that the auxiliary integrals [Eq. (16)], themselves, are independent of primitive exponents. In addition, the only contracted quantity in Eq. (16) is the auxiliary vector, which is required to compute the integrals [Eq. (12)] *anyway*. In fact, the summation of translation matrix products appearing in Eqs. (12) and (16) are also in common. Finally, some of the terms in Eqs. (17)–(19) depend on l_a and others depend on $l_a - 1$ (and similarly for l_b); therefore, if a Gaussian multipole expansion of the density is considered, then only a single matrix of auxiliary integrals needs to be generated, the elements of which are reused multiple times for the derivatives corresponding to higher angular momentum functions.

III. RESULTS AND DISCUSSION

A. Implementation

This section describes the practical implementation of the method derived in Sec. II. The procedure for computing the integrals differs only by the calculation of the auxiliary vector and we, therefore, begin by providing expressions for these quantities.

The Coulomb integrals [Eq. (4)] require the calculation of the auxiliary vector [Eq. (14)] with operator $O = |\mathbf{r} - \mathbf{r}'|^{-1}$.

$$
[_0^0|J|_0^0]^{(n)} = \frac{2}{\sqrt{\pi}}\sqrt{\zeta_{\alpha\beta}}(-\zeta_{\alpha\beta})^n F_n(\zeta_{\alpha\beta}R_{ab}^2). \tag{20}
$$

where $\zeta_{\alpha\beta} = \zeta_\alpha \zeta_\beta/(\zeta_\alpha + \zeta_\beta)$ and $F_n(x)$ is the nth order Boys function. The Gaussian multipole-point multipole Coulomb integral auxiliary vector is a limiting case of Eq. (20), i.e.,

$$
[_0^0|V|_0^0]^{(n)} = \frac{2}{\sqrt{\pi}}\sqrt{\zeta_\alpha}(-\zeta_\alpha)^n F_n(\zeta_\alpha R_{ab}^2). \tag{21}
$$

Lastly, the overlap between two normalized spherical Gaussian functions is

TABLE I. Comparison of Coulomb integral FLOP counts. k_0 and k_2 indicate the distribution of independent and quadratic dependencies on contraction length, respectively (i.e., FLOPs=$k_0+k_2K^2$). The maximum angular momentum L_{max} and contraction length of either function are chosen to be identical. The total number of FLOPs correspond to the construction of the $(L_{max}+1)^4$ integral matrix elements (left set) or the $4(L_{max}+1)^4$ elements of integrals and derivatives (right set).

| | Integrals | | | | Integrals+Derivatives | | | |
| | H-L | | G-Y | | H-L | | G-Y | |
L_{max}	k_0	k_2	k_0	k_2	k_0	k_2	k_0	k_2
0	8	10	8	10	8	21	14	13
1	8	66	32	17	20	235	108	21
2	173	448	219	25	800	1292	792	29
3	933	1 929	1034	33	4 380	4 932	3 504	37
4	3353	6 381	3517	41	15 740	14 823	11 108	45
5	9713	17 501	9636	49	45 380	37 525	28 602	53

$$\begin{bmatrix}0\\0\end{bmatrix}|S|\begin{bmatrix}0\\0\end{bmatrix} = \left(\frac{\zeta_{\alpha\beta}}{\pi}\right)^{3/2} e^{-\zeta_{\alpha\beta}R_{ab}^2}, \tag{22}$$

which is used to initiate the following recurrence formula for the overlap auxiliary vector:

$$\begin{bmatrix}0\\0\end{bmatrix}|S|\begin{bmatrix}0\\0\end{bmatrix}^{(n)} = (-\zeta_{\alpha\beta})\begin{bmatrix}0\\0\end{bmatrix}|S|\begin{bmatrix}0\\0\end{bmatrix}^{(n-1)}. \tag{23}$$

The algorithm for computing the Coulomb and overlap integrals and derivatives differs only by the definition of the auxiliary vector described above and, therefore, the description of the implementations is made generic. To compute the $(l_{max,a}+1)^2(l_{max,b}+1)^2$ matrix of integrals, one performs the following steps: (1) Compute and contract the auxiliary vector (for $0 \leq n \leq l_a+l_b$) using Eq. (14) and either Eqs. (20), (21), and (23). (2) Compute $\widetilde{W}(\mathbf{R}_{ab})$ using Eq. (13). (3) Compute the integrals using Eq. (12). If derivatives are to be computed, then step (1) should compute an additional element, i.e., $0 \leq n \leq l_a+l_b+1$, and one would compute Eqs. (16)–(19). Assuming $l_a \geq l_b$, Eqs. (12) and (16)–(19) would only need to be evaluated for the $l_a \geq l_b$ elements, and the $l_b > l_a$ elements can be reconstructed from Eq. (15).

B. Performance and comparison with other methods

This section compares floating point operation (FLOP) counts and empirical timings of the integral and derivative method derived in Sec. II with a commonly used method employing Cartesian Gaussian functions. The Cartesian-based method involves the calculation of unnormalized Cartesian Gaussian integrals via recurrence relations, followed by normalization and linear transformation into solid harmonic representation. The Cartesian Gaussian recurrence relations are based on the works of Hamilton and Schaefer[33] and Lindh et al.,[34] and this method will henceforth be denoted as H-L. It has previously been noted that the Cartesian recurrence relations simplify for these integrals.[49,50] For example, Gill et al.[49] developed an OCL PRISM path for a more general case of two-center integrals, whereas we describe our H-L implementation as an OLC path written specifically to capture all intermediates necessary to reconstruct the $(l_{max,a}+1)^2(l_{max,b}+1)^2$ matrix of integrals. When $l_{max,a}=l_{max,b}$, for example, only half of the Cartesian integrals are required since Eq. (15) can reconstruct the missing values,

and all of the required Cartesian integrals are obtained as a consequence of recursion upon computing the maximum angular momentum target class. The method of Gill et al. will likely perform better than our H-L implementation for highly contracted functions; however, this section demonstrates the benefits of our method even for primitive integrals. For the purposes of differentiating the current and H-L methods in the tables and text, the algorithms outlined in Sec. III A are denoted as G-Y.

Table I compares the H-L and G-Y FLOP counts used in the evaluation of Coulomb integrals. The total number of FLOPs depends on the angular momentum L_{max} and contraction lengths K of either Gaussian function, which have been chosen to be identical for the purposes of discussion. The calculation of the Boys function, which would contribute identically to either method, is not included in Table I.

The H-L and G-Y FLOP distributions differ most significantly in the effort spent in the double loop over contractions; the Cartesian recurrence relations depend on primitive ζ exponents and, therefore, the entire lower diagonal of the Cartesian integral matrix needs to be constructed in the k_2 loop. In contrast, the G-Y method requires only the calculation of the auxiliary vector within the k_2 loop. The effect of this difference is significant at large L_{max} because the number of Cartesian integrals, for the cases considered here, scales proportionally to L_{max}^6, as opposed to the linear L_{max} dependence of the auxiliary vector. In addition, the H-L method requires a transformation from Cartesian to solid harmonic representation in the k_0 region. This constitutes nearly all H-L k_0 FLOPs in Table I, which is very close to the G-Y k_0 FLOP count. Examination of the derivative evaluation FLOP counts results in similar conclusions.

As a second measure of comparison, Table II provides empirical timings observed in the calculation of Coulomb integrals and integrals+derivatives, respectively. Table II indicates that the G-Y method is generally superior to the H-L method. For primitive functions with nonzero angular momentum, the G-Y integral evaluation is 2.5–6.4 times faster than H-L, and 4.4–8.2 times faster when derivatives are considered. G-Y is also faster when using highly contracted functions; the extent of which is related to the balance of effort expended within the k_0 and k_2 regions.

TABLE II. Comparison of Coulomb integral timings.

L_{max} [a]	K [a]	Integrals [b]			Integrals+Derivatives [c]		
		H-L	G-Y	Ratio	H-L	G-Y	Ratio
0	1	0.21	0.21	1.0	0.22	0.21	1.0
	2	0.64	0.65	1.0	0.71	0.66	1.1
	3	1.36	1.33	1.0	1.53	1.41	1.1
	4	2.36	2.31	1.0	2.66	2.46	1.1
1	1	0.66	0.27	2.5	1.76	0.40	4.4
	2	1.84	0.76	2.4	3.47	0.97	3.6
	3	4.05	1.54	2.6	6.17	1.90	3.3
	4	6.17	2.65	2.3	10.00	3.20	3.1
2	1	2.31	0.49	4.7	8.60	1.04	8.2
	2	5.11	1.14	4.5	13.55	1.73	7.8
	3	9.90	2.19	4.5	22.09	2.85	7.7
	4	16.15	3.67	4.4	33.11	4.41	7.5
3	1	8.05	1.25	6.4	33.62	4.84	7.0
	2	16.11	2.02	8.0	51.72	5.70	9.1
	3	29.62	3.22	9.2	81.66	7.07	11.6
	4	48.17	4.92	9.8	124.01	8.96	13.8
4	1	23.91	6.02	4.0	94.70	16.43	5.8
	2	53.43	6.94	7.7	153.09	17.38	8.8
	3	101.77	8.44	12.1	249.47	18.99	13.1
	4	168.09	10.55	15.9	384.64	21.29	18.1
5	1	56.39	16.32	3.5	229.81	38.68	5.9
	2	137.42	17.38	7.9	377.04	39.79	9.5
	3	267.43	19.14	14.0	615.91	41.67	14.8
	4	452.71	21.52	21.0	954.81	44.23	21.6

[a]L_{max} and K are the angular momentum and contraction length of each function, which are chosen to be identical.
[b]The observed time (microseconds) required to compute the set of $(L_{max}+1)^4$ contracted integrals using the H-L and G-Y methods. Ratio is H-L/G-Y.
[c]The observed time required to compute the integrals and the $3(L_{max}+1)^4$ derivatives. These timings were performed on an Intel Core2 6300 1.8 GHz processor with 2 Mbytes of cache and 2 Gbytes of random access memory, and computer code was compiled with the Intel FORTRAN COMPILER V10.0 using the options "-axT -O3 -static."

IV. CONCLUSION

The present work used Hobson's theorem to derive expressions for the efficient evaluation of Coulomb and overlap SHG integrals and derivatives important for molecular simulation quantum and empirical force field models that utilize a Gaussian basis to represent the electron density. The method presented herein has been shown, by measure of FLOP counts and empirical timings, to be superior to traditional Cartesian Gaussian-based methods for both primitive and contracted basis sets for nontrivial angular momentum; and to depend very weakly on contraction length, making it ideal for contracted Gaussians.

Expressions for the Cartesian derivatives were shown to be compactly written in terms of auxiliary integrals, and involve no more than five terms. It has also been shown that inclusion of normalization constants leads to integral and derivative expressions that are independent of primitive ζ exponents. In addition, by choosing to contract each angular momentum in a consistent way, only a single set of auxiliary integrals need to be generated to compute the derivatives for *all* angular momentum. Utilization of these properties leads to a method that requires the calculation and contraction of a single auxiliary vector, whose length scales linearly with respect to angular momentum.

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