A multipole acceptability criterion for electronic structure theory

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(August 18, 1998)

Abstract

Accurate and computationally inexpensive estimates of multipole expansion errors are crucial to the success of several fast electronic structure methods. In this paper, a new non-empirical multipole acceptability criterion is described that is directly applicable to expansions of high order moments. Several model calculations typical of electronic structure theory are presented to demonstrate its performance. For cases involving small translation distances, accuracies are increased by up to five orders of magnitude over an empirical criterion. The new multipole acceptance criterion is on average within an order of magnitude of the exact expansion error. Use of the multipole acceptance criterion in hierarchical multipole based methods as well as in traditional electronic structure methods is discussed.

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I. INTRODUCTION

New computational methods have greatly extended the applicability of electronic structure theory. In particular, hierarchical methods such as treecodes [1–5] and the fast multipole method [6–11], originally developed to solve the classical N-body problem, have recently been generalized to accelerate computation of the Coulomb matrix [12–16]. In addition, a number of non-multipole based methods have appeared for linear scaling computation of the Hartree-Fock exchange matrix [17–20].

The efficiency of hierarchical multipole based methods depends to a large extent on how aggressively the multipole approximation is applied. When the approximation is used to represent a sufficiently large number of direct interactions a savings can be achieved. However, these savings do not come for free. As expansions are truncated at a finite order, errors accumulate, and must be controlled to ensure a reliable and accurate method.

Truncation errors are controlled primarily with a multipole acceptability criterion (MAC) in treecodes, or with a well separated index in the fast multipole method. Both MACs and well separated indices serve a similar purpose, which is to estimate the truncation error in a given multipole expansion. Since treecodes and fast multipole methods have their origin in classical particle simulations, error estimates have traditionally been developed for systems of interacting point (monopole) charges. However, in electronic structure calculations translations of higher order moments are encountered. In these situations it is common practice to use empirical error estimates based on expansions of monopole moments [12,14,15]. In continuous fast multipole methods such as CFMM [12] or GvFMM [14] an empirical error estimate is acceptable as interactions are tested on the basis of worst-case cell-cell interactions, where "cell" refers to a collection of particles represented by a multipole expansion. However in the quantum chemical tree code (QCTC) [15], MACs are applied on a finer level to multipole-cell interactions. In this case, substantial benefits may be gained by using non-empirical, numerically tight MACs.

The importance of tight MACs may be even greater for the direct evaluation of electron repulsion integrals (ERIs). For example, large savings can be achieved when individual ERIs are computed in a multipole representation [21–24]. In electronic structure methods, ERIs are usually computed between products of Gaussian-type basis functions, also referred to as Gaussian distributions. The Gaussian product theorem states that the product of two Gaussians can be expressed exactly as a finite sum of one-center Gaussians. For example, the product of two s-type Gaussians is

$$e^{\zeta_a(\mathbf{r}-\mathbf{A})^2} e^{\zeta_b(\mathbf{r}-\mathbf{B})^2} = e^{\xi(\mathbf{A}-\mathbf{B})^2} e^{\zeta_{r_1}(\mathbf{r}-\mathbf{r}_1)^2}, \tag{1}$$

where $\xi = \zeta_a\zeta_b/\zeta_{r_1}$, $\mathbf{r}_1 = (\zeta_a\mathbf{A} + \zeta_b\mathbf{B})/\zeta_{r_1}$, and $\zeta_{r_1} = \zeta_a + \zeta_b$. In addition, basis functions may consist of a contraction of K primitive functions where each primitive has a different exponent, ζ_a. Rather than a single center, $\mathbf{r}_1$, contracted distributions form finite expansions at K^2 centers between the originating basis functions. Therefore, evaluation of a contracted ERI involves computation of K^4 primitive ERIs, which is a computationally demanding requirement.

One approach for avoiding the contraction problem involves using the multipole approximation to translate sets of primitive distributions about common centers [25–27]. This is illustrated in Figure 1, which shows a typical set of primitive distributions centered at $\mathbf{r}_1'$, $\mathbf{r}_1''$, and $\mathbf{r}_1'''$ between basis functions at $\mathbf{A}$ and $\mathbf{B}$. For those ERIs that involve well separated distributions, contractions can be precomputed at the level of basis function products instead of on primitive ERIs, which leads to a reduction in computational work from $\mathcal{O}(K^4)$ to $\mathcal{O}(1)$. As contraction lengths of high quality basis sets can be on the order of ten, this method offers the possibility of large improvements in the computation of ERIs.

In addition to avoiding contraction steps in ERI evaluation, the multipole representation also allows a straightforward reduction in the complexity of ERI computation with respect to their total angular symmetry. For a given total angular symmetry $\mathcal{L}$, spherical multipole interaction tensors can be used that involve only $\mathcal{O}(\mathcal{L}^2)$ work as compared to the $\mathcal{O}(\mathcal{L}^4)$ work required in corresponding Cartesian representations.

Since electronic structure methods involve continuous distributions, errors may also arise from penetration effects when a multipole representation is used [13]. This situation is illustrated in Figure 2. However, preliminary results indicate that penetration errors are secondary to truncation errors [28].

Despite the important advantages to both hierarchical and direct methods for ERI evaluation, no attention has been given to the development of a tight non-empirical MAC for the high order moments encountered in quantum chemistry. In this paper, truncated multipole expansions are examined in detail. Existing error estimates for the expansion of $|\mathbf{r}_1 - \mathbf{r}_2|^{-1}$ are reviewed and extended to high angular symmetry moments. In this development emphasis is placed on balancing numerical accuracy with computational simplicity so that the resulting MAC can be used effectively on the fly. The paper is organized as follows: In the next Section, the multipole limit of Gaussian based ERIs is discussed. In Section III A, existing methods for the expansion and corresponding error estimate of $|\mathbf{r}_1 - \mathbf{r}_2|^{-1}$ are reviewed. Then, in Section III B, the error estimates are extended to high order moments and simplified to a form suitable for use as a MAC. In Section IV, several model systems similar to those found in electronic structure theory are used to demonstrate the performance of the new MAC. These results are discussed in Section V, and in Section VI, we present our conclusions.

II. THE MULTIPOLE LIMIT OF ERIS

In modern quantum chemistry, the basis functions of choice are the Cartesian Gaussian type functions (CGTFs) [29],

$$\phi_a(\mathbf{r}) = (r_x - A_x)^{l_a} (r_y - A_y)^{m_a} (r_z - A_z)^{n_a} \times \exp\left[-\zeta_a (\mathbf{r} - \mathbf{A})^2\right], \tag{2}$$

which enable the analytic evaluation of electron repulsion integrals (ERIs) [29–36],

$$(\phi_a \phi_b | \phi_c \phi_d) = \int\int d\mathbf{r} d\mathbf{r}' \phi_a(\mathbf{r}) \phi_b(\mathbf{r}) \frac{1}{|\mathbf{r} - \mathbf{r}'|} \phi_c(\mathbf{r}') \phi_d(\mathbf{r}'). \tag{3}$$

Throughout this paper, basis functions with $l_a + m_a + n_a = 0, 1, 2$ are referred to as s, p, and d-type respectively.

It is often convenient to represent products of CGTFs, which we will refer to as distributions, with exact one center expansions in Hermite Gaussian type functions (HGTFs):

$$\phi_a(\mathbf{r})\,\phi_b(\mathbf{r}) = \sum_{L=0}^{l_a+l_b} \sum_{M=0}^{m_a+m_b} \sum_{N=0}^{n_a+n_b} e^{ab}_{LMN} \Lambda^{\mathbf{r}_1}_{LMN}(\mathbf{r})\,, \tag{4}$$

where e^{ab}_{LMN} are the expansion coefficients obtained with the McMurchie-Davidson two term recurrence relations [32] and multiplied by the appropriate radial overlap. The HGTFs centered at $\mathbf{r}_1$ are

$$\Lambda^{\mathbf{r}_1}_{LMN}(\mathbf{r}) = \frac{\partial^L}{\partial r^L_{1x}} \frac{\partial^M}{\partial r^M_{1y}} \frac{\partial^N}{\partial r^N_{1z}} \exp\left[-\zeta\,(\mathbf{r}-\mathbf{r}_1)^2\right]. \tag{5}$$

In the multipole limit, HGTFs are related to derivatives of the Dirac delta function by

$$\begin{aligned}\delta^{\mathbf{r}_1}_{LMN}(\mathbf{r}) &= \frac{\partial^L}{\partial r^L_{1x}} \frac{\partial^M}{\partial r^M_{1y}} \frac{\partial^N}{\partial r^N_{1z}}\ \delta(\mathbf{r}-\mathbf{r}_1) \\ &= \lim_{\zeta\to\infty} \left(\frac{\zeta}{\pi}\right)^{3/2} \Lambda^{\mathbf{r}_1}_{LMN}(\mathbf{r})\,,\end{aligned} \tag{6}$$

which enables ERIs over HGTFs to be evaluated with the Cartesian multipole interaction tensor [13,37] as

$$\begin{aligned}(\Lambda^{\mathbf{r}_1}_{LMN}|\Lambda^{\mathbf{r}_2}_{L'M'N'}) &= (-1)^{L+M+N} \left(\frac{\pi}{\sqrt{\zeta_{ab}\zeta_{cd}}}\right)^3 \\ &\times \frac{\partial^{L+L'}}{\partial r^{L+L'}_{12x}} \frac{\partial^{M+M'}}{\partial r^{M+M'}_{12y}} \frac{\partial^{N+N'}}{\partial r^{N+N'}_{12z}} \frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}.\end{aligned} \tag{7}$$

III. ERROR ESTIMATES

Since matrix elements in electronic structure theory involve summation of interactions spanning many orders of magnitude, we focus on estimates of absolute error. Relative error estimates are non-optimal because computing small interactions to a high relative accuracy leads to unnecessary computational work that has little or no effect on the total accumulated error of each matrix element.

A. Estimates for $|\mathbf{r}_1 - \mathbf{r}_2|^{-1}$

The truncated bipolar expansion of $|\mathbf{r}_1 - \mathbf{r}_2|^{-1}$ about centers $\mathbf{P}$ and $\mathbf{Q}$, as in Figure 3, can be carried out in several different representations [37–41]. For example, in terms of the associated Legendre polynomials, $P_l^m(x)$, the truncated expansion is [42]

$$\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \approx \sum_{l_p=0}^{p} (-1)^{l_p} \sum_{m_p=-l_p}^{l_p} O_{l_p}^{m_p}[\mathbf{r}_1 - \mathbf{P}] \times \sum_{l_q=0}^{q} \sum_{m_q=-l_q}^{l_q} M_{l_p+l_q}^{m_p+m_q}[\mathbf{P} - \mathbf{Q}] \, O_{l_q}^{m_q}[\mathbf{r}_2 - \mathbf{Q}] \tag{8}$$

where

$$O_l^m[\mathbf{r}] = \frac{r^l}{(l+m)!} P_l^m(\cos\theta_{\mathbf{r}}) \, e^{-im\phi_{\mathbf{r}}} \tag{9}$$

and

$$M_l^m[\mathbf{R}] = \frac{(l-m)!}{R^{l+1}} P_l^m(\cos\theta_{\mathbf{R}}) \, e^{im\phi_{\mathbf{R}}}. \tag{10}$$

The orders of expansion about the new centers $\mathbf{P}$ and $\mathbf{Q}$ are p and q respectively. Expansions in both Cartesian and spherical representations that are truncated at the same level yield equivalent errors.

Recently, the error of expanding $|\mathbf{r}_1 - \mathbf{r}_2|^{-1}$ in the context of the fast multipole method has been thoroughly investigated [43–45]. For expansions truncated at order p and q, the absolute error

$$\epsilon = \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} - \sum_{l_p=0}^{p} (-1)^{l_p} \sum_{m_p=-l_p}^{l_p} O_{l_p}^{m_p}[\mathbf{r}_1 - \mathbf{P}] \times \sum_{l_q=0}^{q} \sum_{m_q=-l_q}^{l_q} M_{l_p+l_q}^{m_p+m_q}[\mathbf{P} - \mathbf{Q}] \, O_{l_q}^{m_q}[\mathbf{r}_2 - \mathbf{Q}] \tag{11}$$

may be partitioned as

$$\epsilon = \epsilon_1 + \epsilon_2 + \epsilon_{12} \tag{12}$$

where

$$\epsilon_1 = \sum_{l=p+1}^{\infty} \frac{|\mathbf{r}_1 - \mathbf{P}|^l}{|\mathbf{P} - \mathbf{r}_2|^{l+1}} P_l\left(\cos\theta_1\right), \tag{13}$$

$$\epsilon_2 = \sum_{l=q+1}^{\infty} \frac{|\mathbf{r}_2 - \mathbf{Q}|^l}{|\mathbf{Q} - \mathbf{r}_1|^{l+1}} P_l\left(\cos\theta_2\right), \tag{14}$$

and $\cos\theta_1 = \left(\widehat{\mathbf{P} - \mathbf{r}_1} \cdot \widehat{\mathbf{P} - \mathbf{r}_2}\right)$. Equations (13) and (14) correspond to one-center expansion errors where the translations $(\mathbf{r}_1 - \mathbf{P})$ and $(\mathbf{r}_2 - \mathbf{Q})$ in Figure 3 are considered independently. The quantity ϵ_{12} represents a cross term in the bipolar expansion error that becomes significant only with $p, q \geq 10$ [45]. Equations (13) and (14) provide a numerically tight estimate and are useful for estimating the total error in the fast multipole method for a given expansion order.

To balance accuracy and computational simplicity, we replace the Legendre polynomials in Eqs. (13) and (14) with the bound $P_l(\cos\theta) \leq 1$ [42,46]. This is equivalent to assuming a one-dimensional worst-case orientation where translations are in opposite directions pointing away from each other. The summations in Eqs. (13) and (14) can then be evaluated exactly to yield the compact forms

$$\epsilon_1 \leq \left(\frac{1}{|\mathbf{r}_2 - \mathbf{P}| - |\mathbf{r}_1 - \mathbf{P}|}\right) \left(\frac{|\mathbf{r}_1 - \mathbf{P}|}{|\mathbf{r}_2 - \mathbf{P}|}\right)^{p+1}, \tag{15}$$

and

$$\epsilon_2 \leq \left(\frac{1}{|\mathbf{r}_1 - \mathbf{Q}| - |\mathbf{r}_2 - \mathbf{Q}|}\right) \left(\frac{|\mathbf{r}_2 - \mathbf{Q}|}{|\mathbf{r}_1 - \mathbf{Q}|}\right)^{q+1}. \tag{16}$$

Further simplifications of ϵ_1 and ϵ_2 are possible by assuming that translations are much smaller than interaction distances (see Figure 3);

$$|\mathbf{r}_1 - \mathbf{P}| \ll |\mathbf{P} - \mathbf{Q}| \;\text{ and }\; |\mathbf{r}_2 - \mathbf{Q}| \ll |\mathbf{P} - \mathbf{Q}|. \tag{17}$$

This assumption leads to the following approximate expression for the total error

$$\epsilon \approx \frac{|\mathbf{r}_1 - \mathbf{P}|^{p+1}}{|\mathbf{r}_2 - \mathbf{P}|^{p+2}} + \frac{|\mathbf{r}_2 - \mathbf{Q}|^{q+1}}{|\mathbf{r}_1 - \mathbf{Q}|^{q+2}}. \tag{18}$$

Equation (18) is a tight and relatively cheap estimate of the absolute error introduced by truncating the bipolar expansion of $|\mathbf{r}_1 - \mathbf{r}_2|^{-1}$.

B. Extension to arbitrary moments

In the evaluation of HGTF-based ERIs, Eq. (7), $|\mathbf{r}_1 - \mathbf{r}_2|^{-1}$ can be replaced with a bipolar expansion about two new centers as in Eq. (8). The corresponding error that the truncated expansion involves can be estimated by replacing $|\mathbf{r}_1 - \mathbf{r}_2|^{-1}$ in Eq. (7) with Eq. (18) to yield

$$
\begin{aligned}
\epsilon \approx\ & (-1)^{L+M+N+L'+M'+N'} \left(\frac{\pi}{\sqrt{\zeta_{ab}\zeta_{cd}}} \right)^3 \\
& \times \frac{\partial^L}{\partial r_{1x}^L} \frac{\partial^M}{\partial r_{1y}^M} \frac{\partial^N}{\partial r_{1z}^N} \frac{\partial^{L'}}{\partial r_{2x}^{L'}} \frac{\partial^{M'}}{\partial r_{2y}^{M'}} \frac{\partial^{N'}}{\partial r_{2z}^{N'}} \\
& \times \left(\frac{|\mathbf{r}_1 - \mathbf{P}|^{p+1}}{|\mathbf{r}_2 - \mathbf{P}|^{p+2}} + \frac{|\mathbf{r}_2 - \mathbf{Q}|^{q+1}}{|\mathbf{r}_1 - \mathbf{Q}|^{q+2}} \right) .
\end{aligned} \tag{19}
$$

Equation (19) is prohibitively expensive for evaluation on the fly. To achieve an inexpensive MAC we once again ignore angular effects and assume a one-dimensional orientation to arrive at

$$
\begin{aligned}
\epsilon \approx\ & \left(\frac{\pi}{\sqrt{\zeta_{ab}\zeta_{cd}}} \right)^3 \\
& \times \left[(-1)^{\mathcal{L}'} \mathcal{M}_1^p [\mathcal{L}, \mathcal{L}'] + (-1)^{\mathcal{L}} \mathcal{M}_2^q [\mathcal{L}', \mathcal{L}] \right] ,
\end{aligned} \tag{20}
$$

where

$$
\begin{aligned}
\mathcal{M}_1^p [0,0] &= \frac{|\mathbf{r}_1 - \mathbf{P}|^{p+1}}{|\mathbf{r}_2 - \mathbf{P}|^{p+2}} , \\
\mathcal{M}_1^p [i,0] &= \mathcal{M}_1^p [i-1,0] \frac{(p-i+2)}{|\mathbf{r}_1 - \mathbf{P}|} , \quad i > 0 \\
\mathcal{M}_1^p [i,j] &= \mathcal{M}_1^p [i,j-1] \frac{(p+j+1)}{|\mathbf{r}_2 - \mathbf{P}|} , \quad j > 0 .
\end{aligned} \tag{21}
$$

By contraction with the MD two-term expansion coefficients, as in Eq. (4), and summing the magnitude of each component, a MAC applicable to CGTF based integrals involving distributions of angular symmetry $l_{ab} = (l_a + l_b + m_a + m_b + n_a + n_b)$ is

$$
\begin{aligned}
& \mathrm{MAC}[l_{ab}, l_{cd}] = \\
& \qquad \sum_{i=0}^{l_{ab}} \sum_{j=0}^{l_{cd}} c_i^{ab} c_j^{cd} \left(|\mathcal{M}_1^p [i,j]| + |\mathcal{M}_2^q [j,i]| \right)
\end{aligned} \tag{22}
$$

where

$$c_i^{ab} = \max_{L+M+N=i} \left[\left| e_{LMN}^{ab} \right| \right] \left(\frac{\pi}{\zeta_{ab}} \right)^{3/2} . \tag{23}$$

It should be noted that Eq. (23) can be precomputed and contracted with the appropriate translation distances ($|\mathbf{r}_1 - \mathbf{P}|$ and $|\mathbf{r}_2 - \mathbf{Q}|$) at the level of distributions, which enables Eq. (22) to be efficiently applied at the level of interactions.

IV. RESULTS

Previous empirical estimates of the truncated multipole expansion error have been based on approximating translation errors of arbitrary angular symmetry moments with expressions derived for the lowest order case [12,14,15]. To compensate for neglecting the effect of higher order terms, an empirically determined safety or fudge factor is usually included in the estimate. In terms of the MAC developed here, this approach is equivalent to using the $i = j = 0$ component only in Eq. (22) to describe higher angular symmetry moments. In the following sections we examine the overall performance as well as the specific cases where MAC$[l_{ab}, l_{cd}]$ offers a significant advantage over MAC$[0, 0]$.

A. Statistical performance

To investigate the statistical performance of the MACs we have constructed several model systems. Each system consists of 100 distributions of particular angular symmetry. The distributions were formed from two-center products of normalized CGTFs that were chosen randomly within a sphere of a given radius. The exponents of the CGTFs were selected as $\zeta = 10^n$ with n distributed uniformly in the range $[-1, 3]$. The radial overlap of the CGTF products used were required to be greater than 10^{-7}. Random expansion centers for each distribution were chosen to be within a given distance from the original distribution centers. Hereafter, the distance between expansion and distribution centers, $|\mathbf{r}_1 - \mathbf{P}|$ in Figure 1, will be referred to as the translation distance.

The relative performance of MAC$[l_{ab}, l_{cd}]$ and MAC$[0,0]$ were compared by observing the order of magnitude deviation of each MAC from the exact multipole expansion error,

$$\mathcal{D} = \mathrm{Log}_{10}\left(\frac{\text{error}}{\text{MAC}}\right). \tag{24}$$

Positive values of $\mathcal{D}$ correspond to an underestimation and negative values to an overestimation of the expansion error.

Tables I and II summarize the statistical behavior of MAC$[l_{ab}, l_{cd}]$ and MAC$[0,0]$ for a variety of integral types. In each case the systems consist of the two interacting spheres shown in Figure 4, which have radii of 2 atomic units (au) and centers that are separated by 10 au. Random translation distances for each distribution were chosen to be within the range $[0, 2]$ au, such that the resulting expansion centers remain within the distribution sphere.

For the systems examined in Tables I and II, the multipole expansions were truncated at the same level ($p = l_{ab}$ and $q = l_{cd}$) as the largest non-zero untranslated distribution moment. In Tables III and IV the effects of increasing the expansion level on the performance of MAC$[l_{ab}, l_{cd}]$ and MAC$[0,0]$ are shown for the integral types $(pp|pp)$ and $(dd|dd)$.

B. Effect of translation distance

For Tables I to IV, the model systems employed involve a mixture of many different exponent sizes, translation distances, as well as orientations. It is therefore difficult to determine the exact conditions for which the MACs perform poorly. In order to examine these issues in more detail we have constructed a simple one-dimensional system. The system consists of a single integral of type $(pp|pp)$ located along the z-axis. The centers of the $(pp|$ and the $|pp)$ distributions are separated by 10 au. Figure 5 illustrates the behavior of $\mathcal{D}$ for MAC$[l_{ab}, l_{cd}]$ and MAC$[0,0]$ as the translation distance, $|\mathbf{r}_1 - \mathbf{P}|$, is increased. This dependence of the MACs on the translation distance holds for other integral types and orientations as well and becomes more pronounced for MAC$[0,0]$ as the angular symmetry is increased. In Table V the behavior of MAC$[0,0]$ is demonstrated for three-dimensional systems of $(pp|pp)$ integrals, for which the random translations have been restricted to the range $[t_{\min}, t_{\max}]$.

V. DISCUSSION

Inspection of Table I reveals that MAC$[l_{ab}, l_{cd}]$ performs quite well for the integral types studied, and is on average less than an order of magnitude from the exact expansion error. In particular, $\mathcal{D}$ is essentially always less than zero, which indicates that the error is not underestimated. The average value of $\mathcal{D}$ is shifted below zero because angular factors have been neglected.

As shown in Table II, MAC$[0,0]$ is not able to effectively represent the expansion error for higher angular symmetry moments. In the highest angular symmetry case considered here, $(dd|dd)$, MAC$[0,0]$ underestimates the expansion error by nearly five orders of magnitude. Although the average deviation of MAC$[0,0]$ remains small, the large positive values of $\mathcal{D}$ make it useless as an estimate for higher order moments.

Figure 5 dramatically shows how the translation distance can affect the performance of the MAC. As expected, MAC$[l_{ab}, l_{cd}]$ remains accurate for the entire range of translation distances. However, for MAC$[0,0]$ it becomes clear that large positive values of $\mathcal{D}$ occur primarily for small translations. As the translation distance is increased the performance of MAC$[0,0]$ also increases. This behavior of MAC$[0,0]$ is demonstrated again for a more general three-dimensional distribution of $(pp|pp)$ type integrals in Table V. By restricting minimum as well as maximum allowed translation distances, the ability of MAC$[0,0]$ to estimate expansion errors of high order moments can be improved to an acceptable level.

VI. CONCLUSIONS

Fast methods for computing long range interaction potentials are rapidly changing the field of electronic structure theory. Importantly, these methods are able to achieve a reduced computational complexity without sacrificing numerical accuracy. However, their efficiency depends critically on accurate estimates of the errors incurred. This situation is quite similar to direct SCF methods [47], which were greatly enhanced with the advent of rigorous integral prescreening techniques [48,49].

The new MAC developed here represents a significant improvement for estimating the expansion error of high order moments. By enabling the aggressive application of the multipole approximation, the MAC is expected to have a large impact on hierarchical methods such as QCTC [15] and direct methods such as ONX [19] and LinK [20]. Although the emphasis has been on moments originating from continuous charge distributions, the basic results apply as well to multipole interactions that arise in semiempirical [50] and classical [11] methods.

The increases in accuracy afforded by the new MAC need to be weighed against the increased cost of its evaluation. The largest improvements in accuracy are shown to occur with systems that involve small translation distances, which are characteristic of the finest levels of spatial decomposition in hierarchical multipole methods, and of multipole based methods for direct ERI evaluation in general.

VII. ACKNOWLEDGMENTS

This work has been supported by the ASCI program at Los Alamos National Laboratory, and by the Laboratory Directed Research and Development Program of the Ernest Orlando Lawrence Berkeley National Laboratory under the U.S. Department of Energy, Contract No. DE-AC03-76SF00098.

TABLES

TABLE I. Statistics of MAC$[l_{ab}, l_{cd}]$ for various integral types with $p = l_{ab}$ and $q = l_{cd}$. Distributions are in spheres of radius 2 au, which have centers separated by 10 au. Translations are restricted to [0,2] and exponents to [0.1,1000]. Max, Avg, and δ are the maximum, average, and standard deviation of $\mathcal{D}$.

Type	p	q	Max($\mathcal{D}$)	Avg($\mathcal{D}$)	δ
$(ss\|ss)$	0	0	0.14	-0.5	0.4
$(ps\|ss)$	1	0	0.17	-0.5	0.5
$(pp\|ss)$	2	0	0.20	-0.5	0.5
$(ps\|ps)$	1	1	0.21	-0.7	0.5
$(pp\|ps)$	2	1	0.23	-0.8	0.5
$(pp\|pp)$	2	2	0.24	-1.0	0.6
$(dd\|dd)$	4	4	0.19	-1.2	0.6

TABLE II. Statistics of MAC$[0, 0]$ for various integral types. Distributions are in spheres of radius 2 au, which have centers separated by 10 au. Translations are restricted to [0,2] and exponents to [0.1,1000].

Type	p	q	Max($\mathcal{D}$)	Avg($\mathcal{D}$)	δ
$(ss\|ss)$	0	0	0.14	-0.5	0.4
$(ps\|ss)$	1	0	0.68	-0.5	0.5
$(pp\|ss)$	2	0	0.53	-0.6	0.6
$(ps\|ps)$	1	1	1.67	-0.5	0.5
$(pp\|ps)$	2	1	2.14	-0.5	0.6
$(pp\|pp)$	2	2	2.42	-0.5	0.7
$(dd\|dd)$	4	4	4.63	-0.2	0.8

TABLE III. Statistics of MAC[l_{ab}, l_{cd}] for the integral types $(pp|pp)$ and $(dd|dd)$ with increasing q. Distributions are in spheres of radius 2 au, which are separated by 10 au. Translations of the $(pp|$ and $(dd|$ distributions are limited to the range $[0, 1]$ and the $|pp)$ and $|dd)$ distributions to the range $[0, 4]$.

Type	p	q	Max($\mathcal{D}$)	Avg($\mathcal{D}$)	δ
$(pp\|pp)$	2	2	0.13	-0.9	0.5
	2	4	0.24	-1.0	0.5
	2	6	0.29	-0.9	0.5
	2	8	0.31	-0.9	0.5
$(dd\|dd)$	4	4	-0.15	-1.3	0.5
	4	6	-0.13	-1.2	0.5
	4	8	-0.28	-1.4	0.5

TABLE IV. Statistics of MAC[0,0] for the integral $(pp|pp)$ and $(dd|dd)$ with increasing q. Distributions are in spheres of radius 2 au, which are separated by 10 au. Translations of the $(pp|$ and $(dd|$ distributions are limited to the range $[0, 1]$ and the $|pp)$ and $|dd)$ distributions to the range $[0, 4]$.

Type	p	q	Max($\mathcal{D}$)	Avg($\mathcal{D}$)	δ
$(pp\|pp)$	2	2	1.35	-1.0	0.6
	2	4	2.31	-0.8	0.7
	2	6	2.33	-0.5	0.8
	2	8	2.34	-0.4	0.8
$(dd\|dd)$	4	4	4.32	-0.9	0.7
	4	6	5.20	-0.7	0.9
	4	8	5.33	0.2	1.0

TABLE V. Statistics of MAC[0, 0] for the integral type $(pp|pp)$. Distributions are in spheres of radius 3 au, which have centers separated by 10 au. Translations are restricted to the interval $[t_{\mathrm{min}}, t_{\mathrm{max}}]$.

t_{min}	t_{max}	Max($\mathcal{D}$)	Avg($\mathcal{D}$)	δ
0.00	0.25	4.4	0.5	0.8
0.25	0.50	1.4	-0.1	0.6
0.50	0.75	0.9	-0.3	0.5
0.75	1.00	0.8	-0.5	0.5
1.00	2.00	0.8	-0.7	0.6
2.00	3.00	0.7	-0.8	0.6

FIGURES

FIG. 1. A set of primitive distributions located at $\mathbf{r}_1'$, $\mathbf{r}_1''$, and $\mathbf{r}_1'''$, which are translated with the multipole approximation to a common center $\mathbf{P}$ and contracted.

FIG. 2. A schematic of penetration effects that can occur between continuous distributions. In a) there is significant penetration between the two distributions that is not accounted for in a multipole representation. In b) the distributions do not involve significant penetration and a multipole representation is acceptable.

FIG. 3. The interaction of two particles located at $\mathbf{r}_1$ and $\mathbf{r}_2$, which is represented with a bipolar expansion about the centers $\mathbf{P}$ and $\mathbf{Q}$. The translations $|\mathbf{r}_1 - \mathbf{P}|$ and $|\mathbf{r}_2 - \mathbf{Q}|$ are assumed to be smaller than the interaction distance $|\mathbf{P} - \mathbf{Q}|$.

FIG. 4. A schematic of the distribution spheres used to investigate the performance of the MACs. The distribution centers are represented by the points within each sphere.

FIG. 5. Deviation, $\mathcal{D}$, of $\mathrm{MAC}[l_{ab}, l_{cd}]$ and $\mathrm{MAC}[0,0]$ for the integral type $(pp|pp)$ at various translations of $(pp|$ in one-dimension. The distribution exponents are $\zeta = 1.0$ and expansions are truncated at $p = q = 2$.

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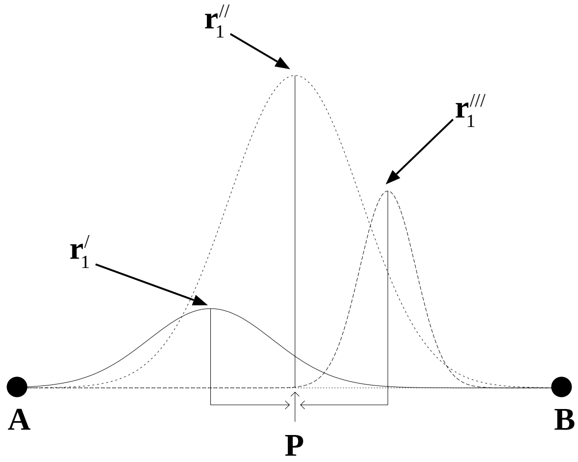


Figure 1, Schwegler, Journal of Chemical Physics

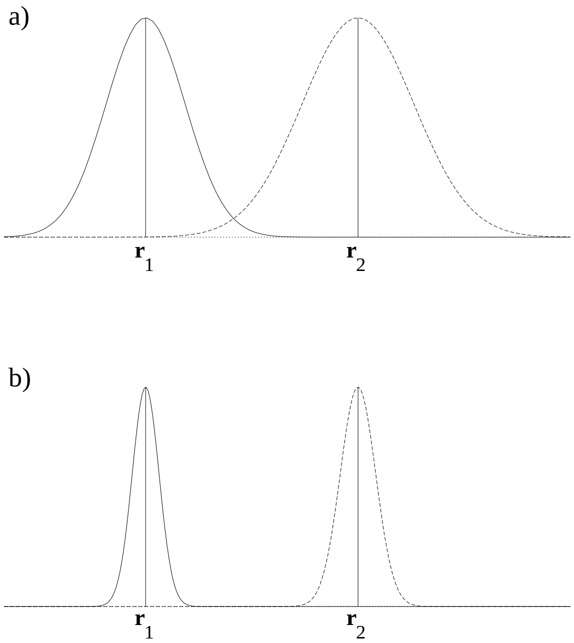
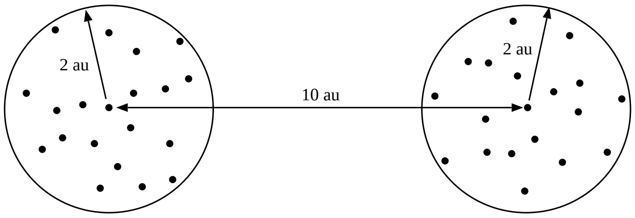


Figure 2, Schwegler, Journal of Chemical Physics

Figure 3, Schwegler, Journal of Chemical Physics



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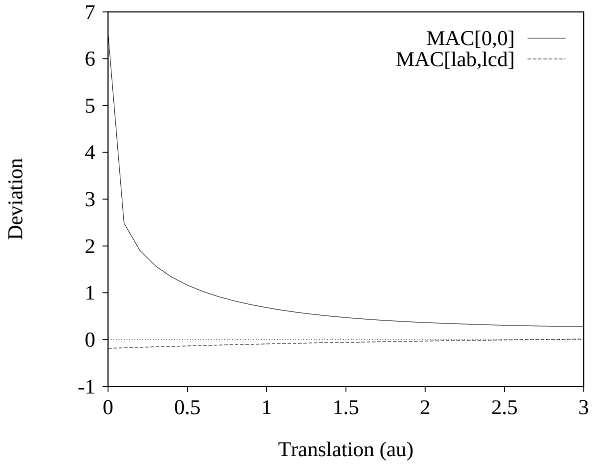

Figure 5, Schwegler, Journal of Chemical Physics