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Rigorous bounds to molecular electron repulsion and electrostatic potential integrals

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Novel rigorous upper and lower bounds, at primitive level, to general electron-repulsion integrals (ERIs) involving Gaussian basis sets have been derived and interconnections with the earlier works in the literature are brought out. New optimal strategies for a preemptive elimination of insignificant ERIs at atom and contraction levels are discussed and tested, resulting in a significant reduction in CPU time. Similar analysis is carried out for the computation of the molecular electrostatic potential for the first time in the literature, leading to a marked savings in computer time.

I. INTRODUCTION

Accurate quantum chemical calculations on atoms and molecules at Hartree-Fock (HF) as well as more refined (viz., CI, MCSCF, etc.) levels invariably employ suitable basis sets. It is the evaluation of electron-repulsion energies that forms "a real bottleneck"¹ to further advancement in this domain. For a set of N real-valued basis functions (e.g., primitive Gaussians²) used in an HF program, one needs to evaluate, excluding molecular symmetries, $(N^4 + 2N^3 + 3N^2 + 2N)/8$ independent types of two-electron-repulsion integrals. Thus, e.g., $N \sim 10^3$ necessitates enumeration of a mammoth ($\sim 10^{11}$) number of two-electron integrals. A general electron-repulsion integral (ERI) is symbolized here as

$$\langle ij|kl \rangle \equiv \int d\tau d\tau' u_i^*(\mathbf{r}) u_j(\mathbf{r}) u_k^*(\mathbf{r}') u_l(\mathbf{r}') / |\mathbf{r} - \mathbf{r}'|, \quad (1)$$

where, the u_i 's denote primitive basis functions. The accurate evaluation and storage of these integrals using Gaussian basis sets, requires large CPU time^{1,3-9} and disk space,¹⁰⁻¹² respectively. However, for large molecular systems, a significant fraction of ERIs is, in fact, negligibly small in magnitude,^{1,3,4} and bypassing evaluation of these integrals^{1,5-7} leads to negligible loss in total energy. These works generally estimate the order of magnitude of ERIs reasonably, but not rigorously; the strict boundedness from above, of a given ERI is not ensured. However, Ahlrichs,⁸ for the first time, derived a *rigorous* upper bound to the ERIs involving only s-type Gaussians.

The electron-repulsion energy also emerges as a functional of the ground-state electron density, $\rho(\mathbf{r})$ within the density functional theory (DFT).^{13,14} A variety of rigorous bounds to functionals involving two-electron energies have become available.¹⁵⁻²²

Another quantity of chemical interest^{15,16} for a many-electron system is the electrostatic potential (ESP) at a location \mathbf{r} (which does not coincide with any nuclear site) defined by

$$V(\mathbf{r}) = \sum_{\alpha} Z_{\alpha} / |\mathbf{r} - \mathbf{R}_{\alpha}| - \int d\tau' \rho(\mathbf{r}') / |\mathbf{r} - \mathbf{r}'|, \quad (2)$$

the first term denotes the bare nuclear potential (BNP) (α labels the (point-) nuclear charges Z_{α} at locations \mathbf{R}_{α}). We derive in the present work, rigorous bounds to primitive-orbital level contributions to ESP for the first time in literature. In summary, the spirit underlying this article is:

- (i) to provide a sound, rigorous theoretical footing to the criteria for discarding seemingly insignificant two-electron-repulsion integrals and establishing connection with the other works mentioned in this section;
- (ii) to derive and test several new upper and lower bounds to the ERIs in a Gaussian context and to put forth new criteria for bypassing computation of insignificant integrals in a preemptive manner and to carry out an analysis of the cumulative error involved in ignoring negligible integrals;
- (iii) to derive appropriate upper bounds to, and to demonstrate the CPU-time savings, for ESP calculations.

II. RIGOROUS BOUNDS TO TWO-ELECTRON INTEGRALS

The inequalities involving two-electron integrals can be classified as (a) density based and (b) wave function/orbital based ones. Schrader and Prager¹⁷ were the first ones to employ electrostatic variation principles in molecular energy calculations to yield a lower bound to the direct Coulomb energy $J[\rho] = (1/2) \int \rho(\mathbf{r}) \rho(\mathbf{r}') d\tau d\tau' / |\mathbf{r} - \mathbf{r}'|$. Thulstrup and Linderberg¹⁸ derived an *upper* bound to $J[\rho]$, which was subsequently rendered into a local form by Gadre *et al.*,¹⁹ viz.,

$$J[\rho] \leq 1.0918 N^{2/3} \int d\tau \rho^{4/3}(\mathbf{r}). \quad (3)$$

Among the density-based bounds to the indirect Coulomb energy $E_{\text{ind}}[\rho] = V_{ee} - J[\rho]$, the elegant study due Lieb²⁰ is especially noteworthy. Further, Lieb and Oxford²¹ improved Lieb's²⁰ bound to E_{ind} yielding, for many-electron systems,

$$E_{\text{ind}}[\rho] \geq c \int d\tau \rho^{4/3}(\mathbf{r}) \quad (4)$$

where $c = -1.68$, which has the same form as that of the famous Dirac–Slater²² exchange energy.

Okiniski²³ derived an upper bound to the magnitude of an ERI in terms of one-electron, overlap-type integrals, with the help of a three-dimensional Sobolev²⁴ inequality. His bound reads

$$|\langle ij|kl \rangle| \leq 3(\pi/2)^{1/3} (\int d\tau |ij|)^{2/3} \times (\int d\tau |kl|)^{2/3} (\int d\tau |ij|^2)^{1/6} (\int d\tau |kl|^2)^{1/6}. \quad (5)$$

Another bound, for an “exchange-type” integral (at the primitive level) was derived by Pathak,²⁵ viz.,

$$\langle ij|ji \rangle \leq (8/3)(2/\pi)^{1/3} \int d\tau |ij|^{4/3}. \quad (6)$$

For a more complete exposition of the works cited above, consult Ref. 26. We derive below several rigorous upper and lower bounds to Gaussian ERIs and ESPs and further establish their connection with the bounds quoted above.

The ERIs over Gaussian basis sets are expressed² in terms of special functions $F_m(t) \equiv \int_0^1 du u^{2m} e^{-tu^2}$. For example the ERI for s-type four-center Gaussians viz. $\langle ss|ss \rangle \equiv \langle s_A s_B | s_C s_D \rangle$ is given by

$$\langle ss|ss \rangle = W \cdot F_0 \cdot E \quad (7)$$

with

$$\begin{aligned} W &= 2\pi^{5/2} (16abcd/\pi^4)^{3/4} / \\ &\quad [(a+b)(c+d)(a+b+c+d)^{1/2}]; \\ F_0 &\equiv F_0(\{(a+b)(c+d)/(a+b+c+d)\}(\mathbf{PQ})^2); \\ \mathbf{P} &= (a\mathbf{A} + b\mathbf{B})/(a+b); \\ \mathbf{Q} &= (c\mathbf{C} + d\mathbf{D})/(c+d) \\ E &= \exp[-ab(\mathbf{AB})^2/(a+b) - cd(\mathbf{CD})^2/(c+d)]. \end{aligned}$$

The computation of $F_m(t)$ forms the most time-consuming aspect of an ERI evaluation. For the case of self-repulsion integral $\langle aa|aa \rangle$, the following sequence of upper bounds is generated via the inequalities due to Ahlrichs⁸ (wherein the result is an equality), Gadre *et al.*,¹⁹ and Okniński²³ (see Appendix B for details), respectively:

$$\begin{aligned} \langle aa|aa \rangle &\leq 2\pi^{-1/2} a^{1/2} \leq 1.0918 (3/2)^{3/2} \pi^{-1/2} a^{1/2}, \\ &\leq 3\pi^{-1/6} 2^{-1/3} a^{1/2}. \end{aligned} \quad (8)$$

Incidentally, as pointed out by Gadre *et al.*¹⁹ and Perdew and Zunger,²⁷ the second upper bound is very tight (off by a mere 0.3% in the present case) and may be used to approximate the Coulomb repulsions. As the orbital exponents range between $\sim 10^{-2}$ – $\sim 10^3$, most self-repulsion integrals are significant, a fact in agreement with Ref. 1.

Analogous results for the exchange-type integrals could be derived

$$\begin{aligned} \langle ab|ba \rangle / (\exp[-ab(\mathbf{AB})^2/(a+b) - cd(\mathbf{CD})^2/(c+d)] (ab)^{3/2} (a+b)^{-5/2}) \\ \leq 2^{7/2} \pi^{-1/2} \leq 2^{10/3} 3^{1/2} \pi^{-5/6} \leq 3 \cdot 2^{13/6} \pi^{-1/6}, \end{aligned} \quad (9)$$

the last three numbers herein being due to Ahlrichs,⁸ Pathak,²⁵ and Okniński,²³ respectively. Owing to the presence of the exponential factor, the exchange-type integrals are expected to evince a rather more diffuse statistical distribution¹ than that for the self-repulsion case.

Rigorous upper bounds to a general Gaussian ERI with a few sample combinations of s-, p-, and d-type primitives based on the results derived in Appendix A are displayed in Table I.

Using simple lower bounds to the functions $F_m(t)$ (cf. Appendix A), it is also possible to derive rigorous lower bounds to ERIs. In particular,

$$\langle aa|aa \rangle \geq 2a^{1/2} \pi^{-1/2}, \quad (10)$$

$$\begin{aligned} \langle ab|ba \rangle &\geq (2ab)^{1/2} (a+b)^{-1/2} \\ &\quad \times \exp[-2ab(\mathbf{AB})^2/(a+b)], \end{aligned} \quad (11)$$

respectively, for self-repulsion-type and exchange-type primitive-level $\langle ss|ss \rangle$ integrals. Table II gives lower bounds to some $\langle ss|ss \rangle$ integrals chosen as representative cases. Lower bounds to general $|\langle ij|kl \rangle|$ integrals may be improved by using tighter lower bounds to $F_m(t)$ vide Appendix A. Like the upper bounds, the lower bounds also can be meaningfully employed to eliminate insignificant integrals: Represent magnitudes of ERIs on a line in a decreasing order.

TABLE I. Electron repulsion integrals and upper bounds to electron repulsion integrals.

Type of integral	Actual value of the integral ^a	Upper bound to the absolute value of the integral ^{a,b}
$\langle s_A s_B s_C s_D \rangle$	$K \cdot F_0$	K
$\langle s_A s_B s_C p_D \rangle$	$K \cdot 2d^{1/2} [F_0 c(C_x - D_x)/(c+d) + F_1 L(P_x - Q_x)/(c+d)]$	$K \cdot 2(d)^{1/2} [c(CD_x)/v + (PQ_x)L/(3v)]$
$\langle s_A p_B s_C p_D \rangle$	$K \cdot 4(bd)^{1/2} [ac(A_x - B_x)(C_x - D_x)F_0 + F_1 L \times [a(A_x - B_x)(P_x - Q_x) - c(C_x - D_x)(P_x - Q_x) + 1/2] - F_2 L^2(P_x - Q_x)^2]/[(a+b)(c+d)]$	$K \cdot 4(bd)^{1/2} [ac(AB_x)(CD_x) + (L/3)[a(AB_x)(PQ_x) + c(CD_x)(PQ_x) + 1/2] + L^2 \times (PQ_x)^2/5]/[(a+b)v]$
$\langle s_A s_B p_C p_D \rangle$	$K \cdot 4(cd)^{1/2} [F_0(-cd(C_x - D_x)^2 + (c+d)/2) + F_1 L \times [(c-d)(C_x - D_x)(P_x - Q_x) - 1/2] + F_2 L^2 \times (P_x - Q_x)^2]/(c+d)^2$	$K \cdot 4(cd)^{1/2} [cd(CD_x)^2 + v/2 + (L/3)[(CD_x)(PQ_x) c-d + 1/2] + L^2(PQ_x)^2/5]/v^2$
$\langle s_A s_B s_C d_{x,D} \rangle$	$K \cdot d(32/3)^{1/2} [-c^2(C_x - D_x)^2 F_0/(c+d)^2 - F_1 L c(C_x - D_x)(P_x - Q_x)/(c+d)^2 + 2cd F_0/(c+d) - F_1 L c(C_x - D_x)(P_x - Q_x)/(c+d) - F_1 L/[2(c+d)] - F_2 \times L^2(P_x - Q_x)^2/(c+d)^2]$	$K \cdot d(32/3)^{1/2} [c^2(CD_x)^2/v^2 + cL(CD_x)(PQ_x)/(3v^2) + 2cd/v + cL(CD_x) \times (PQ_x)/(3v) + L/(6v) + (PQ_x)^2 L^2/(5v^2)]$

^a $K = 2\pi^{5/2}/[(a+b)(c+d)(a+b+c+d)^{1/2}](16abcd/\pi^4)^{3/4} \exp[-ab(\mathbf{AB})^2/(a+b) - cd(\mathbf{CD})^2/(c+d)]$,

$L = (a+b)(c+d)/(a+b+c+d)$; $\mathbf{P} = (a\mathbf{A} + b\mathbf{B})/(a+b)$; $\mathbf{Q} = (c\mathbf{C} + d\mathbf{D})/(c+d)$.

^b $v = c+d$; $AB_x = |A_x - B_x|$; $CD_x = |C_x - D_x|$; $PQ_x = |P_x - Q_x|$.

TABLE II. Lower bounds to electron repulsion integrals of the type $\langle ss|ss \rangle$.

Type of integral	Lower bound to the absolute value of the integral ^a
$\langle s_A s_B s_C s_D \rangle$	$(16abcd)^{3/4} \cdot 2 \cdot \exp[-ab(\mathbf{AB})^2/(a+b) - cd(\mathbf{CD})^2/(c+d) - t]/[\pi^{1/2}(a+b)(c+d)(a+b+c+d)^{1/2}]$
$\langle s_A s_B s_C s_D \rangle$	$(16abcd)^{3/4} \exp[-ab(\mathbf{AB})^2/(a+b) - cd(\mathbf{CD})^2/(c+d)] [1 - \exp(-t)]/[t\pi^{1/2}(a+b)(c+d)(a+b+c+d)^{1/2}]$

$$^a t = (a+b)(c+d)(\mathbf{PQ})^2/(a+b+c+d); \mathbf{P} = (a\mathbf{A} + b\mathbf{B})/(a+b); \mathbf{Q} = (c\mathbf{C} + d\mathbf{D})/(c+d).$$

Lower bounds falling to the *left* of a prechosen cutoff represent *significant* integrals, a criterion complementary to its upper bound counterpart, wherein integrals whose upper bounds fall to the *right* of the cutoff are *negligible*.

For molecular ESP evaluation (at a point) as well, one can employ upper bounds to the functions F_m and in turn derive those for ESP. Table IV summarizes all these upper bounds with their actual values for s- and p-type ESP primitives. Schemes towards a gainful utilization of these bounds with numerical tests are featured in subsequent sections.

III. STRATEGIES FOR ELIMINATING INSIGNIFICANT ERI AND ESP INTEGRALS

Some of the foregoing upper bounds to ERIs were harnessed accomplishing the desired CPU-time saving. Two schemes, viz., the most-diffuse-orbital (MDO) strategy and the upper-bound (UB) strategy were used in conjunction, with the $\langle ss|ss \rangle$ -type ERIs chosen for demonstration (cf. Table III).

A. MDO strategy

Implementation of the MDO scheme is carried out as follows: Find the maximum value of W , viz., W_{\max} for a given system; the factor W now denoted to incorporate the absolute value of the products of coefficients of the respective primitive Gaussians in a given contraction; this maximum needs to be evaluated only once. Now for any $a' \geq a$, $b' \geq b$, $c' \geq c$, and $d' \geq d$ and for a fixed geometry of a molecule, it follows that

$$e^{-\alpha'} \leq e^{-\alpha} \equiv E_{\max}, \quad (12)$$

with $\alpha = ab(\mathbf{AB})^2/(a+b) + cd(\mathbf{CD})^2/(c+d)$ and a similar definition for α' . The inequality (12) implies that the exponential attains its maximal value for the *minimal* values of the orbital exponents, viz., a, b, c, d , i.e., for the corresponding most diffuse s-type orbitals.

Evidently,

$$q \equiv \langle ss|ss \rangle = W \cdot E \cdot F_0 \leq W_{\max} \cdot E_{\max} \equiv u, \quad (13)$$

where use has been made of the fact that $F_0(t) \leq 1$ for $t \geq 0$ (cf., Appendix A). Thus, all q integrals are bounded from above by u . Notice that only the factors F_0 and E depend on the nuclear configuration, while the first two factors depend exclusively on the primitive orbital exponents and coefficients for a given set of atoms and hence determinable ahead of time.

Given a threshold $\epsilon = 10^{-p}$ (usually p ranges from 8 to 12), if $u < \epsilon$ or, equivalently if

$$\ln W_{\max} + p \ln 10 < \alpha', \quad (14)$$

(α' being the exponent in the q integral at hand), it follows that $q < u$ and such an $\langle ss|ss \rangle$ integral turns out to be insignificant. Here the only comparison that needs to be made is that of the *exponent* α' (and *not* the *exponential*) with the fixed, predetermined left-hand side of the inequality (14). The CPU-time saving is thus accomplished by completely avoiding the computation of the function F_0 , the evaluation of which is rather expensive.¹

Two levels of filters are employed to implement the above prescriptions.

1. Atom-level filter (ALF)

Represent each atom in the given molecule by its own most diffuse primitive Gaussian. Compute the exponent α with these most diffuse Gaussians and check for the validity of inequality (14). If it is in the affirmative, skip the evaluation of *all* the ERIs centered at the respective atomic sites.

2. Contraction-level filter (CLF)

The integrals that have escaped ALF are tested at the contraction level. Here analogous to ALF, MDOs *per contraction* in a given atom are traced out. Proceeding exactly on the lines of ALF, but at the *contraction* level, integrals pertinent to those particular combinations of contractions are further eliminated.

B. UB strategy

Upper bounds (Table I) to the integrals that have survived the above two filters are computed, and compared directly with the given threshold, i.e., cut-off value of $\epsilon = 10^{-p}$. The integrals that are numerically less than ϵ are ignored, leaving behind the significant ones. Unlike ALF and CLF, the UB strategy is slightly time consuming for the actual evaluation of the exponential becomes necessary at this stage (cf. Table I). However, the evaluation of F_0 is still avoided. Since the values of the coefficient W_{\max} range from $\sim 10^1$ to 10^2 , for first row atoms, the elimination of a given four-center q integral based on rigorous upper bound, again hinges on the value of the exponent α' . Thus, in turn, the ubiquitous exponential $e^{-\alpha'}$ is the decisive entity, as had been proposed earlier by Clementi and others.^{1,3-9} The methods proposed in this work, on the other hand, put these criteria on a rigorous footing for bypassing evaluation of numerically insignificant integrals.

Analogous to the foregoing study on ERIs, it is hoped that computing upper bounds to ESP also would result in a sizable insignificant fraction of integrals at the primitive

TABLE III. Algorithm for a preemptive elimination of insignificant molecular electron-repulsion integrals of the type $\langle ss|ss \rangle$, using the MDO and upper bound criteria.

- (1) Determine the most diffuse orbital for each constituent atom.
- (2) Determine the most diffuse orbital per contraction per atom.
- (3) Calculate W_{\max} (cf. Sec. III)
criterion $\tau = \ln(W_{\max} 10^p)$; $\epsilon \equiv \text{cutoff} = 10^{-p}$.
- (4) Loops over atoms.
- (5) Loops over contractions.
- (6) Loops over primitive Gaussians
(consider only independent types of integrals *vide* the symmetries of the primitive indices $\langle i|j|kl \rangle$)
- (7) Compare τ with $\alpha' = a'b'(AB)^2/(a' + b') + c'd'(CD)^2/(c' + d')$ within the MDO strategy per atom (cf. Sec. III).
If $\alpha' > \tau$, skip the corresponding atomic loop (go to the "end of atomic loop"), or else continue.
- (8) Compare τ with $\alpha'' = a''b''(AB)^2/(a'' + b'') + c''d''(CD)^2/(c'' + d'')$ within the MDO strategy per contraction per atom.
If $\alpha'' > \tau$, skip the corresponding contraction loop, or else continue.
- (9) Compute upper bound u *vide* Table I.
If $u < 10^{-p}$ skip the primitive Gaussian loop, or else compute the actual value of the integral after computing the function F_0 .
End of the primitive Gaussian loop.
End of the contraction loop.
End of the atomic loop.

Gaussian level, resulting in an enhanced CPU-time efficiency. The general strategy of exploiting upper bounds in the ESP-context now follows:

Circumscribe the given molecular system in a rectangular parallelepiped of definite dimensions. In addition, extend the boundaries of this box to 2 a.u. on each side, forming the region of interest. Calculate $f_{\max} \equiv \max \{u_{ss}, u_{sp}, u_{pp}\}$, where the u 's denote the respective upper bounds to primitive-ESP elements as in Table IV. Unlike the ERI case, ESP involves only two centers at a time. The neglect of an integral is chiefly attributed to the small value of exponential, viz., $e^{-\alpha''}$, i.e., with large enough $\alpha'' = a''b''(AB)^2/(a'' + b'')$ giving rise to a criterion $\ln f_{\max} + p \ln 10 < \alpha''$. Integrals escaping this filter would be expected to be, by and large, significant. Numerical tests on sample molecular systems bringing out the utility of the above schemes form the theme of the next section.

IV. NUMERICAL TESTS AND DISCUSSION

The following molecular systems were chosen for a demonstration of the schemes put forth in the last section, for the $\langle ss|ss \rangle$ -ERI case: (i) a hypothetical linear chain of 21 hydrogen atoms with an interatomic separation of 1.4 a.u.; (ii) *trans*-butadiene; and (iii) octatetraene. The double-zeta Gaussian basis set tabulated by Snyder and Basch²⁸ was employed for this purpose. The case of a hypothetical H chain is particularly interesting as it has exclusively *s*-type contractions. Table V summarizes the results of ERI investigations, giving the CPU time and per cent insignificant integrals for two cutoffs, viz., $\epsilon = 10^{-8}$ and $\epsilon = 10^{-12}$. It is gratifying that an impressive reduction, in the number of significant integrals and a consequent one, in CPU time is noticed by a factor ranging from 1.5 to 2.4. It must be emphasized that the decisive factor for the neglect of an ERI is manifested in the exponent α' being overwhelmingly large. Note that the molecules considered here can by no means be termed as very large, yet they have a remarkable fraction of negligible $\langle ss|ss \rangle$ integrals, implying that larger systems would exhibit even more dramatic results.

For the ESP computation, the neglect of an integral is chiefly attributed to $\alpha'' = a''b''(AB)^2/(a'' + b'')$ in the exponent being overwhelmingly large. The results, therefore, are not expected to be as dramatic as for the case of ERIs. Numerical tests carried out on the systems cyclopropane and *trans*-butadiene show that 31% and 37% of the ESP integrals are negligible right at their respective primitive levels, accompanied by a CPU-time reduction by $\sim 33\%$, which is indeed an encouraging result.

It may be inquired at this stage about the loss of accuracy brought about by ignoring insignificant integrals. A naive estimate of the accumulated error in the ERI would be $N_0 \epsilon$, when N_0 is the number of integrals ignored. However, round-off errors being random in nature, one expects that the actual error swings towards a more optimistic (or less drastic) error estimate²⁹ δ_{mp} ($mp \Rightarrow$ "most probable") given by

$$\delta_{mp} = 0.1947 \epsilon N_0^{1/2}. \quad (15)$$

To investigate the accuracy for a given cut-off value, we formed a cumulative sum of all the $\langle ss|ss \rangle$ integrals for the H

TABLE IV. Electrostatic potential integrals and upper bounds to electrostatic potential integrals.

Type of integral ^a	Actual value of the integral ^b	Upper bound to the absolute value of the integral ^{b,c}
$\langle s_A 1/r_{12} s_B \rangle$	$2 K \cdot F_0$	$2 K$
$\langle s_A 1/r_{12} p_{xB} \rangle$	$2 K [(x_2 - C_x)F_1 + a(A_x - B_x)F_0/(a + b)]$	$2 K \cdot (M_x/3) [(4a + b)/(a + b)]$
$\langle p_{xA} 1/r_{12} s_B \rangle$	$2 K [(x_2 - C_x)F_1 - b(A_x - B_x)F_0/(a + b)]$	$2 K \cdot (M_x/3) [(4b + a)/(a + b)]$
$\langle p_{xA} 1/r_{12} p_{xB} \rangle$	$K \{ F_1 [2(a - b)(A_x - B_x)(x_2 - C_x) - 1]/(a + b) + F_2 \times 2(x_2 - C_x)^2 + [F_0/(a + b)] [1 - 2ab(A_x - B_x)^2/(a + b)] \}$	$K [(31/15) M_x^2 + 1/(a + b)]$
$\langle p_{xA} 1/r_{12} p_{yB} \rangle$	$2 K \{ [F_1/(a + b)] [a(A_y - B_y)(x_2 - C_x) - b(A_x - B_x) \times (y_2 - C_y)] - [ab/(a + b)^2] (A_x - B_x)(A_y - B_y)F_0 + (x_2 - C_x)(y_2 - C_y)F_2 \}$	$K \cdot (31/15) M_x M_y$

^a The bracket denotes integration over the entire r_1 space.

^b $K = [\pi/(a + b)] \exp[-ab(AB)^2/(a + b)]$. The argument of functions F_m ($m = 0, 1, 2$) is $(a + b)(r_2 - C)^2$ with $C = (aA + bB)/(a + b)$.

^c M_x, M_y, M_z are the dimensions of the box encompassing the region of interest (cf. Sec. III).

TABLE V. Percent ignorable electron repulsion integrals with corresponding CPU time^a.

Threshold cutoff value	Molecule	Filters					
		Actual evaluation		"UB-OFF" evaluation		"ALL-ON" evaluation	
		Integrals discarded (percent)	Time (min)	Integrals discarded (percent)	Time (min)	Integrals discarded (percent)	Time (min)
10 ⁻⁸	H chain	0.0	222	74.1	99.2	88.2	93.4
	TBD ^b	0.0	74.5	36.3	58.3	77.4	52.1
	OTE ^c	0.0	892	72.5	409	91.7	378
10 ⁻¹²	H chain	0.0	222	65.1	117	82.0	110
	TBD	0.0	74.5	25.2	65.3	66.7	59.3
	OTE	0.0	892	63.5	483	85.8	445

^a Computations performed on an HP-9050 AM computer facility.

^b TBD corresponds to the *trans*-butadiene molecule.

^c OTE corresponds to the octatetraene molecule.

chain, with very accurate ERI evaluations. For $\epsilon = 10^{-8}$, the most pessimistic error estimate $\delta = 5.6 \times 10^{-2}$, compared against the most probable error estimate $\delta_{mp} = 4.6 \times 10^{-6}$, the actual deviation δ_{act} , being around 10^{-4} . The δ counterparts for $\epsilon_0 = 10^{-12}$ were found to be $\delta = 5.2 \times 10^{-6}$, $\delta_{mp} = 4.5 \times 10^{-10} = \delta_{act}$. The remarkable agreement between δ_{mp} and δ_{act} appears to stem from smaller ϵ accompanied by the artifacts of computer arithmetic.²⁹ Of course, since the charge-density-bond-order matrix is a sparse one and contains nonvanishing entries which range between 10^{-1} – 10^{-6} (cf. Ref. 28), the error in the total electron–electron interaction energy is expected to be further *reduced* by a factor of 100.

Similar considerations were applied to *actual* ESP calculations at several points in different directions within the region of interest, for the cases of *trans*-butadiene and cyclopropane. It was revealed that for a six-significant figure accuracy, a threshold (cutoff) of a mere 10^{-2} at the primitive level sufficed. Here, the density-matrix elements also played their role in mitigating the error. Also, as the integral elements here occur with both the signs (positive as well as negative), a further increase in accuracy is accomplished owing to cancellation of errors.

V. CONCLUDING REMARKS

In this article, the authors have endeavored to present *rigorous* bounds to general electron-repulsion integrals. A direct link has been established with many diverse rigorous works reported in the literature, leading to a coherent perspective. New upper and lower bounds to two-electron-repulsion integrals with a special reference to Gaussian basis sets have been derived. To the authors' knowledge, derivations of lower bounds appear for the first time in the literature. Further, a utility of the upper bounds under the new strategies, viz., MDO and UB (cf. Sec. III), has been demonstrated for the ERIs with s-type Gaussians, endowing rigor to the existing, rather heuristic criteria for discarding

seemingly insignificant integrals judged solely by the ubiquitous exponential factor. An analysis of cumulative errors has also been presented. Similar analysis using rigorous upper bounds is carried out for the first time for a complete molecular electrostatic potential calculation, again showing a marked CPU-time efficiency enhancement, with no loss in the required accuracy.

The $\langle ss|ss \rangle$ type ERIs chosen in the present case served only as test cases. The upper bounds (samples of which have been presented in the tables) are expected to lead to similar CPU-time savings for other types of integrals as well, viz., $\langle ss|sp \rangle$, $\langle ss|pp \rangle$, etc., a detailed exposition of which would fall beyond the scope of the present study. To facilitate the utility of the bounds in general by rendering them into more simple, closed forms, one may determine the maximal geometry-independent factors ahead of time.

The present study thus unravels the potential in rigorous upper bounds to ERIs and ESPs. A significant reduction in CPU time is accomplished with no loss of rigor and practically with no loss in accuracy. The present work is expected to impart an impetus to use of rigorous bounds in molecular energy calculations within a direct-SCF framework employing primitive Gaussian bases.

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APPENDIX A

Expressions for electron repulsion integrals over Gaussian basis sets involve² special functions

$$F_m(t) \equiv \int_0^1 u^{2m} e^{-tu^2} du.$$

A variety of upper and lower bounds to F_0 , F_1 , and F_2 will be derived here.

1. Bounds to $F_0(t)$

Note that $F_0(t)$ is a monotone decreasing function, since $F'_0(t) < 0$ for finite $t > 0$. The maximum value attained by F_0 is 1, viz., $F_0(0) = 1$.

$$\text{Hence, a trivial bound is } F_0(t) \leq 1. \quad (\text{A1})$$

Also note the following: for $0 \leq u \leq 1$,

$$F_0(t) = \int_0^1 e^{-tu^2} du \geq \int_0^1 e^{-tu} du = (1 - e^{-t})/t. \quad (\text{A2})$$

Another bound is obtained by the following considerations:

$$F_0(t) \geq \int_0^1 e^{-t} du = e^{-t}. \quad (\text{A3})$$

For $t \leq 3$, the following bounds are obtained by series expansion:

$$F_0(t) \leq 1 - t/3 + t^2/10$$

and

$$F_0(t) \geq 1 - t/3 + t^2/10 - t^3/42. \quad (\text{A4})$$

2. Bounds to $F_1(t)$

$$\begin{aligned} F_1(t) &= \int_0^1 u^2 e^{-tu^2} du \leq \int_0^1 u e^{-tu^2} du \\ &= [-1/(2t)] e^{-tu^2} \Big|_0^1 \\ &= (1 - e^{-t})/(2t), \end{aligned} \quad (\text{A5})$$

yet another upper bound to $F_1(t)$ may also be readily derived:

$$\begin{aligned} F_1(t) &= \int_0^1 u^2 e^{-tu^2} du \leq \int_0^1 u^2 e^{-tu} du \\ &= (2/t^3) - (2 + 2t + t^2) \exp(-t)/t^3. \end{aligned} \quad (\text{A6})$$

Some simpler upper bounds to F_1 and F_2 are given by

$$F_1 \leq 1/3 \text{ and } F_2 \leq 1/5$$

and, in general,

$$F_m \leq 1/(2m + 1). \quad (\text{A7})$$

For some further inequalities, note that $x \leq e^{x-1}$. Substitute $x = tu^2$ to obtain $tu^2 \leq e^{tu^2-1} = e^{tu^2}/e$. Hence, $e \cdot t \cdot u^2 \leq \exp(tu^2)$ yielding $\exp(-tu^2) \leq (etu^2)^{-1}$. This leads to the result

$$F_1(t) = \int_0^1 u^2 e^{-tu^2} du \leq [1/(et)]. \quad (\text{A8})$$

APPENDIX B

Using Okniński's result [cf. inequality (9) in the text], the desired upper bounds are readily obtainable for primitive Gaussians. Recall that

$$\begin{aligned} |\langle ij|kl \rangle| &\leq 3(\pi/2)^{1/3} (\int |ij| d\tau)^{2/3} (\int |kl| d\tau)^{2/3} \\ &\quad \times (\int |ij|^2 d\tau)^{1/6} (\int |kl|^2 d\tau)^{1/6}. \end{aligned}$$

For a basis set involving only s- and p-type primitive Gaussians, one needs to compute in general, for different centers A and B , only the following independent integrals in the up-

per bounds (normalization factors incorporated and primitive Gaussian coefficients not included): Setting

$$\begin{aligned} K &= (2a2b/\pi^2)^{3/4} (\pi/(a+b))^{3/2} \\ &\quad \times \exp[-ab(\mathbf{AB})^2/(a+b)], \end{aligned}$$

one obtains

$$\langle s_A | s_B \rangle = K, \quad (\text{B1})$$

$$\langle s_A | p_{xB} | \rangle \leq K 2b^{1/2} \{ [\pi(a+b)]^{-1/2} + |P_x - B_x| \} \quad (\text{B2})$$

$$\begin{aligned} \langle p_{xA} | p_{xB} | \rangle &\leq K 4(ab)^{1/2} \{ [2(a+b)]^{-1} + |2P_x - A_x - B_x| \\ &\quad \times [\pi(a+b)]^{-1/2} + |P_x - A_x| \cdot |P_x - B_x| \} \end{aligned} \quad (\text{B3})$$

$$\begin{aligned} \langle p_{xA} | p_{yB} | \rangle &\leq K 4(ab)^{1/2} \{ [\pi(a+b)]^{-1/2} + |P_x - A_x| \} \\ &\quad \times \{ [\pi(a+b)]^{-1/2} + |P_y - B_y| \}. \end{aligned} \quad (\text{B4})$$

Also declaring

$$\begin{aligned} M &= (2a2b/\pi^2)^{3/2} \{ \pi/[2(a+b)] \}^{3/2} \\ &\quad \times \exp[-2ab(\mathbf{AB})^2/(a+b)], \end{aligned}$$

one can get

$$\langle (s_A)^2 | (s_B)^2 \rangle = M, \quad (\text{B5})$$

$$\langle (s_A)^2 | (p_{xB})^2 \rangle = 4 \cdot b \cdot M \{ [4(a+b)]^{-1} + (P_x - B_x)^2 \}, \quad (\text{B6})$$

$$\begin{aligned} \langle (p_{xA})^2 | (p_{xB})^2 \rangle &= 16 \cdot a \cdot b \cdot M \{ (3/4) [2(a+b)]^{-2} + [(P_x - A_x)^2 \\ &\quad + (P_x - B_x)^2 + 4(P_x - A_x)(P_x - B_x)] \\ &\quad \times [4(a+b)]^{-1} + (P_x - A_x)^2 (P_x - B_x)^2 \}, \end{aligned} \quad (\text{B7})$$

$$\begin{aligned} \langle (p_{xA})^2 | (p_{yB})^2 \rangle &= 16 \cdot a \cdot b \cdot M \{ [4(a+b)]^{-1} + (P_x - A_x)^2 \\ &\quad \times \{ [4(a+b)]^{-1} + (P_y - B_y)^2 \}. \end{aligned} \quad (\text{B8})$$

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