# An Efficient Algorithm for the Generation of Two-Electron Repulsion Integrals over Gaussian Basis Functions

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## Abstract

A synthesis of certain of the features of the recently developed HGP method of Head-Gordon and Pople with some of the constructs of the well-established McMurchie-Davidson (MD) scheme has led to the development of a new algorithm for the computation of the two-electron repulsion integrals which arise in conventional *ab initio* quantum chemical calculations using Gaussian basis sets. As in the MD scheme, derivatives of the two-electron integrals with respect to the nuclear coordinates are obtained very efficiently by the new algorithm. Moreover, in the spirit of the HGP approach, as much of the computational effort as possible is performed outside the contraction loops. This is achieved through the intermediacy of scaled, partially contracted integral sets and through the use of a near-optimal solution to the central tree-search problem. Explicit FLOP (floating point operation) counts suggest that the new algorithm is typically a factor of 2 cheaper than the HGP method for contracted basis sets.

## Introduction

There has been a recent resurgence in the development of highly efficient algorithms [1,2] for the evaluation of two-electron repulsion integrals (ERIs) over Gaussian basis functions [3]. Because their number increases with the fourth power of the size of the basis set used, the computation and handling of these (six-dimensional) integrals constitutes the rate-limiting step in most implementations of the widely-used algebraic Hartree-Fock (HF) approximation [4]. Moreover, for large problems, the storage and retrieval of the ERIs from disk can pose considerable practical difficulties, and this has led to the development of so-called "direct" methods in which the ERIs are recomputed whenever they are needed. Direct algorithms have been applied to the calculation of HF energies and gradients [5] and, more recently, second-order Møller-Plesset perturbation (MP2) energies [6,7] and HF frequencies [8]. Not surprisingly, the viability of such direct calculations is found to be critically dependent on the efficiency of the method used to compute the required ERIs.

The state of the art in ERI evaluation prior to the contributions of Obara and Saika and Schlegel (OSS [1]) and of Head-Gordon and Pople (HGP [2]) has been thoroughly reviewed [9]. Of the pre-OSS approaches, the Pople-Hehre method (PH [10]) has generally been considered to be the most efficient for ERIs involving only *s* and *p* functions (particularly if these are significantly contracted and/or in the form of *sp* shells) while the Rys (DRK [11]) and McMurchie-Davidson (MD [12])

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methods are often used for ERIs involving $d$ (or higher) functions. For the calculation of the *derivatives* of ERIs with respect to nuclear positions, a variety of methods [1a,11,12] have proven useful.

However, in their seminal paper [1b], Obara and Saika demonstrated that an eight-term recurrence relation (RR) (which had been implicit in earlier work [1a] by Schlegel on derivatives) connecting a given ERI to others of lower angular momentum may be used to reduce the desired ERIs very efficiently to readily evaluated [3] ERIs involving only $s$ functions. More recently, HGP have improved upon the OS procedure by demonstrating that a two-term RR (termed the "horizontal" recurrence relation, HRR) can, significantly, be applied to *contracted* ERIs. HGP showed [2] that a judicious combination of the eight-term and two-term RRs leads to a particularly efficient scheme which is as fast, or faster, than all previous algorithms (except the PH method for highly contracted *sp* basis sets) for the generation of ERIs and their *first* derivatives.

In the present paper, following a careful examination of the features which lead to the remarkably good performance of the HGP algorithm, we propose a synthesis of the HGP and MD algorithms which appears to be superior to either approach and which, additionally, appears well-suited to the computation of ERI first (and higher) derivatives.

## Definitions and Conventions

We begin by defining some fundamental quantities, adopting conventions similar to those used by HGP. Thus, an unnormalized primitive Cartesian *Gaussian* function $\psi_{\mathbf{a}k}$ centered at **A** and with exponent $\alpha_k$, is

$$\psi_{\mathbf{a}k}(\mathbf{r}) = (x - A_x)^{a_x}(y - A_y)^{a_y}(z - A_z)^{a_z} \exp[-\alpha_k(\mathbf{r} - \mathbf{A})^2] \tag{1}$$

and is uniquely defined by the vectors $\mathbf{a} = (a_x, a_y, a_z)$ and **A** and by the scalar $\alpha_k$. The angular momentum of $\psi_{\mathbf{a}k}$ is $a = (a_x + a_y + a_z)$. A *contracted* Gaussian function centred at **A** is defined as

$$\phi_{\mathbf{a}}(\mathbf{r}) = \sum_{k=1}^{K} D_{\mathbf{a}k}\psi_{\mathbf{a}k}(\mathbf{r}) \tag{2}$$

where $K$ is known as the degree of contraction of $\phi_{\mathbf{a}}$. A primitive ERI over four primitive unnormalized Gaussians is the six-dimensional integral

$$[\mathbf{a}_k\mathbf{b}_l|\mathbf{c}_m\mathbf{d}_n] = \int\int \psi_{\mathbf{a}k}(\mathbf{r}_1)\psi_{\mathbf{b}l}(\mathbf{r}_1)r_{12}^{-1}\psi_{\mathbf{c}m}(\mathbf{r}_2)\psi_{\mathbf{d}n}(\mathbf{r}_2)\, d\mathbf{r}_1\, d\mathbf{r}_2 \tag{3}$$

We will frequently drop the subscripts when they are not of interest, thereby denoting this primitive four-center Gaussian ERI by $[\mathbf{ab}|\mathbf{cd}]$. Finally, from Eq. (2) we define a fully contracted Gaussian ERI $(\mathbf{ab}|\mathbf{cd})$, distinguished from a primitive ERI by the use of parentheses in place of brackets, by

$$(\mathbf{ab}|\mathbf{cd}) = \sum_{k_A}^{K_A}\sum_{k_B}^{K_B}\sum_{k_C}^{K_C}\sum_{k_D}^{K_D} D_{\mathbf{a}k_A}D_{\mathbf{b}k_B}D_{\mathbf{c}k_C}D_{\mathbf{d}k_D}[\mathbf{a}_{k_A}\mathbf{b}_{k_B}|\mathbf{c}_{k_C}\mathbf{d}_{k_D}] \tag{4}$$

In an entirely analogous fashion, we define an unnormalized primitive Cartesian *Hermite* function $\bar{\psi}_{\mathbf{a}k}$ centered at **A** and with exponent $\alpha_k$ by

$$\bar{\psi}_{\mathbf{a}k}(\mathbf{r}) = \alpha^{a/2} H_{a_x}[\alpha_k^{1/2}(x - A_x)] H_{a_y}[\alpha_k^{1/2}(y - A_y)] H_{a_z} \times [\alpha_k^{1/2}(z - A_z)] \exp[-\alpha_k(\mathbf{r} - \mathbf{A})^2] \tag{5}$$

where $H_n$ represents the usual $n$th degree Hermite polynomial. Henceforth, we will retain the convention that a bar above a function indicates that it is Hermite. Likewise, we define a *contracted* Hermite function $\bar{\phi}_{\mathbf{a}}$, a primitive Hermite ERI $[\bar{\mathbf{a}}_k \bar{\mathbf{b}}_l | \bar{\mathbf{c}}_m \bar{\mathbf{d}}_n]$, and a contracted Hermite ERI $[\bar{\mathbf{a}}\bar{\mathbf{b}} | \bar{\mathbf{c}}\bar{\mathbf{d}})$ by analogy with Eqs. (2), (3), and (4), respectively.

Finally, we will also consider "generalized" ERIs which may

(1) Contain both Gaussian and Hermite functions

(2) Be $n$-centered, where $n$ is not necessarily 4

(3) Be contracted with respect to the functions of *either* or *both* electrons 1 and 2

These are straightforward extensions of the ERIs described above. For example, an $(\mathbf{ab} | \bar{\mathbf{q}}]$ ERI might be described as a "left-contracted, three-center, mixed ERI" because it contains contracted Gaussian functions of electron 1 and an uncontracted Hermite function of electron 2.

## The Motivation for the New Algorithm

In the paper by HGP [2], a number of contemporary procedures for ERI computation were evaluated by comparing the number of floating-point operations (FLOPS, i.e., adds, subtracts, multiplies, and divides) required by each procedure to generate $(pp|pp)$, $(sp, sp|sp, sp)$, $(dd|dd)$, and $(ff|ff)$ integral classes. For clarity, it was assumed in each case that each of the four shells is on a distinct center and has a degree of contraction $K$. Each FLOP count is then expressed (Table III of Ref. 2) as a quadratic in $K^2$, viz.,

$$N = xK^4 + yK^2 + zK^0 \tag{6}$$

The utility of such an expression lies in the fact that it indicates not only how much total computational effort is required by a given algorithm but, also, how that effort is distributed between

(1) FLOPS inside all four contraction loops ($xK^4$)

(2) FLOPS outside the two innermost contraction loops ($yK^2$)

(3) FLOPS outside all of the contraction loops ($zK^0$)

For example, the margin by which the HGP method [2] is faster than the Rys method [11] increases with increasing contraction of the basis set used, and this is directly indicated by the fact that, although $z(\text{HGP}) > z(\text{DRK})$, it is also found that $x(\text{HGP}) < x(\text{DRK})$.

One key, then, to the impressive performance of the PH and HGP algorithms with contracted integral classes is their comparatively modest $x$ parameters. That is, they perform relatively little work within the innermost contraction loop. In the PH approach [10] this is achieved by the use of carefully chosen axis systems which enable most of the computational effort to be "factored" outside the two innermost

contraction loops (thereby decreasing $x$ at the expense of $y$) while, in the HGP algorithm, the fact that the HRR (horizontal recurrence relation) can be applied to *fully contracted* integrals enables much of the work to be "factored" outside all four contraction loops (thereby decreasing $x$ at the expense of increasing $z$). Any scheme for ERI evaluation which aims to be competitive with the PH and HGP algorithms for contracted basis sets must likewise "factor" work outside as many of the contraction loops as possible.

Another promising approach to the problem of ERI (and, particularly, ERI derivative) evaluation is that due to McMurchie and Davidson (MD). A decade ago, MD argued [12] that, since it is straightforward to express a primitive four-center Gaussian ERI $[\mathbf{ab}|\mathbf{cd}]$ as a linear combination of primitive two-center Hermite ERIs $[\bar{\mathbf{p}}|\bar{\mathbf{q}}]$ (and since integrals of this latter type are comparatively easy to evaluate), contracted Gaussian ERIs $(\mathbf{ab}|\mathbf{cd})$ can be efficiently computed via such a pathway. Moreover, essentially because the derivative of one Hermite function is another, e.g.,

$$\frac{\partial}{\partial x}(\bar{\psi}_{\mathbf{a}}) = -\bar{\psi}_{\mathbf{a}+\mathbf{1}_x} \tag{7}$$

it is easy to show that *arbitrary-order derivatives* of an intermediate primitive two-center Hermite ERI $[\bar{\mathbf{p}}|\bar{\mathbf{q}}]$ with respect to the coordinates of $\mathbf{P}$ (or $\mathbf{Q}$) are trivial to obtain. The MD technique is superficially quite different from the HGP and OS approaches. However, closer inspection reveals that the algorithms have structural similarities, and a very satisfactory synthesis of the two is possible.

On the basis of the lessons learned from the performances of previous algorithms, we list below five guidelines for the construction of an efficient procedure for calculating ERIs:

(1) Contract primitive functions as *early* as possible.

(2) Where possible, employ recurrence relations over *contracted* functions.

(3) Use recurrence relations with as *few* terms as possible.

(4) Solve implicit tree-search problems as well as possible.

(5) In constructing desired ERIs from intermediate ones, use *one*-electron transformations (wherever possible), since it will then be possible to loop (vectorize) efficiently over the functions of the other electron.

## A New Algorithm for ERI Evaluation

In both the HGP and MD approaches, a complete class of the desired $(\mathbf{ab}|\mathbf{cd})$ ERIs is formed through a combination of well-defined and distinct stages which, henceforth, we will term *generation, contraction,* and *transformation* steps. Below, we summarize first the HGP and MD methodologies and then our synthesis of these into a new algorithm for ERI computation.

### *Head-Gordon-Pople Algorithm*

(1) The *generation* step begins with the calculation of the necessary $F_m(T)$ integrals and, thence, of a set of auxiliary $[\mathbf{00}|\mathbf{00}]^{(m)}$ ERIs. Finally, $[\mathbf{e0}|\mathbf{f0}]$

are generated from these (using HGPs five-term "vertical" RR [2], a special case of the Obara-Saika RR [1]).

(2) In the *contraction* step, $(\mathbf{e0}|\mathbf{f0})$ are formed from $[\mathbf{e0}|\mathbf{f0}]$.

(3) Finally, in the *transformation* step, desired $(\mathbf{ab}|\mathbf{cd})$ are derived from $(\mathbf{e0}|\mathbf{f0})$ using HGP's two-term "horizontal" RR [2].

*McMurchie-Davidson Algorithm*

(1) The *generation* step includes the calculation of the necessary $F_m(T)$ integrals and the subsequent generation (using MDs two-term RR [12]) of $[\bar{\mathbf{p}}|\bar{\mathbf{q}}]$ ERIs from these.

(2) In the *transformation* step, $[\mathbf{ab}|\mathbf{cd}]$ are derived from $[\bar{\mathbf{p}}|\bar{\mathbf{q}}]$ using coefficients determined from MDs three-term RR [12].

(3) Finally, in the *contraction* step, desired $(\mathbf{ab}|\mathbf{cd})$ are formed from $[\mathbf{ab}|\mathbf{cd}]$.

*The New Algorithm*

Loop over primitives on centers **C** and **D**

  Loop over primitives on centers **A** and **B**

    (1) A *generation* step, similar to that in the MD method, in which the necessary $[\bar{\mathbf{p}}|\bar{\mathbf{q}}]$ are computed from the $F_m(T)$ using one- and two-term recurrence relations (after considering the relevant minimum-FLOPS tree-search problem).

    (2) A *bra-contraction* step in which $[\bar{\mathbf{p}}|\bar{\mathbf{q}}]$ are used to form several sets of "left-contracted scaled" $(\bar{\mathbf{p}}|\bar{\mathbf{q}}]_{u,v}$.

  (3) A *bra-transformation* step leading to $(\mathbf{e0}|\bar{\mathbf{q}}]$.

  (4) A *ket-contraction* step leading to several sets of $(\mathbf{e0}|\bar{\mathbf{q}})_{u,v}$.

(5) A *ket-transformation* step leading to $(\mathbf{e0}|\mathbf{f0})$.

(6) A second *bra-transformation* step leading to $(\mathbf{ab}|\mathbf{f0})$.

(7) A second *ket-transformation* step leading to $(\mathbf{ab}|\mathbf{cd})$.

These seven steps are discussed in depth below with reference to the evaluation of a class of contracted $(\mathbf{ab}|\mathbf{cd})$ ERIs. Throughout, we assume that

(1) Each of the four shells involved is on a distinct center (i.e., that we are dealing with four-center integrals)

(2) Each shell has a degree of contraction of $K$

(3) The Gaussian exponents and contraction coefficients, Eqs. (1) and (2), of the primitive functions at **A**, **B**, **C**, and **D** are $\alpha$ and $D_A$, $\beta$ and $D_B$, $\gamma$ and $D_C$, and $\delta$ and $D_D$, respectively.

$L$ will represent the total angular momentum of the ERI class ($L = a + b + c + d$), and $N$ will represent the total number of shells in the basis set being used.

*The Generation Step*

Initially, as with many ERI algorithms, the $F_m(T)$ integrals ($0 \le m \le L$) must be computed for each of the $K^4$ primitive $[\mathbf{ab}|\mathbf{cd}]$ classes. For a given primitive class, we evaluate the following:

$$\zeta = \alpha + \beta \qquad \eta = \gamma + \delta \tag{8}$$

$$\mathbf{P} = \frac{\alpha\mathbf{A} + \beta\mathbf{B}}{\zeta} \qquad \mathbf{Q} = \frac{\gamma\mathbf{C} + \delta\mathbf{D}}{\eta} \tag{9}$$

$$K_P = \frac{2^{1/2}\pi^{5/4}}{\zeta} \exp\left[\frac{-\alpha\beta}{\zeta}(\mathbf{A} - \mathbf{B})^2\right] \quad K_Q = \frac{2^{1/2}\pi^{5/4}}{\eta} \exp\left[\frac{-\gamma\delta}{\eta}(\mathbf{C} - \mathbf{D})^2\right] \tag{10}$$

$$D_P = D_A D_B \qquad D_Q = D_C D_D \tag{11}$$

$$\mathbf{R} = \mathbf{Q} - \mathbf{P} \tag{12}$$

$$\vartheta^2 = \frac{\zeta\eta}{\zeta + \eta} \tag{13}$$

$$T = \vartheta^2 R^2 \tag{14}$$

$$F_m(T) = \int_0^1 t^{2m} \exp(-Tt)\, dt \tag{15}$$

The quantities defined in Eqs. (8)–(11) are two-center quantities and can be precomputed in a preliminary $N^2$-loop. The evaluations of Eqs. (12)–(15) must necessarily be performed in the $N^4$-loop but, when $L \gg 0$, they are computationally insignificant in relation to the later steps of the algorithm.

We then form a set of $[\mathbf{0}]^{(m)}$ integrals from the $F_m(T)$, defined thus

$$\omega = \frac{K_P D_P K_Q D_Q}{(2\zeta)^{a+b}(2\eta)^{c+d}(\zeta + \eta)^{1/2}} \tag{16}$$

$$[\mathbf{0}]^{(m)} = \omega(2\vartheta^2)^m F_m(T) \tag{17}$$

which have Gaussian-prefactor, contraction-coefficient and $u, v$-scaling (*vide infra*) factors "built into" them. Introducing these factors early leads to enhanced overall efficiency because, at this stage, we are handling so few (only $L + 1$) integrals.

The next stage in the generation step is to form $[\bar{\mathbf{p}}|\bar{\mathbf{q}}]$ integrals. As MD [12] have shown, $[\bar{\mathbf{p}}|\bar{\mathbf{q}}]$ integrals are readily reduced to one-center $[\bar{\mathbf{r}}]$ integrals. Thus,

$$[\bar{\mathbf{p}}|\bar{\mathbf{q}}] = (-1)^q[\overline{\mathbf{p} + \mathbf{q}}] \tag{18}$$

where

$$[\bar{\mathbf{r}}] = \omega \int_0^1 (\vartheta t)^r H_{r_x}(R_x\vartheta t) H_{r_y}(R_y\vartheta t) H_{r_z}(R_z\vartheta t) \exp(-R^2\vartheta^2 t^2)\, dt \tag{19}$$

In order to compute these $[\bar{\mathbf{r}}]$ integrals efficiently, we follow MD in defining auxiliary integrals $[\bar{\mathbf{r}}]^{(m)}$ such that $[\bar{\mathbf{r}}] \equiv [\bar{\mathbf{r}}]^{(0)}$ and then using their RR

$$[\bar{\mathbf{r}}]^{(m)} = R_i[\overline{\mathbf{r} - \mathbf{1}_i}]^{(m+1)} - (r_i - 1)[\overline{\mathbf{r} - \mathbf{2}_i}]^{(m+1)} \tag{20}$$

where $\mathbf{1}_i = (\delta_{ix}, \delta_{iy}, \delta_{iz})$ and $\mathbf{2}_i = (2\delta_{ix}, 2\delta_{iy}, 2\delta_{iz})$.

To form the full set of $[\bar{\mathbf{r}}]^{(0)}$ integrals (there are ${}_{L+2}C_3$ of them) from the $[\mathbf{0}]^{(m)}$ using Eq. (20) as FLOP-efficiently as possible, it is desirable to solve the implicit minimum-FLOP tree-search problem. This is difficult and, to this point, we have been able to do so only for $L < 6$. In lieu of the general solution, we have developed a rapid preliminary "sieve" (see Appendix) which determines many of the ${}_{L+3}C_4$ auxiliary $[\bar{\mathbf{r}}]^{(m)}$ integrals which are redundant in the computation of the desired $[\bar{\mathbf{r}}]^{(0)}$ integrals. The sieve is equivalent to the exact solution when $L < 5$ and seems to work well for $L \geq 5$.

*The Bra-contraction Step*

McMurchie and Davidson have shown [12] how the $[\bar{\mathbf{p}}|\bar{\mathbf{q}}]$ integrals, once formed, may be transformed to $[\mathbf{ab}|\mathbf{cd}]$ integrals by using the elementary recurrence relation for Hermite polynomials. Proceeding in this way, we have

$$\begin{aligned}
&\zeta^{(p_i+1)/2} H_{p_i+1}[\zeta^{1/2}(i - P_i)] \\
&\quad \equiv \zeta^{(p_i+1)/2}\{2\zeta^{1/2}(i - P_i)H_{p_i}[\zeta^{1/2}(i - P_i)] - 2p_i H_{p_i-1}[\zeta^{1/2}(i - P_i)]\} \\
&\quad \equiv 2\zeta\{[(i - A_i) - (P_i - A_i)]\zeta^{p_i/2} H_{p_i}[\zeta^{1/2}(i - P_i)] \\
&\qquad - p_i \zeta^{(p_i-1)/2} H_{p_i-1}[\zeta^{1/2}(i - P_i)]\}
\end{aligned} \tag{21}$$

(where, as usual, $i = x$, $y$, or $z$). Multiplying Eq. (21) by $\psi_{\mathbf{a}-\mathbf{1}_i}/(2\zeta)$ and using the definition of $\mathbf{P}$ [Eq. (9)] gives rise to the transformation identity

$$\psi_{\mathbf{a}}\bar{\psi}_{\mathbf{p}} \equiv p_i \psi_{\mathbf{a}-\mathbf{1}_i}\bar{\psi}_{\mathbf{p}-\mathbf{1}_i} - (A_i - B_i)\left(\frac{2\beta}{2\zeta}\right)\psi_{\mathbf{a}-\mathbf{1}_i}\bar{\psi}_{\mathbf{p}} + \left(\frac{1}{2\zeta}\right)\psi_{\mathbf{a}-\mathbf{1}_i}\bar{\psi}_{\mathbf{p}+\mathbf{1}_i} \tag{22}$$

which can be used to relate $[\bar{\mathbf{p}}|\bar{\mathbf{q}}]$ integrals to $[\mathbf{ab}|\mathbf{cd}]$ ones. At this point, we note an important feature of this identity, namely that it involves only functions of the coordinates of *one* electron and hence leads to a transformation which affects only *one* side of the bar in an ERI. This suggests that, for conciseness, we adopt a "bra-ket" notation henceforth. For example, the bra transformation implied by Eq. (22) is

$$\begin{aligned}
[\mathbf{a}\bar{\mathbf{p}}| &= p_i[(\mathbf{a} - \mathbf{1}_i)(\overline{\mathbf{p} - \mathbf{1}_i})| - (A_i - B_i)\left(\frac{2\beta}{2\zeta}\right)[(\mathbf{a} - \mathbf{1}_i)\bar{\mathbf{p}}| \\
&\quad + \left(\frac{1}{2\zeta}\right)[(\mathbf{a} - \mathbf{1}_i)(\overline{\mathbf{p} + \mathbf{1}_i})|
\end{aligned} \tag{23}$$

and, of course, the complementary ket transformation is entirely analogous. Since Eq. (23) pertains to uncontracted bras, we will refer to it as the uncontracted transformation equation (UTE).

In constructing this algorithm, our primary aim is to reduce the amount of work which is performed within the innermost contraction loop. That is, we wish to introduce a contraction step as early in the method as is feasible. However, it would appear that it is not sensible to contract the $[\bar{\mathbf{p}}|\bar{\mathbf{q}}]$ integrals because the UTE involves

Gaussian exponents and, as a result, could not be applied to contracted integrals. Nonetheless, if we introduce *u,v-scaled bras,* defined thus

$$[\bar{\mathbf{p}}|_{u,v} = \frac{(2\beta)^u}{(2\zeta)^v}[\bar{\mathbf{p}}| \tag{24}$$

then we can recast the UTE into the following form:

$$[\mathbf{a}\bar{\mathbf{p}}|_{u,v} = p_i[(\mathbf{a}-\mathbf{1}_i)(\overline{\mathbf{p}-\mathbf{1}_i})|_{u,v} - (A_i - B_i)[(\mathbf{a}-\mathbf{1}_i)\bar{\mathbf{p}}|_{u+1,v+1} + [(\mathbf{a}-\mathbf{1}_i)(\overline{\mathbf{p}+\mathbf{1}_i})|_{u,v+1} \tag{25}$$

Equations (23) and (25) have identical content, but the latter is written in a form which is *not explicitly exponent dependent.* This formulation is crucial to the new algorithm, for it implies that Eq. (25) *can* be directly applied to contracted ($u$,$v$-scaled) bras, i.e.,

$$(\mathbf{a}\bar{\mathbf{p}}|_{u,v} = p_i((\mathbf{a}-\mathbf{1}_i)(\overline{\mathbf{p}-\mathbf{1}_i})|_{u,v} - (A_i - B_i)((\mathbf{a}-\mathbf{1}_i)\bar{\mathbf{p}}|_{u+1,v+1} + ((\mathbf{a}-\mathbf{1}_i)(\overline{\mathbf{p}+\mathbf{1}_i})|_{u,v+1} \tag{26}$$

Since Eq. (26) pertains to contracted bras, we will refer to it as the contracted transformation equation (CTE).

Thus, the final step of the $K^4$-work in the new algorithm is the preparation of a set of left-contracted, $u$,$v$-scaled $(\bar{\mathbf{p}}|\bar{\mathbf{q}}]_{u,v}$ integrals for each $(u,v)$ pair which will be required when the CTE is applied in the next step of the method. We note that the largest of these sets is that for ($u = 0$, $v = a + b$), and the first factor in the denominator of the $\omega$ factor, Eq. (16), was included precisely so that scaling could be avoided for this set.

Equation (18) may be used to bypass redundant calculations when the $(\bar{\mathbf{p}}|\bar{\mathbf{q}}]_{u,v}$ sets are being formed, thus

$$(\bar{\mathbf{p}}|\bar{\mathbf{q}}]_{u,v} = \sum_{k_A}^{K_A}\sum_{k_B}^{K_B}\frac{(2\beta)^u}{(2\zeta)^v}[\bar{\mathbf{p}}|\bar{\mathbf{q}}] = (-1)^q\sum_{k_A}^{K_A}\sum_{k_B}^{K_B}\frac{(2\beta)^u}{(2\zeta)^v}[\overline{\mathbf{p}+\mathbf{q}}] \tag{27}$$

As there are only $O(L^3)$ of the $[\bar{\mathbf{r}}]$ integrals which need to be scaled and contracted in this way, the total $K^4$ work in this algorithm is strikingly less than in almost all previous methods.

### *The First Bra-transformation Step*

Once the left-contracted $(\bar{\mathbf{p}}|\bar{\mathbf{q}}]_{u,v}$ integrals have been evaluated, we enter the $K^2$ region of the algorithm. We are now in a position to use the CTE to transform our ERIs from the framework of **P**-centered Hermite bras to that of **AB**-centered Gaussian bras. Following HGP, we choose to use the CTE to form $(\mathbf{e0}|$, rather than $(\mathbf{ab}|$, bras because there are $O(L^4)$ of the latter but only $O(L^3)$ of the former. (Proceeding in this way reduces $K^2$ work at the expense, later on, of increased $K^0$ work.) At the completion of this step, the sets of left-contracted $(\bar{\mathbf{p}}|\bar{\mathbf{q}}]_{u,v}$ integrals have been transformed into a single set of $(\mathbf{e0}|\bar{\mathbf{q}}]$ integrals.

*The Ket-contraction Step*

By this stage, we have transformed uncontracted **P**-centered Hermite bras to contracted **AB**-centered Gaussian bras. It is now the turn of the kets. We proceed very similarly for these, except that a simplification comparable to Eq. (27) no longer applies. All the required $(\mathbf{e0}|\bar{\mathbf{q}}]_{u,v}$ sets are prepared by scaling and then ket-contracting the appropriate $(\mathbf{e0}|\mathbf{q}]$ integrals.

$$(\mathbf{e0}|\bar{\mathbf{q}})_{u,v} = \sum_{k_C}^{K_C} \sum_{k_D}^{K_D} \frac{(2\delta)^u}{(2\eta)^v} (\mathbf{e0}|\bar{\mathbf{q}}] \tag{28}$$

*The First Ket-transformation Step*

Having found the requisite $(\mathbf{e0}|\bar{\mathbf{q}})_{u,v}$ integrals, we enter the $K^0$-region of the algorithm, i.e., all subsequent work is outside the contraction loops. The CTE (in its ket form) can now be used to transform our ERIs from the framework of uncontracted **Q**-centered Hermite kets to that of contracted **CD**-centered Gaussian kets. As before, we choose to transform to $|\mathbf{f0})$, rather than $|\mathbf{cd})$, kets and this eventually leads to a set of all the necessary $(\mathbf{e0}|\mathbf{f0})$ ERIs.

*The Second Bra-transformation Step*

At this point, outside all of the contraction loops, we rejoin the HGP algorithm which, by the conclusion of its VRR and contraction steps, has produced the same set of $(\mathbf{e0}|\mathbf{f0})$ ERIs as we now have. At this point, HGP use their HRR (horizontal recurrence relation) to transform from $(\mathbf{e0}|$ to $(\mathbf{ab}|$ bras, *viz.*,

$$(\mathbf{ab}| = ((\mathbf{a} + \mathbf{1}_i)(\mathbf{b} - \mathbf{1}_i)| + (A_i - B_i)(\mathbf{a}(\mathbf{b} - \mathbf{1}_i)| \tag{29}$$

and this eventually leads to the set of all necessary $(\mathbf{ab}|\mathbf{f0})$ ERIs.

When the integral class in question contains $d$ (or higher) functions, the HRR can be applied in more than one way and another tree-search problem is implied. Solving this tree-search problem leads to significant savings in the total computational effort required by the HRR, and we use a preliminary sieve (like that in the generation step) for this purpose.

*The Second Ket-transformation Step*

The last step of the algorithm is also shared with that of HGP (except that, as above, we begin by sieving), who employ their HRR again to transform from $|\mathbf{f0})$ to $|\mathbf{cd})$ kets, thus

$$|\mathbf{cd}) = |(\mathbf{c} + \mathbf{1}_i)(\mathbf{d} - \mathbf{1}_i)) + (C_i - D_i)|\mathbf{c}(\mathbf{d} - \mathbf{1}_i)) \tag{30}$$

and this eventually leads to the desired $(\mathbf{ab}|\mathbf{cd})$ integral class.

## Theoretical Performance Assessment

In Tables I and II, we compare the FLOP counts of the present algorithm (henceforth referred to as GHP) against those of the Pople-Hehre [10], Rys [11], Mc-

TABLE I. FLOP counts[a] for the formation of a $(pp/pp)$ integral class.

| | PH | DRK | MD | HGP | GHP |
|---|---|---|---|---|---|
| $x (\times K^4)$ | 220 | 1800 | 1100 | 840 | 300 |
| $y (\times K^2)$ | 2300 | 50 | 600 | 30 | 610 |
| $z (\times K^0)$ | 4000 | 0 | 0 | 330 | 680 |
| Cost ($K = 1$) | 6,500 | 1,900 | 1,700 | 1,200 | 1,600 |
| Cost ($K = 2$) | 17,000 | 29,000 | 20,000 | 14,000 | 7,900 |
| Cost ($K = 3$) | 43,000 | 150,000 | 95,000 | 69,000 | 30,000 |
| Cost ($K = 4$) | 97,000 | 460,000 | 290,000 | 220,000 | 87,000 |
| Cost ($K = 5$) | 200,000 | 1,100,000 | 700,000 | 530,000 | 200,000 |

[a] The coefficients $x$, $y$, and $z$ refer to Eq. (6) (see text). PH = The axis-switch method of Pople and Hehre, see Ref. 10. DRK = The Rys polynomial method of Dupuis, Rys, and King, see Ref. 11. MD = The Hermite method of McMurchie and Davidson, see Ref. 12. HGP = The recurrence relation method of Head-Gordon and Pople, see Ref. 2. GHP = The present algorithm. The PH, DRK, MD, and HGP results are computed from values given in Ref. 2. Two significant figures are given. The $x$ coefficient includes one square root and one $F_m(T)$ evaluation.

TABLE II. FLOP counts[a] for ERI formation.

| Class | PH | DRK | MD | HGP | GHP |
|---|---|---|---|---|---|
| $(pp/pp)$ | | | | | |
| $x$ | 220 | 1,800 | 1,100 | 840 | 300 |
| $y$ | 2,300 | 50 | 600 | 30 | 610 |
| $z$ | 4,000 | 0 | 0 | 330 | 680 |
| $(sp)^4$ | | | | | |
| $x$ | 220 | 3,600 | 1,500 | 1,400 | 450 |
| $y$ | 2,300 | 50 | 1,700 | 30 | 1,300 |
| $z$ | 4,000 | 0 | 0 | 800 | 1,700 |
| $(dd/dd)$ | | | | | |
| $x$ | — | 30,900 | 27,300 | 14,600 | 2,450 |
| $y$ | — | 220 | 24,000 | 30 | 25,800 |
| $z$ | — | 0 | 0 | 11,300 | 28,900 |
| $(ff/ff)$ | | | | | |
| $x$ | — | 276,000 | 342,000 | 108,000 | 11,000 |
| $y$ | — | 600 | 383,000 | 30 | 600,000 |
| z | — | 0 | 0 | 135,000 | 600,000 |

[a] See footnotes for Table I.

Murchie-Davidson [12], and Head-Gordon-Pople [2] schemes for the generation of $(pp|pp)$, $(sp, sp|sp, sp)$ [abbreviated $(sp)^4$], $(dd|dd)$, and $(ff|ff)$ integral classes. The FLOP counts are conveniently expressed via the quartic coefficients of Eq. (6) but, in Table I, the total FLOP counts are also given explicitly for a range of degrees of contraction $K$. It is clear from both tables that the new algorithm represents a significant advance over previous methods for the computation of contracted ERI classes.

For uncontracted $(pp|pp)$ classes (Table I), the HGP methodology appears to be superior to GHP but, as we will discuss in another paper [13], it is more efficient for GHP to transform uncontracted bras and kets using the UTE, rather than the CTE, and this leads to substantial savings in the $K = 1$ case.

As a rule of thumb, since common basis sets consist of both uncontracted and contracted basis functions, the $K = 2$ FLOP counts give a good indicator of "overall" algorithm performance in a typical molecular calculation. From Table I we see that GHP represents an improvement by a factor of roughly 2 over the HGP and PH approaches for this degree of contraction. The DRK and MD methods are even less competitive.

As the degree of contraction increases, GHP improves even further relative to all other methods except PH, which eventually ($K \geq 5$) becomes the cheapest algorithm. Even in the $(sp)^4$ case (for which the PH method was optimized), GHP is cheaper than PH for $K = 2$ and is comparable for $K = 3$.

From Table II it is apparent that GHP retains its comparative efficiency for ERI classes of higher angular momentum. The fact that the $x$ parameters in the GHP algorithm are so much smaller than those for previous algorithms implies that, for sufficiently contracted ERI classes, GHP will inevitably be the cheapest approach. We note, however, that the degree of contraction necessary for GHP to be better than HGP seems to increase somewhat as the angular momentum of the ERI class increases. For example, HGP is superior to GHP when $K \leq 2$ for $(ff|ff)$ classes.

The ramifications of a faster algorithm for calculating ERIs will be most significant in the increasingly popular "direct" procedures [5–8], where integrals must be recalculated many times. Moreover, as the new algorithm promises to be even more efficient for ERI *derivatives* [13] than it is for ERIs themselves, we expect it to render the new "simultaneous" optimization methods [14,15] even more competitive with their conventional analogues.

## Appendix: The Generation-Step Sieve

In the present algorithm, we employ a "sieve" to eliminate as much unnecessary work as possible in the generation step where the $[\bar{\mathbf{r}}]$ are derived recursively from the $[\mathbf{0}]^{(m)}$. There are $O(L^4)$ "auxiliary" $[\bar{\mathbf{r}}]^{(m)}$, but it turns out that many of these are not needed in order to form the complete set of $[\bar{\mathbf{r}}]$, of which there are only $O(L^3)$.

Our sieve systematically eliminates, from an originally complete list, those $[\bar{\mathbf{r}}]^{(m)}$ which do not need to be computed. It works as follows:

For each integral $I = [\bar{\mathbf{r}}]^{(m)}$
  Find all integrals $J_I$ which could be formed from $I$ using (20)
  If, for each $J_i$, there is at least one other integral $I'$ (still on the list) from which $J_I$ could be formed, then $I$ is not needed and is removed from the list.

Multiple passes of this type may be made through the list until no further integrals are eliminated. This conceptually simple algorithm appears to work very well. For example, it finds that *almost a third* of the auxiliary integrals are unnecessary in forming the complete set of $[\bar{\mathbf{r}}]$ with $r \leq 16$.

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## Bibliography

[1] (a) H. B. Schlegel, J. Chem. Phys. 77, 3676 (1982); (b) S. Obara and A. Saika, J. Chem. Phys. **84**, 3963 (1986); (c) H. B. Schlegel, J. Chem. Phys. **90**, 5630 (1989).
[2] M. Head-Gordon and J. A. Pople, J. Chem. Phys. **89**, 5777 (1988).
[3] S. F. Boys, Proc. Roy. Soc. (London) A**200**, 542 (1950).
[4] (a) C. C. J. Roothaan, Rev. Mod. Phys. **23**, 69 (1951); (b) J. A. Pople and R. K. Nesbet, J. Chem. Phys. **22**, 571 (1954).
[5] J. Almlöf, K. Faegri, and K. Korsell, J. Comput. Chem. **3**, 385 (1982).
[6] M. Head-Gordon, J. A. Pople, and M. J. Frisch, Chem. Phys. Letters **153**, 503 (1988).
[7] S. Saebø and J. Almlöf, Chem. Phys. Letters **154**, 83 (1989).
[8] M. J. Frisch, M. Head-Gordon and J. A. Pople, to be published.
[9] (a) I. Shavitt, in *Methods in Computational Physics,* B. Alder, S. Fernbach, and M. Rotenberg, Eds. (Academic, New York, 1963), Vol. 2, p. 1; (b) V. R. Saunders, in *Computational Techniques in Quantum Chemistry and Molecular Physics,* G. H. F. Diercksen, B. T. Sutcliffe, and A. Veillard, Eds. (Reidel, Dordrecht, 1975), p. 347; (c) V. R. Saunders, in *Methods in Computational Physics,* G. H. F. Diercksen and S. Wilson, Eds. (Reidel, Dordrecht, 1973), p. 1; (d) D. Hegarty and G. Van Der Velde, Int. J. Quantum Chem. **23**, 1135 (1983); (e) D. Hegarty in *Advanced Theories and Computational Approaches to the Electronic Structure of Molecules,* C. E. Dykstra, Ed. (Reidel, Dordrecht, 1984), p. 39.
[10] J. A. Pople and W. J. Hehre, J. Comput. Phys. **27**, 161 (1978).
[11] (a) M. Dupuis, J. Rys, and H. F. King, J. Chem. Phys. **65**, 111 (1976); (b) H. F. King and M. Dupuis, J. Comput. Phys. **21**, 44 (1976); (c) J. Rys, M. Dupuis, and H. F. King, J. Comput. Chem. **4**, 154 (1983).
[12] L. E. McMurchie and E. R. Davidson, J. Comput. Phys. **26**, 218 (1978).
[13] P. M. W. Gill, M. Head-Gordon, and J. A. Pople, to be published.
[14] M. Head-Gordon and J. A. Pople, J. Phys. Chem. **92**, 3063 (1988).
[15] M. Head-Gordon, J. A. Pople, and M. J. Frisch, Int. J. Quantum Chem., Quantum Chem. Symp. **23**, 291 (1989).

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*Note Added in Proof:* Further investigations have established that, in certain circumstances, the loop structure given in this paper is not optimal. Two straightforward improvements are as follows:

(1) When the desired ERI class is sufficiently highly contracted, it is more efficient to reverse the order of the ket-contraction and bra-transformation steps. Such a reversal serves to reduce the $y$ parameter of Eq. (6) at the expense of increasing the $z$ parameter.
(2) For certain types of integral class, it is more efficient to transform directly from (**p**| bras to (**ab**| bras than to form intermediate (**e0**| bras.

For example, if both of these modifications are employed in generating a $(pp|pp)$ class, the $x$, $y$, and $z$ parameters (which are otherwise 300, 610, and 680 respectively) become 300, 215, and 1035, respectively. As we will discuss further in an upcoming paper [13], we suggest that an efficient computer program should be capable of rapidly predetermining the optimal loop structure for the production of any given type of integral class.