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Two-Electron Integrals over Gaussian Geminals

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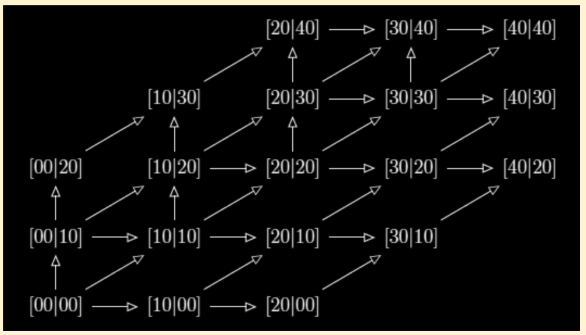
ABSTRACT: The evaluation of contracted two-electron integrals over a Gaussian geminal operator is pivotal to diverse quantum chemistry methods. In this article, using the unique factorization properties and the sparsity of these integrals, a novel, near-optimal computation algorithm is presented. Our method employs a combination of recently developed upper bounds, recurrence relations in the spirit of the Head-Gordon–Pople approach, and late- and early-contraction paths in the PRISM style. A detailed study of the FLOP (floating-point operations) cost reveals that the new algorithm is computationally much cheaper than any other previous scheme.



1. INTRODUCTION

Fashions come and go in quantum chemistry, but Gaussian functions are here to stay. Their unique combination of desirable properties—strong localization, infinite differentiability, and closure under multiplication—have cemented their status as near-ideal computational building blocks, and they enjoy an almost unchallenged pre-eminence in most of the popular molecular orbital software packages.

However, they have not always been so admired. Following Boys's landmark proposal[1] that they be used as basis functions for molecular orbitals, many of the field's leading exponents were skeptical and continued to persevere with exponential functions of various types, either devoting years of effort to the multicenter two-electron integrals that such functions entail or approximating those integrals by ingenious combinations of fitting and neglect.

It is less well-known that, 10 years after the paper of Boys and long before Gaussian basis functions had garnered universal approval, Boys[2] and Singer[3] proposed that a Gaussian in the distance r_{12} between two electrons, the so-called Gaussian geminal

$$\hat{G}(r_{12}) = \exp(-\lambda {r_{12}}^2) \tag{1}$$

could be a similarly potent two-electron basis function because (quoting Boys[2]) "there are explicit formulas for all of the necessary many-dimensional integrals" that arise.

Over the years, a number of other geminal functions have been contemplated, primarily because the lack of cusps[4] in Gaussians has been perceived as a serious deficiency. Ten-no showed that although the Slater geminal $\exp(-\lambda r_{12})$ is more difficult to handle than its Gaussian cousin the integrals that it generates can be computed, albeit with some effort.[5,6] Soon afterward, in an elegant comparative study,[7] Tew and Klopper concluded that the Slater geminal is superior to three other non-Gaussian alternatives. However, although one-electron Gaussians are inherently incapable of modeling nuclear–electron cusps and two-electron Gaussian geminals are likewise unable to capture electron–electron cusps, it has been established both theoretically[8−11] and empirically that a "brute force" saturation of function space, including Gaussians with large exponents, can reduce the cusp-related errors to any desired level. As a consequence, the Boys–Singer idea has taken root and flourished over the years in a number of groups.[12−34]

Twenty years ago, Gill and Adamson suggested[35] that the short-range part of the Coulomb operator could be systematically improved toward the full operator by adding Gaussians, that is

$$\frac{1}{r_{12}} \approx \frac{\mathrm{erfc}(\omega r_{12})}{r_{12}} + \frac{2\omega}{\sqrt{\pi}} \sum_{j=1}^{m} c_j \exp(-\omega^2 {\alpha_j}^2 {r_{12}}^2) \tag{2}$$

where erfc is the complementary error function[36] and the coefficients c_j and exponents α_j are dimensionless constants. If c_j and α_j are chosen to match the first $4m - 2$ derivatives at $r_{12} = 0$, one obtains a family of Coulomb-attenuated potentials that we termed CAP(m), and we explored the performance of several of these potentials for the prediction of chemical properties.[37] A few years later, Sirbu and King[38] proposed a single-Gaussian expansion in which the parameters were instead tailored for a subsequent perturbation theory. In 2004, Toulouse et al.[39] adopted the CAP(1) potential, renaming it "erfgau" and using it to explain the accuracy of the Local Density Approximation (LDA) in density functional theory (DFT). The erfgau potential was adopted by Song and co-workers,[40,41] who later discovered problems for which it is useful to drop the erfc term[42−44] and subsequently to add a second Gaussian,[45] to form the "2Gau" potential. In 2Gau, the more diffuse Gaussian ($\alpha = 0.006$) is used to estimate the medium-range part of the exchange energy.

Boys–Singer, CAP(m), erfgau, and 2Gau calculations all require the evaluation of two-electron integrals over the geminal

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operator (eq 1), and for efficient applications to large chemical systems, it is desirable to be able to compute these fast. If the molecular orbitals are expanded in a Gaussian basis, that is, the basis functions and the two-electron operator are both Gaussian, the resulting integrals factorize immediately into their Cartesian components[46] and can be formed without the need for an "auxiliary index" m. This offers important computational advantages, and the usual recurrence relations (RRs) that are effective for forming traditional Coulomb integrals[46−61] must be appropriately simplified and optimized in order to be maximally effective.

In addition to constructing optimal RRs and using them intelligently, one must also fully exploit the fact that the Gaussian geminal (eq 1) is a short-range operator whose matrix elements between spatially well-separated charge distributions are negligible and should be systematically avoided. It is easy to show that if the basis set contains N functions there are $O(N^4)$ two-electron integrals but only $O(N)$ of these are non-negligible in a large molecule. We[62] and others[63] have discussed special techniques for identifying this tiny subset of worthwhile integrals and avoiding the others.

In the following sections, we present a near-optimal algorithm for constructing two-electron integrals over eq 1 in a basis set of contracted Gaussian functions. After defining our notation in section 2, we discuss a detailed algorithm in section 3 and its application to the formation of a (pp|pp) class in section 4. Finally, computational costs are examined in section 5.

2. NOTATION

A contracted Gaussian basis function

$$\psi_{\mathbf{a}}(\mathbf{r}) = \sum_{i=1}^{K_A} \phi_{\mathbf{a}}^{i}(\mathbf{r}) \tag{3}$$

is a sum of primitive Gaussians

$$\phi_{\mathbf{a}}^{i}(\mathbf{r}) = D_A^i n_A^i (x - A_x)^{a_x} (y - A_y)^{a_y} (z - A_z)^{a_z} e^{-\alpha_i |\mathbf{r}-\mathbf{A}|^2} \tag{4}$$

and K_A is typically between 1 and 20. A primitive is defined by its contraction coefficient D_A^i, normalization factor n_A^i, exponent α_i, center $\mathbf{A} = (A_x,A_y,A_z)$, angular momentum vector $\mathbf{a} = (a_x,a_y,a_z)$, and total angular momentum $a = a_x + a_y + a_z$. We will usually suppress the primitive index i.

A contracted Gaussian pair (indicated by a parenthesis)

$$(\mathbf{ab}| = \psi_{\mathbf{a}}(\mathbf{r})\psi_{\mathbf{b}}(\mathbf{r}) \tag{5}$$

is a sum of primitive Gaussian pairs (indicated by a bracket)

$$[\mathbf{ab}| = \phi_{\mathbf{a}}(\mathbf{r})\phi_{\mathbf{b}}(\mathbf{r}) \tag{6}$$

A pair of contracted pairs is a contracted quartet and yields a contracted integral

$$(\mathbf{ab}|\mathbf{cd}) = \iint \psi_{\mathbf{a}}(\mathbf{r}_1)\psi_{\mathbf{b}}(\mathbf{r}_1)\hat{G}(r_{12})\psi_{\mathbf{c}}(\mathbf{r}_2)\psi_{\mathbf{d}}(\mathbf{r}_2)\, d\mathbf{r}_1\, d\mathbf{r}_2 \tag{7}$$

which is a sum of primitive integrals

$$[\mathbf{ab}|\mathbf{cd}] = \iint \phi_{\mathbf{a}}(\mathbf{r}_1)\phi_{\mathbf{b}}(\mathbf{r}_1)\hat{G}(r_{12})\phi_{\mathbf{c}}(\mathbf{r}_2)\phi_{\mathbf{d}}(\mathbf{r}_2)\, d\mathbf{r}_1\, d\mathbf{r}_2 \tag{8}$$

It is easy to show that

$$[\mathbf{ab}|\mathbf{cd}] = G_{AB}G_{CD}T_{a_xb_xc_xd_x}T_{a_yb_yc_yd_y}T_{a_zb_zc_zd_z} \tag{9}$$

where the Gaussian product exponents, centers, and prefactors are

$$\zeta = \alpha + \beta \qquad \mathbf{P} = \frac{\alpha\mathbf{A} + \beta\mathbf{B}}{\alpha + \beta}$$

$$G_{AB} = D_A n_A D_B n_B (\pi/\zeta)^{3/2} \exp\left[-\frac{|\mathbf{AB}|^2}{\alpha^{-1} + \beta^{-1}}\right] \tag{10a}$$

$$\eta = \gamma + \delta \qquad \mathbf{Q} = \frac{\gamma\mathbf{C} + \delta\mathbf{D}}{\gamma + \delta}$$

$$G_{CD} = D_C n_C D_D n_D (\pi/\eta)^{3/2} \exp\left[-\frac{|\mathbf{CD}|^2}{\gamma^{-1} + \delta^{-1}}\right] \tag{10b}$$

Here, and elsewhere, we use **AB** to represent the vector **A**−**B**. The Rys integrals are

$$T_{abcd} = \frac{\sqrt{\zeta\eta}}{\pi} \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} (s - A)^a (s - B)^b (t - C)^c (t - D)^d \times e^{-\zeta(s-P)^2} e^{-\lambda(s-t)^2} e^{-\eta(t-Q)^2}\, ds\, dt \tag{11}$$

and the simplest of these is

$$T_{0000} = \left[\frac{\lambda^{-1}}{\zeta^{-1} + \lambda^{-1} + \eta^{-1}}\right]^{1/2} \exp\left[-\frac{(P - Q)^2}{\zeta^{-1} + \lambda^{-1} + \eta^{-1}}\right] \tag{12}$$

When discussing RRs, we use a compact vector notation that we introduced recently[61] wherein $\mathbf{a}^{\pm}$ represents the three angular momentum vectors formed by incrementing or decrementing the x, y, or z components of **a**. For example, Boys's famous formula[1] for the derivatives of the primitive Gaussian (eq 4) with respect to the components of its center is

$$\nabla_{\mathbf{A}}[\mathbf{a}| = 2\alpha[\mathbf{a}^+| - \mathbf{a}[\mathbf{a}^-| \tag{13}$$

This notation avoids the need for the $\mathbf{a} \pm \mathbf{1}_i$ motifs that arise in the Obara−Saika notation.[50]

We will use nonbold indices to indicate shells of Gaussians. For example, [11| denotes a primitive Gaussian shell pair arising from two p shells. Similarly, (22|10) denotes a class of $6 \times 6 \times 3 \times 1 = 108$ contracted integrals that arise from two d shells, a p shell, and an s shell.

3. ALGORITHM

In this section, we present an efficient algorithm for generating an $(ab|cd)$ class from shell data. We use L to denote the maximum angular momentum in the basis set. For example, if the basis contains only s, p, and d functions, then $L = 2$.

3.1. Significant shell-pairs. We have recently derived[64] the primitive class bound

$$|[ab|\mathrm{cd}]| \le [\mathrm{ab}]^{\hat{G}}[cd] \tag{14}$$

where the primitive bound factor is

$$[ab]^{\hat{G}} = [ab]\left[\frac{(1 - \xi)(\alpha + \beta)}{\lambda + (1 - \xi)(\alpha + \beta)}\right]^{3/2} \tag{15}$$

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and

$$[ab] = |D_A D_B| \sqrt{\frac{a^a e^{-a}}{(1/2)_a} \frac{b^b e^{-b}}{(1/2)_b}} \frac{(4\alpha\beta)^{3/4}}{(\alpha+\beta)^{3/2}} \times \frac{\xi^{-(a+b)/2}}{(1-\xi)^{3/2}} \exp\left[-(1-\xi)\frac{|\mathbf{AB}|^2}{\alpha^{-1}+\beta^{-1}}\right] \quad (16)$$

$(z)_n$ is a Pochhammer symbol,[36] and ξ is an adjustable parameter that we set to

$$\xi = \frac{(a+b)(\alpha+\beta+\lambda)}{(a+b+3)(\alpha+\beta) + 2\frac{|\mathbf{AB}|^2}{\alpha^{-1}+\beta^{-1}}(\alpha+\beta+\lambda)} \quad (17)$$

The bound factor $[cd]$ is defined similarly, and we have shown[64] that it is bounded by

$$[cd] \le M = \frac{(L+3/2)^{L+3/2} e^{-L}}{(3/2)^{3/2}(1/2)_L} \quad (18)$$

Thus, to build a list of "significant" contracted shell pairs, that is, those that could yield integrals over $\hat{G}(r_{12})$ that exceed a user-specified threshold τ, we follow the scheme in Algorithm 1 in Chart 1. In an extended system with N shells, this generates only $O(N)$ significant shell pairs.

Chart 1. Algorithm 1: Construction of Significant Shell Pairs for Computing Integrals over $\hat{G}(r_{12})$

```
Compute M using eq 18
Compute τ/M
nSigShellPairs = 0
foreach contracted shell (a| do
  foreach contracted shell (b| do
    K_ab = 0;  ζ_min = 10^6;  (ab) = 0
    foreach primitive shell [a_i| in (a| do
      foreach primitive shell [b_j| in (b| do
        Compute ξ using eq 17
        Compute primitive bound factor [a_i b_j] using eq 16
        Compute primitive bound factor [a_i b_j]^Ĝ using eq 15
        if [a_i b_j]^Ĝ > τ/M then
          K_ab = K_ab + 1
          ζ_min = min((1−ξ)(α_i + β_j), ζ_min)
          (ab) = (ab) + [a_i b_j]
        end
      end
    end
    if K_ab = 0 then
      Discard contracted shell-pair (ab|
    else
      nSigShellPairs = nSigShellPairs + 1
      Store degree of contraction K_ab
      Store minimum exponent ζ_min
      Store contracted bound factor (ab)
    end
  end
end
```

3.2. Significant Shell Quartets. Shell quartets are produced by pairing significant shell pairs. However, because $\hat{G}(r_{12})$ is short-ranged, most of the quartets in an extended system are not significant, and we therefore require a strong upper bound to identify and discard these as cheaply as possible. Bounds[65−67] for Coulomb integrals are weak when applied to integrals over $\hat{G}(r_{12})$, but we have derived[64] the strong bound

$$|(ab|cd)| \le (ab)(cd)G_{abcd} \quad (19)$$

where

$$G_{abcd} = \exp\left[-\frac{R^2}{\zeta_{\min}^{-1} + \lambda^{-1} + \eta_{\min}^{-1}}\right] \quad (20)$$

$\zeta_{\min}$ is the smallest exponent in the $(ab|$ shell pair (see Algorithm 1 in Chart 1) and

$$R = \max\left[0, \left|\frac{\mathbf{A}+\mathbf{B}}{2} - \frac{\mathbf{C}+\mathbf{D}}{2}\right| - \left|\frac{\mathbf{A}-\mathbf{B}}{2}\right| - \left|\frac{\mathbf{C}-\mathbf{D}}{2}\right|\right] \quad (21)$$

is the distance between a sphere with diameter $\overline{\mathbf{AB}}$ and another with diameter $\overline{\mathbf{CD}}$. Thus, to identify the significant contracted shell quartets, we follow the scheme in Algorithm 2 in Chart 2. In an extended system with N shells, this generates only $O(N)$ significant quartets.

Chart 2. Identifying Significant Shell Quartets for Computing Integrals over $\hat{G}(r_{12})$

```
foreach significant shell-pair (ab| do
  foreach significant shell-pair |cd) do
    if (ab)(cd) < τ then
      (ab|cd) is not significant
    else
      Compute G_abcd using eqs 20 and 21
      if (ab)(cd)G_abcd < τ then
        (ab|cd) is not significant
      else
        (ab|cd) is significant
      end
    end
  end
end
```

3.3. Construct [00|00]. For each of the primitive quartets in a significant contracted shell quartet, we form

$$f_\zeta = \frac{\zeta^{-1}}{\zeta^{-1}+\lambda^{-1}+\eta^{-1}} \qquad f_\lambda = \frac{\lambda^{-1}}{\zeta^{-1}+\lambda^{-1}+\eta^{-1}}$$
$$f_\eta = \frac{\eta^{-1}}{\zeta^{-1}+\lambda^{-1}+\eta^{-1}} \quad (22)$$

It then follows from eqs 9 and 12 that

$$[00|00] = G_{AB} G_{CD} f_\lambda^{3/2} \exp\left[-\frac{|\mathbf{PQ}|^2}{\zeta^{-1}+\lambda^{-1}+\eta^{-1}}\right] \quad (23)$$

For optimal efficiency, the exponential should be computed via a Chebyshev interpolation.[68]

If the class angular momentum $a+b+c+d > 0$, we need a pathway to form the required $(e0|f0)$ classes. If the degree of contraction $K_{tot} = K_A K_B K_C K_D$ is small, we use the late-contraction path (section 3.4). If K_{tot} is large, the early contraction path (section 3.5) is more economical.

3.4. Construct (e0|f0) by Late Contraction. When K_{tot} is small, it is best to build angular momentum and then contract,

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Table 1. Cost (Multiplications + Additions) of Forming an $[e0|f0]$ Class Using Equations 26 and 27

|60]	41 + 13	138 + 54	303 + 135	537 + 257	840 + 420	1212 + 624	1653 + 869
|50]	30 + 9	102 + 39	225 + 99	399 + 189	624 + 309	900 + 459	1212 + 624
|40]	21 + 6	72 + 27	159 + 69	282 + 132	441 + 216	624 + 309	840 + 420
|30]	13 + 3	48 + 18	105 + 45	185 + 85	282 + 132	399 + 189	537 + 257
|20]	9 + 3	30 + 12	66 + 30	105 + 45	159 + 69	225 + 99	303 + 135
|10]	3 + 0	12 + 3	30 + 12	48 + 18	72 + 27	102 + 39	138 + 54
|00]	0 + 0	3 + 0	9 + 3	13 + 3	21 + 6	30 + 9	41 + 13
	[00|	[10|	[20|	[30|	[40|	[50|	[60|

Table 2. Cost (Multiplications + Additions) of Forming an $(e0|f0)$ Class Using Equations 35 and 36

|60)	118 + 125	354 + 396	723 + 813	1231 + 1383	1884 + 2106	2682 + 2982	3626 + 4011
|50)	87 + 93	261 + 297	537 + 609	915 + 1035	1401 + 1575	1995 + 2229	2697 + 2997
|40)	63 + 66	189 + 207	387 + 429	657 + 732	1002 + 1116	1425 + 1581	1926 + 2127
|30)	43 + 43	129 + 138	261 + 285	445 + 485	681 + 738	969 + 1044	1310 + 1403
|20)	24 + 27	72 + 84	147 + 174	249 + 297	381 + 453	543 + 642	735 + 864
|10)	12 + 12	36 + 39	75 + 81	129 + 138	198 + 210	282 + 297	381 + 399
|00)	0 + 0	12 + 9	27 + 24	46 + 36	69 + 57	96 + 81	131 + 110
	(00|	(10|	(20|	(30|	(40|	(50|	(60|

in the spirit of the Head-Gordon–Pople approach.[51] We form the Gaussian centroids

$$\mathbf{R}_A = \mathbf{PA} + f_\zeta \mathbf{QP} \qquad \mathbf{R}_C = \mathbf{QC} + f_\eta \mathbf{PQ} \tag{24}$$

and the inverse exponents

$$g_\zeta = \frac{1 - f_\zeta}{2\zeta} \qquad g_\lambda = \frac{f_\zeta}{2\eta} = \frac{f_\eta}{2\zeta} \qquad g_\eta = \frac{1 - f_\eta}{2\eta} \tag{25}$$

and then use RRs to transform $[00|00]$ into the required $[e0|f0]$ classes. We call the following algorithm the late path.

To form an $[e0|f0]$ class in which $e \geq f$, we use the three-term RR[34]

$$[\mathbf{e}^+\mathbf{0}|\mathbf{f}\mathbf{0}] = \mathbf{R}_A[\mathbf{e}\mathbf{0}|\mathbf{f}\mathbf{0}] + \mathbf{e}\, g_\zeta[\mathbf{e}^-\mathbf{0}|\mathbf{f}\mathbf{0}] + \mathbf{f}\, g_\lambda[\mathbf{e}\mathbf{0}|\mathbf{f}^-\mathbf{0}] \tag{26}$$

To form an $[e0|f0]$ class in which $e < f$, we use the three-term RR[34]

$$[\mathbf{e}\mathbf{0}|\mathbf{f}^+\mathbf{0}] = \mathbf{R}_C[\mathbf{e}\mathbf{0}|\mathbf{f}\mathbf{0}] + \mathbf{e}\, g_\lambda[\mathbf{e}^-\mathbf{0}|\mathbf{f}\mathbf{0}] + \mathbf{f}\, g_\eta[\mathbf{e}\mathbf{0}|\mathbf{f}^-\mathbf{0}] \tag{27}$$

Finally, the $[e0|f0]$ are contracted into $(e0|f0)$ using the simple sum

$$(\mathbf{e}\mathbf{0}|\mathbf{f}\mathbf{0}) = \sum_{i=1}^{K_A}\sum_{j=1}^{K_B}\sum_{k=1}^{K_C}\sum_{l=1}^{K_D}[\mathbf{e}\mathbf{0}|\mathbf{f}\mathbf{0}] \tag{28}$$

There are many ways to use eqs 26 and 27 because, in general, an $[\mathbf{e}\mathbf{0}|\mathbf{f}\mathbf{0}]$ integral can be formed in three ways, namely, by incrementing the x, y, or z component of its angular momentum. The pursuit of an optimal strategy to form the required $[e0|f0]$ classes therefore leads to an optimization problem related to the McMurchie–Davidson tree-search problem.[54] Optimal flop costs (decomposed into multiplications and additions) for forming various $[e0|f0]$ classes are shown in Table 1.

3.5. Construct $(e0|f0)$ by Early Contraction. When K_{tot} is large, it is better to contract the $[00|00]$ and then build angular momentum, in the spirit of the Pople–Hehre axis switch method[69] and the CCTTT path in the PRISM algorithm.[57] To achieve this, we substitute the identities[57]

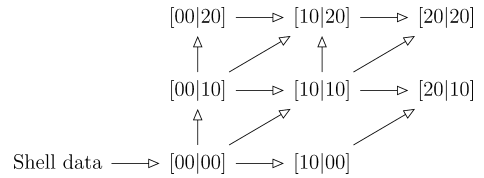

Figure 1. $[e0|f0]$ classes needed to form a (pp|pp) class on the late path.

$$\mathbf{PA} = \mathbf{BA}\frac{2\beta}{2\zeta} \tag{29a}$$

$$\mathbf{QC} = \mathbf{DC}\frac{2\delta}{2\eta} \tag{29b}$$

$$\mathbf{PQ} = \mathbf{BA}\frac{2\beta}{2\zeta} + \mathbf{CD}\frac{2\delta}{2\eta} + \mathbf{AC} \tag{29c}$$

into the primitive RRs (eqs 26 and 27) to obtain the "contraction-ready" RRs

$$[\mathbf{e}^+\mathbf{0}|\mathbf{f}\mathbf{0}] = \left[\mathbf{BA}\frac{2\beta}{2\zeta}(1 - f_\zeta) + \mathbf{DC}\frac{2\delta}{2\eta}f_\zeta + \mathbf{CA}f_\zeta\right][\mathbf{e}\mathbf{0}|\mathbf{f}\mathbf{0}] + \mathbf{e}\frac{1 - f_\zeta}{2\zeta}[\mathbf{e}^-\mathbf{0}|\mathbf{f}\mathbf{0}] + \mathbf{f}\frac{f_\zeta}{2\eta}[\mathbf{e}\mathbf{0}|\mathbf{f}^-\mathbf{0}] \tag{30}$$

$$[\mathbf{e}\mathbf{0}|\mathbf{f}^+\mathbf{0}] = \left[\mathbf{DC}\frac{2\delta}{2\eta}(1 - f_\eta) + \mathbf{BA}\frac{2\beta}{2\zeta}f_\eta + \mathbf{AC}f_\eta\right][\mathbf{e}\mathbf{0}|\mathbf{f}\mathbf{0}] + \mathbf{e}\frac{f_\eta}{2\zeta}[\mathbf{e}^-\mathbf{0}|\mathbf{f}\mathbf{0}] + \mathbf{f}\frac{1 - f_\eta}{2\eta}[\mathbf{e}\mathbf{0}|\mathbf{f}^-\mathbf{0}] \tag{31}$$

Subtracting eq 31 from eq 30 yields a symmetrical RR

$$[\mathbf{e}^+\mathbf{0}|\mathbf{f}\mathbf{0}] - [\mathbf{e}\mathbf{0}|\mathbf{f}^+\mathbf{0}] = \left[\mathbf{BA}\frac{2\beta}{2\zeta}f_\lambda + \mathbf{CD}\frac{2\delta}{2\eta}f_\lambda + \mathbf{CA}(1 - f_\lambda)\right][\mathbf{e}\mathbf{0}|\mathbf{f}\mathbf{0}] + \mathbf{e}\frac{f_\lambda}{2\zeta}[\mathbf{e}^-\mathbf{0}|\mathbf{f}\mathbf{0}] - \mathbf{f}\frac{f_\lambda}{2\eta}[\mathbf{e}\mathbf{0}|\mathbf{f}^-\mathbf{0}] \tag{32}$$

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Table 3. Steps and Flop Costs Required to Form a (pp|pp) Class on the Late Path[a]

			cost				
step	equation	computed quantity	M	A	D	S	E
1	22	$1/(\zeta^{-1} + \lambda^{-1} + \eta^{-1})$		2	1		
2	22	$f_\zeta, f_\lambda, f_\eta$	3				
3	23	$f_\lambda^{3/2}$	1			1	
4	23	**PQ**		3			
5	23	$\|\mathbf{PQ}\|^2/(\zeta^{-1} + \lambda^{-1} + \eta^{-1})$	4	2			
6	23	[00|00]	3				1
7	24	$\mathbf{R}_A, \mathbf{R}_C$	6	6			
8	25	$g_\zeta, g_\lambda, g_\eta$	3	2			
9	26	[10|00]	3	0			
10	27	[00|10], [10|10], [20|10]	45	15			
11	27	[00|20], [10|20], [20|20]	105	45			
12	28	(20|20), (10|20), (20|10), (10|10)		81			
		total K^4 work	173	156	1	1	1
13	37	(11|20), (11|10)	81	81			
14	38	(11|11)	81	81			
		total K^0 work	162	162			

[a]A, M, D, S, and E are addition, multiplication, division, square root, and exponential, respectively.

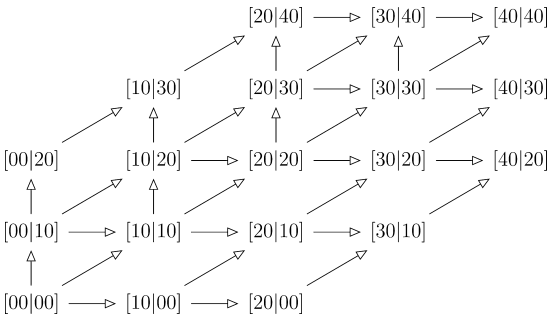

Figure 2. [e0|f0] classes needed to form a (dd|dd) class on the late path.

that relates an integral to its four neighbors and involves f_λ, rather than f_ζ or f_η.

Contracted seven-term RRs emerge from eqs 30−32 by substituting the identities $f_\zeta = (2\lambda/2\zeta)f_\lambda$ and $f_\eta = (2\lambda/2\eta)f_\lambda$ and summing over primitives.[53] This leads to the following algorithm, which we call the early path.

First, [00|00] are half-contracted into [00|00) using the scaled ket contraction[52]

$$[\mathbf{00}|\mathbf{00})^r_{dq} = \sum_{k=1}^{K_C}\sum_{l=1}^{K_D}\frac{(2\delta)^d}{(2\eta)^q} f_\lambda^r [\mathbf{00}|\mathbf{00}] \tag{33}$$

Then, [00|00) are fully contracted into (00|00) using the scaled bra contraction[52]

$${}_{bp}(\mathbf{00}|\mathbf{00})^r_{dq} = \sum_{i=1}^{K_A}\sum_{j=1}^{K_B}\frac{(2\beta)^b}{(2\zeta)^p}[\mathbf{00}|\mathbf{00})^r_{dq} \tag{34}$$

Then, (00|00) are transformed into (e0|00) using the six-term RR (from eq 30)

$$\begin{aligned}{}_{bp}(\mathbf{e}^+\mathbf{0}|\mathbf{00})^r_{dq} &= \mathbf{BA}_{(b+1)(p+1)}(\mathbf{e0}|\mathbf{00})^r_{dq} \\ &- 2\lambda\mathbf{BA}_{(b+1)(p+2)}(\mathbf{e0}|\mathbf{00})^{r+1}_{dq} + 2\lambda\mathbf{DC}_{b(p+1)}(\mathbf{e0}|\mathbf{00})^{r+1}_{(d+1)(q+1)} \\ &+ 2\lambda\mathbf{CA}_{b(p+1)}(\mathbf{e0}|\mathbf{00})^{r+1}_{dq} + \mathbf{e}_{b(p+1)}(\mathbf{e}^-\mathbf{0}|\mathbf{00})^r_{dq} \\ &- 2\lambda\mathbf{e}_{b(p+2)}(\mathbf{e}^-\mathbf{0}|\mathbf{00})^{r+1}_{dq}\end{aligned} \tag{35}$$

Finally, (e0|00) are transformed into (e0|f0) using the seven-term RR (from eq 32)

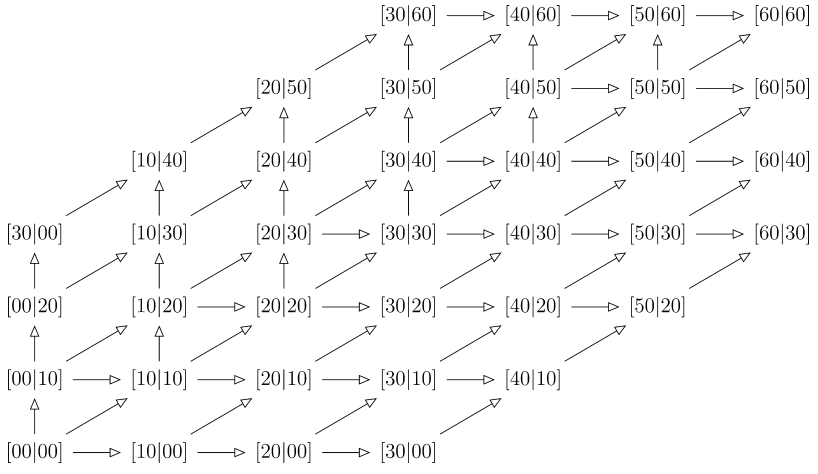

Figure 3. [e0|f0] classes needed to form an (ff|ff) class on the late path.

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Table 4. The 178 ${}_{bp}(00|00)^{r}_{dq}$ Integrals Required to Form a (pp|pp) Class on the Early Path[a]

	(0,0)	(1,1)	(2,2)	(3,3)	(4,4)	(0,1)	(1,2)	(2,3)
(1,1)	0,1,2	1,2	2			1		
(2,2)	0,1,2	1,2	2			1		
(3,3)	0,1,2	1,2						
(4,4)	0,1,2							
(0,1)	0,1,2,3	1,2,3	2,3	3		1,2	2	
(1,2)	0,1,2,3	1,2,3	2,3	3		2	2	
(2,3)	0,1,2,3	1,2,3	2,3			2		
(3,4)	1,2,3	1,2,3						
(4,5)	1,2,3							
(0,2)	0,1,2,3,4	1,2,3,4	2,3,4	3,4	4	2,3	3	3
(1,3)	1,2,3,4	1,2,3,4	2,3,4	3,4		3	3	
(2,4)	1,2,3,4	2,3,4	2,3,4			3		
(3,5)	2,3,4	2,3,4						
(4,6)	2,3,4							
(0,3)	1,2,3,4	2,3,4	2,3,4	3,4	4			
(1,4)	2,3,4	2,3,4	3,4	3,4				
(2,5)	2,3,4	3,4	3,4					
(3,6)	3,4	3,4						
(4,7)	3,4							
(0,4)	2,3,4	3,4	3,4	4	4			
(1,5)	3,4	3,4	4	4				
(2,6)	3,4	4	4					
(3,7)	4	4						
(4,8)	4							
all	0,1,2,3,4	1,2,3,4	2,3,4	3,4	4	1,2,3	2,3	3

[a]The row index is (b,p), the column index is (d,q), and the entries in the body are the required r values. The final row shows the 21 half-contracted $[00|00)^{r}_{dq}$ integrals that are required.

Table 5. Steps and Flop Costs Required to Form a (pp|pp) Class on the Early Path[a]

			Cost				
step	equation	computed quantity	M	A	D	S	E
1	22	$1/(\zeta^{-1}+\lambda^{-1}+\eta^{-1})$		2	1		
2	22	$f_\zeta, f_\lambda, f_\eta$	3				
3	23	$f_\lambda^{3/2}$	1			1	
4	23	$\mathbf{PQ}$		3			
5	23	$\lvert\mathbf{PQ}\rvert^2/(\zeta^{-1}+\lambda^{-1}+\eta^{-1})$	4	2			
6	23	$[00\lvert00]$	3				1
7	33	$[00\lvert00)^{r}_{dq}$	20	21			
		total K^4 work	31	28	1	1	1
8	34	${}_{bp}(00\lvert00)^{r}_{dq}$	178	178			
		total K^2 work	178	178			
9	35	${}_{bp}(a0\lvert00)^{r}_{dq}$	2411	1953			
10	36	$(20\lvert20)$, $(10\lvert20)$, $(20\lvert10)$, $(10,10)$	840	927			
11	37	$(11\lvert20)$, $(11\lvert10)$	81	81			
12	38	$(11\lvert11)$	81	81			
		total K^0 work	3413	3042			

[a]A, M, D, S, and E are addition, multiplication, division, square root, and exponential, respectively.

$$
\begin{aligned}
{}_{bp}(\mathbf{e0}|\mathbf{f}^{+}\mathbf{0})^{r}_{dq} = {}& {}_{bp}(\mathbf{e}^{+}\mathbf{0}|\mathbf{f0})^{r}_{dq} + \mathbf{AB}_{(b+1)(p+1)}(\mathbf{e0}|\mathbf{f0})^{r+1}_{dq} \\
& + \mathbf{DC}_{bp}(\mathbf{e0}|\mathbf{f0})^{r+1}_{(d+1)(q+1)} + \mathbf{AC}_{bp}(\mathbf{e0}|\mathbf{f0})^{r}_{dq} \\
& - \mathbf{AC}_{bp}(\mathbf{e0}|\mathbf{f0})^{r+1}_{dq} - \mathbf{e}_{b(p+1)}(\mathbf{e}^{-}\mathbf{0}|\mathbf{f0})^{r+1}_{dq} \\
& + \mathbf{f}_{bp}(\mathbf{e0}|\mathbf{f}^{-}\mathbf{0})^{r+1}_{d(q+1)} \qquad (36)
\end{aligned}
$$

Optimal flop costs for forming various $(e0|f0)$ classes in this way are shown in Table 2.

3.6. Construct (ab|cd).

Finally, we transform $(e0|f0)$ into $(ab|f0)$ and then into $(ab|cd)$ using the two-term RRs[49,51,56]

$$(\mathbf{ab}^{+}|\mathbf{f0}) = (\mathbf{a}^{+}\mathbf{b}|\mathbf{f0}) + \mathbf{AB}(\mathbf{ab}|\mathbf{f0}) \qquad (37)$$

$$(\mathbf{ab}|\mathbf{cd}^{+}) = (\mathbf{ab}|\mathbf{c}^{+}\mathbf{d}) + \mathbf{CD}(\mathbf{ab}|\mathbf{cd}) \qquad (38)$$

4. EXAMPLES: FORMING A (PP|PP) CLASS

We now consider in detail the steps required to form a (pp|pp) class from shell pair data. We assume, as usual, that each shell has a degree of contraction K. We measure the cost of each step

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by the number of flops (floating-point operations) that it requires, assuming that all useful shell pair data (e.g., $2\delta/2\eta$, G_{AB}, **PA**, etc.) have been precomputed.

4.1. Late Path. Figure 1 shows how the late path builds angular momentum, and Table 3 lists all of the steps needed. In addition to K^4 divisions, square roots, and exponentials, the (pp|pp) flop cost is

$$C^{\text{late}}_{\text{pppp}} = 329K^4 + 324 \tag{39}$$

Figure 1 shows that the [20|00] class can be avoided for (pp|pp) construction, illustrating a general feature of the strategy in section 3.4, which avoids the construction of unnecessary intermediate classes. This saving grows with the angular momentum of the target class, as can be seen in Figures 2 and 3 in the Appendix.

Table 3 reveals that building angular momentum on **C** (eq 27) represents two-thirds of the primitive work and contraction (eq 28) represents only a quarter. We also see that the horizontal recurrence relations (HRRs), eqs 37 and 38, perform half of the work to form an uncontracted (pp|pp) class but that as K increases their contribution becomes a minor component.

4.2. Early Path. Table 4 shows the ${}_{bp}(00|00)^{r}_{dq}$ required on the early path, and Table 5 lists all of the steps required. In addition to K^4 divisions, square roots, and exponentials, the (pp|pp) flop cost is

$$C^{\text{early}}_{\text{pppp}} = 59K^4 + 356K^2 + 6455K^0 \tag{40}$$

Table 4 shows that, whereas (pp|pp) requires 24 distinct bra scalings (rows), it needs only 8 ket scalings (columns). This illustrates a general feature of the strategy in section 3.5, which first builds on **A** using eq 35 and later on **C** using eq 36, creating a strong asymmetry in the number of required bra and ket scalings. This decreases the cost of the ket contraction (eq 33) but increases the cost of the bra contraction (eq 34). These changes create the tiny K^4 coefficient, significantly larger K^2 coefficient, and huge K^0 coefficient in eq 40.

An ($aa|aa$) class consists of $O(a^8)$ integrals, and yet, one can show that on the early path there are only $(a+1)(3a+1)$ ket scalings and the number of ket-contracted $[00|00)^{r}_{dq}$ is only

$$\text{No. of } [00|00)^{r}_{dq} = \frac{(a+1)(4a+3)(7a+2)}{6} \tag{41}$$

For this reason, the early path does remarkably little work at the primitive level (Table 5). As each primitive [00|00] is formed by eq 23, it is immediately contracted into the required $[00|00)^{r}_{dq}$ integrals using eq 33. If done efficiently (Algorithm 3 in Chart 3), each ket-contraction requires only a single multiplication and addition. The subsequent bra-contraction is similarly simple.

In this way, most of the computational effort is shifted to the contracted level, where eq 35 does 68% of the work, eq 36 does 27%, and the HRRs do 5%. Equation 40 shows that the cost of the early path grows only slowly with K, and comparison with eq 39 reveals that the early path is cheaper than the late path for any (pp|pp) class with $K_{\text{tot}} \geq 30$.

5. COMPUTATIONAL COSTS

As shown in the examples above, the flop cost to form a given class by a given algorithm is

$$\text{cost} = xK^4 + yK^2 + zK^0 \tag{42}$$

Chart 3. Forming the [00|00) Integrals Required for (pp|pp) on the Early Path

foreach *bra primitive shell-pair* **do**
  Initialize all $[00|00)^{r}_{dq}$ to zero
  foreach *ket primitive shell-pair* **do**
    $s_{01} = 1/2\eta$ and $s_{11} = 2\delta/2\eta$ (pre-computed)
    Compute f_λ using eq 22
    Compute [00|00] using eq 23
    $T^0_{00} = [00|00]$; Add T^0_{00} to $[00|00)^0_{00}$
    $T^1_{00} = T^0_{00} * f_\lambda$; Add T^1_{00} to $[00|00)^1_{00}$
    $T^2_{00} = T^1_{00} * f_\lambda$; Add T^2_{00} to $[00|00)^2_{00}$
    $T^3_{00} = T^2_{00} * f_\lambda$; Add T^3_{00} to $[00|00)^3_{00}$
    $T^4_{00} = T^3_{00} * f_\lambda$; Add T^4_{00} to $[00|00)^4_{00}$
    $T^1_{11} = T^1_{00} * s_{11}$; Add T^1_{11} to $[00|00)^1_{11}$
    $T^2_{11} = T^1_{11} * f_\lambda$; Add T^2_{11} to $[00|00)^2_{11}$
    $T^3_{11} = T^2_{11} * f_\lambda$; Add T^3_{11} to $[00|00)^3_{11}$
    $T^4_{11} = T^3_{11} * f_\lambda$; Add T^4_{11} to $[00|00)^4_{11}$
    $T^2_{22} = T^2_{11} * s_{11}$; Add T^2_{22} to $[00|00)^2_{22}$
    $T^3_{22} = T^2_{22} * f_\lambda$; Add T^3_{22} to $[00|00)^3_{22}$
    $T^4_{22} = T^3_{22} * f_\lambda$; Add T^4_{22} to $[00|00)^4_{22}$
    $T^3_{33} = T^3_{22} * s_{11}$; Add T^3_{33} to $[00|00)^3_{33}$
    $T^4_{33} = T^3_{33} * f_\lambda$; Add T^4_{33} to $[00|00)^4_{33}$
    $T^4_{44} = T^4_{33} * s_{11}$; Add T^4_{44} to $[00|00)^4_{44}$
    $T^1_{01} = T^1_{00} * s_{01}$; Add T^1_{01} to $[00|00)^1_{01}$
    $T^2_{01} = T^1_{01} * f_\lambda$; Add T^2_{01} to $[00|00)^2_{01}$
    $T^3_{01} = T^2_{01} * f_\lambda$; Add T^3_{01} to $[00|00)^3_{01}$
    $T^2_{12} = T^2_{01} * s_{11}$; Add T^2_{12} to $[00|00)^2_{12}$
    $T^3_{12} = T^2_{12} * f_\lambda$; Add T^3_{12} to $[00|00)^3_{12}$
    $T^3_{23} = T^3_{12} * s_{11}$; Add T^3_{23} to $[00|00)^3_{23}$
  end
end

The x, y, and z parameters have been discussed in many previous papers, and in Table 6, we give their values for forming (pp|pp), (dd|dd), and (ff|ff) classes by the early and late paths described above, comparing these with Pople–Hehre (PH),[69] Head-Gordon–Pople (HGP),[51] and McMurchie–Davidson (MD)[48] algorithms.

For all classes studied, the late path is systematically cheaper than the HGP and MD algorithms. For $K_{\text{tot}} = 1$, the late path is roughly twice as fast as HGP, and for large K_{tot}, the late path is between 2.75 and 4.5 times faster. The early path is uncompetitive for small K_{tot} but quickly overtakes all other algorithms as K_{tot} increases. It outperforms the late path if $K_{\text{tot}} \geq 30$ for (pp|pp), if $K_{\text{tot}} \geq 81$ for (dd|dd), or if $K_{\text{tot}} \geq 158$ for (ff|ff).

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Although the flop cost remains a useful comparator between different algorithms, it has been recognized for many years[70] that the number of memory operations (mop cost) is even more important. This is particularly relevant for classes where the early path generates more ${}_{bp}(00|00)^{r}_{dq}$ integrals (see Table 4, for example) than can fit in the computer's L1 data cache. The L1 cache in a Core i7 Xeon 5500 processor is 32 KB and is sufficient for the contracted fundamentals in a (dd|dd) class (which require 16.5 KB) but not for those in an (ff|ff) class (which require 84 KB). Fortunately, however, the early path is preferred primarily for strongly contracted classes, and this usually limits its application to classes of low-to-moderate angular momentum. High-momentum classes such as (dd|dd) and (ff|ff) are normally either weakly contracted or uncontracted and therefore prefer the late path.

The efficiency of the early path for strongly contracted classes is even more attractive for calculations in which eq 1 is replaced by the contracted Gaussian geminal[27]

$$\hat{G}(r_{12}) = \sum_{m=1}^{K_G} c_m \exp(-\lambda_m {r_{12}}^2) \tag{43}$$

The total degree of contraction is now $K_{tot} = K_A K_B K_C K_D \times K_G$, and the ket contraction (eq 33) naturally generalizes to include the geminal contraction, becoming

$$[\mathbf{00}|\mathbf{00}]^{r}_{dq} = \sum_{k=1}^{K_C}\sum_{l=1}^{K_D}\sum_{m=1}^{K_G} \frac{(2\delta)^d}{(2\eta)^q} f^{r}_{\lambda}[\mathbf{00}|\mathbf{00}] \tag{44}$$

It is therefore immediately clear that calculations using contracted Gaussian geminals with $K_G \gg 1$ will benefit greatly from the early path.

6. CONCLUDING REMARKS

We have presented an efficient algorithm to construct two-electron integrals over a Gaussian geminal operator. Our method employs vertical and horizontal RRs in the spirit of the Head-Gordon−Pople approach and offers late and early contraction paths in the PRISM style. Flop cost parameters reveal that the new algorithm is much cheaper computationally than previous schemes. We therefore expect that efficient implementations of the new approach will significantly reduce the cost of calculations in which the interelectronic Coulomb operator is approximated by expansions such as eq 2.

Table 6. Flop Cost Parameters for Forming Integral Classes by Present and Previous Algorithms

		present algorithms		previous algorithms[51]		
class	flop cost parameter	early	late	PH	HGP	MD
(pp|pp)	x	59	329	220	920	1100
	y	356	0	2300	30	600
	z	6455	324	4000	324	0
(dd|dd)	x	193	3864		14 600	27 300
	y	4130	0		30	24 000
	z	273 736	11 256		11256	0
(ff|ff)	x	477	23 960		108 000	342 000
	y	20 986	0		30	383 000
	z	3 574 460	135 024		135 024	0

Table 7. Steps and Flop Costs Required to Form a (dd|dd) Class on the Late Path[a]

			cost				
step	equation	computed quantity	M	A	D	S	E
1	22	$1/(\zeta^{-1} + \lambda^{-1} + \eta^{-1})$		2	1		
2	22	$f_\zeta, f_\lambda, f_\eta$	3				
3	23	$f_\lambda^{3/2}$	1			1	
4	23	$\mathbf{PQ}$		3			
5	23	$\|\mathbf{PQ}\|^2/(\zeta^{-1} + \lambda^{-1} + \eta^{-1})$	4	2			
6	23	[00|00]	3				1
7	24	$\mathbf{R}_A, \mathbf{R}_C$	6	6			
8	25	$g_\zeta, g_\lambda, g_\eta$	3	2			
9	26	[{0,1,2}0|00]	12	3			
10	27	[{0,1,2,3}0|10]	93	33			
11	27	[{0,1,2,3,4}0|20]	369	159			
12	27	[{1,2,3,4}0|30]	620	280			
13	27	[{2,3,4}0|40]	882	417			
14	28	(20|20), ..., (40|40)		961			
		total K^4 work	1996	1868	1	1	1
15	37	({2,3}1|{2,3,4}0)	1488	1488			
16	37	(22|{2,3,4}0)	1116	1116			
17	38	(22|{2,3}1)	1728	1728			
18	38	(22|22)	1296	1296			
		total K^0 work	5628	5628			

[a]A, M, D, S, and E are addition, multiplication, division, square root, and exponential, respectively.

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Table 8. Steps and Flop Costs Required to Form an (ffff) Class on the Late Path[a]

			cost				
step	equation	computed quantity	M	A	D	S	E
1	22	$1/(\zeta^{-1} + \lambda^{-1} + \eta^{-1})$		2	1		
2	22	$f_\zeta, f_\lambda, f_\eta$	3				
3	23	$f_\lambda^{3/2}$	1			1	
4	23	**PQ**		3			
5	23	$\|\mathbf{PQ}\|^2/(\zeta^{-1} + \lambda^{-1} + \eta^{-1})$	4	2			
6	23	[00|00]	3				1
7	24	$\mathbf{R}_A, \mathbf{R}_C$	6	6			
8	25	$g_\zeta, g_\lambda, g_\eta$	3	2			
9	26	[{0,1,2,3}0|00]	25	6			
10	27	[{0,1,2,3,4}0|10]	165	60			
11	27	[{0,1,2,3,4,5}0|20]	594	258			
12	27	[{0,1,2,3,4,5,6}0|30]	1569	729			
13	27	[{1,2,3,4,5,6}0|40]	2418	1173			
14	27	[{2,3,4,5,6}0|50]	3360	1680			
15	27	[{3,4,5,6}0|60]	4242	2170			
16	28	(30|30), ..., (60|60)		5476			
		total K^4 work	12393	11567	1	1	1
17	37	({3,4,5}1|{3,4,5,6}0)	10212	10212			
18	37	({3,4}2|{3,4,5,6}0)	11100	11100			
19	37	(33|{3,4,5,6}0)	7400	7400			
20	38	(33|{3,4,5}1)	13800	13800			
21	38	(33|{3,4}2)	15000	15000			
22	38	(33|33)	10000	10000			
		total K^0 work	67512	67512			

[a]A, M, D, S, and E are addition, multiplication, division, square root, and exponential, respectively.

These include the CAP(n), LCgau and LC2gau models. The new algorithm should also be useful in F12 calculations where Gaussian geminals are used.

APPENDIX: FORMING (DD|DD) AND (FF|FF) ON THE LATE PATH

In Figures 2 and 3, the classes needed to form (dd|dd) and (ff|ff) on the late path are given, and the steps and flop costs are presented in Tables 7 and 8, respectively.

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