



# Rapid Evaluation of Two-Center Two-Electron Integrals

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**ABSTRACT:** We present optimal formulae for two-center two-electron repulsion integrals (ERIs) over Cartesian Gaussian basis functions. Floating-point operations (flop) counts reveal that two-center ERIs are often an order of magnitude cheaper than their four-center analogues. © 2000 John Wiley & Sons, Inc. *J Comput Chem* 21: 1505–1510, 2000

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## Introduction

The award of the 1998 Nobel Prize for Chemistry to Kohn and Pople acknowledged that the quantum chemical investigation of chemical problems is now a mature branch of the field. Nonetheless, there is still much to be done and, in particular, there remains a dearth of generally applicable methods that yield quantitative accuracy for large biochemical or biological systems. If quantum chemistry hopes eventually to provide a first-principles solution to Grand Challenge problems such as protein folding, it must first undergo a radical reformation, and almost all of its traditional computational framework must be reconsidered.

Fortunately, the writing on the wall has been visible for some time, and a large number of groups

have been contributing to the reformation process. Twenty years ago, the introduction<sup>1</sup> of direct methods by Almlöf et al. dramatically altered the range of applicability of Hartree–Fock theory and laid the conceptual foundation for the subsequent development of analogous integral-driven schemes in configuration interaction, perturbation theory, and MCSCF theory.<sup>2–6</sup>

In more recent times, the design of so-called linear methods has become fashionable, and has attracted a number of researchers from both the physical and chemical communities. Such approaches, which are also called  $O(n)$  methods, seek to compute the energy of a system via computational work that scales only linearly with the system's size. By alleviating some of the key bottlenecks in density functional theory (DFT) and Hartree–Fock (HF) calculations, these methods have significantly enhanced the range of applicability of these types of calculation.

The Fast Multipole Method<sup>7</sup> (FMM) of Green-gard and Rokhlin is an  $O(n)$  algorithm for computing the Coulomb energy of an ensemble of  $n$

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point charges, and underlies the CFMM algorithm introduced<sup>8</sup> into quantum chemistry by White et al. and later embraced by several groups.<sup>9,10</sup> The Quantum Chemical Tree Code<sup>11</sup> (QCTC) of Challacombe et al., the various KWIK algorithms<sup>12–14</sup> from our group, and the Recursive Bisection Method<sup>15</sup> (RBM) of Pérez-Jordá and Yang are other linear, or near-linear, approaches to the Coulomb problem.

The development of linear methods for the evaluation of the Fock exchange energy has proven to be a more difficult task, and the ONX and Link schemes<sup>16–18</sup> in current use show linear cost scaling only for systems where the HOMO–LUMO gap is large. A similar caveat applies to the method<sup>19</sup> of Ayala and Scuseria for MP2 and coupled-cluster calculations.

Notwithstanding the ingenious tricks and shortcuts that underlie this impressive array of fast techniques, it is sobering to observe that every one of them still requires the notorious two-electron integrals (ERIs)

$$(\mathbf{ab}|\mathbf{cd}) = \iint \phi_{\mathbf{a}}(\mathbf{r}_1)\phi_{\mathbf{b}}(\mathbf{r}_1)\vartheta(r_{12})\phi_{\mathbf{c}}(\mathbf{r}_2) \times \phi_{\mathbf{d}}(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (1)$$

$$\phi_{\mathbf{a}}(\mathbf{r}) = (x - A_x)^{a_x}(y - A_y)^{a_y}(z - A_z)^{a_z} \times \sum_{i=1}^{K_a} D_{ai} e^{-\alpha_i|\mathbf{r}-\mathbf{A}|^2} \quad (2)$$

that have haunted quantum chemistry ever since its birth. The stubborn persistence of ERIs has fueled an on-going interest in their computation, and the last 3 decades have witnessed the development of several efficient algorithms.<sup>20–30</sup>

It follows from the Schwarz inequality

$$(\mathbf{ab}|\mathbf{cd})^2 \leq (\mathbf{ab}|\mathbf{ab})(\mathbf{cd}|\mathbf{cd}) \quad (3)$$

that, if either of the distributions  $\phi_{\mathbf{a}}\phi_{\mathbf{b}}$  and  $\phi_{\mathbf{c}}\phi_{\mathbf{d}}$  is small, the ERI  $(\mathbf{ab}|\mathbf{cd})$  will also be small. Conversely, if  $\mathbf{A} = \mathbf{B}$  and  $\mathbf{C} = \mathbf{D}$ , the integral (1) reduces to a two-center ERI of the form

$$(\mathbf{a}|\mathbf{c}) = \iint \phi_{\mathbf{a}}(\mathbf{r}_1)\vartheta(r_{12})\phi_{\mathbf{c}}(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (4)$$

and is often large. The efficient generation of these concentric integrals is our present concern.

The preeminence of two-center integrals has been known, or assumed, for years, and is the basic premise of the Pople approximations wherein differential overlap (i.e., nonconcentric  $\phi_{\mu}\phi_{\nu}$  distributions) is either neglected (NDDO<sup>31</sup>) or projected onto nearby nuclei (PDDO<sup>32</sup>). Although these approximations are rarely used in their original

Hartree–Fock context, a variant of the PDDO approximation has become a popular technique<sup>33–35</sup> in DFT calculations where the electron density is expanded in an auxiliary nuclear-centered basis.

The electron count, Coulomb energy, and exchange energy in a system are given by

$$n = \sum_{\mu} \sum_{\nu} P_{\mu\nu} S_{\mu\nu} \quad (5)$$

$$J = \frac{1}{2} \sum_{\mu} \sum_{\nu} \sum_{\lambda} \sum_{\sigma} P_{\mu\nu} P_{\lambda\sigma} (\mu\nu|\lambda\sigma) \quad (6)$$

$$K = \frac{1}{2} \sum_{\mu} \sum_{\nu} \sum_{\lambda} \sum_{\sigma} P_{\mu\lambda} P_{\nu\sigma} (\mu\nu|\lambda\sigma) \quad (7)$$

where  $P_{\mu\nu}$  and  $S_{\mu\nu}$  are elements of the density matrix and overlap matrix, respectively. The parts of these quantities originating exclusively from the concentric  $\phi_{\mu}\phi_{\nu}$  are

$$n_{\text{NDDO}} = \sum_{(\mu\nu)} P_{\mu\nu} S_{\mu\nu} \quad (8)$$

$$J_{\text{NDDO}} = \frac{1}{2} \sum_{(\mu\nu)} \sum_{(\lambda\sigma)} P_{\mu\nu} P_{\lambda\sigma} (\mu\nu|\lambda\sigma) \quad (9)$$

$$K_{\text{NDDO}} = \frac{1}{2} \sum_{(\mu\nu)} \sum_{(\lambda\sigma)} P_{\mu\lambda} P_{\nu\sigma} (\mu\nu|\lambda\sigma) \quad (10)$$

where the notation  $(\mu\nu)$  implies that only concentric  $\phi_{\mu}\phi_{\nu}$  are included in the sum. The data in Table I show that, although concentric  $\phi_{\mu}\phi_{\nu}$  are relatively rare, they are disproportionately important. They account for between 70 and 100% of the electron count in typical molecules and similarly dominate both the Coulomb and exchange energies, yet computing the concentric  $(\mu\nu|\lambda\sigma)$  occupies only about 1% of the total ERI time in medium-sized molecules.

## Notation

We use square and round brackets for primitive and contracted integrals, respectively. Thus, the four-center ERI  $(\mathbf{ab}|\mathbf{cd})$  is a sum of primitive ERIs  $[\mathbf{ab}|\mathbf{cd}]$  and we have

$$(\mathbf{ab}|\mathbf{cd}) = \sum^{K_{\text{bra}}} [\mathbf{ab}|\mathbf{cd}] \quad (11)$$

$$[\mathbf{ab}|\mathbf{cd}] = \sum^{K_{\text{ket}}} [\mathbf{ab}|\mathbf{cd}] \quad (12)$$

where  $K_{\text{bra}}$  and  $K_{\text{ket}}$  are the number of bra and ket primitives, respectively. In the recursive schemes pioneered by Obara and Saika,<sup>23</sup> recurrence relations (RRs) are used to construct the  $[\mathbf{ab}|\mathbf{cd}]$  from s-type

**TABLE I.** Electron Counts, Coulomb, and Exchange Energies, ERI Timings, and Their Concentric Fractions.<sup>a</sup>

Molecule	$n$	$\frac{n_{\text{NDDO}}}{n}$	$J$	$\frac{J_{\text{NDDO}}}{J}$	$K$	$\frac{K_{\text{NDDO}}}{K}$	$\frac{T_{\text{NDDO}}}{T}$
H <sub>2</sub>	2	0.595	1.303	0.354	0.651	0.354	b
LiH	4	0.800	5.587	0.801	2.141	0.865	b
BeH <sub>2</sub>	6	0.712	11.388	0.681	3.454	0.787	b
BH <sub>3</sub>	8	0.709	20.142	0.641	4.930	0.751	b
CH <sub>4</sub>	10	0.721	32.649	0.638	6.582	0.736	b
NH <sub>3</sub>	10	0.819	39.075	0.769	7.664	0.836	b
OH <sub>2</sub>	10	0.899	46.706	0.876	8.941	0.917	b
FH	10	0.956	55.854	0.949	10.443	0.967	b
C <sub>6</sub> H <sub>6</sub>	42	0.767	312.428	0.652	33.239	0.805	0.038
C <sub>6</sub> H <sub>14</sub>	50	0.766	356.726	0.647	36.153	0.782	0.036
Camphor	84	0.808	907.295	0.699	65.856	0.827	0.011
Caffeine	102	0.854	1264.452	0.763	88.404	0.871	0.015
Diazepam	148	0.837	2183.515	0.742	136.883	0.874	0.012

<sup>a</sup> Based on HF/6-31G\* calculations. Geometries available upon request.

<sup>b</sup> Measured timings too short to yield a reliable ratio.

ERIs  $[00|00]^{(m)}$  which we denote by  $[m]$  and which can be found very efficiently.<sup>25</sup> The Obara–Saika algorithm is thereby an OLC path<sup>30</sup>

$$[m] \rightarrow [\mathbf{ab}|\mathbf{cd}] \rightarrow [\mathbf{ab}|\mathbf{cd}] \rightarrow (\mathbf{ab}|\mathbf{cd}) \quad (13)$$

In the PRISM methods,<sup>26, 28, 30</sup> recurrence relations are used to build the  $(\mathbf{ab}|\mathbf{cd})$  from scaled and contracted  $s$ -type ERIs that we denote by  ${}_{a'b'p'}(m)_{c'd'q'}$  and which are defined by

$${}_{a'b'p'}(m)_{c'd'q'} = \sum^{K_{\text{bra}}} \frac{(2\alpha)^{a'}(2\beta)^{b'}}{(2\zeta)^{p'}} [m]_{c'd'q'} \quad (14)$$

$$[m]_{c'd'q'} = \sum^{K_{\text{ket}}} \frac{(2\gamma)^{c'}(2\delta)^{d'}}{(2\eta)^{q'}} [m] \quad (15)$$

where  $\zeta = \alpha + \beta$  and  $\eta = \gamma + \delta$ . This corresponds to an OCL path<sup>30</sup>

$$[m] \rightarrow [m]_{c'd'q'} \rightarrow {}_{a'b'p'}(m)_{c'd'q'} \rightarrow (\mathbf{ab}|\mathbf{cd}) \quad (16)$$

### Formulae for Two-Center Integrals

Equation (97) of our review<sup>28</sup> is a modified version of the eight-term Obara–Saika RR. In the concentric  $\mathbf{A} = \mathbf{B} = \mathbf{P}$  and  $\mathbf{C} = \mathbf{D} = \mathbf{Q}$  case, four of the terms vanish to yield

$${}_{p'}(\mathbf{p} + \mathbf{1}_i|\mathbf{q})_{q'}^{(m)} = R_i {}_{p'+1}(\mathbf{p}|\mathbf{q})_{q'}^{(m+1)} + q_i {}_{p'+1}(\mathbf{p}|\mathbf{q} - \mathbf{1}_i)_{q'+1}^{(m+1)}$$

$$+ p_i [{}_{p'+1}(\mathbf{p} - \mathbf{1}_i|\mathbf{q})_{q'}^{(m)} - {}_{p'+2}(\mathbf{p} - \mathbf{1}_i|\mathbf{q})_{q'}^{(m+1)}] \quad (17)$$

where  $\mathbf{R} = \mathbf{Q} - \mathbf{P}$  is simply an internuclear vector. Like the 10-term RR that underpins the  $L_2$  step<sup>30</sup> of COLD PRISM, the four-term RR (17) yields compact explicit ERI formulae, for example,

$$(s|s) = {}_0(0)_0 \quad (18)$$

$$(p_i|s) = R_i {}_1(1)_0 \quad (19)$$

$$(p_i|p_j) = -R_i R_j {}_1(2)_1 + \delta_{ij} {}_1(1)_1 \quad (20)$$

$$(d_{ij}|s) = R_i R_j {}_2(2)_0 + \delta_{ij} [{}_1(0)_0 - {}_2(1)_0] \quad (21)$$

Each of these expressions can be interpreted in terms of simple multipole–multipole interactions. Specifically,  $(s|s)$ ,  $(p|s)$ ,  $(p|p)$ , and  $(d|s)$  integrals describe charge–charge, dipole–charge, dipole–dipole, and quadrupole–charge interactions, respectively. Because axial  $d$  functions also contain an  $s$ -like component, the  $(d|s)$  expression also includes the charge–charge term  ${}_1(0)_0$ .

Expressions for higher ERI classes are easy to derive from (17), but mixed terms, like that in (21), arise frequently, and it proves convenient to define the angle bracket  $s$ -type ERIs

$${}_0\langle m \rangle_0 = {}_a(m)_c \quad (22)$$

$${}_1\langle m \rangle_0 = {}_{a-1}(m-1)_c - {}_a(m)_c \quad (23)$$

$${}_0\langle m \rangle_1 = {}_a(m-1)_{c-1} - {}_a(m)_c$$

**TABLE II.** Explicit Formulae for Two-Center ERI Classes.

Class	Formula
$(s s)$	${}_0\langle 0 \rangle_0$
$(\rho_i s)$	$R_i {}_0\langle 1 \rangle_0$
$(d_{ij} s)$	$R_i R_j {}_0\langle 2 \rangle_0 + \delta_{ij} {}_1\langle 1 \rangle_0$
$(\rho_i \rho_j)$	$-R_i R_j {}_0\langle 2 \rangle_0 + \delta_{ij} {}_0\langle 1 \rangle_0$
$(f_{ijk} s)$	$R_i R_j R_k {}_0\langle 3 \rangle_0 + (\delta_{ij} R_k + \delta_{ik} R_j + \delta_{jk} R_i) {}_1\langle 2 \rangle_0$
$(d_{ij} \rho_k)$	$-R_i R_j R_k {}_0\langle 3 \rangle_0 - \delta_{ij} R_k {}_1\langle 2 \rangle_0 + (\delta_{ik} R_j + \delta_{jk} R_i) {}_0\langle 2 \rangle_0$
$(\mathcal{G}_{ijkl} s)$	$R_i R_j R_k R_l {}_0\langle 4 \rangle_0 + (\delta_{ij} R_k R_l + \delta_{ik} R_j R_l + \delta_{il} R_j R_k + \delta_{jk} R_i R_l + \delta_{jl} R_i R_k + \delta_{kl} R_i R_j) {}_1\langle 3 \rangle_0 + (\delta_{ij} \delta_{kl} + \delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}) {}_2\langle 2 \rangle_0$
$(f_{ijk} \rho_l)$	$-R_i R_j R_k R_l {}_0\langle 4 \rangle_0 - (\delta_{ij} R_k R_l + \delta_{ik} R_j R_l + \delta_{jk} R_i R_l) {}_1\langle 3 \rangle_0 + (\delta_{il} R_j R_k + \delta_{jl} R_i R_k + \delta_{kl} R_i R_j) {}_0\langle 3 \rangle_0 + (\delta_{ij} \delta_{kl} + \delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}) {}_1\langle 2 \rangle_0$
$(d_{ij} d_{kl})$	$R_i R_j R_k R_l {}_0\langle 4 \rangle_0 + \delta_{ij} R_k R_l {}_1\langle 3 \rangle_0 + \delta_{kl} R_i R_j {}_0\langle 3 \rangle_1 - (\delta_{ik} R_j R_l + \delta_{il} R_j R_k + \delta_{jk} R_i R_l + \delta_{jl} R_i R_k) {}_0\langle 3 \rangle_0 + \delta_{ij} \delta_{kl} {}_1\langle 2 \rangle_1 + (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}) {}_0\langle 2 \rangle_0$

$$\begin{aligned}
 {}_2\langle m \rangle_0 &= {}_{a-2}(m-2)_c - 2{}_{a-1}(m-1)_c + {}_a(m)_c \\
 {}_1\langle m \rangle_1 &= {}_{a-1}(m-2)_{c-1} - {}_{a-1}(m-1)_c \\
 &\quad - {}_a(m-1)_{c-1} + {}_a(m)_c \\
 {}_0\langle m \rangle_2 &= {}_a(m-2)_{c-2} - 2{}_a(m-1)_{c-1} + {}_a(m)_c
 \end{aligned}
 \tag{24}$$

Table II lists ERI formulae in this notation for all classes with total angular momentum  $L \leq 4$ .

### Flop Counts

The ERI formulae in Table II appear simpler than their four-center analogues, which can be derived from the 10-term RR that underpins the  $L_2$  step<sup>30</sup> of the COLD PRISM. But how much practical difference does this make? Do we expect the construction of two-center ERIs to be 50% faster than that of four-center ERIs? Or a factor of two? Or more? It is traditional to quantify the difference by comparing the number of floating-point operations (flops) required to form classes of two- and four-center

ERIs from  $[m]$  integrals. Following earlier work,<sup>24</sup> we write the total costs in the form

$$\text{Cost} = xK_{\text{tot}} + yK_{\text{bra}} + z \tag{25}$$

where  $K_{\text{tot}} = K_{\text{bra}} * K_{\text{ket}}$  is the total degree of contraction, and  $x$ ,  $y$ , and  $z$  are the numbers of flops expended in the primitive, half-contracted and fully contracted parts of the algorithm, respectively. Before presenting the flop counts, however, we illustrate our strategy for the case of a two-center ( $pp|ss$ ) ERI class. The six steps of our recipe are based on the  $(d_{ij}|s)$  entry in Table II and are summarized in Table III.

In Step 1, we construct the  $[0]$ ,  $[1]$ , and  $[2]$  integrals. We have discussed an efficient algorithm for this elsewhere,<sup>25</sup> and do not reproduce our methodology here. However, we note that, unlike the four-center case, all of the primitives in a two-center contracted shell quartet share the same  $\mathbf{R}$  and, if this is fully exploited, it leads to significant computational savings. For further efficiency, we

**TABLE III.** Strategy for Forming a Two-Center ( $pp|ss$ ) Class from  $[m]$  Integrals.

Step	Agenda	Flop Cost	Method
1	${}_2[0]_0, {}_2[1]_0, {}_2[2]_0$	—	refs. 25 and 26
2	${}_2[0]_0, {}_2[1]_0, {}_2[2]_0$	$3K_{\text{tot}}$	eq. (15)
3	${}_1(0)_0 - {}_2(1)_0, {}_2(2)_0$	$K_{\text{bra}}$	eq. (14)
4	${}_1(\rho_i s)_0^{(1)}$	3	eq. (17)
5	$(d_{ij} s)$	9	eq. (17)
6	$(\rho_i\rho_j ss)$	0	$(\rho_i\rho_j ss) \equiv (d_{ij} s)$

**TABLE IV.**  
**Flop-Cost Parameters for Forming an ERI Class from  $[m]$  Integrals.**

Class	<b>A <math>\neq</math> B and C <math>\neq</math> D</b>			<b>A = B and C = D</b>		
	x	y	z	x	y	z
(ss ss)	1	0	0	1	0	0
(ps ss)	6	8	15	1	0	3
(ds ss)	12	24	78	3	1	12
(pp ss)	12	30	93	3	1	12
(ps ps)	16	28	93	2	0	12
(fs ss)	20	56	305	3	1	24
(dp ss)	20	76	411	3	1	24
(ds ps)	30	76	411	3	1	36
(pp ps)	30	94	477	3	1	36
(gs ss)	30	116	1032	5	3	49
(fp ss)	30	162	1230	5	3	49
(dd ss)	30	176	1467	5	3	49
(fs ps)	48	166	1230	4	2	85
(dp ps)	48	224	1698	4	2	85
(ds ds)	68	198	1467	10	3	115
(ds pp)	80	242	1698	10	3	115
(pp pp)	80	296	2349	10	3	115

apply principal scaling<sup>26</sup> to the shell-pair data. In the  $(pp|ss)$  case, this means that we begin with  ${}_2[0]_0$ ,  ${}_2[1]_0$ , and  ${}_2[2]_0$  integrals.

Step 2 is the ket contraction to form  ${}_2[0]_0$ ,  ${}_2[1]_0$ , and  ${}_2[2]_0$ . Because the scalings do not change, the contraction (15) involves only an add (no multiply) for each of the  $K_{\text{tot}}$  primitives and, consequently, the flop cost for this step is  $3K_{\text{tot}}$ .

Step 3 is the bra contraction step to form  ${}_1\langle 1\rangle_0$  and  ${}_0\langle 2\rangle_0$ . To form the required  ${}_1\langle 0\rangle_0$  integral, the  ${}_2[0]_0$  integrals (of which there are  $K_{\text{bra}}$ ) are scaled by  $2\zeta$  in contraction (14) and, as a result, the flop cost for this step is  $K_{\text{bra}}$ .

In Step 4, we use the RR (17) to form the three  ${}_1(p_i|s)_0^{(1)}$  integrals. Only the first term of the RR survives, and thus, each application requires only a single multiply. Consequently, the flop cost for the step is 3.

Step 5 again uses the RR, this time to form the six  $(d_{ij}|s)$  integrals. Like the  ${}_1(p_i|s)_0^{(1)}$  in Step 4, each of the three  $(d_{ij}|s)$  with  $i \neq j$  needs only a single multiply. In contrast, each of the  $(d_{ii}|s)$  requires both a multiply and the Kronecker addition. In total, nine flops are expended.

In Step 6, the desired  $(p_i p_j|ss)$  are identified with the  $(d_{ij}|s)$ , and the task of forming a two-center

$(pp|ss)$  class from  $[m]$  integrals is complete, having cost  $3K_{\text{tot}} + K_{\text{bra}} + 12$  flops.

By tabulating such flop costs for a selection of two-center and four-center ERI classes, Table IV invites and facilitates direct comparisons between equivalent classes. The precise ratio between the costs of a four-center and a two-center class depends on  $K_{\text{tot}}$  and  $K_{\text{bra}}$ , but it is clear that the ratio grows quickly as the total angular momentum  $L$  rises, from 1.0 for (ss|ss) to approximately 10.0 for (pp|pp).

## Concluding Remarks

We have introduced a highly efficient algorithm for the construction of two-center ERIs, and have shown that these can be computed several times more efficiently than their four-center analogues. Although two-center ERIs are much less numerous than four-center ERIs in normal *ab initio* quantum chemical calculations, they are the most common integrals in semiempirical NDDO-based models, and the existence of this new algorithm provides a major incentive for the future evolution of such models. We are currently developing such models and will report our progress in the near future.

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