

Three-electron integrals over Gaussian basis functions

Pierre-François Loos, Giuseppe Barca, and Peter Gill

Research School of Chemistry, Australian National University,
Canberra, Australia

Molecular Electronic Structure, Buenos Aires

19th Sep 2016



Why do we want to compute these?

Potentially useful in many cases

- Gaussian-type geminals (GTGs) calculations
Szalewicz & Jeziorski, Mol. Phys. 108, 3191 (2010)
Komornicki & King, JCP 134 (2011) 244115
- GTGs and Gaussian-type orbitals (GTOs)
Persson & Taylor, JCP 105 (1996) 5915; TCA 97 (1997) 240
- Transcorrelated-type methods
Ten-no, CPL 330 (2000) 175
- Explicitly-correlated F12 methods: MP2-F12, CC-F12, etc.
(RI world)
Hattig et al. Chem Rev 112 (2012) 4
Ten-no & Noga, WIREs Comput Mol Sci 2 (2012) 114

What do we want to calculate?

Three-electron integral

$$\begin{aligned} \langle \mathbf{a}_1 \mathbf{a}_2 \mathbf{a}_3 | \mathbf{b}_1 \mathbf{b}_2 \mathbf{b}_3 \rangle &\equiv \langle \mathbf{a}_1 \mathbf{a}_2 \mathbf{a}_3 | f_{123} | \mathbf{b}_1 \mathbf{b}_2 \mathbf{b}_3 \rangle \\ &= \iiint \psi_{\mathbf{a}_1}^{\mathbf{A}_1}(\mathbf{r}_1) \psi_{\mathbf{a}_2}^{\mathbf{A}_2}(\mathbf{r}_2) \psi_{\mathbf{a}_3}^{\mathbf{A}_3}(\mathbf{r}_3) f_{123} \psi_{\mathbf{b}_1}^{\mathbf{B}_1}(\mathbf{r}_1) \psi_{\mathbf{b}_2}^{\mathbf{B}_2}(\mathbf{r}_2) \psi_{\mathbf{b}_3}^{\mathbf{B}_3}(\mathbf{r}_3) d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \end{aligned}$$

Gaussian-type orbital (GTO)

$$\text{Primitive GTO} = |\mathbf{a}\rangle = (x - A_x)^{a_x} (y - A_y)^{a_y} (z - A_z)^{a_z} e^{-\alpha |\mathbf{r} - \mathbf{A}|^2}$$

$$\text{Contracted GTO} = |\mathbf{a}\rangle \equiv \psi_{\mathbf{a}}^{\mathbf{A}}(\mathbf{r}) = \sum_i^K D_i |\mathbf{a}\rangle_i$$

- Exponent α
- Center $\mathbf{A} = (A_x, A_y, A_z)$
- Angular momentum $\mathbf{a} = (a_x, a_y, a_z)$ and total angular momentum $a = a_x + a_y + a_z$

Three-electron operator

Three-electron operators

$$f_{123} = f_{12}g_{13}h_{23}$$

Two-electron operators

- **Long-range** Coulomb operator

$$C_{12} = r_{12}^{-1}$$

- **Short-range** Slater geminal

$$S_{12} = \exp(-\lambda r_{12})$$

- **Short-range** Gaussian geminal

$$G_{12} = \exp(-\lambda r_{12}^2)$$

- **Short-range** operator

$$E_{12} = r_{12} \operatorname{erfc}(\sqrt{\lambda} r_{12})$$

Asymptotic scaling

Operator		Scaling
Two-electron	Three-electron	
<i>S</i>	<i>SS, SSS, SSL</i>	$\mathcal{O}(N)$
<i>L</i>	<i>SL, SLL</i>	$\mathcal{O}(N^2)$
—	<i>LL, LLL</i>	$\mathcal{O}(N^3)$

S = short range

L = long range

Asymptotic scaling of two-electron integrals

Number of significant two-electron integrals for polyenes

$$N_{\text{sig}} = c N^\alpha$$

Molecule	N	C_{12}		G_{12}	
		N_{sig}	α	N_{sig}	α
propene	12	1 625	—	1 650	—
butadiene	16	5 020	3.9	5 020	3.9
hexatriene	24	24 034	3.9	23 670	3.8
octatetraene	32	63 818	3.4	52 808	2.8
decapentaene	40	119 948	2.8	81 404	1.9
dodecahexaene	48	192 059	2.6	109 965	1.6

Helgaker, Jorgensen & Olsen, Molecular Electronic-Structure Theory

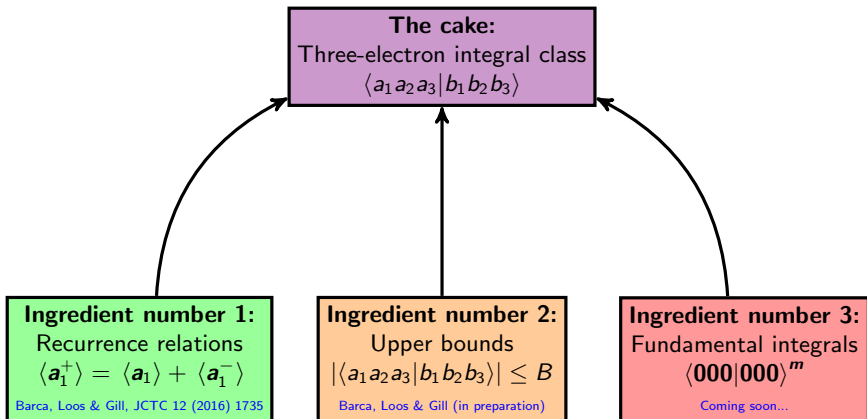
Asymptotic scaling of three-electron integrals

Number of significant three-electron integrals for polyenes

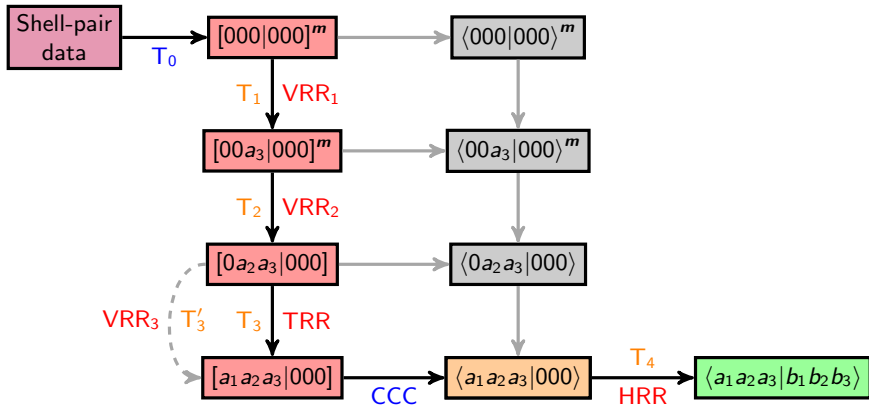
$$N_{\text{sig}} = c N^\alpha$$

Molecule	N	$C_{12}C_{13}$		$G_{12}C_{13}$		$G_{12}G_{13}$	
		N_{sig}	α	N_{sig}	α	N_{sig}	α
propene	12	123 480	—	243 071	—	123 480	—
butadiene	16	650 034	5.8	1 288 614	5.8	649 796	5.8
hexatriene	24	6 259 263	5.6	10 992 400	5.3	4 436 162	4.7
octatetraene	32	22 875 778	4.5	31 511 030	3.7	9 273 218	2.6
decapentaene	40	53 576 923	3.8	59 315 069	2.8	14 101 575	1.9
dodecahexaene	48	101 224 185	3.5	94 176 325	2.5	18 927 362	1.6

Recipe for three-electron integrals



Late-contraction path algorithm (Head-Gordon-Pople & PRISM inspired)



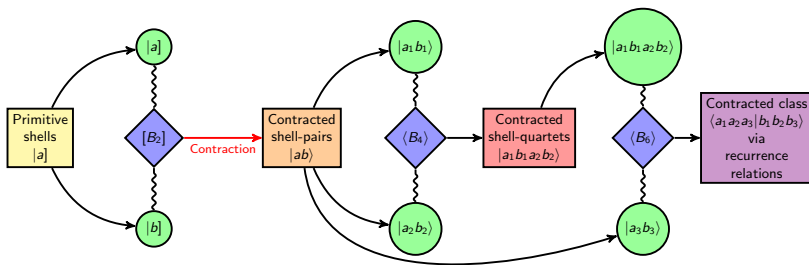
Recurrence relations for three-electron integrals

Number of terms in the recurrence relations for cyclic and chain operators

Step	RR type	Three-electron operator		Two-electron operator
		$f_{12} g_{13} h_{23}$ (cyclic)	$f_{12} g_{13}$ (chain)	f_{12}
T_1	VRR_1	8	6	4
T_2	VRR_2	10	7	6
T'_3	VRR_3	12	12	—
T_3	TRR	6	6	4
T_4	HRR	2	2	2

If one uses GTGs, the RRs become even simpler!
Barca & Gill, JCTC (in press)

Screening algorithm for three-electron integrals



What is a “good” upper bound?

A good upper bound must be

- **simple**

⇔ significantly less computationally expensive than the true integral

- **strong**

⇔ as close as possible from the true integral in the threshold region
(10^{-14} – 10^{-8})

- **scaling-consistent**

⇔ $N_{\text{sig}} = \mathcal{O}(N_{\text{UB}})$ where N_{UB} is the number estimated by the UB

Shell and shell-pair bounding Gaussians

Shell bounding Gaussian (SBG)

$$\tilde{a}(\mathbf{r}) = \mathcal{N}_a e^{-(1-\sigma)\alpha|\mathbf{r}-\mathbf{A}|^2} \geq \|a\|$$

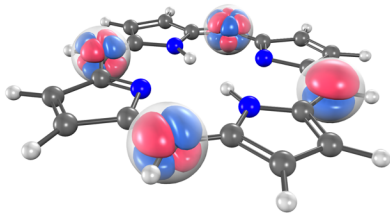
Shell-pair bounding Gaussian (SPBG)

$$\tilde{z}(\mathbf{r}) = \tilde{a}(\mathbf{r})\tilde{b}(\mathbf{r}) = h e^{-\xi|\mathbf{r}-\mathbf{Z}|^2} \geq \|ab\|$$

$$\zeta = \alpha + \beta$$

$$\mathbf{Z} = (\alpha\mathbf{A} + \beta\mathbf{B})/\zeta$$

$$\xi = (1 - \sigma)\zeta$$



© Andrew Gilbert aka Mr. IQMol

A tale of three strategies

■ Integral bound

We seek a single number that bounds a particular integral

$$|[a_1 a_2 | b_1 b_2]| \leq [a_1 a_1 | b_1 b_1]^{1/2} [a_2 a_2 | b_2 b_2]^{1/2}$$

With $\mathcal{O}(N^2)$ $[a_1 a_1 | b_1 b_1]$ bound factors, we can upper bound $\mathcal{O}(N^4)$ $[a_1 a_2 | b_1 b_2]$ integrals

■ Non-factorizable class bound

We seek a single number that bounds an entire class*

$$|[a_1 a_2 | b_1 b_2]| \leq [\check{a}_1 \check{a}_2 | \check{b}_1 \check{b}_2]$$

■ Factorizable class bound

We combine the two previous ideas

$$\begin{aligned} |[a_1 a_2 | b_1 b_2]| &\leq [\check{a}_1 \check{a}_2 | \check{b}_1 \check{b}_2] \\ &\leq [\check{a}_1 \check{a}_1 | \check{b}_1 \check{b}_1]^{1/2} [\check{a}_2 \check{a}_2 | \check{b}_2 \check{b}_2]^{1/2} \end{aligned}$$

*The simple $[ppp|ppp]$ class is made of 729 integrals!

Our home-made bounds

- We always use **class bounds via SPBGs**

$$|[a_1 a_2 a_3 | b_1 b_2 b_3]| \leq [\hat{a}_1 \hat{a}_2 \hat{a}_3 | \hat{b}_1 \hat{b}_2 \hat{b}_3]$$

⇒ σ is optimized with an **operator-specific metric**

- $[B_2]$, $[B_4]$ and $[B_6]$ are derived with **Hölder's inequality**

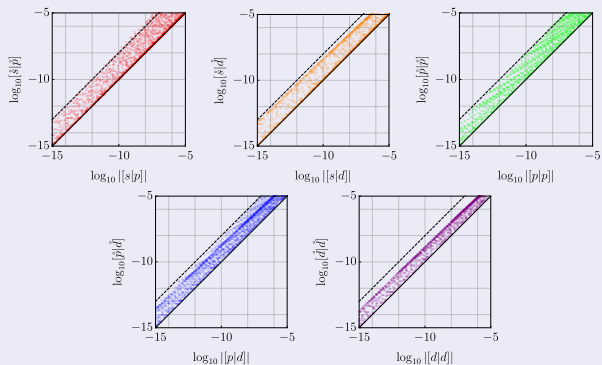
$$\left| \int \phi_1(\mathbf{r}) \phi_2(\mathbf{r}) d\mathbf{r} \right| \leq \left[\int |\phi_1(\mathbf{r})|^p d\mathbf{r} \right]^{1/p} \left[\int |\phi_2(\mathbf{r})|^q d\mathbf{r} \right]^{1/q},$$

for $p^{-1} + q^{-1} = 1$ and $p, q > 1$.

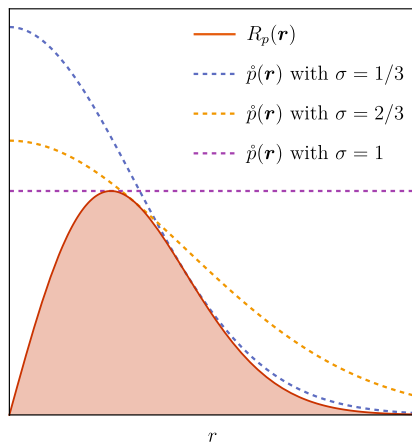
- We are **not** using Cauchy-Schwartz (i.e. $p = q = 2$)!
 - 1 they are usually weaker
 - 2 for three-electron integrals, they are not always simple

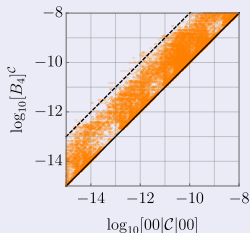
Performance of SPBGs

One-electron overlap integrals: $|[a|b]| \leq [\tilde{a}|\tilde{b}]$

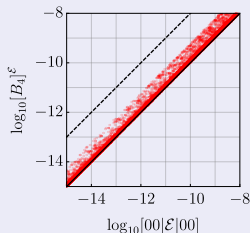


Performance of SPBGs



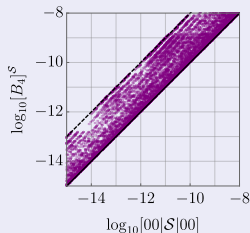
Performance of shell-quartet bounds $[B_4]$ for two-electron integralsLR operator C_{12} 

(factorizable bound)

NB: tighter than
Cauchy-Schwartz!SR operator \mathcal{E}_{12} 

(non-factorizable bound)

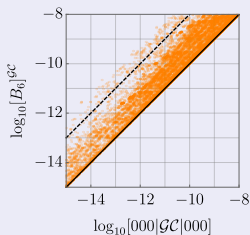
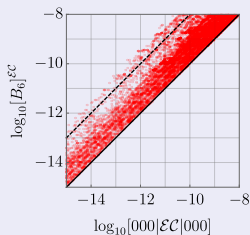
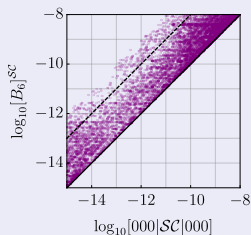
$$\sqrt{\pi\lambda} \frac{\mathcal{E}_{12}}{\mathcal{G}_{12}} \leq 1$$

SR operator \mathcal{S}_{12} 

(non-factorizable bound)

NB: we upper bound the
fundamental integral!

Performance of shell-sextet bounds $[B_6]$ for three-electron integrals

Operator $\mathcal{G}_{12}\mathcal{C}_{13}$ Operator $\mathcal{E}_{12}\mathcal{C}_{13}$ Operator $\mathcal{S}_{12}\mathcal{C}_{13}$ 

NB: All these integrals scale quadratically unlike $\mathcal{G}_{12}\mathcal{G}_{13}$, $\mathcal{E}_{12}\mathcal{E}_{13}$ or $\mathcal{S}_{12}\mathcal{S}_{13}$

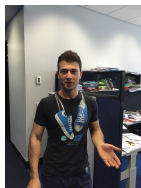
Things to do...

Future work

- Efficient computation of **fundamental integrals** (Slater-based operators in particular)
- Recurrence relations and upper bounds for **four-electron integrals** (under progress)
- Specific recurrence relations for **GTGs** (three- and four-electron integrals) (under progress)
- **Implementation** in quantum chemistry softwares

Collaborators and Funding

■ Collaborators:



Giuseppe Barca



Peter Gill

- Research School of Chemistry & Australian National University
- Australian Research Council:
Discovery Early Career Researcher Award 2013 & Discovery Project 2014



Australian Government
Australian Research Council