Searching efficient inequalities for 2-e AO integrals screening

Alexander A. Granovsky*

Vladimir I. Pupyshev[+]

***Laboratory of Chemical Cybernetics**
[+]Laboratory of Molecular Structure and Quantum Mechanics
M.V. Lomonosov Moscow State University, Moscow, Russia

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Notations

- p, q, r, s - atomic orbitals
- (pq|rs) - 2-e integral in AO basis
- Chemical notation: p(1) q(1), r(2), s(2)

Simple known inequalities

- Schwarz inequalities:
  - Most powerful and most useful:
  - $|(pq|rs)| \le |(pq|pq)(rs|rs)|^{1/2}$ (1)
    - Simple sequences (weaker inequalities):
      - $|(pq|rs)| \le |(pq|pq)(rs|rs)|^{1/2} \le |(pp|qq)(rs|rs)|^{1/2}$
      - $|(pq|rs)| \le |(pq|pq)(rs|rs)|^{1/2} \le |(pq|pq)(rr|ss)|^{1/2}$
      - $|(pq|rs)| \le |(pq|pq)(rs|rs)|^{1/2} \le |(pp|qq)(rr|ss)|^{1/2}$
      - $|(pq|rs)| \le |(pp|pp)(qq|qq)(rr|rr)(ss|ss)|^{1/4}$
  - Less useful but different:
  - $|(pq|rs)| \le |(pp|rr)(qq|ss)|^{1/2}$ (2)
  - $|(pq|rs)| \le |(pp|ss)(qq|rr)|^{1/2}$ (3)

Much less trivial

- Hardy-Littlewood-Sobolev inequality:
  - $\forall$p,r>1, 0< λ< n, $\frac{1}{p}+\frac{\lambda}{n}+\frac{1}{r}=2$, $\forall f\in L_p(R^n), h\in L_r(R^n)$

$$\left|\int_{R^n}\int_{R^n}\frac{f(x)h(y)}{|x-y|^{\lambda}}d^n x\, d^n y\right| \le C(n,\lambda,p)\,\|f\|_p\,\|h\|_r$$

  - where $\|f\|_p=\left(\int_{R^n}|f(x)|^p d^n x\right)^{1/p}$

$$C(n,\lambda,p)\le\frac{3}{3-\lambda}\left(\frac{4\pi}{3}\right)^{\lambda/3}\frac{1}{pr}\left[\left(\frac{\lambda/3}{1-1/p}\right)^{\lambda/3}+\left(\frac{\lambda/3}{1-1/r}\right)^{\lambda/3}\right]$$

  - p = r = 2n/(2n–λ): $C(n,\lambda,p)=\pi^{\lambda/2}\frac{\Gamma(n/2-\lambda/2)}{\Gamma(n-\lambda/2)}\left(\frac{\Gamma(n/2)}{\Gamma(n)}\right)^{\lambda/n-1}$

Simple sequences, symmetric case

- For n = 3, λ = 1, f, h ∈ $L_{6/5}(\mathrm{R}^3)$:

$$\left| \int_{R^3}\int_{R^3} \frac{f(x)h(y)}{|x-y|} d^3x\, d^3y \right| \leq \frac{8}{3}\left(\frac{2}{\pi}\right)^{1/3} \| f \|_{6/5} \| h \|_{6/5}$$

$$\left|(pq\,|\,rs)\right| = \left| \int_{R^3}\int_{R^3} \frac{p(x)q(x)r(y)s(y)}{|x-y|} d^3x\, d^3y \right| \leq \frac{8}{3}\left(\frac{2}{\pi}\right)^{1/3} \| pq \|_{6/5} \| rs \|_{6/5} \quad (4)$$

Great disappointment

- Inequality (4) is weaker than much simpler Schwarz inequality (1):
- **<u>Statement (1):</u>**
- Let $|(pq|rs)| \leq |G(p,q)G(r,s)|^{1/2}$
- Then: $|(pq|rs)| \leq |(pq|pq)(rs|rs)|^{1/2} \leq$

$$\leq \quad ||G(p,q)G(p,q)|^{1/2}\,|G(r,s)G(r,s)|^{1/2}|^{1/2} =$$

$$= \quad |G(p,q)G(r,s)|^{1/2}$$

- **<u>Sequence:</u>** the only way to improve (1) is to use non-symmetric Sobolev inequalities

Fully non-symmetric case

- p = 1, r = n/(n–λ) = 3/2: $C(n, \lambda, p = 1) \leq \infty$
  - Finite C: does it exist at all?
- Our numerical experiments show that at least for GTOs:

$$C(3,1,1) \equiv C(3,1,6/5) = \frac{8}{3}\left(\frac{2}{\pi}\right)^{1/3}$$

- Promising result!

Applying this to estimate (pq|rs)

$$\left|(pq\,|\,rs)\right| = \left|\int_{R^3}\int_{R^3} \frac{p(x)q(x)r(y)s(y)}{|\,x-y\,|}\,d^3x\,d^3y\right| \le \frac{8}{3}\left(\frac{2}{\pi}\right)^{1/3} \|\,pq\,\|_1 \|\,rs\,\|_{3/2} \quad (5)$$

$$\left|(pq\,|\,rs)\right| = \left|\int_{R^3}\int_{R^3} \frac{p(x)q(x)r(y)s(y)}{|\,x-y\,|}\,d^3x\,d^3y\right| \le \frac{8}{3}\left(\frac{2}{\pi}\right)^{1/3} \|\,pq\,\|_{3/2} \|\,rs\,\|_1 \quad (6)$$

Combining them together

- $|(pq|rs)| \leq G1(p,q)G2(r,s)$ (5)
- $|(pq|rs)| \leq G2(p,q)G1(r,s)$ (6)
  - $|(pq|rs)| \leq \min(G1(p,q)G2(r,s), G2(p,q)G1(r,s))$ (7)
- The statement (1) above is no longer applicable!

Results of numerical experiments

- Inequality (7) is not identical to (1)
- Inequality (7) seems to be slightly more accurate in most cases
- The best way is to use both (1) and (7) at the same time
- Considerable CPU time required for evaluation of non-trivial integrals entering inequality (7) makes its practical applications senseless!
  - The only acceptable case: fully uncontracted basis sets

Conclusions: what are the inequalities we actually need?

- Inequality (1) does not include 1/r dependence
- Inequalities (2) and (3) include 1/r dependence but do not decay exponentially
- **We need the set of inequalities combining properties of both (1) and (2)-(3)!**
- Our hope: strengthened Schwarz inequality

Thank you for your attention!