A simple yet powerful upper bound for Coulomb integrals

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A new simple upper bound for Coulomb integrals is presented and shown to be significantly more powerful than the bound based on the Schwarz inequality.

1. Introduction

The last decade has witnessed remarkable progress in the development and application of quantum chemistry [1,2] and readily available computer programs can now be used to study chemical systems which, until a few years ago, would have been considered prohibitively large. Moreover, there is every reason to believe that the next decade will be just as fruitful as the last. At present, the most computationally demanding step in well-implemented Hartree–Fock (HF) and density functional theory (DFT) calculations [3] [#1] is the treatment of the non-local electron–electron interactions which, within finite basis set methods [4], reduce to classical Coulomb integrals

$$(P|Q) = \int \int \frac{P(r_1)Q(r_2)}{|r_1 - r_2|} \, dr_1 \, dr_2 \qquad (1)$$

between charge distributions $P(r)$ and $Q(r)$. It can not be over-emphasized, however, that HF and DFT calculations on very large systems are currently feasible *only* because the costs of such calculations do *not* obey the frequently cited $\mathcal{O}(N^3)$ and $\mathcal{O}(N^4)$ "laws", where N is the size of the basis set employed. In fact, it is easy to show that, although the total number of Coulomb integrals (ERIs) which arise in large systems is $\mathcal{O}(N^3)$ or $\mathcal{O}(N^4)$ (depending upon whether or not density-projection techniques [5] are used), the number of *non-negligible* ERIs is only $\mathcal{O}(N^2)$.

To take advantage of the fact that most of the ERIs in large systems are negligible, modern quantum chemistry programs use upper bound formulae to estimate the magnitudes of ERIs in order to avoid computing and handling any that would be sufficiently small. To be maximially effective, such bounds must be both *strong* (i.e. not too conservative) and *simple* (i.e. based only on information about $P(r)$ and $Q(r)$ individually). Although many sophisticated bounds have been proposed over the years, relatively few satisfy both of these criteria.

In section 2 of this Letter, we develop three simple upper bounds on the ERI (1) and then propose a

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[#1] CADPAC5: The Cambridge Analytic Derivatives Package Issue 5, Cambridge, 1992. A suite of quantum chemistry programs developed by R.D. Amos with contributions from I.L. alberts, J.S. Andrews, S.M. Colwell, N.C. Handy, D. Jayatilaka, P.J. Knowles, R. Kobayashi, N. Koga, K.E. Laidig, P.E. Maslen, C.W. Murray, J.E. Rice, J. Sanz, E.D. Simandiras, A.J. Stone and M-D. Su.

fourth which is the minimum of these. In section 3, we use an elementary ERI to define the *power* of these bounds and, in section 4, we examine their performance.

2. Four simple bounds

It has been pointed out by many authors [6–11] that, since the Coulomb operator defines an inner product, the Schwarz inequality [12] can be invoked to yield the simple bound

$$|(P|Q)| \leqslant I_P^* I_Q^* = B_1 ,$$ (2)

where

$$I_P^* = \left(\int \int \frac{P(r_1)P(r_2)}{|r_1 - r_2|} \, dr_1 \, dr_2 \right)^{1/2} .$$ (3)

Following a detailed empirical study of its performance, Häser and Ahlrichs concluded that B_1 is "relatively sharp" [10] and it has been advocated by Ahlrichs and co-workers [10,11] ever since. These authors have also suggested that, because (2) becomes an equality when $P(r) = Q(r)$, the bound B_1 cannot be improved without further assumptions. We disagree, however, with this contention. Indeed, as we will demonstrate in section 3, B_1 can greatly overestimate $(P|Q)$, that is, it can be a very weak bound.

Suppose now that we carry out the integration over r_1 in (1) to yield

$$(P|Q) = \int V_P(r)Q(r) \, dr ,$$ (4)

where $V_P(r)$ is, therefore, the potential due to the charge distribution $P(r)$. In the spirit of Gadre et al. [13], we can apply Hölder's inequality [12] to (4) to obtain

$$|(P|Q)| \leqslant \left(\int |V_P(r)|^m \, dr \right)^{1/m} \left(\int |Q(r)|^n \, dr \right)^{1/n}$$ (5)

for any m and n satisfying $(1/m) + (1/n) = 1$, m, $n > 1$. Eq. (5) provides us with an infinite family of bounds on $(P|Q)$, parametrically determined by m.

Letting m tend to infinity in (5) yields

$$|(P|Q)| \leqslant V_P^* S_Q^* = B_2 ,$$ (6)

where

$$V_P^* = \underset{R}{\mathrm{Max}} \left| \int \frac{P(r)}{|r - R|} \, dr \right|$$ (7)

is the maximum absolute potential due to $P(r)$ and

$$S_Q^* = \int |Q(r)| \, dr$$ (8)

is the absolute content of $Q(r)$. Of course, by the symmetry in (1), it must also be true that

$$|(P|Q)| \leqslant S_P^* V_Q^* = B_3 .$$ (9)

Since the simple bounds B_1, B_2 and B_3 defined by (2), (6) and (9) are independent, an even stronger simple bound on $(P|Q)$ is given by

$$|(P|Q)| \leqslant \mathrm{Min}\{B_1, B_2, B_3\} = B_4 .$$ (10)

In order to use (10) efficiently, one must precompute and store the I^*, V^* and S^* values defined in (3), (7) and (8). The I^* are simply square roots of two-center ERIs and can be computed by standard integral methods [3]. The V^* and S^* are novel quantities whose computation requires special techniques which we will discuss elsewhere [14].

We note that (5) generates additional rigorous bounds if other values of m are chosen and the resulting extensions of (10) are even stronger bounds. For each such choice, the integrals of the absolute potential of $P(r)$ raised to the power of m and of the absolute content of $Q(r)$ raised to the power of $m(m-1)^{-1}$ must be found. However, as we will show, the B_4 bound is already powerful enough for many purposes and we will not consider such generalizations here.

3. The power of a simple bound

We have chosen to develop our definition of the *power* of the B_1, B_2, B_3 and B_4 bounds with reference to the Coulomb repulsion between two Gaussian charge distributions because, in this prototypical case, all quantities of interest can be expressed in closed form. Suppose that the distributions $P(r)$ and $Q(r)$ are Gaussian with exponents ζ and η, respectively. The Coulomb repulsion between them is then given by the Boys formula [15],

$$(P|Q) = \frac{2\pi^{5/2}}{\zeta\eta(\zeta+\eta)^{1/2}} F_0(t) \,, \qquad (11)$$

where $F_0(T)$ has its usual meaning and it is straightforward to evaluate (3), (7) and (8) to obtain

$$I_P^* = 2^{1/4}(\pi/\zeta)^{5/4} \,, \qquad (12)$$

$$V_P^* = 2(\pi/\zeta) \,, \qquad (13)$$

$$S_P^* = (\pi/\zeta)^{3/2} \qquad (14)$$

and similarly for I_Q^*, V_Q^* and S_Q^*.

The differences between the bounds are very clearly demonstrated by constructing the ratio of the exact integral (11) to the B_n ($n=1$–4) defined by (2), (6), (9) and (10). Proceeding in this way, it is not difficult to show that

$$(P|Q)/B_n = F_0(T)P_n(x) \,, \qquad (15)$$

where

$$x = \ln\sqrt{\zeta/\eta} \qquad (16)$$

and the functions $P_n(x)$ (not to be confused with Legendre functions) are given by

$$P_1(x) = \sqrt{\operatorname{sech} x} \,, \qquad (17)$$

$$P_2(x) = \sqrt{\tfrac{1}{2}(1-\tanh x)} \,, \qquad (18)$$

$$P_3(x) = \sqrt{\tfrac{1}{2}(1+\tanh x)} \,, \qquad (19)$$

$$P_4(x) = \operatorname{Max}\{P_1(x), P_2(x), P_3(x)\} \,. \qquad (20)$$

Since it is certainly not possible for a simple bound (one based only on information about $P(r)$ and $Q(r)$ individually) to account for the $F_0(T)$ factor (which depends upon the distance between the distributions), we can measure its performance by $P_n(x)$ which we will term the *power* of the bound B_n. We will describe a bound as *strong* whenever its power is close to unity and *weak* whenever its power is close to zero. The $P_n(x)$ ($n=1, 2, 3$) are plotted in fig. 1 and $P_4(x)$ is simply the maximum of these.

Inspection of fig. 1 reveals that the four bounds differ dramatically from one another: the Schwarz bound B_1 is strong if and only if x is close to zero, that is, when ζ and η are of the same order of magnitude; B_2 is strong if and only if ζ is much smaller than η; B_3 is strong if and only if ζ is much larger than η; B_4 is strong for all x. It is easily shown that the

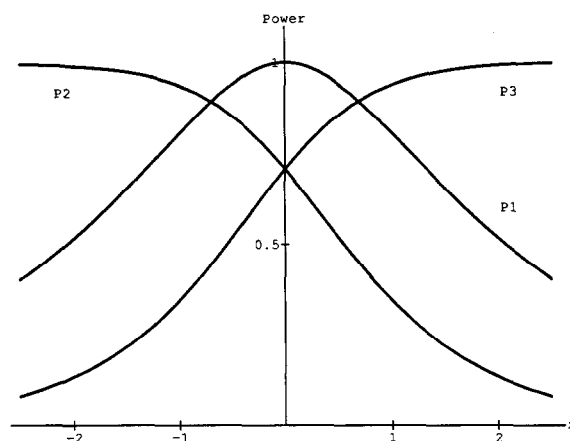Fig. 1. Powers of the bounds B_1, B_2 and B_3.

minimum power of B_4 is 0.89 and arises when $\zeta/\eta = \tfrac{1}{4}$ or 4.

The fact that the power of the Schwarz bound drops exponentially as $|x|$ increases explains the observation that this bound loses its effectiveness (i.e. becomes weak) when the charge distributions $P(r)$ and $Q(r)$ differ grossly in size. This occurs, for example, when one pertains to valence electrons and the other to core electrons, a common combination in molecular quantum chemical calculations, and it has been found empirically [16] that the overall performance of the Schawarz bound in direct SCF calculations is inferior to that of the nonrigorous bound (with a safety factor of 10) described by Head-Gordon and Pople [17]. It occurs, a fortiori, when constructing electrostatic potential maps by the evaluation of ERIs in which $Q(r)$ is a normalized s Gaussian with infinite exponent (i.e. a delta function); this is a case for which the Schwarz bound B_1 is vacuous but B_4 performs very well [18].

4. The performance of the bounds

Although, by definition, the B_4 bound can never be inferior to the Schwarz bound B_1, the degree to which it is superior in practical applications depends on the *range* of sizes of charge distributions present: in the extreme case of a completely homogeneous basis set (one in which all exponents are equal), B_1 and

B_4 are equivalent; at the other extreme (the potential-mapping problem mentioned above), B_1 is useless and $B_4 \equiv B_2$ is optimal.

To quantify the performances of the bounds under various conditions, we may consider all of the possible Coulomb repulsions in the one-parameter model system consisting of a large number of Gaussian charge distributions whose exponents ζ_i are such that the $\ln \zeta_i$ are uniformly distributed between 0 and N. Clearly, the parameter N measures the heterogeneity of the charge distributions. The mean power

$$\langle P_i \rangle = \frac{1}{N^2} \int_0^N \int_0^N P_i\left(\frac{u-v}{2}\right) du \, dv \qquad (21)$$

of each bound B_i can then be computed within this model as a function of N. The $\langle P_i \rangle$ obtained by evaluating (21) numerically for $N = 0, 1, ..., 10$ are given in table 1.

Although the mean power of the Schwarz bound B_1 eventually falls to zero for large N, it does so rather slowly which explains the empirical usefulness of this bound. For example, even when the largest Gaussian exponent is as much as 1000 times larger than the smallest one, $\langle P_1 \rangle$ is still greater than 0.9. Nonetheless, for the highly heterogeneous model systems ($N > 3$), the mean power of the bound B_4 is significantly greater than that of B_1.

Table 1
Mean powers $\langle P_i \rangle$ of the bounds B_1–B_4 as a function of the heterogeneity parameter N for a model system

N	$\langle P_1 \rangle$	$\langle P_2 \rangle = \langle P_3 \rangle$	$\langle P_4 \rangle$
0	1.000	0.707	1.000
1	0.990	0.704	0.990
2	0.962	0.694	0.967
3	0.924	0.681	0.958
4	0.881	0.668	0.957
5	0.836	0.655	0.960
6	0.792	0.642	0.963
7	0.751	0.631	0.966
8	0.711	0.621	0.969
9	0.675	0.613	0.971
10	0.641	0.605	0.973

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