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J. L. Whitten

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J. L. Whitten

Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York 11790

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Theorems are derived which establish a method of approximating two-particle Coulombic potential energy integrals, $[\phi_a(1) r_{12}^{-1} |\phi_b(2)]$, in terms of approximate charge densities ϕ_a' and ϕ_b'. Rigorous error bounds, $|[\phi_a(1)|r_{12}^{-1}|\phi_b(2)] - [\phi_a'(1)|r_{12}^{-1}|\phi_b'(2)]| \leq \delta$, are simply expressed in terms of information calculated separately for the pair of densities ϕ_a and ϕ_a' and the pair ϕ_b and ϕ_b'. From the structure of the bound, a simple method of optimizing charge density approximations such that δ is minimized is derived. The framework of the theory appears to be well suited for application to the approximation of electron repulsion integrals which occur in molecular structure theory, and applications to the approximation of integrals over Slater orbitals or grouped Gaussian functions are discussed.

I. INTRODUCTION

In problems involving the electrostatic interaction of particles simplifications are sometimes sought by introducing approximations for the two-particle Coulombic potential energy integral,

$$[\phi_a(1) \mid r_{12}^{-1} \mid \phi_b(2)] = \int \phi_a(1)\phi_b(2) r_{12}^{-1} dv_1 dv_2,$$

where ϕ_a and ϕ_b are charge densities for particles 1 and 2, respectively, and r_{12} is the interparticle distance. Error bounds on the magnitude of the difference between exact and approximate integrals are desirable of course, and if the method of approximation is such that the only approximation is to express ϕ_a and ϕ_b in terms of other densities, then such error bounds can be derived. Given that this is true, then the next step, ideally, would be to relate the method of determination of approximate densities directly to the error bound, provided that the structure of the argument leads to sufficiently small bounds, and in this paper an approach of this type is considered. Several theorems are derived which establish a method of approximation of individual Coulombic integrals in terms of approximate charge densities ϕ_a' and ϕ_b', and rigorous error bounds,

$$\mid [\phi_a(1) \mid r_{12}^{-1} \mid \phi_b(2)] - [\phi_a'(1) \mid r_{12}^{-1} \mid \phi_b'(2)] \mid \leq \delta,$$

are expressed simply in terms of integrals minimized to determine charge density approximations.

In addition to their general applicability, the theorems appear to be particularly useful when applied to the approximation of electron repulsion integrals, $[\phi_i(1)\phi_j(1) \mid r_{12}^{-1} \mid \phi_k(2)\phi_l(2)]$, which arise in quantum mechanical molecular structure problems where the ϕ_m are basis functions centered at arbitrary points in space. Two different ways of representing approximate densities $\phi_a' \approx \phi_i\phi_j$ and $\phi_b' \approx \phi_k\phi_l$ are discussed as examples; the first is most readily applicable to Gaussian basis functions and the second to either Gaussian or Slater functions. The introduction of integral approximations into quantum mechanical calculations on molecules is currently being investigated and here there

are important and unanswered practical questions concerning the magnitude of tolerable errors, δ. These questions are not dealt with in this paper, however, numerical results showing comparisons of exact and approximate integrals and studies of the sensitivity of the molecular descriptions to integral approximations will be reported at a later date.

II. THEORY

In the following, charge densities are denoted by $\phi_l(k) = \phi_l(x_k, y_k, z_k)$ for particle k and density l and by $\phi_l'(k)$ where the prime often denotes an approximation of the corresponding density. All functions are assumed to be defined on the full three-dimensional space to satisfy necessary differentiability and integrability requirements. In particular, functions are always assumed to vanish sufficiently rapidly at infinity to eliminate the surface integral which occurs in the use of Green's theorem. These conditions are always satisfied by the ordinary basis functions ϕ_k used in bound state molecular structure theory. Formally, in the derivations, functions are also assumed to be real, but extensions to complex functions can be made without difficulty.

A. Theorem A

If ϕ_a is a charge density function, then,

$$\epsilon = \int \phi_a(1)\phi_a(2) r_{12}^{-1} dv_1 dv_2 = [\phi_a(1) \mid r_{12}^{-1} \mid \phi_a(2)] \geq 0.$$

Proof: Define a potential $\chi(2) = \int r_{12}^{-1}\phi_a(1) dv_1$. Since the function ϕ_a is the same in $\phi_a(1)$ and $\phi_a(2)$, by Poisson's theorem

$$\nabla_2^2 \chi(2) = -4\pi\phi_a(2),$$

and thus,

$$\epsilon = -(4\pi)^{-1} \int \chi(2) \nabla_2^2 \chi(2) dv_2.$$

The anti-Hermitian nature of ∇, $\nabla^+ = -\nabla$, proved

using Green's theorem for suitably behaved functions ϕ_a, gives

$$\epsilon = (4\pi)^{-1}\int |\nabla_2\chi(2)|^2 dv_2 \geq 0.$$

This proof is the same as used by Slater to prove that exchange integrals are positive.[1]

B. Theorem B

If ϕ_a and $\phi_a{}'$ are charge density functions, then

$$|[\phi_a(1)|r_{12}^{-1}|\phi_a{}'(2)]|$$

$$\leq [\phi_a(1)|r_{12}^{-1}|\phi_a(2)]^{1/2}[\phi_a{}'(1)|r_{12}^{-1}|\phi_a{}'(2)]^{1/2}.$$

Proof: Define

$$\epsilon = [\phi_a(1)-\lambda\phi_a{}'(1)|r_{12}^{-1}|\phi_a(2)-\lambda\phi_a{}'(2)].$$

By theorem A, $\epsilon \geq 0$. Minimization of ϵ with respect to λ gives

$$\partial\epsilon/\partial\lambda = -[\phi_a{}'(1)|r_{12}^{-1}|\phi_a(2)-\lambda\phi_a{}'(2)]$$

$$-[\phi_a(1)-\lambda\phi_a{}'(1)|r_{12}^{-1}|\phi_a{}'(2)]=0.$$

Or, from the identity of the two integrals for the Hermitian operator r_{12}^{-1}, assuming real functions,

$$\lambda = [\phi_a(1)|r_{12}^{-1}|\phi_a{}'(2)]/[\phi_a{}'(1)|r_{12}^{-1}|\phi_a{}'(2)].$$

Evaluation of ϵ for this choice of λ gives

$$[\phi_a(1)|r_{12}^{-1}|\phi_a(2)]$$

$$-\{[\phi_a(1)|r_{12}^{-1}|\phi_a{}'(2)]^2/[\phi_a{}'(1)|r_{12}^{-1}|\phi_a{}'(2)]\}\geq 0.$$

The statement of the theorem follows since the integrals under the square root are positive for ϕ_a and $\phi_a{}'$ not identically zero. *Corollary:* If ϕ_a is a given density, an approximation $\phi_a{}'$ can be found by maximizing

$$[\phi_a(1)|r_{12}^{-1}|\phi_a{}'(2)]^2/[\phi_a{}'(1)|r_{12}^{-1}|\phi_a{}'(2)]$$

with respect to variations of the parameters of $\phi_a{}'$.

On application to electron repulsion integrals over basis functions ϕ_k, the theorem is simply a statement of the known inequality,

$$|[\phi_i(1)\phi_j(1)|r_{12}^{-1}|\phi_k(2)\phi_l(2)]|$$

$$\leq [\phi_i(1)\phi_j(1)|r_{12}^{-1}|\phi_i(2)\phi_j(2)]^{1/2}$$

$$\times[\phi_k(1)\phi_l(1)|r_{12}^{-1}|\phi_k(2)\phi_l(2)]^{1/2},$$

and a variety of other inequalities follow immediately from different choices of ϕ_a and ϕ_b.[2] Another approach to the determination of upper and lower bounds on $[\phi_a(1)|r_{12}^{-1}|\phi_b(2)]$, based on certain choices of trial electric fields and electrostatic potentials, is discussed in Ref. 3.

C. Theorem C

If ϕ_a and ϕ_b are given charge density functions and $\phi_a{}'$ and $\phi_b{}'$ are the corresponding approximate densities,

then

$$|[\phi_a(1)|r_{12}^{-1}|\phi_b(2)]-[\phi_a{}'(1)|r_{12}^{-1}|\phi_b{}'(2)]|$$

$$\leq \epsilon_a^{1/2}\epsilon_b^{1/2}+K_a^{1/2}\epsilon_b^{1/2}+K_b^{1/2}\epsilon_a^{1/2},$$

where

$$\epsilon_m = [\phi_m(1)-\phi_m{}'(1)|r_{12}^{-1}|\phi_m(2)-\phi_m{}'(2)],$$

$$K_m = [\phi_m{}'(1)|r_{12}^{-1}|\phi_m{}'(2)]$$

or

$$K_m = [\phi_m(1)|r_{12}^{-1}|\phi_m(2)],$$

and $m=a$ or b.

Proof: In the inequality of Theorem B, let $\phi_a=\phi_c-\phi_c{}'$ and $\phi_a{}'=\phi_d-\phi_d{}'$, then

$$|[\phi_c(1)-\phi_c{}'(1)|r_{12}^{-1}|\phi_d(2)-\phi_d{}'(2)]|\leq\epsilon_c^{1/2}\epsilon_d^{1/2},$$

$$|[\phi_c(1)|r_{12}^{-1}|\phi_d(2)-\phi_d{}'(2)]-[\phi_c{}'(1)|r_{12}^{-1}|\phi_d{}'(2)]$$

$$-[\phi_c{}'(1)|r_{12}^{-1}|\phi_d(2)-\phi_d{}'(2)]$$

$$-[\phi_d{}'(1)|r_{12}^{-1}|\phi_c(2)-\phi_c{}'(2)]|\leq\epsilon_c^{1/2}\epsilon_d^{1/2}.$$

Using the inequality $|A|\leq|A+B|+|B|$ gives

$$|[\phi_c(1)|r_{12}^{-1}|\phi_d(2)]-[\phi_c{}'(1)|r_{12}^{-1}|\phi_d{}'(2)]|$$

$$\leq\epsilon_c^{1/2}\epsilon_d^{1/2}+|[\phi_c{}'(1)|r_{12}^{-1}|\phi_d(2)-\phi_d{}'(2)]|$$

$$+|[\phi_d{}'(1)|r_{12}^{-1}|\phi_c(2)-\phi_c{}'(2)]|.$$

By Theorem B, the integrals on the right satisfy

$$|[\phi_m{}'(1)|r_{12}^{-1}|\phi_n(2)-\phi_n{}'(2)]|$$

$$\leq[\phi_m{}'(1)|r_{12}^{-1}|\phi_m{}'(1)]^{1/2}$$

$$\times[\phi_n(2)-\phi_n{}'(2)|r_{12}^{-1}|\phi_n(2)-\phi_n{}'(2)]^{1/2},$$

where $m=c$ and $n=d$ or $m=d$ and $n=c$. Relabeling the functions ϕ_c, ϕ_d, $\phi_c{}'$, and $\phi_d{}'$ gives the statement of the theorem for the first choice of K_m; the second choice of K_m follows on interchange of the primed and unprimed functions in all expressions.

D. Optimization of Approximate Charge Densities and the Integral Approximation

Consider the problem of approximating the integral

$$I_{\text{exact}} = \int\phi_a(1)\phi_b(2)r_{12}^{-1}dv_1dv_2 = [\phi_a(1)|r_{12}^{-1}|\phi_b(2)],$$

where ϕ_a and ϕ_b are given charge density functions. Theorem C provides a simple and direct way of determining approximate densities $\phi_a{}'$ and $\phi_b{}'$ such that the error bound, δ, on the magnitude of the difference between exact and approximate integrals, $|I_{\text{exact}}-I_{\text{approx}}|$, is minimized.[4] Assume that density approximations are taken as $\phi_a\approx\phi_a{}'=\lambda_a\phi_a{}''$ and $\phi_b\approx\phi_b{}'=\lambda_b\phi_b{}''$ where the functions ϕ'' may contain variable parameters. Minimization of δ is achieved by minimization of

$$\epsilon_a = [\phi_a(1)-\lambda_a\phi_a{}''(1)|r_{12}^{-1}|\phi_a(2)-\lambda_a\phi_a{}''(2)]$$

with respect to λ_a and the parameters of $\phi_a{}''$, and by

independent minimization of ϵ_b, defined similarly. For the optimum λ_a,

$$\lambda_a = [\phi_a(1) \mid r_{12}^{-1} \mid \phi_a''(2)] / [\phi_a''(1) \mid r_{12}^{-1} \mid \phi_a''(2)],$$

ϵ_a becomes

$$\epsilon_a = [\phi_a(1) \mid r_{12}^{-1} \mid \phi_a(2)] - \lambda_a^2 [\phi_a''(1) \mid r_{12}^{-1} \mid \phi_a''(2)]$$

$$= [\phi_a(1) \mid r_{12}^{-1} \mid \phi_a(2)] - [\phi_a'(1) \mid r_{12}^{-1} \mid \phi_a'(2)],$$

and similarly for λ_b and ϵ_b. The integral approximation is

$$I_{\text{exact}} = [\phi_a(1) \mid r_{12}^{-1} \mid \phi_b(2)]$$

$$\approx \lambda_a \lambda_b [\phi_a''(1) \mid r_{12}^{-1} \mid \phi_b''(2)]$$

$$= [\phi_a'(1) \mid r_{12}^{-1} \mid \phi_b'(2)] = I_{\text{approx}}$$

with error bound δ,

$$\mid I_{\text{exact}} - I_{\text{approx}} \mid \leq \delta,$$

where

$$\delta = \epsilon_a^{1/2} \epsilon_b^{1/2} + [\phi_a(1) \mid r_{12}^{-1} \mid \phi_a(2)]^{1/2} \epsilon_b^{1/2}$$

$$+ [\phi_b(1) \mid r_{12}^{-1} \mid \phi_b(2)]^{1/2} \epsilon_a^{1/2}.$$

Thus, the error bound δ is proportional to quantities ϵ minimized to determine the charge density approximations. From the expression for ϵ_a,

$$[\phi_a(1) \mid r_{12}^{-1} \mid \phi_a(2)] \geq \lambda_a^2 [\phi_a''(1) \mid r_{12}^{-1} \mid \phi_a''(2)]$$

$$= [\phi_a'(1) \mid r_{12}^{-1} \mid \phi_a'(2)]$$

and thus the first choice of K_m in Theorem C gives the better bound,[4]

$$\delta = \epsilon_a^{1/2} \epsilon_b^{1/2} + [\phi_a'(1) \mid r_{12}^{-1} \mid \phi_a'(2)]^{1/2} \epsilon_b^{1/2}$$

$$+ [\phi_b'(1) \mid r_{12}^{-1} \mid \phi_b'(2)]^{1/2} \epsilon_a^{1/2}.$$

E. An Improved Error Bound

The error bound of Theorem C applies to any choice of approximate densities, ϕ_a' and ϕ_b', regardless of their method of determination; however, if $\phi_a' = \lambda_a \phi_a''$ and $\phi_b' = \lambda_b \phi_b''$ are determined by minimization of ϵ_a and ϵ_b, as in the previous section, an important improvement in the bound is possible.

Theorem D

If ϕ_a and ϕ_b are given charge density functions and if $\phi_a' = \lambda_a \phi_a''$ and $\phi_b' = \lambda_b \phi_b''$ are the corresponding approximate densities, determined by minimization of

$$\epsilon_m = [\phi_m(1) - \lambda_m \phi_m''(1) \mid r_{12}^{-1} \mid \phi_m(2) - \lambda_m \phi_m''(2)]$$

with respect to λ_m, for $m = a, b$, then

$$\mid [\phi_a(1) \mid r_{12}^{-1} \mid \phi_b(2)] - [\phi_a'(1) \mid r_{12}^{-1} \mid \phi_b'(2)] \mid$$

$$\leq \epsilon_a^{1/2} \epsilon_b^{1/2} + K_a^{1/2} \epsilon_b^{1/2} + K_b^{1/2} \epsilon_a^{1/2},$$

where

$$K_a = [\phi_a'(1) \mid r_{12}^{-1} \mid \phi_a'(2)]$$

$$- \{[\phi_a'(1) \mid r_{12}^{-1} \mid \phi_b'(2)]^2 / [\phi_b'(1) \mid r_{12}^{-1} \mid \phi_b'(2)]\}$$

or

$$K_a = [\phi_a(1) \mid r_{12}^{-1} \mid \phi_a(2)]$$

$$- \{[\phi_a'(1) \mid r_{12}^{-1} \mid \phi_b'(2)]^2 / [\phi_b(1) \mid r_{12}^{-1} \mid \phi_b(2)]\}$$

and K_b is obtained from K_a by interchanging a and b.

Proof: Adopting the notation $[\phi_m(1) \mid r_{12}^{-1} \mid \phi_n(2)] = (\phi_m \mid \phi_n)$, minimization of ϵ_m gives

$$\lambda_m = (\phi_m'' \mid \phi_m) / (\phi_m'' \mid \phi_m'')$$

and

$$\epsilon_m = (\phi_m \mid \phi_m) - (\phi_m' \mid \phi_m'),$$

thus it follows from the general definition of ϵ_m that

$$(\phi_m' \mid \phi_m) - (\phi_m' \mid \phi_m') = 0.$$

As in the proof of Theorem C, $\mid (\phi_a - \phi_a' \mid \phi_b - \phi_b') \mid \leq \epsilon_a^{1/2} \epsilon_b^{1/2}$, and

$$\mid (\phi_a \mid \phi_b) - (\phi_a' \mid \phi_b') - (\phi_a' \mid \phi_b - \phi_b') - (\phi_b' \mid \phi_a - \phi_a') \mid$$

$$\leq \epsilon_a^{1/2} \epsilon_b^{1/2}.$$

Introducing the two new parameters λ_a' and λ_b' and adding the quantities $\lambda_b'(\phi_b' \mid \phi_b - \phi_b')$ and $\lambda_a'(\phi_a' \mid \phi_a - \phi_a')$ which are both identically zero, gives

$$\mid (\phi_a \mid \phi_b) - (\phi_a' \mid \phi_b') - (\phi_a' - \lambda_b' \phi_b' \mid \phi_b - \phi_b')$$

$$- (\phi_b' - \lambda_a' \phi_a' \mid \phi_a - \phi_a') \mid \leq \epsilon_a^{1/2} \epsilon_b^{1/2}$$

It follows that

$$\mid (\phi_a \mid \phi_b) - (\phi_a' \mid \phi_b') \mid$$

$$\leq \epsilon_a^{1/2} \epsilon_b^{1/2} + (\phi_a' - \lambda_b' \phi_b' \mid \phi_a' - \lambda_b' \phi_b')^{1/2} \epsilon_b^{1/2}$$

$$+ (\phi_b' - \lambda_a' \phi_a' \mid \phi_b' - \lambda_a' \phi_a')^{1/2} \epsilon_a^{1/2}.$$

The choice of $\lambda_b' = (\phi_a' \mid \phi_b') / (\phi_b' \mid \phi_b')$ and $\lambda_a' = (\phi_a' \mid \phi_b') / (\phi_a' \mid \phi_a')$ minimizes the right hand side, and gives

$$\mid (\phi_a \mid \phi_b) - (\phi_a' \mid \phi_b') \mid \leq \epsilon_a^{1/2} \epsilon_b^{1/2} + K_a^{1/2} \epsilon_b^{1/2} + K_b^{1/2} \epsilon_a^{1/2},$$

where

$$K_a = (\phi_a' \mid \phi_a') - [(\phi_a' \mid \phi_b')^2 / (\phi_b' \mid \phi_b')]$$

and K_b is obtained from K_a by interchanging a and b. From the definition of ϵ_a (minimum) and ϵ_b (minimum),

$$K_a = (\phi_a \mid \phi_a) - \epsilon_a - \{(\phi_a' \mid \phi_b')^2 / [(\phi_b \mid \phi_b) - \epsilon_b]\}$$

$$\leq (\phi_a \mid \phi_a) - [(\phi_a' \mid \phi_b')^2 / (\phi_b \mid \phi_b)]$$

and similarly for K_b which gives the two definitions of K_a and K_b in the theorem. The information required to evaluate K_a and K_b is the same as used to evaluate ϵ_a and ϵ_b except for $(\phi_a' \mid \phi_b')$ which is known if the integral approximation has been evaluated prior to evaluation of the bound.

F. Bounds from the Schwarz Inequality

It is apparent from the proof of Theorem C that any inequality of the form

$$| (\phi_a \mid r_{12}^{-1} \mid \phi_a') | \le (\phi_a \mid r_{12}^{-1} \mid \phi_a)^{1/2}(\phi_a' \mid r_{12}^{-1} \mid \phi_a')^{1/2}$$

would lead to a bound,

$$| (\phi_a \mid r_{12}^{-1} \mid \phi_b) - (\phi_a' \mid r_{12}^{-1} \mid \phi_b') | \le \delta,$$

and that this applies also to the case of two-particle functions $\phi_a(1, 2)$ and $\phi_b(1, 2)$. Minimization of

$$\epsilon_a' = \int r_{12}^{-1}[\phi_a(1, 2) - \lambda\phi_a'(1, 2)]^2 dv_1 dv_2$$

with respect to λ gives the Schwarz inequality

$$| \phi_a(1, 2) \mid r_{12}^{-1} \mid \phi_a'(1, 2) |$$
$$\le [\phi_a(1, 2) \mid r_{12}^{-1} \mid \phi_a(1, 2)]^{1/2}$$
$$\times [\phi_a'(1, 2) \mid r_{12}^{-1} \mid \phi_a'(1, 2)]^{1/2}.$$

If the two-particle functions are approximated, $\phi_a(1, 2) \approx \phi_a'(1, 2)$ and $\phi_b(1, 2) \approx \phi_b'(1, 2)$ then

$$| [\phi_a(1, 2) \mid r_{12}^{-1} \mid \phi_b(1, 2)]$$
$$- [\phi_a'(1, 2) \mid r_{12}^{-1} \mid \phi_b'(1, 2)] |$$
$$\le (\epsilon_a')^{1/2}(\epsilon_b')^{1/2} + (K_a')^{1/2}(\epsilon_b')^{1/2} + (K_b')^{1/2}(\epsilon_a')^{1/2},$$

where

$$\epsilon_m' = \int r_{12}^{-1}[\phi_m(1, 2) - \phi_m'(1, 2)]^2 dv_1 dv_2,$$
$$K_m' = [\phi_m'(1, 2) \mid r_{12}^{-1} \mid \phi_m'(1, 2)],$$

and $m = a$ or b.

Taking $\phi_m(1, 2) \approx \lambda_m \phi_m''(1, 2) = \phi_m'(1, 2)$ and minimizing ϵ_m' with respect to λ gives

$$\lambda = \frac{[\phi_m(1, 2) \mid r_{12}^{-1} \mid \phi_m''(1, 2)]}{[\phi_m''(1, 2) \mid r_{12}^{-1} \mid \phi_m''(1, 2)]}$$

and a minimum ϵ_m',

$$\epsilon_m' = [\phi_m(1, 2) \mid r_{12}^{-1} \mid \phi_m(1, 2)]$$
$$- \lambda^2[\phi_m''(1, 2) \mid r_{12}^{-1} \mid \phi_m''(1, 2)]$$
$$= [\phi_m(1, 2) \mid r_{12}^{-1} \mid \phi_m(1, 2)]$$
$$- [\phi_m'(1, 2) \mid r_{12}^{-1} \mid \phi_m'(1, 2)].$$

The special choice of

$$\phi_m''(1, 2) = \frac{[\phi_m(1, 2) \mid r_{12}^{-1} \mid \phi_m(2, 1)]}{[\phi_m(1, 2) \mid r_{12}^{-1} \mid \phi_m(1, 2)]} \phi_m(2, 1)$$

gives the well-known relation between Coulombic and Coulombic exchange integrals,

$$[\phi_m(1, 2) \mid r_{12}^{-1} \mid \phi_m(1, 2)] \ge [\phi_m(1, 2) \mid r_{12}^{-1} \mid \phi_m(2, 1)].$$

A significant disadvantage of the present bound, however, is the occurrence of Coulombic integrals in K_m' and ϵ_m', and the relative largeness of these inte-grals compared to the integral to be approximated can render the bound useless. On the other hand, if the problem is such that either one- or two-particle functions could be approximated, for example, if $\phi_m(1) = \phi_a(1)\phi_b(1)$ and $\phi_n(1, 2) = \phi_a(1)\phi_c(2)$ then in the bound of theorem C there occur only exchange integrals, $[\phi_m(1) \mid r_{12}^{-1} \mid \phi_m(2)] = [\phi_a(1)\phi_b(2) \mid r_{12}^{-1} \mid \phi_a(2)\phi_b(1)]$, plus corresponding integrals over approximate densities for ϕ_m'. If the exchange integrals which occur in the approximation of ϕ_m are significantly smaller than the Coulomb integrals which occur in the approximation of $\phi_n(1, 2)$ then the bound of theorem C becomes superior. Such is often the case in problems involving nonlocalized densities, and the multicenter electron re-pulsion integrals discussed in the next section provide an example of a case in which there can be several orders of magnitude superiority of the bound of theorm C over the bound based on the Schwarz inequality.

III. APPROXIMATION OF ELECTRON REPULSION INTEGRALS

Consider a set of N basis functions $\{g_k\}$ and the problem of approximating certain, but not necessarily all, electron repulsion integrals

$$[g_i(1)g_j(1) \mid r_{12}^{-1} \mid g_k(2)g_l(2)]$$

of which there is a total of $\sim \frac{1}{8}N^4$ for large N. Further, assume as in the preceding sections that charge densi-ties will be approximated by $g_i(1)g_j(1) \simeq \lambda_{ij}\Phi_{ij}(1) = \Phi_{ij}'(1)$ and $g_k(2)g_l(2) \simeq \lambda_{kl}\Phi_{kl}(2) = \Phi_{kl}'(2)$ where func-tions Φ_{mn} are of some chosen functional form possibly containing variable parameters. There are $\frac{1}{2}N(N+1)$ product densities $g_m g_n$ and for each density to be ap-proximated, $\lambda_{mn}\Phi_{mn}$ is determined by minimization of

$$\epsilon_{mn} = [g_m(1)g_n(1)$$
$$- \lambda_{mn}\Phi_{mn}(1) \mid r_{12}^{-1} \mid g_m(2)g_n(2) - \lambda_{mn}\Phi_{mn}(2)]$$

with respect to λ_{mn} and parameters of Φ_{mn}. After the mn pair information is calculated, four index integrals can be approximated by

$$[g_i(1)g_j(1) \mid r_{12}^{-1} \mid g_k(2)g_l(2)]$$
$$\simeq \lambda_{ij}\lambda_{kl}[\Phi_{ij}(1) \mid r_{12}^{-1} \mid \Phi_{kl}(2)]$$

and error bounds δ evaluated. Certainly, in applica-tions it will be of interest to examine δ and to reject the use of the approximation if δ is not sufficiently small. It should be noted that optimization of $\lambda_{mn}\Phi_{mn}$ occurs at the N^2 stage of the computation and that the error bound computation at the N^4 stage is trivial.

Two possible choices of approximate densities Φ_{mn} are interesting to consider. If the functions g_m them-selves consist of component functions as is the case with grouped or contracted Gaussian functions (linear

TABLE I. Some numerical results on charge density approximations, comparison of exact and approximate values of electron repulsion integrals, and theoretical error bounds. Comparisons are for certain multicenter integrals of ethylene over a basis of linear combinations of Gaussian functions, g_i, where g_i contains three to seven single Gaussian components. Densities $g_i g_j$ are approximated by $\lambda_{ij} g_i' g_j'$ (see text) where the primed functions are single Gaussians with a single variable scale factor for the pair.

Density approximations				Electron repulsion integrals								
i	j	$[i(1)j(1)/$ $i(2)j(2)]$	ϵ_{ij}	$[i(1)j(1)/k(2)l(2)]$				Approx[a]	Exact	δ (actual)	δ_1[b]	δ_2[b]
1	13	0.00391	0.000093	1	1	1	13	−0.02617	−0.02649	0.0003	0.0073	0.0061
2	9	0.01514	0.000124	1	1	4	7	−0.06780	−0.06852	0.0007	0.0085	0.0058
3	10	0.01463	0.000280	1	1	10	11	0.04934	0.04949	0.0002	0.0072	0.0033
4	7	0.01514	0.000124	1	1	11	12	0.05153	0.05221	0.0007	0.0071	0.0036
5	9	0.00412	0.000038	2	9	5	9	0.00783	0.00789	0.0001	0.0015	0.0003
7	11	0.01561	0.000300	2	9	4	7	−0.00338	−0.00369	0.0003	0.0029	0.0028
7	12	0.01561	0.000300	7	11	7	12	0.01156	0.01087	0.0007	0.0046	0.0032
10	11	0.00534	0.000089	7	11	9	9	−0.05705	−0.05827	0.0012	0.0324	0.0315
10	12	0.00534	0.000089	5	5	10	12	0.04985	0.04998	0.0001	0.0095	0.0033
11	12	0.00623	0.000088	3	10	8	10	0.02687	0.02788	0.0010	0.0058	0.0045

[a] Pair densities not included in the list of density approximations were not approximated in the evaluation of electron repulsion integrals.

[b] Theoretical error bounds, δ_1 from Theorem C, and δ_2 from Theorem D, see text.

combinations of simple Gaussians), a smaller number of components could be selected to define a function g_m'. Taking the product density approximation as $g_m g_n \simeq \lambda_{mn} \Phi_{mn} = \lambda_{mn} g_m' g_n'$ gives, after the parameter optimization, the integral approximation

$$[g_i(1)g_j(1) \mid r_{12}^{-1} \mid g_k(2)g_l(2)]$$
$$\simeq \lambda_{ij}\lambda_{kl}[g_i'(1)g_j'(1) \mid r_{12}^{-1} \mid g_k'(2)g_l'(2)].$$

As an example, consider an application to integrals over five-component Gaussian group orbitals, g_m; taking g_m' as a single Gaussian would lead to an approximation of the linear combination of 625-component integrals by one integral over a single Gaussian function, multiplied by the appropriate λ_{ij} and λ_{kl}. Numerical examples of this type of approximation are given at the end of this section. It should be noted here that the present approximation is entirely different from an approximation of the integral using single Gaussians which have maximum overlap with the group functions; λ factors exist, and Gaussian exponents when optimized do not necessarily lead to maximum overlap.

A second choice of Φ_{mn}' of interest is an expansion

$$g_m g_n \simeq \Phi_{mn}' = \sum_k^M c_k \Omega_k,$$

where Ω_k denotes a product of basis functions $g_p g_q$. If g_p and g_q are restricted to have the same origin and if this origin is the same as the origin of one of the functions g_m or g_n, then the expansion is particularly applicable to the evaluation of Slater integrals since only two-center integrals are required throughout. Mini-

mization of

$$\epsilon_{mn} = [g_m(1)g_n(1)$$
$$- \sum_k^M c_k \Omega_k(1) \mid r_{12}^{-1} \mid g_m(2)g_n(2) - \sum_k^M c_k \Omega_k(2)]$$

with respect to coefficients c_l gives the set of equations,

$$[g_m(1)g_n(1) \mid r_{12}^{-1} \mid \Omega_l(2)]$$
$$= [\Omega_l(1) \mid r_{12}^{-1} \mid \sum_k c_k \Omega_k(2)], \qquad l = 1, 2, \cdots, M,$$

which can be solved to determine the coefficients. Near-linear dependence of the equations can occur in practice, but such problems can be circumvented. Given the expansions, the integral approximation becomes

$$[g_i(1)g_j(1) \mid r_{12}^{-1} \mid g_k(2)g_l(2)]$$
$$\simeq [\Phi_{ij}'(1) \mid r_{12}^{-1} \mid \Phi_{kl}'(2)],$$

where as a result of the restrictions only two-center integrals occur. The determination of approximate charge densities and the subsequent integral approximation by such a procedure has in fact been proposed previously by Harris and Rein,[5] and has been further investigated by Billingsley and Bloor.[6] The present argument provides a theoretical basis for the procedure and in addition gives error bounds for the appraisal of the suitability of the expansion.

Finally, in order to demonstrate that relatively small values of ϵ_{mn} can be achieved simply in practice and to give some indication of the actual error in the integral approximation, some numerical values are reported in Table I for the simplest possible case, that of using a

single Gaussian with optimized exponent and λ to approximate products of three- to seven-component linear combinations of Gaussians. These integrals were selected from a list of multicenter electron repulsion integrals of the ethylene molecule, but the tabulation is only for numerical illustration, and inferences concerning the entire distribution of integrals are not intended. Values in the table show actual integral errors to be significantly smaller than the theoretical bounds, but for rigorous applications, it is the theoretical bound which must be reduced and this would require additional terms in the density approximations. The latter observation should not be regarded as discouraging, however, since the present level of approximation is one of the simplest imaginable; doubling the number of terms in the density approximations would still lead to a 10^2 reduction in computational time per integral approximated for integrals over five-component Gaussian orbitals. As mentioned previously, the over-all improvement in computational time for the entire set of integrals required in a molecular structure problem is of course a different question which depends on the fraction of integrals to which an approximation method is applicable.[7]

IV. CONCLUSIONS

The problem of approximation of two-particle Coulombic potential energy integrals can be organized simply in a way which is theoretically well defined by application of theorems of electrostatics. Rigorous error bounds on the difference between exact and approximate integrals exist,

$$| [\phi_a(1) \mid r_{12}^{-1} \mid \phi_b(2)] - [\phi_a'(1) \mid r_{12}^{-1} \mid \phi_b'(2)] | \leq \delta,$$

and the structure of the expression for δ provides a powerful method of optimizing the charge density approximations by minimization of

$$\epsilon_a = [\phi_a(1) - \phi_a'(1) \mid r_{12}^{-1} \mid \phi_a(2) - \phi_a'(2)]$$

with respect to parameters of the density approximations ϕ_a' and similarly for ϕ_b' treated independently. Thus, δ can be evaluated simply from information calculated separately for the pair of densities ϕ_a and ϕ_a' and the pair ϕ_b and ϕ_b'. Two expressions for the bound δ are presented: The first is applicable to any choice of approximate densities ϕ' and the second is applicable to functions ϕ' obtained by minimization of ϵ.

The framework of the theory appears to be particularly well suited for applications to the approximation of electron repulsion integrals which occur in molecular structure theory since error bounds can be evaluated simply prior to the use of a proposed approximation.

ACKNOWLEDGMENT

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